Hydrogen detection near surfaces and shallow interfaces with resonant nuclear reaction analysis

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This review introduces hydrogen depth profiling by nuclear reaction analysis (NRA) via the resonant $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction as a versatile method for the highly depth-resolved observation of hydrogen (H) at solid surfaces and interfaces. The technique is quantitative, non-destructive, and readily applied to a large variety of materials. Its fundamentals, instrumental requirements, advantages and limitations are described in detail, and its main performance benchmarks in terms of depth resolution and sensitivity are compared to those of elastic recoil detection (ERD) as a competing method. The wide range of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA applications in research of hydrogen-related phenomena at surfaces and interfaces is reviewed.

Special emphasis is placed on the powerful combination of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA with surface science techniques of *in-situ* target preparation and characterization, as the NRA technique is ideally suited to investigate hydrogen interactions with atomically controlled surfaces and intact interfaces. In conjunction with thermal desorption spectroscopy, ^{15}N NRA can assess the thermal stability of absorbed hydrogen species in different depth locations against diffusion and desorption. Hydrogen diffusion dynamics in the near-surface region, including transitions of hydrogen between the surface and the bulk, and between shallow interfaces of nanostructured thin layer stacks can directly be visualized. As a unique feature of ^{15}N NRA, the analysis of Doppler-broadened resonance excitation curves allows for the direct measurement of the zero-point vibrational energy of hydrogen atoms adsorbed on single crystal surfaces.

Keywords: Nuclear reaction analysis, Hydrogen depth profiling, Surface and interface analysis, Hydrogen adsorption, Hydrogen absorption, Hydrogen diffusion

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Acronyms

AES	Auger electron spectroscopy
BGO	Bismuth germanium oxide ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$)
CRB	Cosmic radiation background
CVD	Chemical vapor deposition
ERD(A)	Elastic recoil detection (analysis)
DFT	Density functional theory
FET	Field effect transistor
FGA	Forming gas annealing
HAS	Helium atom scattering
H _{at}	Atomic hydrogen
H-ERD(A)	High-resolution elastic recoil detection (analysis)
HIERD	Heavy ion elastic recoil detection
HREELS	High resolution electron energy loss spectroscopy
IAEA	International Atomic Energy Agency
IRAS	Infrared absorption spectroscopy
LAPW	Linear augmented plane wave
LEED	Low energy electron diffraction
LEERS	Low energy recoil scattering
MBE	Molecular beam epitaxy
MOS	Metal-oxide-semiconductor
NR(A)	Nuclear reaction (analysis)
PSD	Position sensitive detector
RBS	Rutherford backscattering
PIXE/PIGE	Particle induced X-ray/Gamma-ray emission
ROI	Region of interest (energy integration window in γ -spectroscopy)
SNICS	Source of negative ions by Cs sputtering
SSBD	Silicon surface barrier detector
SSD	Solid state detector
STM	Scanning tunneling microscopy
TC	Transmission channeling

TD(S)	Thermal desorption (spectroscopy)
TOF	Time-of-flight
UHV	Ultrahigh vacuum
UPS	Ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy

Symbols

α_i	Incidence angle (ion beam direction relative to the surface normal)
A	Mass ratio (M_2/M_1) of incident (M_1) and scattered ion ($M_2=M_s$) or recoiled target atom ($M_2=M_r$)
B	Magnetic flux [Gauss]
c	Speed of light in vacuum [2.998×10^8 m s ⁻¹]
c_b	Bulk H concentration [cm ⁻³]
c_{ref}	Reference H concentration in a standard for sensitivity calibration
d	Depth in the target (measured perpendicular from the surface) [nm]
D	H diffusion coefficient [m ² s ⁻¹]
δ_D	Gaussian width parameter of Doppler broadening distribution [keV]
δ_b	Gaussian width parameter of incident beam energy distribution [keV]
δE_d	Channel width of ERD detection energy
δ_G	Total Gaussian energy broadening (Doppler, straggling, beam) [keV]
$\delta_s(z)$	Gaussian width parameter of energy straggling distribution [keV]
ΔE	Energy loss (due to ion stopping in a target material) [keV]
ΔE_b	Beam energy spread (FWHM) [keV]
ΔE_{tot}	Total energy width (FWHM) of the NRA instrumental function [keV]
Δh	Thickness of a thin film or height of an adlayer [nm]
ΔH_s	Enthalpy of H solution [eV]
$\Delta \phi$	Work function change [eV]
$\Delta \Omega$	Detector solid angle [sr]
e	Elemental charge (1.60218×10^{-19} As)
ε	Stopping cross section [eV cm ² /10 ¹⁵ atoms] or [MeV/(mg/cm ²)]
E	Energy (general) [eV]

E_{ads}	Adsorption energy [eV]
E_{d}	Detection energy channel (ERD)
E_{des}	Activation energy for desorption [eV]
E_{diff}	Activation energy of H diffusion [eV]
E_{H}	Zero-point vibrational energy of surface-adsorbed H atoms
E_{i}	Incident ion beam energy in NRA
E_1	Incident projectile ion energy in ERD and RBS
E_{R}	Resonance energy (in a nuclear reaction cross section)
E_{r}	Energy of a recoiled target atom
E_{T}	Kinetic (translational) energy
E_{th}	Threshold energy (of an endothermic nuclear reaction)
$F(E, E_{\text{i}}, z)$	NRA instrumental function; its convolution with the H depth distribution yields the NR excitation curve $Y(E_{\text{i}})$
ϕ	Fluence (ion beam exposure) [ions/cm ²]
Γ	Width of a nuclear reaction cross section resonance [keV]
θ_{H}	Hydrogen surface coverage [ML]
θ_{R}	Recoil angle (ERD, laboratory system)
K	γ -detection efficiency factor
k_{B}	Boltzmann constant
L_{D}	(Thermal) diffusion length in a time interval Δt , $L_{\text{D}} = (D \cdot \Delta t)^{1/2}$ [m]
m_{e}	Electron rest mass
m_{H}	Proton mass
M_1	Mass of the projectile ion
M_2	Mass of a target atom (scattered or recoiled)
m_{C}	Mass of a carbon ion
m_{H}	Mass of a proton
m_{N}	Mass of a nitrogen ion
M_{R}	Mass of a recoiled target atom
n_{H}	Hydrogen number density [cm ⁻³]
N	Atomic density [cm ⁻³]
N_{i}	Incident beam flux [cm ⁻² s ⁻¹]

N_s	Surface areal density [atoms cm ⁻²]
q	Charge state (projectile ion)
Q_i	Acquisition time-integrated incident beam charge [C]
Q_s	Straggling cross section [eV ² /nm]
R	Probing depth range [μm]
s_0	Initial sticking coefficient
S	Stopping power (dE/dz) [keV nm ⁻¹]
S_s	Solution entropy [eV/K]
$\sigma(E)$	Nuclear reaction cross section [barn]
σ_{off}	Off-resonant nuclear reaction cross section
σ_R	Nuclear reaction cross section (resonance amplitude)[barn]
σ_r	Rutherford recoil cross section [barn]
σ_s	Straggling cross section [keV]
T	Temperature [K]
T_s	Surface temperature [K]
v	ion velocity [m s ⁻¹]
V_i	Injection voltage (accelerator ion source) [keV]
V_T	Terminal voltage (Tandem accelerator) [keV]
v_0	Bohr velocity (2.188×10 ⁶ m s ⁻¹)
Ω_s	Bohr straggling cross section [cm ²]
$Y(E_i)$	Excitation function of the nuclear reaction (γ-yield vs. E_i)
z	Ion trajectory length below the target surface, $z = d/\cos\alpha_i$ [nm]
Z	Nuclear charge
Z_1	Nuclear charge of the projectile ion
Z_2	Nuclear charge of a target element

Units

C	Coulomb (1 C = 1 As)
L	Langmuir (unit of gas exposure: 1 L = 1.33 x 10 ⁻⁴ Pa·s)
ML	Monolayer (relative unit of H coverage)
mb	Millibarn, cross section unit. 1 mb = 10 ⁻³ barn = 10 ⁻²⁷ cm ²

1. Introduction

The great wealth of surface and interface interactions of hydrogen and water has caught the keen attention of the Surface Science community for a long time [1-8]. The weak Van-der-Waals forces (and surface-catalyzed ortho-para conversion processes [9-16]) in the physisorbed state of molecular H₂ are of lasting fundamental interest, and recently heightened from the viewpoint of hydrogen in energy applications [17, 18]. Dissociative chemisorption [19-24], surface diffusion, and reaction of adsorbed H atoms with coadsorbates enable hydrogenation catalysis and fuel cell reactions. Recombination of H₂ is important in astrophysics as well as in photocatalysis and electrochemistry. Hydrogen surfactant effects in epitaxy and passivation of semiconductor interfaces impact fabrication and reliability of electronic devices. Adsorption of hydrogen or water can tremendously change the physical and chemical properties of the substrate surface, giving rise to work function shifts, relaxation lifting, reconstruction, conductivity, hydrophilicity, corrosion, etc. Owing to its light mass, the dynamics of hydrogen are subject to quantum effects that may influence the rate of reactions, diffusion, and surface penetration at low temperatures.

Many materials also exhibit volume solubility for hydrogen [25-27]. Bulk-dissolved hydrogen may dramatically affect the electrical and mechanical properties of its host [27-29]. Metal hydride formation, essential for hydrogen storage [18, 30] and optically switchable windows [31-33], the embrittlement of technical alloys [34],

getter pumping and H₂-outgassing in the ultrahigh vacuum (UHV) environment [35, 36], the permeation through diffusion membranes for H₂ purification [37], H-induced conductivity [38, 39], or, conversely, dopant passivation in semiconductors [40], are but a few prominent examples to highlight the diversity of bulk hydrogen-material interactions and their enormous technological impact. Interfacial hydrogen is recognized to influence the electrical performance of Schottky-contacts [41-43] and semiconductor devices [44-46].

Despite its ubiquitous abundance, hydrogen behaves rather elusive in standard surface analysis, as only a few techniques can detect it directly. Since hydrogen has only a single electron and interacts weakly with common analytical electron or X-ray probes, it is barely visible by low energy electron diffraction (LEED) and cannot be detected by photoemission (UPS, XPS) and Auger electron spectroscopy (AES). Widely utilized Thermal Desorption Spectroscopy (TDS) removes hydrogen from the sample and is in this sense destructive to the original adsorption (or absorption) state. Vibrational techniques such as reflection absorption infrared spectroscopy (RAIS), high resolution electron energy loss spectroscopy (HREELS), and helium atom scattering (HAS) are non-invasive, hydrogen-sensitive, and capable of identifying surface-adsorbed H species, but they are neither quantitative nor able to reveal the presence and depth location of hydrogen below surfaces [47] [48]. Hence, the distinction of hydrogen species on a surface from those situated closely below a surface or deeper in the bulk and their respective quantifications pose delicate analytical challenges.

This review therefore introduces hydrogen depth profiling by nuclear reaction analysis (NRA) via the resonant $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction as a powerful tool for the investigation of hydrogen near solid surfaces and interfaces, which can ideally complement conventional methods of surface analysis and overcome the said limitations with respect to hydrogen detection. Resonant $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA determines hydrogen surface coverages and absorbed concentrations quantitatively, non-destructively, and, in particular at 6.385 MeV, with high depth resolution. The specific nuclear reaction renders ^{15}N -NRA sensitive to the proton only, i.e., it is selective to the nucleus of the ^1H isotope, yet indifferent towards its chemical oxidation state.

Among NRA variants that use other nuclear reactions, the resonant $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ technique at 6.385 MeV with energy monochromatized ^{15}N ion beams is appreciated for its excellent near-surface depth resolution in the order of a few nanometers, for its high sensitivity (H concentrations of $\sim 10^{18} \text{ cm}^{-3}$ ($\sim 100 \text{ at. ppm}$) in bulk materials and $\sim 10^{13} \text{ cm}^{-2}$ ($\sim 1\%$ of a monolayer) on surfaces), and a reasonably versatile in-depth probing range of at least $2 \mu\text{m}$ [49-53]. As the measurement delivers absolute hydrogen concentrations, ^{15}N -NRA is frequently applied as a reference for the calibration of other H-sensitive detection methods, especially infrared absorption spectroscopy [54, 55]. An eminent advantage that distinguishes NRA from other forms of depth-resolved elemental analysis such as sputter profiling or Secondary Ion Mass Spectroscopy (SIMS) is its ability to obtain the in-depth H-concentration information non-destructively. Thus the benefits of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA for hydrogen analysis at surfaces and interfaces are near at hand: Subtle distinctions of surface-

adsorbed and near-surface absorbed H are routinely achieved on a depth scale of a few nanometers [51, 52, 56, 57]. Under grazing ^{15}N ion incidence conditions, the depth resolution can be enhanced further to below 1 nm [58], allowing for monolayer depth distinctions in particular situations [59]. Even the discrimination of surface-adsorbed from volume-absorbed hydrogen in size-controlled nanocrystals has recently been achieved [60]. NRA is particularly powerful in investigating hydrogen diffusion processes in the near surface region, including transitions of hydrogen between the surface and the subsurface crucial to the hydrogen absorption phenomenon. Especially in combination with TDS unambiguous identifications of thermal desorption features and assignments to hydrogen in different depth locations become possible, thus allowing for a depth-resolved assessment of the thermal stability of respective H species against diffusion and desorption [61, 62]. The essentially non-destructive nature of the NRA measurement enables repeated analysis of the same specimen conditioned by *in-situ* treatments. Evidently this is an enormous advantage in studies of adsorbed and absorbed hydrogen states at well-defined surfaces that are in principle sensitive to air contact, as well as for the investigation of hydrogen interactions with intact interfaces.

Besides delivering depth information, for which NRA has been devised primarily, the ^{15}N technique is also suited for the analysis of surface hydrogen, and its powerful potential can be exploited fully on well-defined single crystal targets. As a unique feature in addition to the quantitative coverage information ^{15}N NRA provides, the pronounced Doppler Effect in the nuclear reaction kinematics allows for direct

measurements of the zero-point vibrational energy of hydrogen atoms in their chemical bonds to the surface [63-67]. This quantity is entirely inaccessible with other methods of vibrational spectroscopy that probe vibrational excitations. Through the zero-point energy the degree of vibrational anharmonicity of the hydrogen adsorption potential between the ground and first excited state can be assessed, which is related to the activation barrier for surface diffusion and to the debated possibility that the hydrogen wave function is delocalized on certain transition metal surfaces [68, 69]. To a limited extent, the zero-point vibrational energy can even be used to discriminate different chemically bound species of surface hydrogen [70].

In view of these capabilities for the analysis of surface and interfacial hydrogen, it is striking that NRA applications to single crystals or thin film systems with well-defined interfaces, in contrast to mere bulk H concentration evaluations, have remained comparatively rare until rather recently, and that apparently the potential of ^{15}N -NRA for surface-near hydrogen analysis is not as widely recognized in the Surface Science community as it might deserve. As we will show, the instrumental techniques for ion beam analysis and UHV-based surface characterization are well compatible, and the combination of NRA with standard Surface Science methods is a versatile and powerful one.

Since its introduction by Lanford in 1976 [49], NRA via the 6.385 MeV resonance of the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction has matured into a well-established ion beam technique for the quantitative measurement of hydrogen depth distributions [51, 52, 71, 72]. Historically, NRA was first mainly applied to determine H concentrations in

bulk materials and thin films. A large body of literature describes NRA measurements of volume-dissolved hydrogen, related to phenomena such as hydrogen-induced embrittlement [73], the retention of H isotopes in plasma-exposed fusion reactor wall materials [74-76], the H content in CVD fabricated films, or the depth-range and internal diffusion of ion implanted hydrogen. Such studies were seldom concerned about the surface quality of their targets, which might bear uncontrolled surface layers, modified by natural oxidation, contamination, or various treatments. The resulting hydrogen profiles often showed ill-defined 'near-surface regions', where the H-content differed considerably from the value deep in the bulk. Focusing on this H bulk content, many such studies simply disregarded the surface region altogether. A notable exception is the thickness evaluation of near-surface hydration layers found on weathered silicate materials [50, 77] with ^{15}N NRA, which has later been proposed as a method for age dating of natural minerals or of glass or quartz artifacts [78-80] (Section 3.2.5.1). The depth-resolving powers of ^{15}N NRA have also been applied to observe H redistribution associated with electrochromic transitions in multilayer systems [81, 82] (Section 3.2.5.2). NRA measurements of hydrogen at surfaces, however, did not emerge before the late 1980s after the discovery of the Doppler Effect that broadens the width of the nuclear reaction resonance [63-66].

The first truly surface-analytical applications of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA allowing for measurements of absolute H coverages and of the zero-point vibrational energy of H at well-defined *in-situ* prepared single crystal targets were developed in Japan by Murata and Komaki [65, 83]. This first 'marriage' of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA with Surface Science instrumentation has largely promoted the recent progress in research of

hydrogen in the near-surface region of atomically controlled targets. At first, H adsorbed on W(100) and W(111) was examined as a well-known benchmark system in Surface Science, which demonstrated the potential of the NRA technique to characterize hydrogen adsorbed on single crystal surfaces [65, 83]. Next, it was confirmed that new scientific information on hydrogen at surfaces and interfaces can be obtained with NRA using the Pb/H/Si(111) [42, 59] and Ag/H/Si(111) [43] model systems (Section 3.3.2). This was followed by the successful real space observation of the zero-point vibrational motion of H atoms chemisorbed on Si(111) and Pt(111) surfaces through a $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ Doppler broadening analysis [67] (Section 3.1). Later, also the possibilities to study the ‘dynamical’ behavior of surface and interfacial hydrogen, such as transient and strongly temperature dependent near-surface hydrogen distributions observable after hydrogen absorption at metal single crystals [61, 84] (the first half of Section 3.2.3), the thermally driven migration of hydrogen atoms between the bulk and the surface of H-absorbing metals [62] (Section 3.2.3.1), as well as hydrogen redistribution phenomena between interfaces of microelectronic device structures [45, 46] (Section 3.3.1) were added to the portfolio of successful ^{15}N NRA applications to the material science of hydrogen at surfaces, at interfaces, and in nanostructured systems (e.g., Section 3.2.3.8).

The present Surface Science Report focuses on $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA applications that investigate hydrogen at and within a ‘close’ range of well-characterized solid surfaces and shallow interfaces. An important criterion to select literature for this review has hence been the sample quality. Surfaces should have been as clean and structurally controlled as possible (ideally single-crystalline), and interfaces been

abrupt and comprised by layers of uniform thicknesses. In order to exclude an enormous amount of literature on ^{15}N NRA applications that simply determined the H content in the volume of materials, we (arbitrarily) restricted our region of interest to a depth of ~ 100 nm below the surface.

A second important objective of this review in addition to describing the ^{15}N NRA technique has been to provide a comprehensive (although by far not exhaustive) introduction to the rich ‘materials science’ of hydrogen at solid surfaces and interfaces. To this end, as well as in order to highlight the relevance of the information that NRA of hydrogen near surfaces and interfaces has contributed in many research fields, due effort has been paid throughout to outline the scientific background for the reviewed NRA investigations. In order to cover as completely as possible the full range of NRA applications in the surface science of hydrogen, we included also several $^2\text{D}(^3\text{He},\text{p})^4\text{He}$ NRA studies at well-defined targets (e.g., Table 3 in Sect. 3.1.2, Sections 3.2.3.2, 3.2.3.5, and 3.2.3.6). NRA via the D-specific, non-resonant $^2\text{D}(^3\text{He},\text{p})^4\text{He}$ reaction principally provides no depth resolution but quantifies the D content in a ~ 0.5 μm deep near-surface region (cf. Sect. 2.1.2), so that – in absence of absorbed deuterium – it can determine absolute surface coverages of adsorbed D. (These ^3He NRA studies did not require depth resolution but could as well have been performed with ^{15}N NRA). We hope that the substantial information on important aspects of hydrogen interactions with surfaces and interfaces of selected materials compiled in this review will be appreciated as helpful by many interested readers.

The article is organized as follows: Chapter 2 will first provide a thorough description of the relevant fundamentals and instrumental aspects of the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA technique for surface applications. A brief comparison to its main competitor will follow, namely high-resolution Elastic Recoil Detection (H-ERD), which (under optimum provisions) can achieve similar performance as ^{15}N NRA in terms of depth resolution and sensitivity. Chapter 3 then reviews (mainly $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$) NRA applications to hydrogen adsorbed at *surfaces*, followed by absorbed hydrogen in *shallow bulk regions* (< 100 nm, including *thin films*, *multilayers*, and *nanoparticles*), and, finally, at *interfaces*. Each subchapter contains sections for different classes of analyzed material such as metals, semiconductors, and insulators. Further subsections then single out particular materials or hydrogen interaction phenomena investigated by (mainly $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$) NRA. Chapter 4 draws brief conclusions.

2. Hydrogen depth profiling by resonant nuclear reaction analysis

This chapter describes the principle and experimental requirements of hydrogen depth profiling by resonant nuclear reaction analysis. It is meant as a practical compendium providing the relations necessary to enable even the reader without profound experience in ion beam analysis or nuclear physics to measure, analyze, and interpret resonant NRA data without extensive need for external references. Several original papers and earlier reviews offer general introductions of H depth profiling by resonant NRA [49-53, 72, 85-90]. Surface-analytical NRA applications with a particular focus on high-resolution measurements at atomic-level controlled single crystal and interface targets have appeared only rather recently [56-58, 65, 83, 91].

2.1 Principles of resonant NRA

2.1.1 Fundamentals

In the laboratory a nuclear reaction can be induced by colliding an accelerated projectile nucleus (a) with a resting target nucleus (A) at an energy that exceeds the Coulomb barrier between the two nuclei. In general, a stable residual nucleus (B) is formed in one direct or several intermediate steps under emission of one or several

particles (B b') (protons, α -particles, β -emission, γ -rays, etc.) that carry characteristic energies. The general notation for a nuclear reaction ($a + A \rightarrow B + b$) is $A(a,b)B$. In nuclear reaction analysis (NRA) one determines the concentration of a nucleus (A) in a specimen by bombarding the target with accelerated projectile ions (a) and detecting the particles (b) emitted in the $A(a,b)B$ nuclear reaction. The reaction yield, Y_B determines the sensitivity to detect an areal density of (A) nuclei (n_A [cm^{-2}]) and is proportional to the flux (N_i [$\text{cm}^{-2} \text{ s}^{-1}$]) of incident projectiles and to the energy-dependent cross section of the nuclear reaction, $\sigma(E)$ [cm^2]: $Y_b(E) = \sigma(E)N_i n_A$. Certain collision energies are resonant to excited levels of stable nuclei that may form as reaction intermediates and are referred to as compound nuclei. At such energy resonances (E_R) the reaction cross section $\sigma_R = \sigma(E_R)$ can be enhanced by several orders of magnitude. Owing to a multitude of excited states in light nuclei ($Z < 20$) that are accessible in particle collisions at several MeV energy [92, 93] [94], a vast variety of reaction channels exists, but only a very few have practical importance. In general, nuclear reaction resonances suited to analytical depth profiling have the following characteristics: (1) a large resonant cross section σ_R and a small off-resonance cross section ($\rightarrow$ sensitivity), (2) a narrow resonance width (Γ) ($\rightarrow$ depth resolution), (3) a low resonance energy E_R ($\rightarrow$ accelerator size required to generate the projectile beam), and (4) a large separation from the next resonance at higher energy ($\rightarrow$ probing depth range).

Table 1 lists several resonant nuclear reactions applicable to hydrogen (H) detection that fulfill the above criteria more or less ideally. The data are compiled from studies that explored the potential of various nuclear reactions for H profiling

[51, 53, 71, 85, 86, 89]. The product $\sigma_R \Gamma$ is proportional to the integral resonant cross section and hence defines the achievable sensitivity for H detection (Eqs. (2.11) and (2.12)); these reaction yield values are also given relative to $\sigma_R \Gamma$ of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ at 6.385 MeV for comparison. The Γ/S entry is a rough indicator for the near-surface depth resolution (S is the stopping power of the ion projectile). The actually realized resolution is worse due to the Doppler broadening effect that depends on the H vibration frequency on a specific sample material [64, 66, 95] (Section 2.2.3). When the Doppler broadening width is known, the achievable near-surface resolution can be evaluated from the listed Γ and S values through Eq. (2.15) at $z = 0$.

Reaction	$^7\text{Li}+\text{H}$	$^{15}\text{N}+\text{H}$	$^{15}\text{N}+\text{H}$	$^{19}\text{F}+\text{H}$	$^{19}\text{F}+\text{H}$
Resonance energy [MeV]	3.07	6.385	13.35	6.418	16.4
Cross section (σ_R) at resonance [mbarn]	4.8	1650	1050	88	440
Resonance width (Γ) [keV]	81	1.8	25.4	44	86
$\sigma_R \Gamma$ [mbarn-keV]	389	2970	26700	3870	37800
Relative yield	0.13	1.0	9.0	1.3	12.7
$S = dE/dz$ in Si [keV/nm]	0.442	1.45	1.35	1.94	1.94
Γ/S [nm]	183	1.2	18.8	22.6	44.3
Energy of next resonance [MeV]	7.11	13.35	18.0	9.1	17.6
Gamma-ray energy [MeV]	14.75, 17.75	4.43	4.43	6.13, 6.98, 7.12	6.13, 6.98, 7.12

Table 1. Characteristics of nuclear reaction resonances useful for H detection with NRA. Data from Refs. [41, 43, 72].

The first resonance of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction at 6.385 MeV has been by far most widely applied for surface-near H depth profiling owing to its particularly narrow ($\Gamma=1.8$ keV) [96, 97], intense ($\sigma_R = 1650$ mbarn), and isolated shape [89, 98-100]. As shown in Fig. 1, the ratio of the on-resonant to the nearby off-resonance cross-section (77 μbarn) is larger than 10^4 , earning it the attribute of ‘Mona Lisa of resonances’ from Amsel, one of the founding fathers of resonant NRA [100].

Fig. 1. The narrow resonance of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction cross section at 6.385 MeV. The resonance peak is more than four orders of magnitude larger than the nearby off-resonant cross section. Reproduced from Ref. [41] with permission from Elsevier.

Together with the large separation to the next resonance at 13.35 MeV, these properties provide for an outstanding near-surface depth resolution ($\sim 1\text{-}5$ nm, Section 2.2.3), good sensitivity (~ 100 ppm, Section 2.2.4), and a practical probing depth range ($2\text{-}4$ μm , Section 2.2.3) at an energy that can still be realized with moderately sized accelerators. All near-surface high resolution work reviewed herein has been performed with this reaction. We therefore choose $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ as the most representative example to describe in the following the principles of hydrogen depth profiling with resonant NRA. A brief comparison to other resonant nuclear reactions in Table 1 will be given in Section 2.1.2.

The hydrogen depth profiling method by resonant NRA via ${}^1\text{H}({}^{15}\text{N},\alpha\gamma){}^{12}\text{C}$ is schematically illustrated in scheme (2.1) and in Fig. 2. The analyzed sample is subjected to a beam of accelerated and energy-monochromatized ${}^{15}\text{N}$ ions that may induce the following nuclear reaction with protons in the target:

At the resonance energy $E_R = 6.385$ MeV, an excited ${}^{16}\text{O}$ nucleus is formed as the intermediate compound, which undergoes an α -decay into the first nuclear excited state of ${}^{12}\text{C}$ [101]. The latter finally relaxes to the ${}^{12}\text{C}$ ground state by releasing characteristic γ -radiation of 4.4389 MeV [102]. The emitted γ -rays (and the α -particles) provide signals proportional to the H concentration at a certain depth in the target. For reasons explained in Section 2.2.4, γ -detection is preferred in practice. The residual ${}^{12}\text{C}$ nucleus retains a large forward velocity component in the incidence direction of the ${}^{15}\text{N}$ projectiles and is deposited into the target (at much larger depth than the analyzed region).

Information on the H depth location is obtained as follows. The resonance in the ${}^1\text{H}({}^{15}\text{N},\alpha\gamma){}^{12}\text{C}$ reaction cross section at $E_R = 6.385$ MeV with a width of only 1.8 keV [95, 96, 98] is extremely sharp (Fig. 1). From the peak value at E_R $\sigma(E)$ falls steeply to a 4 orders of magnitude smaller off-resonance cross section [51], setting a very narrow energy window for the nuclear reaction. Only ${}^{15}\text{N}$ projectiles incident with the energy $E_i = E_R$ can thus undergo the nuclear reaction with H atoms on the target surface (Fig. 2). The MeV ${}^{15}\text{N}$ ions penetrate into the target and experience energy

loss by electronic stopping while travelling through the material (they eventually come to rest at an implantation depth of several μm , far beyond the analyzed depth region of interest).

Fig. 2. Depth-resolved H detection with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA. ^{15}N ions accelerated to E_i strike the sample. For $E_i = E_R$, ^{15}N reacts with H on the surface, whereas for $E_i = E_R + \Delta E$, ^{15}N reacts with H in a depth $d = \Delta E \cdot \cos \alpha_i / S$. The excitation curve $Y(E_i)$ (γ -ray yield as a function of the incident ^{15}N energy (E_i)) reveals the H depth distribution in the target convolved with the instrumental function. The latter broadens with increasing depth due to energy straggling of the ^{15}N ion.

This energy loss ΔE is proportional to the trajectory length z that the ion has propagated inside the target ($z = 0$ at the surface) and to the material specific stopping power $S = (dE/dz)$:

$$\Delta E = S \cdot z. \quad (2.2)$$

Stopping powers for ^{15}N near 6.4 MeV range in the order of $\sim 1\text{--}4 \text{ keV/nm}$ [103, 104] for elemental targets, so that the energy loss by penetrating only a few atomic

layers suffices to shift the ^{15}N ion energy out of the nuclear reaction energy window spanned by the narrow cross section resonance. When the ^{15}N beam strikes the target at an angle α_i with the surface normal ($0 \leq \alpha_i < 90^\circ$), the trajectory length to penetrate into a depth d below the surface is $z = d/\cos\alpha_i$ (d is measured in the surface normal direction). Thus a ^{15}N incident energy $E_i = E_R + \Delta E$ corresponds to a well-defined probing depth $d = \Delta E \cos\alpha_i / S$ inside the target (Fig. 2). To obtain hydrogen depth profiles the incident energy of the ^{15}N ions is scanned stepwise to position the resonant reaction energy window at varying depths within the target while collecting the γ -yield. The experimental excitation curve $Y(E_i)$ (reaction yield versus incident projectile energy) thus displays the depth distribution of the hydrogen density projected into the ion beam direction, $n_H(z)$, yet in a convolution (*) with an effective instrumental function $F(E, E_i, z)$:

$$Y(E_i) = KN_i \int_0^\infty F(E, E_i, z) * n_H(z) dz \quad . \quad (2.3)$$

K denotes the γ -detection efficiency of the experimental system, which includes the quantum efficiency and solid angle of the detector, as well as its position relative to the beam axis (Section 2.2.4). $F(E, E_i, z)$ is defined in Eq. (2.4) and reflects the broadening of the reaction energy window beyond the nuclear reaction resonance width Γ by three physical effects that independently cause variations of the ^{15}N -H collision energy: (i) the energy distribution of the incident ion beam, $B(E, E_i)$, Eq. (2.6), (ii) a Doppler effect due to zero-point vibration of the H atoms within their bonds to the target, $D(E)$, Eq. (2.7), and (iii) trajectory length dependent energy straggling of the ^{15}N projectiles in the target material, $S(E, z)$, Eq. (2.9). In the instrumental

function $F(E, E_i, z)$ the nuclear reaction cross section $\sigma(E)$ is convolved with these three spectral components:

$$F(E, E_i, z) = \sigma(E) * B(E, E_i) * D(E) * S(E, z) . \quad (2.4)$$

The cross section resonance of the nuclear reaction has the Lorentzian line shape of a Breit-Wigner dispersion function, where E_R , σ_R , and Γ denote the resonance energy, the maximum, and the spectral width of the cross section, respectively:

$$\sigma(E) = \sigma_R \frac{\Gamma^2 / 4}{\Gamma^2 / 4 + (E - E_R)^2} . \quad (2.5)$$

The incident ion beam energy distribution (as delivered by the accelerator) can usually be approximated by a Gaussian function with a width parameter δ_B (standard deviation) [96]:

$$B(E, E_i) = \frac{1}{\sqrt{2\pi}\delta_B} \exp\left(-\frac{(E - E_i)^2}{2\delta_B^2}\right) . \quad (2.6 \text{ a})$$

The experimentally accessible beam energy spread ΔE_B is the full width at half maximum (FWHM) of this distribution:

$$\Delta E_B = [8 \ln(2)]^{1/2} \delta_B = 2.3548 \delta_B . \quad (2.6 \text{ b})$$

(In the special situation that the ion beam is monochromatized, $B(E)$ has a triangular shape (cf. Fig. 3), which reflects the transmission function of the entrance and exit slits of the energy analyzer and the approximately linear relationship between the beam energy and small distances from the center beam axis in the focal plane of the analyzing sector magnet (Section 2.2.1):

$$B(E, E_i) = \begin{cases} 0 & E \leq E_i - \Delta E_B \\ 1 + (E - E_i)/\Delta E_B & E_i - \Delta E_B < E \leq E_i \\ 1 - (E - E_i)/\Delta E_B & E_i < E < E_i + \Delta E_B \\ 0 & E \geq E_i + \Delta E_B \end{cases} \quad (2.6 \text{ c})$$

The spatial confinement of the hydrogen atoms inside their chemical bond potentials causes an inevitable uncertainty of their momentum according to the Heisenberg relation, and the wave function of the resulting zero-point vibration is Gaussian in momentum space (assuming a harmonic oscillator model for the nuclear motion). Although the zero-point vibrational energy E_H of the H nuclei is small (some tens of meV) compared to the nuclear reaction energy E_R , the resulting Doppler shift of the ^{15}N -H collision energy translates into a sizeable Gaussian broadening $D(E)$ [63, 64, 66, 95] of several keV FWHM (cf. Section 3.1.3, $\text{Si}_{1-x}\text{Ge}_x$):

$$D(E) = \frac{1}{\sqrt{2\pi}\delta_D} \exp\left(-\frac{E^2}{2\delta_D^2}\right). \quad (2.7)$$

As derived in Ref. [64], the width parameter (δ_D) of this Doppler-broadening distribution relates as follows to E_H , E_R , and the masses of the H (m_H) and ^{15}N (m_N) nuclei [67, 95]:

$$\delta_D = \sqrt{\frac{2m_N E_H E_R}{m_H}}, \quad (2.8)$$

i.e., the Doppler broadening width $\Delta E_D = 2.3548 \delta_D$ (FWHM) increases in proportion to the square root of the H zero-point vibrational energy E_H .

Along the trajectory of the probing ions in the target, the center of their energy distribution decreases linearly with the propagation length z from the surface due to electronic stopping (Eq. 2.2). Straggling, an energy fluctuation caused by multiple weak scattering interactions of the ion with the target electrons, simultaneously broadens this energy distribution. Due to the stochastic nature of the straggling process the energy broadening function is Gaussian and its width parameter increases in proportion to the square root of the ion trajectory length in the analyzed material ($\delta_s(z) \propto (z)^{1/2}$, Section 2.1.4) [105, 106]:

$$S(E, z) = \frac{1}{\sqrt{2\pi}\delta_s(z)} \exp \left(-\frac{(E - \Delta E(z))^2}{2(\delta_s(z))^2} \right). \quad (2.9)$$

Since all broadening components (i)-(iii) are Gaussian [approximately also for monochromatized beams] they convolve into a Gaussian broadening function $G(E, E_i, z) = B(E, E_i) * D(E) * S(E, z)$ with a spectral width parameter $\delta_G^2 = \delta_B^2 + \delta_D^2 + (\delta_s(z))^2$. Convolution with the Lorentzian reaction resonance $\sigma(E)$ has to be done numerically [96], which finally yields the instrumental function $F(E, E_i, z) = \sigma(E) * G(E, E_i, z)$ in shape of a Voigt profile. There is no analytical expression for the spectral width of the Gaussian-broadened Lorentzian resulting from this convolution, but Briere et al. have suggested a numerical approximation for the resulting total energy width ΔE_{tot} (FWHM) of the instrumental function as [107]:

$$\Delta E_{\text{tot}} = 0.56 \Gamma + [8 \ln(2) (\delta_B^2 + \delta_D^2 + (\delta_s(z))^2)]^{1/2}. \quad (2.10)$$

With the known components $\sigma(E)$, $B(E, E_i)$, $D(E)$, and $S(E, z)$ of the instrumental function $F(E, E_i, z)$, the H concentration distribution $n_H(d)$ can be determined from

experimental excitation curves $Y(E_i)$ by numerical deconvolution (Section 2.2.7). Resonance width parameters (Γ) of several nuclear reactions relevant to H-profiling are listed in Table 1. The incident ion beam energy spread ΔE_B must be determined experimentally [108] or can be calculated from the resolution of the accelerator's energy analyzer (Section 2.2.1). Refer to Section 2.1.4 for methods to estimate the straggling cross section $\delta_s(z)$.

For surface hydrogen the Doppler broadening function $D(E)$ can be determined experimentally by providing a target on which hydrogen is present exclusively on the surface. Since the H solubility in crystalline silicon is immeasurably small [109], the NRA excitation function obtained from a H-terminated Si(111)(1x1) surface shown in Fig. 3 is a good example for this situation. A perfectly symmetric resonance profile centered at $E_R = 6.385$ MeV is observed, its integral being proportional to the surface H coverage according to Eq. (2.11) (below). $D(E)$ is obtained through numerically deconvoluting $\sigma(E)$ and $B(E, E_i)$ from the experimental yield curve. (In practice, the known $\sigma(E)$ and $B(E, E_i)$ functions are convolved with a series of test Gaussian $D(E)$ functions of various width parameters (δ_D in Eq. (2.7)) until the δ_D value is found for which the total convolution result $Y(E_i) = \sigma(E_i) * B(E, E_i) * D(E)$ adequately reproduces the experimental data.) For the example in Fig. 3, this analysis yields $\delta_D = 4.9$ keV [67]. It is seen in Fig. 3 that the Doppler broadening ($\Delta E_D = 2.3548 \delta_D = 11.4$ keV, FWHM) is by far the dominant contribution to the total width of the surface resonance curve, which therefore appears almost Gaussian in shape (the Lorentzian tails of the actual Voigt profile become visible by plotting the γ -yield on a logarithmic scale).

Fig. 3. Spectral decomposition of a surface resonance excitation curve (filled symbols) measured at Si(111)(1×1)-H with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA near $E_R = 6.385$ MeV in surface-normal ^{15}N incidence, showing the nuclear resonance (Lorentzian, $\Gamma=1.8$ keV, long-short-dashed line), the incident ion beam energy distribution (triangular, $\Delta E_B = 3$ keV, dashed line), the Doppler broadening (Gaussian, red dotted line), and their convolution (solid line through data points). Data from Ref. [67].

Since the Doppler broadening effect is so significantly manifested in the surface resonance excitation curves, the zero-point vibrational energy of surface-adsorbed H atoms (E_H) can be determined directly from the width parameter δ_D via Eq. (2.8.) [63-65, 67, 95]. This is a unique feature of resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA at 6.385 MeV. More examples of this application for the systems H/W(100), H/Ir(111), H/Pt(111), H/Rh(111), H/Si(111), and H adsorbed on SiGe(100) alloy surfaces are discussed in Sections 3.1.2 and 3.1.3.

The vibrational frequency of low-coordinated H at surfaces and interfaces is expected to be harder than that of bulk-dissolved H in interstitial sites. Hence, the Doppler broadening width parameter of surface H determined above must be

regarded an upper limit estimate for δ_D of H absorbed below the surface of a given material. Measuring the Doppler width of the latter directly with NRA seems impossible due to the difficulty to provide a target in which absorbed H would assume a delta function like depth distribution (confined to a single atomic layer such as on the surface or at an interface). If available, substituting H zero-point energies (E_H) deduced in a harmonic approximation from vibrational spectroscopic data of H in bulk materials into Eq. (2.8) may thus provide a more appropriate estimate of δ_D for interstitial hydrogen below the surface.

Fig. 4. Principle shape of the NRA excitation function $Y(E_i)$ resulting from (a) H situated exclusively on the surface and (b) from a uniform H concentration in the target volume (bulk).

For the quantitative determination of hydrogen surface coverages and volume concentrations it is instructive to consider two idealized limiting cases of hydrogen depth-concentration distributions $n_H(d)$:

1.) *Surface hydrogen*: The first situation is a surface layer of adsorbed H atoms without any hydrogen below the surface (as in the above example). Let N_s be the (substrate) surface areal density [atoms/cm²] and θ_H the hydrogen coverage in monolayers (ML). Then the H distribution is $n_H(d) = \theta_H \cdot N_s$ at the surface ($d = 0$) and zero elsewhere ($d \neq 0$), and Eq. (2.3) becomes:

$$Y(E_i) = K \cdot N_i \cdot \theta_H \cdot N_s \cdot F(E, E_i, 0), \text{ and}$$

$$\int Y(E_i) dE_i = K N_i N_s \sigma_R \left(\frac{\pi \Gamma}{2} \right) \theta_H. \quad (2.11)$$

The characteristic excitation curve of surface hydrogen is a peaked profile centered at E_R that reflects the Gauss-Lorentz (Voigt) shape of the instrumental function (Fig. 4 (a)). The integrated γ -yield under the profile is proportional to the number of hydrogen atoms on the surface, $\theta_H \cdot N_s$. By normalizing the yield $Y(E_i)$ to the number of incident ¹⁵N ions (N_i) the hydrogen coverage can be evaluated quantitatively once the γ -detection efficiency of the setup (K) has been determined through calculation or calibration with a standard of known H concentration (Section 2.2.6).

2.) *Bulk hydrogen*: The second situation to consider is a homogeneous H volume density c_b [atoms/cm³] in the target, i.e. a rectangular concentration jump at the surface ($d = 0$): $n_H(d) = c_b$ for $d > 0$. Convolving this H distribution with the instrumental function yields an excitation curve $Y(E_i)$ that rises in a sigmoid shape and asymptotically approaches an intensity plateau as depicted in Fig. 4 (b), attaining

its half-height at E_R . At incident projectile energies sufficiently far above E_R ($E_{>}$), the γ -yield becomes constant and is then proportional to the bulk H concentration:

$$Y(E_{>}) = KN_i \sigma_R \left(\frac{\pi \Gamma}{2} \right) c_b / S . \quad (2.12)$$

Equation (2.12) shows that the H volume concentration c_b in a target can be evaluated by a single measurement of the γ -yield at any projectile energy ($E_{>}$) sufficiently far above the rising surface edge of the excitation curve (Fig. 4). In such measurements (such as for sensitivity calibration, Section 2.2.6) it is always recommendable to experimentally verify the energy $E_{>}$ at which $Y(E_i)$ attains the bulk plateau height, since the H distribution may be inhomogeneous in the near-surface region (Section 3.2.3.6). If the H concentration in the target is ideally depth-independent, one may estimate $E_{>}$ from the nuclear reaction resonance width (Γ). The $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ cross section width near the 6.385 MeV resonance ($\Gamma = 1.8$ keV) is much smaller than the Gaussian width components in the NRA instrumental function (convolved Doppler and beam energy broadenings, typically $\delta_G \sim 6.5$ keV, Fig. 3), yet its broad Lorentzian wings still contribute significant γ -yield at energies quite far above E_R . The cumulative integral of the Lorentzian (Cauchy distribution) indicates that the full plateau height is approached except for a small percentile (p) when $E_{>}$ is chosen as: $E_{>} = E_R + \frac{1}{2} \Gamma \cdot \tan [((1-p) - 0.5) \pi]$. If one accepts 1% error ($p = 0.01$), this evaluates $E_{>}$ to $E_R + 29.4$ keV ($E_R + 404$ keV) for the 6.835 MeV (13.35 MeV, $\Gamma = 25.4$ keV) resonance, which is considerably larger than even a $3\delta_G$ interval of the Gaussian component.

Note that Eq. (2.12) resembles Eq. (2.11), but that the stopping power $S = (dE/dz)$ enters as an additional factor resulting from substituting the integration variable from z to E in Eq. (2.3) ($dz = dE/S$). This means that if two materials contain the same absolute H density, the one with the larger stopping power will give a smaller γ -yield. The physical implication is that a large stopping power shifts the energy of the projectile ion away from the resonance within a short traveling distance, thus reducing the probability of the ion to encounter H atoms while its energy is within the resonant reaction window.

2.1.2 Merits of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$

Having laid out the principles of resonant NRA, the suitability of the various nuclear reaction resonances in Table 1 for H profiling can now be compared. As noted, the well isolated first resonance of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction at $E_R^{(1)} = 6.385$ MeV offers the most versatile combination of favorable properties. Its narrow resonance width ($\Gamma^{(1)} = 1.8$ keV), large cross section ($\sigma_R = 1650$ mbarn, Fig. 1), and large separation to the next resonance provide excellent near-surface depth resolution ($\sim 1\text{-}5$ nm), high sensitivity (~ 100 ppm, Section 2.2.4), and a reasonable probing range ($2\text{-}4$ μm , Section 2.2.3). At the expense of near-surface depth resolution, also the considerably wider ($\Gamma^{(2)} = 25.4$ keV) second resonance of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ at $E_R^{(2)} = 13.35$ MeV is available, which offers ~ 9 fold increased sensitivity owing to its larger cross section integral ($\propto \sigma_R \Gamma$).

This is demonstrated in Fig. 5, which compares the NRA profiles of a ~ 40 nm thick hydrogenated SiN layer on a H-free Si(100) backing recorded with the first and second $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonances, respectively. Observe the strongly increased γ -yield in the 13.35 MeV profile (Fig. 5 (b)). The intensity ratio of two curves [$I(13.35 \text{ MeV})/I(6.385 \text{ MeV})$] amounts to 8.7 ± 0.2 , which reflects the integral ratio of the cross-section resonances. The much inferior depth resolution of the 13.35 MeV profile is also apparent. The slight inclination of the H plateau concentration against the surface of the thin SiN film - clearly seen in the high-resolution yield curve at 6.385 MeV - induces only a barely recognizable asymmetry in the 13.35 MeV profile [110]. This resolution disadvantage of the broader 13.35 MeV resonance will never vanish but be less significant for probing H in deeper target regions where ^{15}N straggling becomes the major resolution limiting factor (Sections 2.1.4 and 2.2.3).

Fig.5. Hydrogen depth profiles of H:SiN/Si(100) measured with the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonances at (a) 6.385 MeV and (b) at 13.35 MeV. Bold lines represent simulated yield curves based on the same H depth distribution. Reproduced from Ref. [110] with permission from Elsevier.

The larger γ -yield at 13.35 MeV can be useful to determine small H bulk contents, yet as explained in Section 2.2.4, disturbing γ -yield due to the interaction of surface

H with the non-resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction cross section above ~ 10 MeV may become a concern for such measurements, since the ratio of the resonant to the off-resonant cross section near 13.35 MeV is far less favorable than at 6.385 MeV (Fig. 10) [98, 100, 110, 111]. Also the probing depth range of 13.35 MeV resonant NRA is shorter as compared to that of the 6.385 MeV resonance, since a third resonance follows already at 18.0 MeV and the ^{15}N stopping power is slightly (up to $\sim 20\%$) smaller at 13.35 MeV than at 6.385 MeV (Table 1 and Section 2.2.3).

The 6.42 MeV and 16.44 MeV resonances of the $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ reaction have inferior near-surface depth resolution and shallower probing depth ranges (Section 2.2.3) relative to the respective resonances of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$, but especially the 16.44 MeV resonance has a large cross section that enables highly sensitive H detection. Several applications of $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ are reported [86, 112-116], among them also the notably very first demonstration of hydrogen profiling measurements with resonant NRA by Leich and Tombrello in 1973 [117] that even preceded Lanford's application of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction by a few years [49]. For a direct comparison of ^{19}F and ^{15}N NRA see Ref. [112]. Compared to the ^{15}N and ^{19}F reactions, the 3.07 MeV resonance of the $^1\text{H}(^7\text{Li}, \gamma)^8\text{Be}$ reaction offers neither a particularly favorable energy width for high-resolution near-surface H profiling nor a suitably large resonance cross section for highly sensitive measurements, although the explorable depth range ($\sim 6 \mu\text{m}$) is the largest of the listed resonances owing to the small stopping power of the ^7Li projectiles [53]. Worth mentioning is also the $^1\text{H}(^{18}\text{O}, \alpha)^{15}\text{N}$ reaction (not listed in Table 1), which has a 43 keV wide resonance of 75 mbarn at 11.25 MeV and produces α particles in an energy region of low background (< 4.3

MeV), and can thus be used for rather sensitive bulk H concentration measurements (<10 ppm) [53, 118].

Although this review focuses primarily on highly depth-resolving resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA, we should mention that also a widely used nuclear reaction technique for deuterium profiling exists, namely $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA [119, 120]. The $\text{D}(^3\text{He}, \text{p})^4\text{He}$ reaction produces protons of ~ 13 MeV and α particles of 2-4 MeV energy that are easily identified [51, 119, 120]. The $\text{D}(^3\text{He}, \text{p})^4\text{He}$ cross section has a very broad (~ 350 keV) peak (~ 900 mbarn total) at 650 keV [121]. Since furthermore the stopping powers for the product He particles and protons are small, the reaction offers almost no depth resolution (~ 500 nm near the surface). Nonetheless, $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA can be conducted with small accelerators (even with 400 keV He^{3+}) and has thus found wide application in studies of important hydrogen-material interactions. The large resonance width allows quantifying the D content in the entire near-surface region [122], which has been instrumental in establishing fundamental surface properties such as absolute D saturation coverages (Chapter 3.1, Table 3) for materials that do not absorb hydrogen, as well as D uptake/release and relocation kinetics in hydrogen absorbing (or D-implanted) materials (cf. Sections 3.2.3.4-6). Notably, Davis and Norton evaluated the differential cross section at 750 keV to (54.5 ± 1.7) mbarn sr^{-1} and performed the first quantitative measurements of D coverages at Pt surfaces [123]. For detailed descriptions of the $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA technique refer to Refs. [119] and [120], which also provide excellent general introductions to hydrogen depth profiling with NRA.

2.1.3 Energy loss and stopping power

In order to convert the energy abscissa of experimental NRA excitation curves (γ -yield vs. incident ^{15}N energy, Figs. 2 and 4) into a probing depth scale ($d = \Delta E \cos \alpha_i / S$), it is necessary to know the specific energy loss $S = (dE/dz)$ of the projectiles. The stopping power S is also required to derive absolute H concentrations from γ -yield measurements at bulk targets (Eq. 2.12); hence it is essential for the sensitivity calibration of the experimental system described in Section 2.2.6. A table with S values for ^{15}N at 6.385 MeV in all elemental targets is provided in Appendix A (data from Ref. [124]). An extensive body of experimental (dE/dz) values has been compiled in large databases, such as the frequently cited ‘Stopping cross section values for energetic ions in all elements’ by Ziegler [103, 104]. This database is included in a simulation program for the calculation of electronic stopping and ranges, SRIM (*The Stopping and Range of Ions in Matter*). The database is expanded and the software updated regularly [125-127] and can be obtained free of charge for non-commercial research purposes from the SRIM website [128]. Stopping cross section curves of light ions in many elements and compounds are also made available in graphic form on the website maintained by Paul at Linz University [129].

The stopping power is characteristic for any given ion projectile-material combination and in principle energy-, more precisely, velocity-dependent [130]. Several theories of the stopping process have been developed by Bohr [105, 131, 132], Bethe [133], Bloch [134, 135], Lindhard and Scharff [136], and Firsov [137]. ‘Slow’ ions traveling at velocities much smaller than the Bohr velocity ($v_0 = e^2 / (4\pi\epsilon_0\hbar) = 2.188 \times 10^6$ m/s, or 25 keV/amu) of the valence electrons (i.e., $v \ll 0.1 v_0$) tend to

get neutralized by electron capture, so that the interaction with the target atoms is one of neutral elastic collisions. This so-called ‘nuclear stopping’ decreases with $1/E$. At ‘intermediate’ velocities, i.e., $v \sim 0.1 v_0$ to $Z_1^{2/3} v_0$ (Z_1 is the atomic number of the ion), the probing particles attain an equilibrium charge state by charge exchange processes with the target material [138]. They propagate at velocities corresponding to multiples of v_0 , which results in energy loss by collision-induced excitations of target electrons. This energy loss process is proportional to the velocity or $E^{1/2}$ and referred to as ‘electronic stopping’. At yet much higher velocities ($v \gg v_0$, ‘swift’ ions) the projectiles become fully stripped of their electrons, after which the stopping cross section decreases with increasing energy as the interaction time gets shorter [133]. The result is an overall energy dependence of the electronic stopping cross section that shows a characteristic broad maximum (‘Bragg peak’) near velocities of $\sim 1\text{-}2$ MeV/amu for light nuclei in most elements [103, 129]. The SRIM program package for electronic stopping and range calculations uses a semi-empirical parameterization of the effective charge state [125, 126].

In the intermediate energy range of typical NRA projectiles (^{15}N of $E_i \geq 6.4$ MeV; $v \geq \sim 4v_0$), the dominant energy loss mechanism is electronic stopping. The nuclear stopping cross section amounts to less than 1% of the electronic stopping cross section and is hence safe to neglect. Stopping powers for ^{15}N at 6.385 MeV are well known in all elements and range from ~ 1 to ~ 4 keV/nm for light (C) and heavy (Pt) elements, respectively [103, 124]. Although S is principally energy-dependent, the stopping-induced energy losses in shallow near-surface H profiling ($z \leq 100$ nm) are so small ($\Delta E \leq \sim 0.4$ MeV) that the (dE/dz) value of ^{15}N at 6.4 MeV can safely be

regarded as a material-specific constant in the applications reviewed herein (*surface approximation*). Note that at a given velocity, $v = (2E/M_1)^{1/2}$, the energy loss by electronic stopping scales with the square of the ion's atomic number, Z_1^2 , so that the (dE/dz) values for ^{15}N are to be taken from data tables or stopping cross section charts of ^{14}N [103].

Except for a limited number of compounds, the databases contain the stopping cross sections (ε) of ions in elemental targets. The stopping cross section for compound materials can be estimated in a first approximation, the so-called *Bragg Rule*, as a linear combination of the respective cross sections of the constituting elements [139]:

$$\varepsilon(A_n B_m) = n \varepsilon_A + m \varepsilon_B, \text{ where } n + m = 1. \quad (2.13)$$

Bragg's rule assumes that the stopping process is independent of the bonding state of the valence electrons between the atoms in a material. This assumption is generally well fulfilled for the velocity range of ^{15}N projectiles used for NRA on heavier targets. Noticeable deviations from Bragg's additivity rule may occur, however, when strong hybridizations in compounds of light elements are present such as in organic hydrocarbons [140, 141] or amorphous hydrogenated silicon carbide [142], especially for light projectile ions at low energy, such as He used in ERD or RBS. To account for the chemical bonding state of elements in compounds, Ziegler and Mayonan introduced corrections to the Bragg rule that consider (atomic) cores and bonds (electrons) separately (CAB model) [140]. The accuracy of different semi-empirical parameterizations of the energy loss in simulation codes relative to

experimental stopping power data is still subject of ongoing research [143-145]. The SRIM program is being refined continuously to achieve an ever better agreement of the simulations with the experimental data [126].

In converting experimental NR excitation curves into H concentration depth profiles, the stopping power quantitatively affects the depth scale (Eq. 2.2) as well as the bulk H content (Eq. 2.12). If the target contains a sizeable H concentration (on the order of several atomic %), the material's stopping power will in turn depend on this H content. To determine stopping power and H concentration in such cases, the (dE/dz) value is first to be approximated with Bragg's rule for a roughly estimated H content. This approximate stopping power is then used to derive a first H concentration value from the experimental NRA data. In a second iteration of the analysis this H concentration is used to calculate a refined (dE/dz) value, with which the H content is evaluated again. After a few repetition cycles the process should converge to produce consistent values of H content and stopping power.

2.1.4 Straggling

Straggling becomes the dominant limitation of the depth resolution (Section 2.2.3) from probing depths beyond several nm, the precise value depending on the stopping power and straggling cross section of the projectile in the target. Straggling is a complicated stochastic process related to multiple scattering of the ions with electrons in the target. It depends on both the analyzing ion beam and the target material, i.e., on the atomic mass (M_1), atomic number (Z_1), energy (E_1), and charge state (q) of the projectile in the target, as well as on the target element (Z_2), its

number density N [atoms cm^{-3}], and its electronic structure [111, 130]. The collisions between the projectile and the target electrons are strongly correlated, i.e. not independent of previous interactions. Various theories have been developed to describe the process in different projectile velocity regimes and for light as well as for heavier ions [105, 146-149]. Bohr's theory [105] assumes that the target atoms are randomly distributed, that the energy loss during a single collision is much smaller than the width of the energy loss distribution, and that the projectile velocity is much greater than the orbital electron velocity of the target atoms, i.e., $v \gg v_0/Z_2^{1/2}$ ($v_0 = e^2/(4\pi\epsilon_0\hbar) = 2.188 \times 10^6 \text{ m s}^{-1}$). In this high velocity regime the energy distribution is Gaussian, with an almost velocity-independent width parameter (the Bohr straggling cross section): $\Omega_s^2 = Z_1^2 Z_2 e^4 N \Delta h / (4\pi\epsilon_0^2)$. $N \Delta h$ gives the density (in atoms/ cm^2) of the target penetrated by a thickness Δh [130]. At medium and low projectile energies the assumption of velocity-independent straggling is not valid. The Lindhard-Scharff theory [147] extends Bohr's theory by adding a correction factor for medium- and low-energy projectiles, where $v^2 \leq 3Z_2 v_0^2$ [130]. The Hvelplund theory [149] applies for heavy ions in the low-velocity range, i.e., $v < v_0 Z_1^{2/3}$, where the electronic stopping is proportional to the projectile velocity, and when Z_1 and Z_2 do not differ by more than a factor of 4. This theory takes the binding of target electrons and their spatial distribution into account [106, 111].

Unfortunately, rather few systematic investigations of straggling cross sections for ^{15}N projectiles in solid targets exist in the NRA relevant energy range, and the agreement with the above theoretical models is sometimes far from satisfactory. Rud et al. compiled a larger body of experimental straggling FWHM values of ^{15}N at

6.5 MeV in various elemental targets (C, Al, Cu, Ge, Ag, Sn, Bi) and found that the straggling width (FWHM) divided by $Z_2^{0.39 \pm 0.02}$ scales proportional to the square root of the penetrated thickness [106]. Hjörvarsson and Ryden measured the straggling of 6.5-10 MeV ^{15}N in Au thin films and found that their data matched Rud's results very closely as seen in Fig. 6. Here, the broken line is a fit to Rud's empirical formula [111]:

$$\delta_s = 2.03 Z_2^{0.39} \text{thickness}^{1/2}, \quad (2.14)$$

with δ_s in keV and the thickness in $10^{16} \text{ atoms/cm}^2$.

Fig. 6. Comparison of experimental straggling width parameters of 6.4 MeV ^{15}N from Refs. [106] (+) and [111] (•) with theoretical estimations of maximum electronic straggling. The dotted line represents the empirical formula by Rud (Eq. (2.14)). Reproduced from Ref. [111].

For ^{15}N projectiles incident on Au above 6.4 MeV, $v > 4v_0$, so in terms of the above theories, the Bohr theory should apply at ^{15}N energies much higher than 5

MeV and the Lindhard-Scharff theory should be valid for ^{15}N energies below 85 MeV. The validity range of the Hvelplund theory for ^{15}N in Au ends at energies below 5 MeV and also $Z_2/Z_1 > 4$, so this model is not expected to describe the straggling well for NRA conditions, which is indeed the case as the comparison to Hjörvarsson's and Rud's data in Fig. 6 shows. The Bohr and Lindhard-Scharff theories, on the other hand, appeared to underestimate the straggling effect. A few years later Briere and Biersack [150] as well as Goppelt-Langer et al. [151] independently made similar measurements of 6.4 MeV ^{15}N ion straggling in thin elemental overlayers on H-terminated Si-backings for several elements ($6 \leq Z_2 \leq 79$), and, surprisingly, obtained rather good agreement of their data with the Bohr straggling theory (Fig. 7).

Fig. 7. Comparison of experimental straggling width parameters for 6.4 MeV ^{15}N obtained by Rud et al. [106], Briere and Biersack [150], and Goppelt-Langer et al. [151] ($\bullet$) with the Bohr straggling theory (solid line) and Rud's empirical $Z_2^{0.39}$ dependence (Eq. (2.14), broken line). Reproduced from Ref. [151].

Ref. [151] notes that this agreement should be regarded as coincidental rather than as a justification for the Bohr theory in this energy range. The Bohr theory assumes the ions to be fully stripped, which is not the case for 6.4 MeV ^{15}N , where the equilibrium charge state is about +5, so charge state fluctuations are expected to contribute to straggling. To our knowledge these discrepancies still stand unresolved as of today, suggesting that gaps exist in the systematic understanding of the straggling process and that apparently also the experimental determination of straggling parameters can have its pitfalls, especially for ultrathin films. Non-uniform film thicknesses, i. e., surface or interface roughness, reactive interfacial diffusion, or island formation come to mind as possible error sources. Fukutani et al. even found indications that the Rud formula may *underestimate* the straggling width in ultrathin Pb deposits on H-terminated Si(111) surfaces [59].

For the important H profiling work with SiO_2/Si systems reviewed in Chapter 3.3.1, Briere and Bräunig established that the energy straggling for 6.4 MeV ^{15}N ions in glow discharge deposited amorphous SiO_2 films expectedly scales as a function of the square root of the film thickness, i.e., $\sigma_s = (Q_s \Delta h)^{1/2}$, where the straggling cross section $Q_s = 1.06 \times 10^6 \text{ eV}^2/\text{nm}$ was again found to be in good agreement with the classical Bohr theory of fully stripped ions [107].

2.2 *Instrumental aspects*

2.2.1 *Ion beam generation (accelerator)*

The MeV ion beams required for nuclear reaction analysis are generated by single stage or tandem accelerators. Several groups have been performing $^1\text{H}(^{15}\text{N}$,

$\alpha\gamma$)¹²C NRA internationally and described their accelerator and measurement facilities to various degrees of detail in the literature, to which we shall refer the interested reader (some of these installations appear to have been decommissioned or to no longer be in active use): Amsel (Paris) [152-154], Wagner and Rauch (Frankfurt) [77, 155, 156], Kalbitzer (Heidelberg) [98, 157, 158], Herrmann and Grambole (FZ Rossendorf) [159], Krauser, Bräunig, Briere, and Weidinger (HMI) [107, 160, 161], Thomas and Fallavier (Cedex) [162], Lanford (SUNY-Albany) [51], Davis (LLNL) [163, 164], Allred, White, Clark, and Appleton (Oak Ridge Natl. Lab.) [112], Saris et al. (FOM, Amsterdam) [165], Pick, Dienes, Davenport, Ruckman, and Strongin (Brookhaven) [166], Hjoervarsson (Uppsala) [167], Andersen, Rud, Bøttiger, Jensen, and Stensgaard (Aarhus) [168], Berheide, Becker, Schulte, Rolfs (Bochum) [118, 169-171], Schwickert, Uhrmacher, Lieb (Göttingen) [172, 173], Yamamoto and Naramoto (JAERI, Takasaki) [151, 174], Sasa (Tsukuba) [116], and de Almeida and Baumvol (Rio Grande do Sul) [175, 176].

Here, we give an exemplary description of the vertically mounted 5 MV van-de-Graff tandem accelerator (5UD Pelletron, National Electrostatics Corporation) in the MALT microanalysis laboratory at the Department of Nuclear Engineering and Management of the University of Tokyo [177].

Accelerator

The MALT accelerator system is schematically illustrated in Fig. 8. It features a negative ion source in which Cs-sputtering of a mixed Ti¹⁵N + C cathode material generates an intense ($\sim 1 \mu\text{A}$) and highly stable beam of primary C¹⁵N⁻ ions which are injected from a negative ion source potential (V_i) into the first acceleration stage. To

produce $^{15}\text{N}^{2+}$ beams of 6.385 MeV the terminal is held at a potential V_T (≈ 2.47 MV). At the terminal the accelerated C^{15}N^- ions pass through a stripper gas canal where collision-induced charge exchange with low pressure Ar gas leads to their break up into mainly $^{15}\text{N}^{2+}$ and $^{15}\text{N}^{3+}$ ions in addition to C^{2+} , C^{3+} , and a smaller number of other charge states. The now positive $^{15}\text{N}^{q+}$ ions are accelerated in the second tandem stage towards the exit of the accelerator, where they attain an energy of $E_i = e((V_i + V_T)[m_N/(m_N+m_C)] + qV_T)$, where V_T is the terminal voltage, e the elemental charge, q the charge state of the ^{15}N ion, and m_N and m_C are the masses of the ^{15}N and ^{12}C atoms, respectively. The accelerated ions then pass through a mass and energy dispersive analyzer that extracts only a single selected $^{15}\text{N}^{q+}$ charge state as the usable beam.

Fig 8. Schematic illustration of the MALT tandem accelerator system used for $^1\text{H}(^{15}\text{N},\text{ag})^{12}\text{C}$ NRA at the University of Tokyo. Reproduced from Ref. [57] with permission from Elsevier.

This monochromator is a double focusing sector magnet in which for a given field B only ions of a specific momentum/charge ratio pass on a trajectory along the center radius r : $B \cdot r = (2mE/q^2)^{1/2}$. The analyzing magnet of the MALT system has adjustable entrance and exit slits and a large orbital radius of $r = 1270$ mm that achieves an excellent energy resolution of $\Delta E/E = \Delta s/2r = 4.7 \times 10^{-4}$ at a $\Delta s = 1.2$ mm slit width setting, delivering a well-monochromatized ($\Delta E_B \leq \sim 3$ keV) $^{15}\text{N}^{2+}$ beam of 6.385 MeV (up to 40 nA) to the target in our UHV analysis chamber. The beam energy defining magnet field is measured with a high precision ^1H NMR probe placed between the magnet pole pieces and stabilized to within 10^{-5} with a feedback system, which warrants superior reproducibility of the beam energy.

The MALT system features a second feedback control for the terminal voltage, which senses the ion current on an upper (lower energy) and lower (high energy) probing slit (width ± 2.5 mm) located just in front of the narrower energy defining exit slit of the analyzer, and regulates the accelerator terminal voltage such that the ions always pass through the center of the analyzer. This minimizes beam current fluctuations due to terminal voltage ripple and drift, thus providing excellent stability of the beam output.

Adjusting the analyzer magnet field with the accelerator in slit feedback mode enables a highly accurate setting of the beam energy and greatly facilitates energy scans for depth profiling. Alternative ways of beam energy scanning employ electrostatic deflectors behind the entrance and in front of the exit slits of the analyzer ('Amsel steerers') [108, 153, 154, 157, 173], or impose a bias voltage to the target. These latter methods are faster and hysteresis-free but have only narrow

scan ranges (8-10% of the central analyzer pass energy [153, 154] or ~ 30 keV, respectively) before retuning of the analyzer and the terminal becomes necessary.

We routinely employ $^{15}\text{N}^{2+}$ beams for $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ measurements of surface-near hydrogen distributions, allowing for energy scans from 6.385 MeV up to ~ 12.5 MeV by raising the terminal voltage towards the maximum of 5 MV. If necessary, higher beam energies up to ~ 17.5 MeV can be realized by selecting the $^{15}\text{N}^{3+}$ charge state with the analyzing magnet.

Ion Source

The generation of the ^{15}N ion beam for NRA with a tandem accelerator requires a negative ion in the first acceleration stage. This cannot be achieved with nitrogen alone since N^- is unstable, leaving plasma sources (Alphatross, Duo-Plasmatron) to produce NH_2^- ions from gaseous NH_3 or the SNICS type source (Source of Negative Ions by Cesium Sputtering, National Electrostatics Corp.) delivering CN^- ions as viable alternatives. At MALT two multi-target SNICS ion sources are available, which allow exchanging exhausted cathodes quickly without disrupting the beam operation by remote-controlled rotation of a cathode wheel that accommodates up to 40 sputter targets. The SNICS ion source delivers a highly stable and intense output of CN^- , routinely generating beams of $-2\mu\text{A}$ and more at the accelerator terminal. In the Ar stripper gas canal, straggling and fragmentation of CN^- by Coulomb explosion after charge exchange induce considerable broadening to the ion energy distribution [178] (see below). Due to this energy broadening a relatively large fraction of the N^{q+} beams is lost in subsequent energy analysis. In our case these losses are affordable since the efficient CN^- output of the SNICS source provides for sufficient remaining

^{15}N ion beam current after monochromatization. At MALT, achieving stable mono-energetic beam output conditions with the gas ion source (Alphatros) to produce NH_2^- ions was found to be difficult, so that we routinely employ CN^- beams from the SNICS ion source.

^{15}N Ion energy width without monochromatization

The energy broadening through Coulomb explosion after charge exchange with the stripper gas is significantly smaller in case of NH^- compared to CN^- as the parent negative molecular ion. According to Hartmann *et al.* [178], the disintegration of the diatomic parent ion (AB) into two fragments A and B of positive charges q_A and q_B superimposes a small randomly directed velocity ($\mathbf{v}_D$) component to the large terminal velocity ($\mathbf{v}_T$) of the fragments (typically $10^{-3} \leq |\mathbf{v}_D/\mathbf{v}_T| \leq 10^{-2}$). This leads to satellite peaks in the fragments' energy distribution that are shifted to higher and lower values by a maximum of $\pm E_{s0} = (kE_T E_D)^{1/2}$ against the center beam energy of neutrally dissociating AB with $k = 4\mu/(1+\mu)^2$ and $\mu = m_A/m_B$. Here, $E_T \approx eV_T$ is the terminal energy of the parent molecular ion, and $E_D = q_A q_B e^2 / 4\pi\epsilon_0 d_{AB}$ the Coulomb energy due to molecular disintegration from an initial interatomic distance d_{AB} . The kinematic factor k is symmetric in the atomic components A and B (i.e., $k(\mu) = k(1/\mu)$), so that the two fragments experience the same energy shift. For the nearly isobaric $^{12}\text{C}^{15}\text{N}$ molecule $k = 0.988$, whereas in the highly asymmetric case of $^{15}\text{N}^1\text{H}$ $k = 0.234$, so that the Coulomb explosion related energy shift of 6.4 MeV $^{15}\text{N}^{2+}$ ions ($E_T = 2.47$ MeV) produced from NH^- ($E_{s0} = 3.8$ keV, $q_H = 1$, $d_{\text{NH}} = 1$ Å) is only about half as large as that of those generated from CN^- ($E_{s0} = 7.8$ keV, $q_C = 1$ and $d_{\text{CN}} = 1.158$ Å). For this reason NH_2^- is often recommended in preference over CN^- as the primary ion in

tandem accelerators for the generation of N^{q+} ion beams with small energy widths [52] [178].

All three peaks in the final $^{15}N^{q+}$ ion energy distribution (the central (E_i) and the two symmetric satellites at $E_i \pm E_{s0}$) have identical width, which is determined by terminal voltage ripple and by straggling in the stripper gas [178]. The intensity of the satellites relative to that of the center beam peak at E_i also depends on the stripper gas density, since the latter influences the probability for Coulomb explosion, i.e., the likelihood that CN^- (or NH^-) become multiply ionized by charge exchange before collision-induced dissociation. Therefore the stripper gas pressure is an important parameter to optimize the yield of a desired N^{q+} charge state and to minimize the Coulomb explosion satellites. For $^{15}N^{2+}$ of 6.4 MeV generated from CN^- Hartmann *et al.* found optimum conditions at a stripper gas (N_2) pressure around 10^{-3} mbar, at which the satellite peaks were almost completely reduced (to only 15% of the center peak intensity) and the straggling-dominated width of the center peak was in the order of ~ 5 keV (Figs. 8 and 10 in Ref. [178]).

We also routinely observe an energy width ΔE_B (FWHM) of similar magnitude for the 6.385 MeV $^{15}N^{2+}$ ion beam produced at MALT from CN^- prior to its monochromatization (measured with a beam profile monitor located in front of the analyzer exit slit). Knowing this figure (ΔE_B) may help estimating the expectable near-surface NRA depth resolution (from Eqs. (2.10) or (2.15)) or be useful for Doppler broadening analysis of surface hydrogen in cases where no monochromator is available. Note also that these ΔE_B values are already smaller than E_{s0} (7.8 keV) for 6.4 MeV $^{15}N^{2+}$ produced from CN^- , which suggests that a major additional resolution improvement by choosing NH_2^- as the primary ion might no longer be expected if the

satellite peaks due to Coulomb explosion are already sufficiently suppressed by suitable adjustment of the stripper gas pressure.

2.2.2 Measurement apparatus and sample requirements

Measurement apparatus

It has been recognized early on in the development of hydrogen depth analysis with ion beams that a very clean vacuum in the target chamber is highly important, since otherwise a gradual build-up of hydrocarbons on the sample surface will cause the depth scale as well as the surface hydrogen concentration to vary during the measurement [71, 162, 179-181]. A vacuum in the 10^{-7} Pa range is necessary to achieve stable conditions for hydrogen analysis at surfaces [179]. Accordingly, our UHV target chamber designated for NRA measurements at single crystal surfaces has a base pressure $< 1 \times 10^{-8}$ Pa. Fig. 10 shows a cross-sectional top view of the vacuum chamber in the plane that contains the NRA ion beam. Our (ca. 4 cm) Pb-shielded 4" BGO γ -detector is positioned outside the vacuum on the beam axis 30 mm behind the sample, which is mounted on a manipulator that enables its positioning along 3-axes (x , y , z) as well as rotation around the vertical chamber axis. The UHV chamber is equipped with all necessary facilities for *in-situ* preparation and characterization of single crystal targets, containing a sputter ion gun and 4-grid LEED optics with capability for AES analysis.

Fig. 9. UHV target chamber at the University of Tokyo's MALT tandem accelerator. The system has a base pressure $<1 \times 10^{-8}$ Pa and is equipped for resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA measurements at in-situ prepared single crystal targets in combination with H_2 TDS.

The sample can be cooled to 80 K with liquid nitrogen (optionally to ~ 20 K with liquid He) and heated to >1400 K by thermal radiation and electron bombardment from a tungsten filament mounted on its backside. Temperature control is achieved with a thermocouple directly spotwelded to the crystal side (in case of metal targets). The pressure is measured with a Bayard-Alpert ion gauge (not shown). A special feature of our apparatus is the shielded and differentially pumped quadrupole mass spectrometer (QMS, Balzers Prisma 200) that can be translated with aid of a linear motion device so that the small aperture in the tip of its shield can be approached as

close as 0.5 mm to the sample surface. This equipment enables TDS measurements at hydrogen-exposed samples in combination with *in-situ* NRA analysis in the same system, which is particularly versatile in investigations of hydrogen adsorption and absorption processes at reactive metal surfaces as described in Sections 3.1 and 3.2. Ultrapure H₂ (7N) from a PdAg membrane diffusion purifier is used for the hydrogen exposures in these experiments. If necessary, atomic H can be produced via partial thermal dissociation by passing the purified H₂ gas through a Mo tube that contains a heated tungsten filament.

To exclude contamination of the sample surface by impurities introduced by the ion beam from the accelerator or the beam lines, the sample is positioned not in direct line of sight from the accelerator but slightly above the beam axis during the NRA measurements. An electrostatic deflector in the last differential pumping stage in front of the UHV chamber is used to steer only the ¹⁵N ion beam onto the sample, while any possible neutral contaminants are stopped by a Faraday cup mounted on the beam line axis. When the deflector state is off during the beam energy tuning intervals, the Faraday cup monitors the ion beam current, which also allows verifying proper beam transport to the UHV system from the accelerator's analyzer, where another Faraday cup monitors the monochromatized beam output. The ion beam is focused onto the target with set of magnetic quadrupole lenses on the beamline between the energy analyzer and the target chamber. In order to monitor the beam profile, the luminescent beam halo is observed on a sheet of sapphire or quartz mounted on the sample manipulator and brought into target position. The magnetic beam focusing projects the energy analyzer slit profile onto the target, i.e., the beam

size is at least ~ 1 mm in diameter for work at maximum depth resolution, but it can be defocused into virtually any shape if necessary, e.g., to reduce beam-induced H desorption from the target surface.

Accurate charge integration is an important requirement to obtain quantitative hydrogen concentration measurements (Section 2.2.6). Ideally, the entire target vacuum chamber is electrically insulated from the accelerator beamline and included in the charge integration system [50, 51]. Alternatively, a Faraday-cup mounted target is recommended. In our system these conditions are not perfectly fulfilled as the facilities for sputtering and LEED/AES/TDS measurements prevent the electrical insulation of the vacuum chamber and also require access to the sample surface during its manipulation for preparation and characterization. We therefore apply a positive bias (on the order of 100 V) to the sample in order to retain the low energy secondary electrons during the NRA measurement.

Sample requirements

^{15}N NRA is highly versatile and almost universally applicable to a wide range of materials. Only a minimum of preconditions with regard to the sample material is required to allow for successful hydrogen depth profiling. Evidently the target must be a material that is stable in high vacuum and ideally shows a certain resistance against degeneration under the ion beam (cf. Section 2.2.5). The elemental composition of the material (except for the H content) and its density should be known as precisely as possible so that the stopping power can be calculated accurately. For a meaningful conversion of the ^{15}N projectile energy loss into an analysis depth axis, the material should have a laterally uniform density (no pores)

and, if possible, a flat surface. Surface roughness can affect the depth resolution as an additional broadening, since within the size of the ion beam diameter (> 1 mm) any height variations of the sample will be averaged in the measurement. While this poses no major concern in the case of a more or less continuous internal hydrogen distribution, it will smear out the locations of strongly localized H, such as at interface positions. The effects of surface roughness become increasingly pronounced at increasing projectile incidence angles, so very flat surfaces are required for measurements under strongly grazing ion incidence. Even steps of atomic height may lead to energy shifts in surface resonance profiles in such geometries (Section 3.3.2) [59].

2.2.3 Depth resolution and range

The depth resolution Δd in H profiling by resonant NRA is determined by the energy width ΔE_{tot} of the instrumental function $F(E_i, z)$ (Eq. 2.10) and the stopping power S of the analyzed material:

$$\Delta d = \Delta E_{\text{tot}} \cos \alpha_i / S = \cos \alpha_i (0.56 \Gamma + [8 \cdot \ln(2)(\delta_B^2 + \delta_D^2 + (\delta_s(z))^2)]^{1/2}) / S. \quad (2.15)$$

Owing to energy straggling of the projectile ions within the target the depth resolution is best at the surface but deteriorates with increasing probing depth: $\delta_s(z) \propto (z)^{1/2}$ [106]. We first discuss the ultimate resolution at the surface, where $\delta_s(z = 0) = 0$. Eq. (2.15) shows that even at the surface the ion beam energy spread (δ_B) and, in particular, the Doppler Effect (δ_D) broaden the experimental resonance profiles considerably beyond the resonance width (Γ). Especially in near-surface H profiling

with the narrow ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ resonance at 6.385 MeV ($\Gamma = 1.8$ keV) and a reasonably monochromatized ${}^{15}\text{N}$ beam, Doppler broadening ($\delta_D \sim 4\text{-}5$ keV) is the major limitation of the energy resolution close to the surface, leading to total spectral widths (ΔE_{tot}) of $\sim 10\text{-}14$ keV for H on semiconductors and $\sim 8\text{-}10$ keV on metals (cf. Fig. 3). With $S = 1\text{-}4$ keV/nm for ${}^{15}\text{N}$ at 6.4 MeV, this translates into near-surface NRA depth resolutions of $\sim 2\text{-}10$ nm if the analyzing ion beam impinges onto the target in the surface normal direction ($\alpha_i = 0$). The near-surface depth resolution can be increased to values around 1 nm by adopting a strongly *grazing incidence* geometry of the ion beam with the target surface ($\alpha_i \rightarrow 90^\circ$), as the stopping-induced energy loss to penetrate into a certain depth d scales with $1/\cos\alpha_i$ ($\Delta E = Sd/\cos\alpha_i$, Fig. 2). Submonolayer thickness variations of a Pb film on a H-terminated Si(111) surface in the order of 0.2 nm have been distinguished in this way by analyzing the energy shift of the surface resonance curve [59], see Section 3.3.2. Caution must be executed in measurements at very large incidence angles ($\alpha_i \geq 80^\circ$), as surface roughness can have disturbing effects, and for ion trajectory lengths $> \sim 10$ nm straggling will again become resolution limiting.

The maximum depth range R in which hydrogen can be probed with NRA for a specific nuclear reaction resonance $E_R^{(L)}$ is determined by the energy separation of this $E_R^{(L)}$ from the next cross section resonance at higher energy ($E_R^{(H)}$) divided by the stopping power of the analyzed material [49, 86]. It is easily verified that:

$$R = \left(E_R^{(H)} - E_R^{(L)} \right) \cos \alpha_i / S \quad . \quad (2.16)$$

For ^{15}N NRA at 6.385 MeV in normal incidence ($\alpha_i = 0$), roughly 7 MeV separation to the 2nd resonance at 13.35 MeV, and elemental ^{15}N stopping powers between 1.5 and 4 keV/nm, the usable H probing depth is typically around 2-4 μm .

Fig. 10. γ -ray emission from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction obtained from 6 to 14 MeV on a low-level detection system with an Fe target of immeasurably small H content in the bulk. H on the surface gives resonance peaks at 6.385 and 13.35 MeV. Additional Au/Fe interface peaks appear after a 1000 Å Au film is deposited. Observe the strong increase of non-resonant reaction yield above ~ 10 MeV. Adapted from Ref.[98] with permission from Elsevier.

Note, however, that H profiling with the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction into extended depth regions may require caution in certain situations. If the target bears a H-rich layer at the surface, such as ubiquitous hydrocarbon contaminations or hydroxyl in oxide skins common on air-exposed materials without *in-situ* surface cleaning, this surface hydrogen will interact with the nuclear reaction cross section between $E_R^{(L)}$

and $E_R^{(H)}$ to produce *non-resonant* γ -yield that bears no depth information but feigns non-existing bulk H content at the depth $d = (E_i - E_R^{(L)}) \cos \alpha_i / S$. As an example, Fig. 10 displays the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ γ -yield between 6 and 14 MeV obtained from an annealed Fe sample before and after deposition of a 1000 Å thick Au layer [98]. Hydrogen contamination on the Fe and Au surfaces gives rise to expected peaks at the 6.385 and 13.35 MeV resonances, and the additional features appearing at slightly higher energies after Au deposition suggest that some H was incorporated at the Au/Fe interface. In the intermediate ^{15}N energy region, observe that the γ -yield begins to increase markedly above ~10 MeV as the 13.35 MeV resonance is approached. Since the H concentration in the Fe substrate was known to be immeasurably small, this yield must have resulted from non-resonant nuclear reactions with the surface (and Au/Fe interface) hydrogen. Fig. 10 thus illustrates the fact that the off-resonant cross section for the $\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction, which is small and usually negligible between 6 and 8.3 MeV [100], increases by two orders of magnitude between ~10 and 13 MeV [52, 100, 111]. Hence, the non-resonant γ -yield at such ^{15}N energies degrades the NRA sensitivity for H in large probing depths and may restrict the usable depth range in which small H concentrations can be detected [52, 98-100, 110, 111], unless the non-resonant γ -yield is corrected for as explained in the following section.

2.2.4 γ -detection, background, and sensitivity

Here we describe the signal detection methods used in resonant NRA and explain the influence of various background sources on the sensitivity of H concentration measurements. For the $(p, \alpha\gamma)$ reactions listed in Table 1, detection of the characteristic γ -rays is usually preferred over the measurement of the product α -

particles, which would also be possible in principle. The major advantage of γ -detection is that unlike any (solid state) detector for α -particles, the appropriate γ -detectors do not require shielding from other energetic particles in the vicinity of the analyzed sample. Due to negligible attenuation of the MeV γ -radiation in the thin stainless steel walls of vacuum chambers, the γ -detector can be placed conveniently on the atmospheric side of the analysis system. This arrangement elegantly circumvents the most intricate problems of alternative α -particle detection, namely to avoid that the intense flux of scattered ^{15}N ions and recoiled target atoms would overwhelm the faint α -signal and possibly even damage the detector, and the additional analytical challenge to discriminate the α -particles from target recoils (especially H) and scattered beam projectiles.

It is apparent that collecting the characteristic γ -rays released in the nuclear reactions with a detector positioned outside the vacuum is the easiest and most efficient way to realize resonant (p, γ) NRA measurements. The γ -rays produced in typical $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ and $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ NRA reactions (Table 1) are sufficiently more energetic than most natural radiation so that high signal-to-noise ratios can be achieved by γ -ray counting. For γ -ray detection NaI(Tl) (thallium doped sodium iodide) and BGO (bismuth germanate, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$) scintillators of several inches in length and diameter are in common use. The scintillation crystals are coupled to photomultiplier tubes, so that the γ -ray energy is first converted into UV-VIS photons and then into an electron pulse of an amplitude proportional to the γ -ray energy. In addition to the signal at the incident γ -ray energy E_γ (full-energy peak, FE), the pulse height spectra also show so-called single-escape (SE) and double-escape (DE) peaks

at the energies $E_\gamma - 0.511$ MeV and $E_\gamma - 1.022$ MeV, respectively (Fig. 11). These features originate from γ -ray-induced electron-positron ($e^- - e^+$) pair production in the scintillation crystal. The positrons quickly annihilate upon collision with an electron, which releases two gamma rays of $h\nu_\gamma = m_e c^2 = 0.511$ MeV. The single and double-escape peaks then result from events when either one or both 0.511 MeV γ -rays leave the scintillation crystal without absorption and conversion into detectable UV-VIS photons.

Fig. 11. Comparison of the gamma-ray spectra from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction recorded with 3 in. x 3 in. BGO and NaI detectors on the same target under the same conditions. Adapted from Ref. [182] with permission from Elsevier.

Due to its higher density BGO offers a superior γ -ray absorption coefficient compared to NaI [183] (on a transmitted length of 4 inches, BGO absorbs $\sim 94\%$ of 4 MeV γ -rays, NaI only $\sim 73\%$ [184]). This is advantageous since the rate of cosmic radiation background (CRB) increases roughly linearly with the volume of the

scintillation crystal [185]; hence at the same sensitivity a smaller BGO detector has a lower CRB count rate than a larger NaI scintillator, which enhances the signal-to-background ratio, cf. Eq. (2.17). BGO also has a ~ 10 times smaller neutron absorption cross section than NaI [182, 183], rendering BGO less susceptible to background in environments near thermal or radiative neutron sources.

Moreover, the signal content in the full-energy (FE) peak relative to that of the single- (SE) and double-escape (DE) features is higher in the energy spectrum of BGO due to the higher γ -ray attenuation coefficient of BGO [182, 185]. This is seen in Fig. 11, which compares the 4.43 MeV γ -ray spectrum of a H containing target recorded under identical $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA conditions with NaI and BGO detectors. The NaI spectrum (dotted line) shows all three (FE, SE, DE) peaks, with an intensity ratio of about 1:2:1. In the BGO spectrum (solid line) the intensity ratio of the FE and SE peaks is about 3:1 and a DE peak is barely discernible. The intrinsic FE peak efficiency ratio of BGO and NaI is about 4:1; hence a BGO scintillator will provide a significantly higher signal-to-background ratio than an NaI detector [183]. If one tries to compensate for the weak FE peak of NaI by including the SE peak into the signal integration, one still recovers only $\sim 3/4$ of the BGO FE peak intensity and the widened energy window will deteriorate the signal-to-noise ratio due to increased background detection.

The sensitivity for H concentration measurements with NRA is limited by the level of background signals in the γ -ray detection system. When the H concentration in the target is low, the small γ -signal will be obscured by fluctuations of the background. For a given acquisition time t , one has to accept a certain relative error

$\Delta Y/Y$, which depends on the true γ -signal ($Y = \dot{Y} \cdot t$) and the background ($U = \dot{U} \cdot t$) [98, 107, 185]:

$$\frac{\Delta Y}{Y} = \frac{(\dot{Y} + 2\dot{U})^{\frac{1}{2}}}{\dot{Y} t^{\frac{1}{2}}} \quad (2.17)$$

In absence of background, the expression recovers the familiar $Y^{-1/2}$ dependence of counting statistics. At the detection limit, small signals prevail on a large background, i.e., $\dot{U}/\dot{Y} \gg 1$, and $\Delta Y/Y = (2\dot{U}/t)^{1/2}/\dot{Y}$. The relative error can then be decreased through long data acquisition ($\Delta Y/Y \propto t^{-1/2}$) and by applying high ion beam fluences ($\Delta Y/Y \propto \dot{Y}^{-1}$). With unshielded detectors, ^{15}N NRA usually achieves H sensitivities better than 1000 at. ppm [107, 182]. To optimize the sensitivity, the signal rate $\dot{Y}$ must be maximized and that of the background $\dot{U}$ suppressed as far as possible. Since the sensitivity constant of a given γ -detector (K in Eq. (2.12)) writes as $K = \eta\Delta\Omega$ ($\Delta\Omega$ is the subtended solid angle and η the γ -absorption efficiency), the NRA signal is obviously maximized by providing an efficient γ -detector (large η : $\rightarrow$ BGO) placed as closely to the sample (large $\Delta\Omega$) as can be arranged without obstructing sample manipulations, and by performing the measurement with the largest possible ion beam current (N_i) that is tolerated by the target without deterioration.

Background signals in γ -spectroscopy arise mainly from cosmic radiation. Solar wind-induced nuclear reactions in the upper atmosphere generate a radiation background at sea level, which consists of a softer γ -component (on the order of ~ 10 MeV) and a dominant (70-80%) shower of hard muons up to 100 GeV [98]. Some of these γ -rays may fall into the ROI for NRA and can be suppressed by γ -absorbing

shields (concrete building walls or high density material (Pb) detector enclosures). The highly penetrating muons cause signals by losing a small portion of their energy upon passing through the scintillation crystal. This background can only be eliminated with anticoincidence techniques [98, 182, 185]. Horn and Lanford describe an efficient way to selectively protect the ROI of the 4.43 MeV γ -ray in $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA with an anticoincidence circuit and a single relatively small (16" x 16" x 1") plastic scintillator sensitive to the cosmic radiation that covers a (4") Pb-shielded 3" x 3" BGO detector [182]. The resulting background suppression (Fig. 12) improves $\dot{U}$ in the NRA ROI from ~ 0.8 to 0.16 cts/min, which allows for a H sensitivity of 10-100 atomic ppm.

Fig. 12. Shielded and unshielded spectra using a 3 in. x 3 in. BGO detector. The “notch” extending from 3.5 to 4.75 MeV corresponds to the region protected by the anticoincidence circuit. Reproduced from Ref. [182] with permission from Elsevier.

A similar low-level system described by Kuhn et al. [185] has a 3" x 3" BGO CRB rate of 0.55 cts/min in the 3.8-4.8 MeV range and a detection efficiency for 4.4 MeV

γ -rays of 14%, providing comparable H sensitivity (< 20 at. ppm). These detection systems are relatively compact and allow easy sample access. This is more versatile than the highly effective but very large and heavily shielded detector case designed by Damjantschitsch et al., which achieves similar sensitivity (10-100 ppm) by reducing the background of a large ($10'' \times 10''$) NaI detector by a factor of 100 [73, 98], and can reduce the CRB rate of a $3'' \times 3''$ BGO to 0.19 cts/min [185].

The NRA sensitivity can further be increased by maximizing the γ -detection efficiency with a large solid angle scintillation crystal that accommodates the target in a center hole, and by completely surrounding the γ -detector with passive and active (anticoincidence) shielding [186-189]. The highest reported H sensitivity achieved in this way is better than 10 ppm [186].

Beside the described natural backgrounds, there are also artificial sources of γ -radiation that may perturb NRA measurements. Possible external sources of artificial background radiation are γ -emitting nuclear reactions induced by neutron capture inside or near the detector, which may occur in laboratories located near neutron sources. Moreover, the NRA analysis itself may produce disturbing γ -radiation if applied to certain types of sample materials. The analyzing ^{15}N ion beam may induce nuclear reactions with light elements in the target, such as Li, Be, and, most notably, D [98, 190]. The likelihood of such undesired nuclear side reactions increases at high ^{15}N energies due to the enhanced probability to overcome the Coulomb barrier with low Z nuclei. In unfavorable cases the released γ -radiation (or its Compton continuum) falls into the ROI for the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA γ -rays.

A notable example for this pitfall is the $D(^{15}\text{N},p)^{16}\text{N}$ reaction, which after beta-decay of ^{16}N to $^{16}\text{O}^*$ releases intense emission of 3.6, 6.1, and 7.1 MeV γ -rays and already has a sizeable cross section below the 6.385 MeV resonance of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ [191, 192]. The $D(^{15}\text{N},p)^{16}\text{N}$ reaction can very seriously disturb H profiling in samples that contain appreciable D concentrations [98, 193]. For instance, it renders H-profiling at $\text{H}_2\text{O}/\text{D}_2\text{O}$ sandwich structures for interdiffusion studies with ^{15}N NRA completely fruitless by overwhelming the 4.4 MeV ROI with γ -yield (an experience also the authors had to make). Unfortunately, also Li-based materials (which currently enjoy bright prospects as potential H storing media) are affected by similar problems due to a large variety of possible $^6\text{Li} + ^{15}\text{N}$ and $^7\text{Li} + ^{15}\text{N}$ reactions [190]. As long as the Li (or D) target concentrations are small (on the order of a few atomic %), one may be able to correct for the resulting side reaction γ -yield after identifying and quantifying a characteristic γ -emission outside the ROI for ^{15}N NRA [190]. Applying this to the γ -emission from $D(^{15}\text{N},p)^{16}\text{N}$ at 6.0 or 7.0 MeV and quantifying the yield this reaction induces within the 4.43 MeV $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ ROI might actually permit the simultaneous detection of H and D with the same ^{15}N beam, although the D signal will not be depth-resolved since the $D(^{15}\text{N},p)^{16}\text{N}$ reaction is non-resonant.

Another source of possibly disturbing γ -radiation is the 4.4 MeV γ -yield produced by the interaction of hydrogen near the target surface with ^{15}N at *non-resonant* energies above ~ 10 MeV described in the previous Section (Fig. 10). This non-resonant γ -yield may reduce the sensitivity for, e.g., small H quantities at deeply buried interfaces. Fortunately, the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ cross section has been characterized over a wide energy region [100, 110, 111], so that the non-resonant γ -yield can be

corrected for. The non-resonant γ -yield Y_{off} is proportional to the total H content in the surface layer, i.e., to the integrated γ -yield measured with the first resonance at 6.385 MeV, $I_{\text{on}}^{(l)}$, and to the off-resonant cross section, σ_{off} : $Y_{\text{off}} = \sigma_{\text{off}} \times I_{\text{on}}^{(l)}$. When σ_{off} is known and the first-resonance γ -yield of surface-H ($I_{\text{on}}^{(l)}$) has been determined from a shallow depth profile near 6.385 MeV, the non-resonant reaction yield can be estimated and, if necessary, subtracted from the raw γ -yield at high ^{15}N energy to determine the H concentration at larger depths correctly [100, 110, 111].

Evaluations of the energy-dependent off-resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction cross section $\sigma_{\text{off}}(E)$ between 6.4 and 13.4 MeV are available for the γ -detector positioned on [98-100, 111] and 90° off the ion beam axis [110]. The distinction of the detector position is necessary because the γ -emission in the resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction is slightly peaked in the forward direction [194], whereas the non-resonant γ -emission is nearly isotropic [100] (Fig. 13), making the relative contribution of the non-resonant yield somewhat higher in the 90° detection geometry [110]. Through the above definition as $\sigma_{\text{off}}(E, \theta_D) = Y_{\text{off}}(E)/I_{\text{on}}^{(1)}(\theta_D)$, the non-resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ cross section becomes also detection angle (θ_D) dependent. In the flat region between 6 and 8.3 MeV σ_{off} amounts to 1.9×10^{-5} with the detector in the 0° position [100], and $\sigma_{\text{off}} = 3.8 \times 10^{-5}$ for the detector 90° off axis [110]. For σ_{off} values at energies from 9 to 13.7 MeV, see Fig. 3 in Ref. [110]. The non-resonant γ -yield from surface H primarily affects measurements of deeply buried H concentrations probed at high ^{15}N energies (> 10 MeV) and therefore does not present a major concern for H detection near surfaces and shallow interfaces reviewed here.

Fig. 13. Comparison of the angular distribution of resonant (6.385 MeV) and non-resonant γ -ray emission from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction. Reproduced from Ref. [100] with permission from Elsevier.

2.2.5 Radiation effects

NRA is widely regarded as a non-destructive technique of quantitative elemental analysis. While this is certainly justified in direct comparison to outright destructive methods of hydrogen detection such as SIMS, metallurgical vacuum extraction, or TDS, the influence of the analyzing ion beam cannot entirely be ignored. An important general concern in hydrogen depth profiling with energetic ion beams is the possibly irreversible alteration of the hydrogen distribution in the course of the analysis that may include redistribution and/or loss of hydrogen from the target. We describe in this section the origin, the correction for, and the analytical value of possible ^{15}N -induced alterations of the H distribution.

The severity of radiation-induced effects strongly depends on the analyzed material as well as on the energy and nuclear charge of the ion projectiles. A general trend is that especially insulating low Z materials such as organic polymers, carbon films, and SiO_xN_y dielectrics are prone to suffer substantial losses of volatile light elements (H, C, N, O) under energetic ion irradiation [180, 195-200], whereas metal and semiconductor targets appear to be much less vulnerable against beam-induced H loss [201]. This difference can be understood by considering the basic interaction mechanism of energetic ions with the sample material. In the energy regime of the ^{15}N ions used in $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA direct nuclear collisions that cause permanent damage by displacing target atoms contribute less than 1% to the total energy loss (Section 2.1.3), whereas the dominant interaction is electronic stopping that generates a large number of excited electrons for each incident ^{15}N ion. In conducting materials, the excited electron energy is almost instantaneously dissipated, so that only the minor nuclear stopping leads to lasting damage in metals and semiconductors. In insulating materials, on the other hand, energetic electron impact causes localized bond cleavage that generates dangling bonds and free, diffusible radicals that may eventually leave the target. This explains the observations that the hydrogen depletion rate from insulating materials is many orders of magnitude larger than the nuclear scattering cross section and that it often scales with the electronic stopping power of the projectile ion [195, 197, 198, 200, 202].

When the hydrogen concentration at a constant depth is monitored with NRA as a function of the incident ion beam fluence ϕ (ions/cm²) one often observes a progressive damage pattern, in which an initially rapid H loss is followed by a slower decrease that may eventually saturate and even lead to a stable H concentration. As a typical example, Fig. 14 (a) shows the evolution of the H content in a thin film of hydrogenated amorphous silicon (α -Si) deposited on a H-terminated Si(100) substrate as tracked with ¹⁵N NRA under UHV conditions [203]. Empirically, such γ -yield decay curves as a function of the incident beam fluence $Y(\phi)$ are often well reproduced by a double exponential form:

$$Y(\phi) = n_1 \cdot \exp(-\sigma_1 \phi) + n_2 \cdot \exp(-\sigma_2 \phi), \quad (2.18)$$

Fig. 14. Decay of the γ -yield from the resonant $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction as a function of irradiation time with a 20 nA $^{15}\text{N}^{2+}$ beam. (a) α -Si/H/Si(001) and (b) H/Si(001). Solid lines are fits to a double (a) and (b) single exponential decay function. Reproduced from Ref. [203] with permission from Elsevier.

where σ_1 and σ_2 are effective decay cross sections describing the initially fast and later more gradual decay channels, and n_1+n_2 represents the γ -yield corresponding to the initial H concentration, $Y(0)$. Retrieving the latter by extrapolating the $Y(\phi)$ dependence to zero ion exposure is important for the quantitative analysis of hydrogen distributions with NRA (Section 2.2.6). Further, with the parameters obtained from a fit of $Y(\phi)$ to Eq. (2.18), the relative H loss during NRA depth profiling can be calculated from the ion fluence accumulated at each data point of a measured excitation curve $Y(E_i)$. These relative losses should be applied as weighting factors to the recorded yield curve data $Y(E_i)$ to compensate for the H loss during the analysis, so that unperturbed H depth distributions and surface resonance profiles can be determined.

The effective decay constants (σ_1, σ_2) in Eq. (2.18) may bear physical significance, for instance, they may be specific to certain hydrogen species in the target. Such a strong material dependence of the beam-induced H decay kinetics is exemplified by Fig. 14 (b), which shows the decrease of the H coverage on H-terminated Si(100) surface in a single, slow depletion process that has the same cross section as the slower decay channel in Fig. 14 (a). In comparison, the data strongly suggest that this slow decay is characteristic of the H-termination layer on the Si(100) surface, whereas the rapid depletion of the initially high γ -yield in Fig. 14 (a) is related to the H content in the α -Si overlayer [203]. In the sense that the effective decay constants may reflect individual H species or be particular to a certain H transport property of the analyzed material, the ion beam-induced H decay is of analytical value, as it may

help distinguish chemically different H species or be useful to evaluate, e.g., the hydrogen diffusion behavior underneath the surface. Examples for the assessment of surface conditions and interfacial H relocation phenomena with the aid of H decay kinetics measured by ^{15}N NRA are presented in Sections 3.1.2 and 3.3.1, respectively.

2.2.6 Quantitation and calibration

In order to obtain absolute values for hydrogen surface coverages or volume concentrations from NRA measurements one has to know the sensitivity factor K in Eqs. (2.11) and (2.12) that describes the efficiency of any given experimental setup to capture the γ -rays emitted in the nuclear reaction. K contains the γ -ray absorption efficiency η and the solid angle $\Delta\Omega$ subtended by the detector. The recorded γ -yield will also slightly depend on the detector position relative to the ion beam direction due to the angle variation of the γ -emission in the nuclear reaction (Fig. 13), over which the detection solid angle partially integrates. Hence, since the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ resonance parameters (σ_R , Γ) are well known, the relation of proportionality between the nuclear reaction γ -yield and the recorded NRA signal can in principle be calculated if $\Delta\Omega$ is evaluated carefully. In practice, it is common convenience to subsume all unknown factors except the parameters specific to the sample (S) and the individual measurement (N_i , t) into an effective sensitivity constant K_{eff} , which is characteristic for a given experimental setup with a particular detector in a defined position relative to the sample and a defined energy integration region (ROI) in the γ -spectrum, so that in acquisition time (t) integrated form Eq. (2.12) gives the detected number of γ -counts $I(E_i)$ at a given ion beam energy E_i as:

$$I(E_i) = \int_0^t Y(E_i) d\tau = K_{eff} Q_i c_b / S \quad , \quad (2.19)$$

where $Q_i = q \int_0^t N_i d\tau$ is the ion beam charge accumulated on the target (q is the charge state of the ^{15}N projectile). The detection system is then calibrated by determining K_{eff} with a reference sample of a precisely known volume H concentration c_{ref} . With such a bulk standard of known stopping power S_{ref} , K_{eff} is readily obtained from a single yield measurement in the calibration target. For the calibration measurement, any standard should be probed in a depth sufficiently far below the surface where not only $E_i = E_{>}$ (Fig. 4), but also the H content is certain to have attained the average bulk composition c_{ref} , since near-surface deviations of the H concentration from the bulk value occur quite commonly on a scale of several 10 or even 100 nm (see 3.2.3.6-7 and, e.g., Fig. 3 in Ref. [204]).

Materials suitable as calibration standards for absolute H concentration measurements with NRA should satisfy several requirements [205]. c_{ref} and the other elemental composition must be precisely known so that the stopping power S_{ref} can be calculated accurately. The material must have a uniform lateral H distribution and density, and be stable in vacuum. Although not necessarily a strict requirement, convenient standards furthermore offer long-term stability, in particular under the ion beam, so that they can be used repeatedly.

A variety of materials that fulfill the above demands more or less ideally has been proposed as calibration standards, among them hydrogenated thin films of Ti [100] and Ta foil [204, 206], hydrogenated films of pyrolytic carbon [204], amorphous silicon [204, 207, 208], and silicon nitride [110], hydrogen-implanted Si [71, 207, 209],

as well as the polymers polystyrene [210], polypropylene (C_3H_6)_n, polyester, Mylar ($\text{C}_{10}\text{H}_8\text{O}_4$)_n, Kapton® ($\text{C}_{22}\text{H}_{10}\text{O}_5\text{N}_2$)_n [205, 211], as well as H_2 gas [212].

The hydrogenated thin film materials have been confirmed to show quite favorable properties, such as long-term stability in UHV as well as under the ^{15}N NRA ion irradiation, and sufficient conductivity for proper charge integration. Some of them, however, must be prepared by deposition and hydrogenation techniques or CVD methods that may not be available in most laboratories. Further, although H stability in these hydrided thin films or hydrogen-annealed metal (Ta, Ti) foils has been verified, the absolute H concentration in the obtained specimens still needs to be determined with another reference. The bulk polymers, on the other hand, have precisely known compositions and are readily available as thin foils, yet they suffer from rapid initial beam-induced H loss that introduces substantial uncertainty into the zero-fluence extrapolation of the decay curves (Eq. (2.18), Section 2.2.5). A once irradiated area of polymer foil must be discarded after acquisition of a single decay curve. To our experience and as also described in Ref. [211], Kapton (a polyimide) has a much better resistance against ^{15}N -induced H loss than most polymers, presumably due to its comparatively lower H content, to which the initial H-loss rate is proportional [195, 198, 199]. To avoid charge up of the Kapton foils one may ideally deposit a thin metal layer onto their surface or alternatively clamp the foil under a thin wire mesh that is wide enough to accommodate the ion beam. The use of H_2 for calibration ($\sim 10^4 - 10^5$ Pa is convenient) by extracting the ^{15}N ion beam into a gas cell, such as through a thin (100 nm) SiN membrane, requires a well-focused ion beam due to the necessarily small membrane size ($\sim 1 \times 1 \text{ mm}^2$) and a separate

detector to measure the beam flux into the gas target, but is otherwise independent of any parameters except the H₂ stopping power [212].

H-implanted Si wafers are probably the most versatile (absolute) calibration standards, although B-doped p-Si should probably be avoided to exclude side nuclear reaction γ -yield. Implantation techniques are well established [213], and in preparing the standard, the H content can be known rather precisely if the charge deposited during the implantation process is measured accurately. $5 \times 10^{16} \text{ cm}^{-2} \text{ H}^+$ implanted at 6 keV has produced quite practical results [209]. To prevent channeling effects in the typically single crystalline Si substrates, the implantation depth region is preferably amorphized with an auxiliary ion beam prior to H introduction. Alternatively, a small beam incidence angle against the surface normal can be adjusted during the calibration measurement to avoid ion incidence along a high-symmetry crystal axis. The implanted H is bound strongly at (implantation generated) dangling bond defects and thus well protected against thermal and irradiation-induced diffusion [207]. H-implanted Si standards thus promise good long-term stability, and influences from the surface (exposure to vacuum or atmosphere) on the implant are expected to be negligible as well. Hydrogen-implanted Si-standards have been used for calibration purposes in many of the quantitative NRA studies reviewed in Chapter 3. A recent international 'Round Robin' test by 6 different laboratories applying various forms of ERD and NRA to determine the H quantity implanted into an amorphized Si wafer achieved indeed a very high reproducibility (2.2% relative error) that even exceeded the combined uncertainty estimates ($\sim 6\%$) of the participating laboratories [209].

2.2.7 Data analysis and simulation

In order to extract actual hydrogen concentration depth profiles from experimental γ -yield excitation curves in NRA one has to unfold the instrumental function from the data. Although solving Eq. (2.3) by numerical deconvolution would be the most direct method, this approach is rather cumbersome and has rarely been pursued. To our knowledge only one numerical deconvolution program for the analysis of experimental resonant NRA data has been developed, WinRNRA [214], which however, appears to have been applied only for ^{15}N profiling with H^+ beams at the inverse laboratory resonance energy of the $^{15}\text{N}(^1\text{H},\alpha\gamma)^{12}\text{C}$ reaction at 429 keV (in the center of mass system relevant to the nuclear reaction the collision energy of 429 keV ^1H and resting ^{15}N is the same as for 6.385 MeV ^{15}N impact on resting ^1H).

The second, easier, and much more widely applied way [215-219] of interpreting the γ -yield excitation functions is to forward-convolve a trial H concentration profile with the NRA instrumental function (Section 2.1.1), to obtain a simulated excitation function that can be compared to the experiment. According to Eq. (2.3) a separate calculation of the expected γ -yield is necessary for each incidence energy value in the scan. The model H depth distribution is then refined within reasonable physical limits until good agreement of the simulated yield curve with the experimental data is achieved. This method is comparatively straightforward to implement from Eqs. (2.3) – (2.9), but the obtained simulations do not allow for an unambiguous determination of the actual H depth profile, as the assumed H model distribution is not necessarily unique. Good physical sense in constructing the model distribution is hence essential.

The authors have implemented this approach for surface-near hydrogen profiling by following the ^{15}N ion trajectory into the depth of the target, calculating the energy resolution function $F(E, E_i, z)$ in trajectory length increments corresponding to atomic layer distances, to obtain a relative measure of the expected γ -yield from model H distributions [110, 220]. This simulation routine is a *surface approximation* (Section 2.1.3) for shallow depth profiling [220], which assumes a constant stopping power at all depths, and a Gaussian straggling distribution with a standard deviation based on Rud's formula [106]. Despite their limitations to uniquely identify hydrogen depth distributions, such simplified simulations can be helpful in judging which of several conceivable H distributions are compatible with a given set of experimental data and may thus aid the interpretation of measured excitation curves by at least excluding incompatible models [220].

More sophisticated ion beam analysis software has been devised that takes full account of the energy dependence of the stopping at larger depths (such as the DEPTH code [221, 222] and SRIM [125, 127]) and offers choices between several theoretical frameworks to describe the straggling such as RUMP [223], RBX [224], and SIMNRA [225, 226]. DataFurnace [227, 228] even provides the convenience of automated fitting in complex layered samples and the calculation of confidence limits. These programs are widely used in ion beam analysis with RBS, ERD, and non-resonant NRA and have recently been evaluated by IAEA [229-231]. These IBA techniques have in common that the material is analyzed at constant beam energy while the energy spectrum of the outgoing (scattered, recoiled, or non-resonantly produced) particles is measured to extract the depth information; hence the

software codes are similar. Since this situation is notably different in narrow resonance profiling (r-NRA) where the incident beam energy is scanned, the above programs have long excluded resonant NRA. Only recently special routines for analysis and simulation of PIXE and high-resolution resonant NRA data have been implemented into the DataFurnace [227] software [228].

2.3 *Comparison to ERDA*

Elastic recoil detection (analysis) (ERDA) is an alternative fast and quasi non-destructive method for hydrogen depth profiling that under certain provisions can achieve similar performance in the near surface region as NRA via $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ in terms of sensitivity and depth resolution. For detailed descriptions of the ERD technique the interested reader is referred to original publications [51, 71, 232-239] and comprehensive reviews [193, 240-246]. A few essential principles of ERD that may help comprehending the following comparison with resonant ^{15}N NRA are outlined in Appendix B.

2.3.1 *Performance (depth resolution, sensitivity, probing range)*

Owing to the variety of ERD configurations with respect to projectile masses and energies, recoil geometries, and detection schemes that are briefly described in Appendix B it is difficult to draw a *general* comparison of ERD to the NRA techniques for H and D detection. We have therefore compiled performance benchmarks of various ERD applications to hydrogen analysis in Table 2 for a case by case comparison with $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA at 6.385 MeV. Recall from Section 2.2 that the

typical performance characteristics of the latter are a near surface depth resolution of 2-5 nm in normal and <1 nm in grazing ($\alpha_i = 80^\circ$) incidence, respectively, a probing depth range of $\sim 2\text{-}4\ \mu\text{m}$, and a sensitivity of $\sim 100\text{-}500\ \text{ppm}$ (0.05-0.01 at.%) for bulk H concentrations or H layer densities of $(1\text{-}5)\times 10^{13}\text{cm}^{-2}$ at the surface.

^{15}N NRA at 6.385 MeV thus obviously outperforms conventional (range foil and SSBD) ERD with ^4He beams in terms of depth resolution, a slightly higher sensitivity, the ability to profile rough surfaces, and a larger probing depth range. On the other hand, ERD with ion projectiles heavier than ^4He (HIERD) offers considerably enhanced depth resolution ($(dE/dz) \propto Z_1^2$), improved sensitivity ($\sigma_r \propto Z_1^2$), and in addition enables detection of other light target elements along with the hydrogen isotopes [247, 248], as long as the sample tolerates the heavy projectile beam.

With specialized high-resolution detection systems ERD achieves similarly good near-surface depth resolution as ^{15}N NRA. Analyzers with large acceptance angles (such as kinematic spread corrected spectrometers) [239, 249, 250] are by all means strongly preferable. If heavier ERD projectile beams can be provided and are safe to be applied to the given sample material from the viewpoint of radiation damage, the routinely achieved sensitivity of the two techniques is very similar, yet extended depth profiles can be obtained much faster with conventional ERD since no energy scanning is required [238]. High sensitivity measurements for small volume H concentrations in the order of a few atomic ppm have been demonstrated with both methods [186, 251].

Projectile	θ_1	θ_r	Target	Analysis (Detection)	Reso- lution (nm)	Sensi- tivity	Ref.
ERD							
2.4 MeV $^4\text{He}^+$	15°	30°	Silicon nitride	Conventional (foil + SSBD)	70	<0.1	[234]
3 MeV ^4He	12.5° 4.5°	23° 15°	α -Si:H	Conventional (foil + SSBD)	75 22	0.1	[235]
4-6 MeV ^4He	90°	0°	Ni foil	Transmission ((foil) + SSD)	-	0.0001	[251]
220 keV Li		44.3°	HF- etched Si(111)	MEIS-ERD TOF, (Toroidal Electrostatic Spectrometer)	0.9	-	[252]
4.3 MeV $^{20}\text{Ne}^{2+}$	19°	38°	Cu	Electrostatic Spectrometer + PSD	1.8 (H) 1.5 (D)	-	[238, 253]
4 MeV $^{12}\text{C}^{2+}$	25°	35°	Polymer film	Magnetic Spectrograph Wien filter + PSD	4	-	[254]
500 keV $^{12}\text{C}^+$	15°	30°	CVD- diamond Si(001)	Magnetic Spectrometer + PSD	0.23 0.28	0.05 <6.8x10 ¹³	[249, 255]
350 keV ^4He	15°	30°	H and D implant in Be	E x B filter	3.3	0.2	[256]
2.54 MeV ^{15}N	15°	30°			2.9	0.02	
3.8 MeV ^4He	15°	30°	Ti Er	ΔE -E Telescope	-	<0.0075	[257]
2 MeV ^4He	90°	0°	Pd(100)	Transmission (foil + SSD)	-	-	[258]
6 MeV F^{3+}	20°	40°	Si(100) Si(111)	Conventional (foil + SSD)	-	-	[259] [260]
2 keV ^4He		26°	SiC(0001)	TOF-ERD	-	-	[261]
NRA							
6.4 MeV ^{15}N (H)	90° 10°	-	Bulk Surface	γ -rays, BGO or NaI	2-5 <1	0.004 ~10 ¹³	[61] [59]
700 keV ^3He (D)	any	-	Bulk & surface D	p, SSD	500		[121]

Table 2. Performance benchmarks of various ERD applications in hydrogen and deuterium analysis compared to NRA. Depth resolution refers to the value near the surface. Sensitivities are given either in at.% (general number) for bulk concentrations or in layer densities (cm⁻², scientific notation) for surface coverages.

Several authors have directly compared the performance of ^{15}N NRA and ERD in specific applications to hydrogen analysis [51, 71, 238, 262, 263]. An instructive comparison of the factors influencing the near-surface depth resolution of ^{15}N NRA and high-resolution H-ERDA (with an electrostatic spectrometer) for the same 6.4 MeV ^{15}N ion beam is given in Ref. [238]. The conclusion that the near-surface resolution achieved by H-ERDA is slightly better and may be further improved by using ^{20}Ne ions instead of ^{15}N and apply grazing ion beam incidence is not entirely fair, as the latter important possibility for improvement has not been considered at all for ^{15}N NRA (cf. Sections 3.2.1.8 and 3.3.2). Under grazing-incidence conditions, near-surface resolutions better than 1 nm have been demonstrated for both techniques [59, 255].

For the depth profiling analysis of 50 nm thick hydrocarbon layers that were sandwiched between multilayer structures of three metal films of 382 nm Al, 193 nm Cu, 208 nm Ag, and 148 nm (Au) prepared on Si wafer backings (the film thicknesses give approximately equivalent energy losses), Wielunski et al. [263] concluded that normal incidence $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA (Fig. 15 (a)) offers the best depth resolution and sensitivity compared to conventional 4.5 MeV ^4He ERD (at 20° and 30° recoil angles, Fig. 15 (b)) and 30 MeV F^{6+} HIERD (38° recoil angle). Conventional ERD with ^4He was found to suffer heavily from multiple scattering effects that degrade the depth resolution at larger analyzing depths [264, 265]. This is seen in Fig. 15 (b) as increased width, reduced height, and increased continuous background in the respective H profiles, and is particularly pronounced in the large Z targets (Ag, Au) [263].

Fig. 15. (a) Excitation curves of the resonant $H(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction for all four multilayer structures. The energy straggling of primary ^{15}N beam in sample material is responsible for the reduction of peak height and the increase in peak width as a function of increasing depth in the sample. (b) 4.5 MeV ^4He ERD spectra taken at tilt 75° and recoil angle 30° for all four multilayer samples. The thin line represents a simple (without multiple scattering effects) computer simulation with the RBX program. The thick line represents a DEPTH program simulation, which includes small angle multiple scattering effects. Reproduced from Ref. [263] with permission from Elsevier.

The comparison to simulated ERD spectra using RBX [224] and DEPTH [221, 222] simulation software, respectively, indicated that the spectral broadening was due to multiple scattering effects, which are not included in the RBX code. The latter thus severely overestimates the ERD depth resolution, which may lead to erroneous interpretations of ERD spectra. DEPTH, on the other hand, does take multiple scattering events into account and apparently reproduced the experimental data in Fig. 15 (b) rather adequately. In HIERD (not shown) the depth resolution shows a

much smaller depth- and material- (Z) dependence since heavier F projectiles tend to be less affected by multiple scattering. For the same reason and due to the normal beam incidence resulting in a much shorter ion trajectory within the analyzed material, as well as due to the additional fact that in ${}^1\text{H}({}^{15}\text{N},\alpha\gamma){}^{12}\text{C}$ NRA only the incident ${}^{15}\text{N}$ ion is subject to straggling, the NRA depth resolution was far superior in this particular application of H analysis in a metallic multilayer stack [263].

2.3.2 Versatility

In addressing practical differences between ERD and NRA for near-surface hydrogen analysis, we first note that there are extremely few variable experimental parameters in high resolution H depth profiling via ${}^1\text{H}({}^{15}\text{N},\alpha\gamma){}^{12}\text{C}$ NRA. Obviously, the ${}^{15}\text{N}$ projectile and its energy, the size and energy width of the reaction cross section, the optimum choice of the detector for the 4.43 MeV γ -rays, etc. are rigidly defined by the characteristics of the nuclear reaction resonance at 6.385 MeV (Table 1). Only the γ -detector's solid angle and background, the beam incidence angle on the target, and the beam energy spread remain 'adjustable' parameters that influence sensitivity and depth resolution. A sufficiently monochromatized ${}^{15}\text{N}$ ion beam provided, the near-surface depth resolution is determined mainly by the vibrational Doppler broadening. Depth resolution and probing range are easily optimized by the angle of incidence. In H profiling with NRA, only straggling of the primary ${}^{15}\text{N}$ ion needs consideration. Sensitivity is clearly maximized by increasing the detection solid angle and the beam flux, and by reducing the detector background. Once the detection system is calibrated only the ${}^{15}\text{N}$ stopping power in the analyzed material

(i.e., the target's chemical composition and density) is required to evaluate H concentrations quantitatively. This very manageable situation leads to ^{15}N NRA measurements of great facility and straightforward data interpretations that are easily accomplished even by experimentalists without extensive experience in ion beam analysis.

For ERD, various detection schemes exist that require a certain understanding of ion optics, and the separation of projectiles and recoiled particles as well as the energy analysis of the latter is by no means trivial. Whereas in NRA the identification of the 4.43 γ -rays of the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction in the scintillation spectrum is simple and the sharp resonance at 6.385 MeV may even be used to calibrate the accelerator energy, the channel-energy conversion in commonly used ERD detectors requires some attention [266, 267].

It might thus be stated that in routine ^{15}N NRA the provision of an easily tunable, well-monochromatized ^{15}N beam of >6.4 MeV is the instrumentally demanding part, whereas the actual measurements are simple to conduct and optimum conditions for the analysis of different sample systems are found easily. ERD, on the other hand, appears to be less demanding on the accelerator side (except to provide sufficient energy and stability), whereas the arrangement of the recoil experiment requires more thought (or experience). The recoil energy analysis is definitely more complex and requires specialized detection equipment for high resolution work (Appendix B).

ERD data analysis also appears to be somewhat more involved compared to ^{15}N NRA, since also the stopping and straggling of the recoiled atoms on their path out of

the target and through the range foil (if used) need to be accounted for in addition to the projectile trajectory into the sample. This requires detailed knowledge of the energy dependent stopping cross sections of the projectiles and recoils in the analyzed sample, which may not be available for novel materials at all energies, even though stopping and range databases are continuously expanded [126]. For quantitative ERD analysis the accurate knowledge of the hydrogen recoil cross section is a further crucial requirement. Non-Rutherford cross section effects and possible nuclear reaction backgrounds need careful attention in ERD with high energy (> 1 MeV/amu) beams of ^4He projectiles on light targets (cf. Appendix B). In comparison, the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ cross section near the 6.385 MeV resonance is very well-characterized and the off-resonance cross section is small and constant at least up to 9 MeV [52, 100, 110, 111] (Section 2.2.4).

In conclusion, ERD and ^{15}N offer quite comparable performance in the analysis of near-surface hydrogen. Both have demonstrated ppm level sensitivity and sub-nanometer surface resolution under certain provisions. ^{15}N NRA routinely provides good surface resolution in the order of a few nm and can easily switch between a high-resolution near-surface mode and standard measurements of extended depth profiles by a simple adjustment of the ion beam incidence angle. ERD, on the other hand, requires specialized spectrometers to achieve high resolution and then has a smaller probing depth range and likely non-maximum sensitivity, although this is apparently sufficient to detect sub-monolayer coverages of H or D on a surface [255]. Sensitivity for bulk H or D is similar in both techniques. HIERD is an attractive option to achieve higher sensitivity and better depth resolution, provided the sample

material withstands the more energetic irradiation. Depth profiling over an extended range with high-resolution spectrometers may require segmental measurements at readjusted analyzer pass energies. Simultaneous detection of several hydrogen isotopes (H, D, and perhaps even T) with the same ion beam is only possible in conventional ERD with absorber foils and may require rather high projectile energies. Zero-point vibration measurements of surface H through Doppler width analysis are exclusive to ^{15}NRA at 6.385 MeV.

3. Applications

3.1 Surface hydrogen

This chapter reviews quantitative NRA hydrogen coverage measurements at single crystal surfaces. Table 3 gives an overview of the studied systems. The chapter is organized into sections for metal, semiconductor, and insulator surfaces, with subdivisions for individual materials and surface orientations. Elements appear in order of their group in the periodic table. Single crystal surfaces of hydrogen-absorbing metals (Ti, Zr, Pd, Pd₇₀Au₃₀) are treated in Section 3.2.3. Since quite a few surface coverage data were obtained with the D(³He,p)⁴He reaction, ‘hydrogen’ will be used to synonymously represent both H and D.

¹⁵N nuclear reaction analysis provides two important sources of information on the properties of surface-adsorbed H: (1) The H coverage is obtained quantitatively in a non-destructive fashion (as is D with D(³He,p)⁴He NRA); (2) NRA via the narrow energy resonance of ¹H(¹⁵N,αγ)¹²C at 6.385 MeV is the only experimental technique that can directly reveal the zero-point energy of the H vibrational motion on the surface, both in the perpendicular and in the parallel direction to the surface [67]. The latter property can be related to the mobility of H in surface diffusion and also to the possibility of H delocalization that has been under debate for H on a variety of metal surfaces (Cu(100), Ni, Pd, Pt) [68, 268, 269].

Table 3. Hydrogen and deuterium (saturation) coverages on single-crystal surfaces quantified with NRA and ERD techniques (materials in alphabetical order).

Surface	ML density (atoms/cm ²)	θ_{sat} (ML)	Structure (LEED)	Method	Preparation Condition	Ref.
Ag(111)	1.38×10^{15}	0.6 ± 0.1	(2×2) + (3×3)	D(³ He,p) ⁴ He	D _{at} (filament)	[270]
Cu(111)	1.77×10^{15}	0.67 ± 0.03	(3×3)	D(³ He,p) ⁴ He	D _{at} (filament)	[271]
Cu(100)	1.54×10^{15}	1.0	p(2×2)- p4g	D(³ He,p) ⁴ He	D _{at} (filament)	[272, 273]
Diamond	1.57×10^{15}	1.0 ± 0.3		HR-ERDA	Plasma CVD	[255]
Ir(111)	1.56×10^{15}	1.0 ± 0.1	(1×1)	¹ H(¹⁵ N,αγ) ¹² C	1000 L H ₂ , 80 K	[274]
Mo _{0.75} Re _{0.25}						[275]
(100)		2.02 ± 0.10	(1×1)	D(³ He,p) ⁴ He	100 L D ₂ , 100 K	
(110)		0.99 ± 0.05	(1×1)			
(111)		2.86 ± 0.24	(1×1)			
Ni(110)		1.0	(2×1)	D(³ He,p) ⁴ He	D ₂ , 175 K	[276, 277]
		1.5	(1×2)			
Ni(111)	1.86×10^{15}	0.5	(2×2)	ERD	D ₂ , 120 K	[278]
		0.8	(1×1)		D ₂ , 120 K	
		1.0 ± 0.1	(1×1)		D _{at} , >150 K	
Pd(100)	1.32×10^{15}	0.5	c(2×2)	ERD	D ₂ , <120 K	[258]
		1.0 ± 0.1	(1×1)			
		1.0 ± 0.1	(1×1)	¹ H(¹⁵ N,αγ) ¹² C	H ₂ , <160 K	[61]
Pd(110)	9.35×10^{14}	1.7 ± 0.3	(1×2)	¹ H(¹⁵ N,αγ) ¹² C	1.3 L H ₂ , 80 K	[279]
Pt(111)	1.5×10^{15}	1.0 ± 0.1	(1×1)	¹ H(¹⁵ N,αγ) ¹² C		[280]
Pt _{0.5} Ni _{0.5}						[281]
(110)	1.0×10^{15}	1.0	(1×1)	¹ H(¹⁵ N,αγ) ¹² C		
(111)	1.64×10^{15}	0.2	(1×1)	¹ H(¹⁵ N,αγ) ¹² C		
Rh(111)		0.84 ± 0.12	(1×1)	¹ H(¹⁵ N,αγ) ¹² C	1×10^{-4} Pa H ₂ , 100 K	[282]
Si(100)	6.78×10^{14}	1.0	(2×1)	D(³ He,p) ⁴ He	'Monohydride'	[283]
		1.5	(1×1)	D(³ He,p) ⁴ He	'Dihydride'	[283]
		1.6	(1×1)	D(³ He,p) ⁴ He		[284]
		1.6 ± 0.1	(3×1)	D(³ He,p) ⁴ He	400 K	[285]
		1.85 ± 0.18	(1×1)	ERD	D _{at} , RT	[259]
		1.3 ± 0.1	-	¹ H(¹⁵ N,αγ) ¹² C	HF etched	[286]
Si(111)	7.83×10^{14}	1.25 ± 0.13	(7×7)	D(³ He,p) ⁴ He	>1000 L D _{at} , RT	[287]
		1.5 ± 0.15	(7×7)	ERD		[260]
		1.11 ± 0.1	(1×1)	MEIS-ERD	NH ₄ F-etched	[288]
SiC(0001)		1.7	$\sqrt{3} \times \sqrt{3}$	TOF-ERD	H _{at} , RT	[261]
Si _{0.7} Ge _{0.3}		1.2 ± 0.1	-	¹ H(¹⁵ N,αγ) ¹² C	HF etched	[286]
SrTiO ₃ (001)	6.6×10^{14}	0.47	(1×1)	¹ H(¹⁵ N,αγ) ¹² C	H _{at} , RT	[289]
W(100)	1.0×10^{15}	2.0	(1×1)	D(³ He,p) ⁴ He	120 L D ₂	[290]
Zn(10 $\bar{1}$ 0)	5.9×10^{14}	1.0	(1×1)	¹ H(¹⁵ N,αγ) ¹² C	H _{at} , 30-100°C	[291]
		2.0			10 ⁻⁸ mbar H ₂ O × 30 min, RT	

Absolute hydrogen coverages are in general difficult to determine experimentally, e.g., by most frequently utilized thermal desorption spectroscopy, unless careful measures of calibration are taken [292, 293]. In surface structure determinations through LEED I(V) analysis or He atom scattering, often the assumption is made that the H coverage is a rational fraction of a monolayer (ML), which corresponds to a periodic arrangement of H atoms in symmetry-equivalent adsorption sites. These assumptions partially arise from the need to reduce the computational effort in the theoretical modeling of the surface structure that is required to analyze (i.e., simulate) diffraction patterns. Since the electron scattering cross section of H is very small, the validity of such assumptions can seldom be verified because LEED much more accurately locates the heavier substrate atoms rather than defining the H positions, especially when only (1×1) structures are observed or when several symmetry-equivalent site occupation patterns are conceivable. A similar problem is encountered in helium atom scattering (HAS). While the fractional loss of diffracted He beam intensity has certainly excellent sensitivity to H on the topmost atomic layer (much superior to LEED), it is not necessarily directly proportional to the H coverage [294]. The difficulty to quantitatively correlate a measured signal with the H coverage is even more severe for work function changes, as the surface dipole is likely H coverage dependent, especially in presence of non-equivalent adsorption sites or due to H-H interactions at high coverage. The quantitative information on the coverage of surface-adsorbed hydrogen provided by NRA is hence extremely valuable as a calibration reference for other H-sensitive techniques that cannot directly deliver absolute coverage values.

3.1.1 Note on adsorption experiments with atomic hydrogen

On a certain class of metals, H₂ dissociates spontaneously and sticks on the surface without any activation barrier. In such cases, hydrogen adsorption can conveniently be studied after admission of molecular H₂. On the other hand, several metal surfaces exist on which an activation barrier impedes molecular H₂ dissociation, so that adsorption studies have been performed with atomic hydrogen in order to populate the chemisorbed H state(s). Atomic hydrogen can be generated by cracking H₂ thermally or in a microwave plasma and thus bears excess energy ($\frac{1}{2}$ of the dissociation energy of a H₂ molecule, ~ 2.23 eV). This excess energy enables several other reactive processes of atomic hydrogen in addition to surface adsorption, among them penetration into subsurface sites. This can be effective even when the substrate does not exothermically absorb hydrogen, such as in the case of Cu(111), where the energy barrier for subsurface penetration amounts to at least 1.3 eV [295].

The transfer of excess energy from the H atoms to the substrate via phonon coupling and electron hole pair excitation occurs on a picosecond timescale [295, 296]. Before their full accommodation either in surface adsorption or subsurface potentials, the H atoms may thus exist on (or below) the surface in a so-called 'hot atom' state for a finite lifetime, during which they remain highly mobile and exert multiple collisions with neighboring (substrate or hydrogen) atoms. On the surface this can lead to Langmuir-Hinshelwood-like abstraction of other adsorbed H atoms, in addition to Eley-Rideal-type H abstraction upon direct impact of H atoms from the gas phase [297, 298]. In subsurface sites, not fully accommodated H atoms may diffuse further into the bulk or return to the surface (as long as vacant sites are

available there). At low temperatures the latter is the preferred diffusion direction, since in general the chemisorption potential minimum is energetically strongly favored over bulk interstitial sites [299] and separated from the subsurface potential by only a relatively small barrier [295, 300-304]. As a further possibility, also a direct stamp-in process of pre-adsorbed surface hydrogen into the subsurface by H atoms impinging from the gas phase has been reported for H/Pd(100) [305].

Since several parallel reaction pathways (absorption, abstraction, desorption, and diffusion into the bulk) exist for energetic H atoms in addition to accommodation in the surface chemisorption potentials, the hydrogen coverage on an atomic H-exposed surface will attain a stationary value that reflects a dynamic equilibrium between these processes. The sticking coefficient, the abstraction probability, and the likelihood of penetration into subsurface sites during atomic H exposure will depend on the energy of the impinging H beam, whereas sticking, desorption and bulk diffusion are strongly sensitive to the surface temperature. To our knowledge, the influence of these parameters has never been characterized systematically for any system, and it is likely that the atomic H energy has varied significantly among studies that employed different methods to supply dissociated H₂ (microwave plasmas, heated tubes, or open filaments). These circumstances may partially explain the appreciable scatter among values of the H 'saturation' coverage reported for certain atomic H-exposed surfaces (see, e.g., Table 4 for H/Cu(111) in Section 3.1.2). The point to be made here is that we consider such variations as likely to reflect different preparation conditions rather than errors in the coverage quantification with NRA.

3.1.2 Metals

W(100), W(110)

The deuterium saturation coverage on W(100) was determined as $\theta_{\text{sat}} = 2.0 \text{ ML}$ ($1 \text{ ML} = 1.0 \times 10^{15} \text{ cm}^{-2}$) by $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA [290], confirming earlier results of flash desorption and flux-calibrated molecular beam experiments [306-308]. A similarly large group of authors [292, 309, 310], however, states a smaller saturation coverage for H/W(100) of $1.5 \times 10^{15} \text{ cm}^{-2}$, including a carefully calibrated TDS measurement by Winkler [292]. As of today this discrepancy stands unresolved, which may exemplify that despite best efforts to reproduce a given adsorption system independently, experimental pitfalls may remain. Even when calibration and stability of the H detection method are guaranteed, differences in the surface preparation procedures may always introduce uncertainty, as the H coverage on metal surfaces tends to be strongly sensitive, e.g., to the presence of surface impurities.

The first $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA applications for the analysis of chemisorbed H layers on well-characterized single crystal surfaces were the measurements of hydrogen on W(100) and W(110) by Iwata et al. [65, 83]. They observed the room temperature uptake and saturation of H on the W(100) surface during dissociative chemisorption under different H_2 background pressures in the range of $6.0 \times 10^{-7} - 1.2 \times 10^{-5} \text{ Pa}$ (Fig. 16) and determined the initial H_2 sticking probability as $s_0 = 0.69 \pm 0.1$ in reasonable agreement with previous publications [307, 308]. Although these early ^{15}N NRA measurements of the H coverage were not quantified relative to a calibration standard and saturation at $2.0 \times 10^{15} \text{ cm}^{-2}$ was merely *assumed* (in line with Refs. [290, 306-308]), the H_2 pressure dependent changes of the adsorption rate and of the H

coverage saturation levels in competition with ^{15}N ion-induced desorption are clearly recognized (Fig. 16). Above 6.0×10^{-6} Pa the ion beam-induced desorption is fully compensated and higher H_2 pressures do not increase the H coverage beyond the saturation value. From the decay of the H-NRA signal in UHV (residual pressure: 6.7×10^{-8} Pa) the cross section for ^{15}N ion-induced desorption was estimated as $2.4 \times 10^{-16} \text{ cm}^2$. Iwata et al. obtained similar results for H/W(110), where the ion-induced desorption cross section was found to be the same and the H saturation coverage (0.7 ± 0.1) times smaller than that on W(100) [83]. The latter observation is fairly consistent with earlier hydrogen adsorption studies on tungsten surfaces, which reported H saturation coverage ratios of W(110) relative to W(100) between 0.7 (Ref. [311]) and 0.9 (Ref. [309]).

Fig. 16. Relative hydrogen coverage obtained from the γ -ray yields as a function of the time elapsed after introducing H_2 at pressures of 1.2×10^{-5} (•), 6.0×10^{-6} (▲), 1.2×10^{-6} (×), and 6.0×10^{-7} (○) Pa. Error bars are shown only at the lowest H_2 pressure. The solid curves show fits to $s = s_0(1 - a\theta)$. Adapted from Ref. [65] with permission.

Iwata et al. also determined the zero-point energy of the H-atom vibration perpendicular to the W(100) surface from the Doppler width of the nuclear reaction resonance profile measured with the ^{15}N ions incident along the surface normal [65]. The obtained value of $E_z = 64 \pm 16$ meV was in sound agreement with the zero-point energy expected in the framework of the harmonic oscillator model for the ν_1 H vibration mode (perpendicular to the surface) as measured by HREELS (65 meV) [312, 313] and RAIS (68 meV) [314] at saturation coverage.

Rh(111)

Hydrogen adsorption on the Rh(111) surface was investigated by $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA combined with dynamical LEED analysis [282] in order to clarify the adsorption site and vibrational properties of the adsorbed H atoms. LEED showed no indications for H-induced surface reconstructions, the diffraction pattern remaining (1×1) up to H-saturation. From the integrated γ -yield of the NRA surface resonance excitation profile (Fig. 17) the H saturation coverage at ~ 100 K under 1×10^{-4} Pa H_2 was determined to be 0.84 ± 0.12 ML, suggesting that the local coverage is close to 1 ML as previously assumed [315, 316]. The small difference to the full monolayer coverage was rationalized by either unavoidable defects, repulsive interactions between large densely packed (1×1) domains in the H adlayer, or possibly by hindrance of the H_2 dissociation near coverage saturation [317]. Shifts in the LEED $I(V)$ curves revealed that H(D) adsorption lifts the first layer relaxation (-1.2% contraction vs. the bulk interlayer distance) of the clean Rh(111) surface already at half saturation coverage, restoring a bulk-like spacing between the two outermost layers of Rh atoms. The H adsorption site was clearly identified as the fcc threefold

hollow site in favor over mixed hollow site + bridge, pure hcp hollow, and on-top occupations [282].

Fig. 17. NRA resonance profile of H-saturated Rh(111) recorded at ~ 100 K with normal incidence ^{15}N . Data are fitted to a Voigt profile (solid line). Inset: D uptake of Rh(111) under D_2 exposure at ~ 80 K determined by TDS. Reproduced with permission from Ref. [282].

The zero-point energy for the H vibration perpendicular to the Rh(111) surface was derived as 53.2 ± 9.2 meV from the Doppler width of the NRA surface resonance excitation profile (Fig. 17), measured under ^{15}N ion incidence along the surface-normal direction. This zero-point energy corresponds to a first vibrational excitation energy of ~ 106 meV within a harmonic oscillator model for the atomic H vibration against the surface. The NRA-derived value represents the average of all H vibrational motion components perpendicular to the surface. It is clearly smaller than the HREELS observed energy loss (136 meV) assigned to surface-perpendicular

vibration excitation [316, 318] and also smaller than the theoretical prediction of a vibrational band with A_1^2 symmetry and predominantly perpendicular character (~ 150 meV) [319]. While the discrepancy could not be resolved conclusively, it was reasoned that the nature of the H wavefunction in the adsorbed state is too complex as to be reproduced in a simple harmonic oscillator model. Apparently the H atoms experience a strongly anharmonic potential, causing substantial mixing of the H motions perpendicular and parallel to the surface.

Ir(111)

Matsumoto et al. investigated the H-adsorption structure on the Ir(111) surface by means of dynamical LEED I(V) analysis [320]. Determining the H adsorption site on Ir(111) was of particular interest because this system is a rare case of an fcc (111) transition metal surface for which the on-top position has been proposed as the most likely H adsorption site. This conjecture was inferred from HREELS data revealing unusually high vibrational frequencies of the H adatom layer [269], and later corroborated by DFT total energy calculations [321]. Matsumoto et al. found no superstructures caused by hydrogen adsorption and the LEED pattern remained (1 $\times$ 1) up to saturation with H [320]. $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA was used to confirm that the H coverage saturated at 1.0 ML ($1.56 \times 10^{15} \text{ cm}^{-2}$) after exposing the clean Ir(111) surface to 1000 L ($2.66 \times 10^{-4} \text{ Pa} \times 500 \text{ s}$) H_2 gas at 80 K [274]. The H saturation coverage and uptake behavior under H_2 exposure was found to be in good agreement with a previous TDS investigation of H_2 adsorption on Ir(111), which discovered a novel mechanism of isotope exchange reactions with preadsorbed D driven by hot H adatoms that are generated in the dissociation process [322]. Based

on the perfectly symmetric Gaussian shape of the NRA resonance excitation curve of H/Ir(111) (Fig. 18), recorded with the ^{15}N ion beam inclined by 60° against the surface normal, it was concluded that it is not necessary to consider potential H absorption into the Ir(111) subsurface in modeling the H adsorption structure [274] (although partial first layer subsurface site occupation is principally indistinguishable, see Section 3.2.1). NRA further confirmed that the H coverage was stable against desorption under UHV at 80 K, the conditions under which the LEED $I(V)$ measurements were performed [320].

Fig. 18. Excitation curve of the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ nuclear reaction resonance from 0.5 ML-H covered Ir(111) recorded under a ^{15}N incidence angle of 60° from the surface normal. The solid curve is a fit to a Gaussian form. Reproduced with permission from Ref. [274].

The NRA-derived information on the H coverage and location provided the background for the structural analysis of H-saturated Ir(111) [320]. The dynamical LEED calculations, however, turned out to be rather insensitive towards modeling the H adsorption for either on-top, fcc hollow, or hcp hollow site occupation; the simulated $I(V)$ curves reproducing the experimental data in the energy range of 100-400 eV nearly equally well. This finding is possibly accounted for by the rather flat H

adsorption potential on Ir(111), which according to DFT calculations shows only marginal corrugation with an only slightly deeper minimum at the on-top site and small energy barriers separating this site from similarly deep wells at neighboring high symmetry sites [321]. In addition, Nobuhara et al. found indications that the H nuclear wavefunction is partially delocalized around the on-top adsorption site in low-lying vibrationally excited states (mainly surface-parallel modes ~50 meV above the ground state) [321]. Although the H adsorption site could thus not be determined conclusively on the particular Ir(111) surface, the LEED analysis clearly revealed that H adsorption removes the small inward relaxation between the two outermost layers of Ir atoms (-0.45% contracted vs. the bulk interlayer spacing) and that it instead produces a slight outward expansion of similar magnitude (+~0.45%) on the H-saturated surface with H in threefold hollow sites (or +0.52% with H on top, respectively) [320].

Ni(110), Ni(111), Ni(100)

Ni(110)

Nickel surfaces readily dissociate molecular hydrogen [323]. The rather open and intensively studied Ni(110) surface shows a somewhat complex behavior in its hydrogen interactions, involving several structurally ordered phases developing under increasing H₂ exposure. After small (0.3~0.7 L) H₂ exposures at low temperatures (< 200 K) first a well-defined (2×1) LEED pattern with faint but clear half-order spots appears that subsequently (~2-3 L H₂) transforms into a H-induced (1×2) phase with intense diffraction spots indicative of substrate reconstruction [324,

325]. Further ordered phases ($c(2\times6)$, $c(2\times4)$, and $c(2\times6)$) of the H adatoms were discovered by helium diffraction in the sub-monolayer coverage regime [326-328]. Quantitative $D(^3\text{He,p})^4\text{He}$ NRA measurements by Norton's group established that the well-defined (2×1) structure corresponds to an ordered H adsorption layer of 1.0 ML ($1.14\times10^{15} \text{ cm}^{-2}$) on an unreconstructed Ni(110) surface, whereas the (1×2) phase holds 1.5 ML H at saturation and involves a pairing row reconstruction of the two topmost Ni atom layers [276, 277, 329, 330]. Fig. 19 shows respective models of the proposed (1×2) -2H and (1×2) -3H structures, which are supported by experiments (LEED, HAS) as well as by theory (DFT) [331, 332]. The DFT calculations additionally identified the most stable adsorption sites in the (1×2) pairing row reconstruction as the pseudo-threefold hollow and long-bridge sites. This information cannot be obtained from TDS due to overlapping desorption peaks and possible reconstruction lifting during the heating ramp [329, 331, 332].

The hydrogen coverages in the (2×1) and (1×2) phases had been debated for some time, but presently the respective values of 1.0 and 1.5 ML are most widely accepted [276, 277, 333]. An earlier calibrated $D(^3\text{He,p})^4\text{He}$ NRA investigation notably determined the same coverage *ratio* of (2:3) for D in the (2×1) and (1×2) phases of H/Ni(110), but arrived at overall smaller saturation coverages of 0.67 and 1.0 ML, respectively [334]. It was speculated that either H_2 impurities in the dosed D_2 gas or H/D exchange on the D-exposed Ni(110) surface with H_2 in the UHV residual gas might have reduced the D coverage [276], pointing out a potential pitfall that might require attention in quantitative D coverage evaluations with $D(^3\text{He,p})^4\text{He}$

NRA. Consequently, one may consider H coverage measurements with $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$

NRA more reliable, since residual D_2 is usually negligible in UHV.

Fig. 19. (a) High-symmetry H adsorption sites on Ni(110). TP: top; LB: long bridge; SB: short bridge; HL: hollow; PT: pseudo-threefold. (b)-(e): Top views of the H adsorption structures on Ni(110): (b) (2×1) -2H lattice gas structure (no reconstruction, $q_{\text{H}} = 1.0$ ML), (c) and (d) two models for the (1×2) -3H pairing-row reconstruction ($q_{\text{H}} = 1.5$ ML), and (e) (1×2) -3H missing row reconstruction. Adapted from Ref. [331] with permission from Elsevier.

Warming the (1×2) -3H phase above ~ 220 K or exposing a clean Ni(110) surface to H_2 at room temperature produces another (1×2) phase that shows streaks along $[001]$ in the LEED pattern [277, 325, 329, 334]. It has been suggested on the basis of first-principle computations (DFT) that the evolution of this streaky (1×2) phase is due to progressive transformation into a missing row structure [331]. This type of reconstruction involves substantial mass transport in the topmost Ni layers, hence the phase formation is expected to be thermally activated, consistent with the finding that it occurs only above ~ 200 K [325, 329]. This interpretation might also explain differences in TD spectra and NRA-determined absolute coverages that depend on the exposure history of the sample. Winkler and Rendulic observed a coverage of 2.3 ML at 140 K for the H_2 -saturated (1×2) phase with calibrated TDS,

which showed a pronounced ' α ' feature at ~ 220 K [333]. Harrington and Norton note that cooling an annealed Ni(110) surface in 10^{-4} Pa D_2 from 350 to 170 K results in a larger D coverage (1.7 ± 0.05 ML) compared to the 1.5 ML value obtained after saturation with D_2 at 170 K, the former giving rise to a new ' β_3 ' desorption state at 435 K in TDS, whereas the low temperature ' α ' peak is missing [330]. No detailed explanations were offered, but one may speculate that different amounts and distributions of H absorbed below the surface and also different degrees of surface reconstruction might account for the observations. Owing to the activated and therefore strongly temperature sensitive trend to progressive reconstruction it is difficult to specify a saturation coverage for the streaky (1×2) phase.

Ni(100)

Although no quantitative NRA measurements are reported for Ni(100), we note for the sake of completeness that the coverage is presumed to saturate at 1 ML (1.6×10^{15} cm $^{-2}$) [331, 335], where H occupies fourfold hollow sites in a (1×1) overlayer as concluded from HREELS [336] and HAS [337]. At half-saturation LEED indicates a faint $p(2 \times 2)$ -H adsorption structure [336]. The fourfold hollow adsorption site was confirmed through transmission channeling by Stensgaard and Jacobsen [338, 339], who also determined the height of the H atoms above the topmost Ni atom layer as 0.5 ± 0.1 Å. The above structures and geometries were consistently reproduced in later theoretical treatments of the H/Ni(100) adsorption system [331, 332, 340].

Ni(111)

Exposure of Ni(111) to molecular H₂ at 120-140 K leads to coverages of ~0.8 ML (1 ML = 1.86×10^{15} cm⁻²) [278, 341], after which an activation barrier appears to prevent further H uptake. The true saturation coverage, $\theta_{\text{sat}} = 1.0$ ML, is only attained after atomic H exposure [278], see below. The dissociated H atoms chemisorb in two binding states (β_1 , β_2) with respective TDS maxima at 355 and 383 K, which are filled sequentially and display equal populations after saturation [323, 333, 341]. Both desorption signals show the typical peak shift to lower temperature with increasing initial coverage characteristic of the second-order kinetics of H₂ recombination.

The absolute D coverage was evaluated [278] through ⁴He elastic recoiling, for which the cross-section is known quantitatively [342]. Up to 250 K and in a coverage range of ~0.3 and 0.6 ML a clear (2×2) LEED pattern with weak (1-2% of the fundamental diffraction spot intensity) half order spots appears, which is best developed at a H coverage of 0.5 ML, where the β_2 TDS signal saturates [341]. This Ni(111)(2×2)-2H superstructure is of the honeycomb type, where the large (2×2) surface unit cell contains 2 non-equivalent H atoms in an hcp and in an fcc threefold-coordinated site (Fig. 20) [341]. This structure model was confirmed by Helium scattering [343] and later refined with improved techniques of dynamical LEED I(V) analysis [344], which demonstrated that this H-induced superstructure involves also a substrate reconstruction (the H-coordinated Ni atoms are pulled out of the surface by 0.04 Å to slightly buckle the top Ni layer). This (2×2)-2H structure is in excellent agreement with DFT calculations [331], just as the absolute H atom positions determined by ion scattering. Transmission channeling (TC) [278] and low energy

recoil scattering (LERS) were used to independently confirm the simultaneous occupation of fcc and hcp sites [345, 346]. The height of the H atoms above the surface was determined to 1.1-1.5 Å by LERS, in reasonable agreement with the results of LEED ((1.15±0.1 Å) [341] and (0.98±0.08 Å) [344]), and HAS (1.18±0.05 Å) [343]. The D adsorption height evaluation by TC tends to be slightly smaller (0.8±0.10 Å) [278], possibly because the TC intensity mostly reflects channeling in the bulk of the thin film single crystal and may be less sensitive to the surface buckling and slight outward relaxations in the H-covered outermost Ni layer [347].

Fig. 20. Model for the (2x2)-2H/Ni(111) honeycomb structure in the top (a) and side (b) views. Reproduced with permission from Ref. [344].

The hydrogen saturation coverage on the Ni(111) surface was quantified as 1.0±0.1 ML, which was obtained by dosing atomic hydrogen (deuterium) at $T \geq 150$ K and resulted in the restoration of a (1×1) LEED pattern [278]. Atomic H exposure at surface temperatures below 150 K may cause hydrogen absorption, so that elevated exposures may produce a near-surface hydride phase [48, 348], in which H populates octahedral interstitial sites [278]. To avoid disturbances by absorbed D near the surface, Mortensen *et al.* prepared the D-saturated (1×1) surface phase by atomic H dosage at 190 K, where subsurface H becomes unstable. Transmission channeling (TC) then revealed that D occupation of fcc sites dominates (~90%) on the D-

saturated (1×1) surface [278]. Also a quite substantial lateral r.m.s. displacement (0.25 Å) of D on the saturated Ni(111) surface was found [278], which was considered consistent with theoretical predictions that chemisorbed H may be delocalized along the surface [268, 349]. On the other hand, HREELS measurements could not conclusively confirm a quantum delocalization of the adsorbed H atom in the ground state wavefunction, although evidence for a delocalized nature of vibrationally excited states was found in the $\theta = 0.5$ (2×2)-2H phase [68]. In the high coverage (1×1)-1H phase at $\theta = 1$, however, repulsive H-H interactions again promote the localization of the mainly surface-parallel vibrational modes [350]. Quantum effects possibly play a role in the low-temperature (< 110 K) surface diffusion behavior of H on Ni(111) [351].

The interaction of atomic hydrogen with Ni surfaces at temperatures below 140 K can lead to the population of subsurface sites, which is evidenced by a characteristic zero-order (α) TDS feature peaking at 180 K that may contain several ML of hydrogen after elevated dosages of atomic H [48, 335, 348]. Notably, hydrogen in octahedral subsurface sites at Ni(111) is the only known case in which this species could be identified by means of HREELS [48, 352]. Much theoretical work has supported this assignment [331, 332, 340, 353-356] and confirmed that the first-layer subsurface-absorbed H is metastable against desorption or returning to the energetically more favorable surface adsorption sites, thereby explaining the experimental observation that subsurface population only occurs below ~150 K and not before all surface adsorption sites have been filled [335]. On Ni(100) the desorption of subsurface hydrogen involves recombination with surface-adsorbed H

atoms [335] and for H/Ni(111) the molecular desorption dynamics have been investigated with angle-resolved TDS [348] and quantum state resolving resonance-enhanced multiphoton ionization [357]. These studies revealed that desorbing subsurface hydrogen has a unique desorption temperature, translational energy, angular distribution, and vibrational frequency that differ distinctly from those of surface-adsorbed hydrogen. The results suggested that hydrogen does not directly recombine from subsurface sites but that diffusion on the surface is involved prior to recombination and molecular desorption.

Subsurface-absorbed hydrogen in Ni(111) exhibits a particular chemical reactivity with respect to hydrogen addition to simple co-adsorbed hydrocarbons, a reaction that notably would not occur with surface-adsorbed H atoms alone, and which is suspected to be of profound importance in the widespread application of nickel as a catalyst for hydrocarbon hydrogenation [48, 358-360]. The enhanced chemical reactivity of subsurface hydrogen has attracted considerable attention from theory [353-358, 361], yet the actual reaction pathways of subsurface hydrogen are still far from being fully understood. As of present, the behavior of subsurface H in Ni surfaces has not been addressed through NRA measurements, although such studies might add insight into the interesting problem of the subsurface hydrogen reactivity. The potential of ^{15}N NRA to distinguish surface-adsorbed H species from subsurface-absorbed H at metal single crystal surfaces and nanoparticles is discussed in Section 3.2.

Pt(111)

As one of the most active materials for hydrogen dissociation platinum finds important industrial applications in heterogeneous catalysis of (de-)hydrogenation reactions, in electrochemistry, and in fuel cells. Hydrogen interactions with Pt surfaces have thus long been subject of intense research [1, 362, 363], and even nowadays the complex H₂ dissociation and surface diffusion dynamics continue to attract attention [69, 364, 365]. Several NRA and recoil scattering investigations unanimously agree on a H saturation coverage of 1.0 ML (1 ML = 1.50×10^{15} cm⁻²) on Pt(111) [67, 280]. Nonetheless, the determination of the saturation coverage has turned out to be not as simple as one might expect. Although there is no activation barrier in the minimum reaction pathway for dissociative chemisorption of molecular hydrogen on Pt(111) [366-368], full saturation of the surface requires temperatures <200 K [280, 364] and rather large H₂ exposures (~1000 L) because the initial sticking coefficient does not exceed $s_0 = 0.1$ even on clean Pt(111) and further reduces substantially as the H coverage increases [364, 367, 369, 370]. The small sticking probability (especially on well-prepared surfaces with low defect densities [365] and its slight enhancement with increasing surface temperature [369], has been explained in terms of preferential H₂ dissociation at step defects from a non-equilibrated mobile precursor [364, 365, 369]. This adsorption mechanism strongly dominates at low H coverage and small incident kinetic energies (≤ 60 meV) typical for conditions of H₂ background gas exposure [365]. A second defect-related chemisorption channel operative at higher H coverages and at larger defect densities involves direct H₂ dissociation at step sites with second-order Langmuir kinetics and

an initial probability of 24% of the step density [364]. Molecular beam studies revealed that the dissociation probability at regular Pt(111) terrace sites increases strongly with the surface-normal kinetic energy component ($50 \text{ meV} < E_T < 550 \text{ meV}$) of the incident H_2 molecules [367].

Fig. 21. Isobars for deuterium adsorbed on Pt(111) determined with $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA. $\theta_{\text{H}} = 1.0 \text{ ML}$ by definition at $1.5 \times 10^{15} \text{ D atoms cm}^{-2}$. Reproduced from Ref. [371] with permission from Elsevier.

The first absolute coverage measurement on Pt(111) with $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA was reported as early as 1980 by Davies and Norton, who found a coverage of $(1.10 \pm 0.05) \times 10^{15} \text{ D atoms cm}^{-2}$ (0.7 ML) after dosing 600 L D_2 ($1.3 \times 10^{-4} \text{ Pa}$) at 185 K [123]. This exposure is insufficient to D-saturate the surface. The same group later performed a set of quantitative NRA equilibrium D coverage measurements on Pt(111) in the temperature and pressure ranges of $180 \leq T \leq 440 \text{ K}$ and $5 \times 10^{-6} \text{ Pa} \leq P$

$\leq 5 \times 10^{-2}$ Pa D_2 (Fig. 21) [371]. Converted into isosteres (families of $\ln(P)$ vs. $1/T$ curves for $\theta = \text{const.}$, Fig. 22), these data allowed deriving the coverage dependence of the isosteric heat of adsorption (E_{ads}) for D/Pt(111). For $\theta \leq 0.3$, $E_{\text{ads}} = 67 \pm 7$ kJ/mol (Fig. 23). At coverages above 0.3 ML E_{ads} reduces to 34 ± 3 kJ/mol at $\theta = 0.7$, presumably due to repulsive nearest neighbor interactions in the adsorbed D layer (~ 6 -8 kJ/mol). The largest D coverage observed in this study was 0.9 ML (1.35×10^{15} cm $^{-2}$) at 230 K under 5.5×10^{-2} Pa D_2 .

Fig. 22. Isosteres for deuterium adsorbed on Pt(111). Reproduced from Ref. [371] with permission from Elsevier.

The above described direct and non-invasive observation of the hydrogen adsorption/desorption equilibrium with NRA [371] further helped resolving an apparent discrepancy between E_{ads} evaluations from TDS and helium atom scattering (77-85 kJ/mol) [372] and a considerably lower figure (44 kJ/mol) deduced from the P-T relationship at constant H-induced work function changes [363]. The latter

estimation had led to a speculation that particularly 'soft vibrational modes' might be involved in the H_2 desorption process from Pt(111), since for $E_{ads} = 44$ kJ/mol the pre-exponential factor ν in the second order rate equation for H_2 recombination [$R_{des} = \nu \cdot (\theta_H \cdot N_S)^2 \cdot \exp(-E_{des}/k_B T)$; $E_{des} = E_{ads}$ for non-activated adsorption] would have to be unusually small [373]. Norton's NRA-derived value for E_{ads} (67 ± 7 kJ/mol) [371], however, reconciled this problem by showing that ν values in the 'normal range' for second order desorption (10^{-5} to 10^{-2} cm² atom⁻¹ s⁻¹) [374] were in fact well compatible with the available He scattering data [375].

Fig. 23. Isosteric heat of adsorption of deuterium on Pt(111). Reproduced from Ref. [371] with permission from Elsevier.

The quantitative D coverage measurements on Pt(111) [280, 371] further revealed independently that the H coverage reduces to ~ 0.05 ML when a H-covered Pt(111) surface prepared by low temperature H_2 admission is warmed to 270-300 K in UHV. This consistent observation invalidated an earlier interpretation of the

disappearance of a H-induced feature in angle-resolved valence band photoemission spectra around 270 K as the irreversible transition of surface-adsorbed hydrogen atoms into subsurface sites [376]. The latter conclusion was encouraged by the observation that at 270 K the work function remained strongly reduced relative to clean Pt(111), which seemingly suggested that H was still present on or very close below the surface. Mortensen *et al.*, however, combined the NRA D coverage measurement with transmission channeling at thin Pt(111) single crystal films, which definitely ruled out D occupation of octahedral interstitial sites below the Pt(111) surface for the questionable temperature regime (110-300 K) [280]. In addition their channeling data specified the D adsorption position on Pt(111) as the fcc three-fold hollow site at a height of 0.58 Å above the surface and thereby clearly ruled out hcp site occupation that also had been given consideration at the time. This result agreed with LAPW calculations that predicted a 0.2 eV higher stability of fcc occupation over hcp [377]. Low energy recoil scattering experiments at H/Pt(111) later confirmed the fcc adsorption site and the small initial H₂ sticking coefficient ($s_0 = 0.1$) [370]. The H height above the surface (i.e., the center of mass position of the first layer Pt atoms) was reported as 1.2 Å.

The microscopic diffusion dynamics of H on Pt(111), possible quantum effects, and the vibrational properties of adsorbed H atoms have been receiving attention until very recently. H atoms on Pt(111) are highly mobile and the low coverage activation barrier for surface diffusion is exceptionally small for H on a transition metal [68]. To investigate the adsorption potential, Fukutani *et al.* measured the Doppler-width of the surface resonance excitation curve of H atoms in the saturated

chemisorption layer on Pt(111) with $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA in surface normal and 45° inclined ^{15}N incidence geometries (Fig. 24) and extracted the zero-point energies for the H vibrational motions perpendicular and parallel to the surface [67]. In comparison with HREELS [378], RAIRS [379], and computational studies [377], the zero-point energy for the H vibration perpendicular to the surface ($E_z = 80.8 \pm 3.9$ meV) was found to match well with approximately $\frac{1}{2}$ of the excitation energy of the surface stretching vibration (153 meV), supporting a harmonic oscillator model for this vibrational mode.

Fig. 24. Resonance excitation curves of the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ nuclear reaction for Pt(111)-H recorded at ^{15}N incidence angles of (a) 0° and (b) 45° with the surface normal. Open and filled circles, respectively, denote data before and after subtraction of subsurface-H induced background in form of a sigmoidal function. The solid curves are fits of the background-corrected data to Gaussian forms. Reproduced with permission from Ref. [67].

On the other hand, the zero-point energy for the vibration parallel to the surface ($E_{||} = 62.1 \pm 6.0$ meV) was found to be of similar magnitude as the full excitation energy of the vibration mode (68 meV) assigned to H bending [378] and as the activation energy for H surface diffusion (68.5 ± 5 meV) [380]. The conclusion was

that the potential for the largely surface-parallel bending vibration is apparently strongly anharmonic [67]; the first excited vibrational state already being close to the transition state for surface diffusion. The notion that the unusually large zero-point energy of the lateral H vibration relates to a strongly anharmonic potential found support by HREELS data and DFT calculations, which demonstrated that in the high coverage regime of Fukutani's NRA measurement ($\theta > 0.75$) a third vibrational excitation loss exists at 112 meV, in which the atomic H motions perpendicular and parallel to the surface are strongly coupled [381]. Roman *et al.* found significant amplitudes of the H wavefunction at neighboring hcp sites, suggesting a partially delocalized character of the first vibrational excited state [382]. Favored by the light H atom mass, quantum-mechanical tunneling was shown to dominate the surface diffusion of H on Pt(111) up to 140 K and to contribute largely even at surface temperatures as high as 250 K [69].

A final noteworthy result of the highly depth-resolving H detection with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA in Ref. [67] is the observation of a small amount of H (0.29 at. %) distributed in a shallow region (0~5 nm) *below* the Pt(111) surface, which has been saturated with 1 ML H under 1×10^{-4} Pa H_2 at 150-200 K. This hydrogen gives rise to a faint but significant high energy tailing in the NRA surface resonance profiles of H/Pt(111) (open symbols in Fig. 24), suggesting that this absorbed H is not confined only to first layer subsurface sites (cf. Section 3.2.1). Prior to the zero-point vibration analysis, the absorbed H signal component was modeled by a sigmoid function and subtracted from the raw γ -yield curves in order to recover the purely Gaussian-shaped signal of surface-adsorbed H (cf. Fig. 4, Section 2.1.1). In light of the large

endothermic H solution enthalpy in Pt ($\Delta H_s = +0.48$ eV/H), such H absorption into the subsurface region of Pt(111) is remarkable since the equilibrium H concentration in bulk Pt would be immeasurably small under the conditions of the above experiment. Although the binding mechanism of the H atoms in the extended Pt subsurface region is unknown (it may, e.g., involve H interactions with vacancies, segregated impurities, or defects), at least the stability of H occupying first-layer subsurface sites beneath a H-saturated Pt(111) surface exposed to H₂ gas has recently been described theoretically [383], and the subsurface H concentration expected for the conditions of Fukutani's experiment [67] agrees quite favorably with the NRA observation. Legare [383] speculates that the presence of such subsurface hydrogen may have implications for certain Pt-catalyzed (de-)/hydrogenation reactions as well as for electrochemistry.

Cu(111), Cu(100), Cu(110)

Copper surfaces have been studied as prime examples of noble metal surfaces for which the dissociative H₂ adsorption is activated due to the lack of d-band holes near the Fermi energy [384]. With monoenergetic H₂ beams Anger *et al.* [385] measured the translational energy (E_T) dependence of the H₂ sticking coefficient, clearly revealing the sizeable activation barrier for H₂ dissociation on the (111), (100), and (110) surfaces of Cu (Fig. 25). To circumvent this dissociation barrier most adsorption studies on Cu surfaces have been conducted with atomic H. This practice introduced considerable ambiguity into the determination of the hydrogen saturation coverage at Cu(111), as in addition to filling surface chemisorption sites, the atomic H exposure may cause population of subsurface sites as well as

abstraction of already surface-adsorbed hydrogen atoms (cf. Section 3.1.1) [297, 335, 348, 386]. Possibly due to different methods of atomic H generation, the relative efficiencies of these three processes have likely been different in various published experiments, which might explain the substantial variation of the H 'saturation' coverage values reported for Cu(111) (Table 4).

Fig. 25. Initial sticking coefficient $S_0(E, \theta)$ of monoenergetic H_2 beams on Cu(111), Cu(100) and Cu(110) surfaces as function of beam energy (E) at a surface temperature of 190 K. The values n denote the empirical exponents characteristic of the incidence angular (θ) variation of the sticking coefficient: $S_0(E, \theta)/S_0(E, 0^\circ) = \cos^n \theta$. Reproduced from Ref. [385] with permission from Elsevier.

Cu(111)

Several studies assessed the H saturation coverage on Cu(111) with a variety of methods for atomic H generation (Table 4). Anger *et al.* [385] observed saturation of the H coverage at 0.5 ML on all three lowest-index ((111), (110), and (100)) Cu surfaces with calibrated TDS [293] after dosing H_2 with a molecular beam of $E_T = 0.4$

eV translational energy. The obtained H₂ desorption spectra from Cu(111) have symmetric shapes with maxima in the 300-360 K range and show low temperature shifts for increasing initial coverages typical for the second-order kinetics of H₂ recombination.

θ_{sat} [ML]	Exposure condition	TDS peaks	Ref.
0.5	H ₂ molecular beam ($E_T=0.4$ eV), $T_s=190$ K	β_2	[385]
0.67±0.03	D _{at} , open W-filament, $T_s=100$ K	β_2, β_1	[271]
0.34 (β_2)	H _{at} , W-tube (2000 K), $T_s=79$ K	β_2, β_1, α	[297]
0.5*	H _{at} , effusive W source, 2300 K	-	[387]
-	H _{at} , microwave source, $T_s=100$ K (80% dissociation, $E_T=70$ meV, 1 ML/s)	α	[387]
0.5* (β_2)	H _{at} , ion gun, 18 eV sample bias, $T_s=98$ K	β_2, β_1, α	[388]

Table 4. Hydrogen saturation coverages (θ_{sat}) on Cu(111) obtained with different methods of atomic H (H_{at}) or D (D_{at}) generation. H detection with calibrated TDS (only Ref. [271] used D(³He,p)⁴He NRA for calibration; the value of Ref. [387] (*) is only assumed). 1 ML = 1.77×10¹⁵ cm⁻² for Cu(111). The TDS feature at ~200 K (α) is considered to be associated with desorption of bulk-absorbed H. E_T : translational energy. T_s : Surface temperature during hydrogen exposure.

Additional deuterium uptake to a saturation coverage of 0.67±0.03 ML was found on atomic D exposed Cu(111) (1 ML = 1.77×10¹⁵ cm⁻²) by Lee *et al.* [271], who calibrated their TDS coverage-exposure relation by quantitative D(³He,p)⁴He NRA and could thereby assign the sequence of hydrogen-induced superstructure phases to absolute D coverage regimes (Fig. 26). A series of (2×2) and mixed (2×2) + (3×3) LEED patterns appear with increasing D coverage, finally converting into a (3×3) phase as the

coverage saturates at 2/3 ML. The D coverage in the (2×2) phase on Cu(111) is 0.5 ML. In addition to the 2nd order desorption peak at 300-340 K (' β_2 ') saturating at 0.5 ML, a low temperature peak at ~ 230 K (denoted as ' β_1 ') develops in the TDS spectrum when the hydrogen coverage is increased from 0.5 ML to 0.67 ML at exposure temperatures below 200 K [271, 297, 389].

Fig. 26. Atomic deuterium coverage on Cu(111) held at 100 K and exposed to atomic D as a function of D_2 in Langmuir. Full and open circles correspond to NRA and TDS data, respectively. The inset is an expanded view of the low exposure range with the observed LEED patterns indicated (the line through the data is a guide for the eye). Reproduced from Ref. [271] with permission from Elsevier.

The hydrogen saturation coverage obtained by Lee *et al.* (0.67 ML) [271] appears to be most generally accepted, possibly because a (3×3)-2H superstructure is well compatible with the (3×3) LEED pattern observed at saturation, although here the fractional superstructure spots are quite strong, suggesting that the substrate reconstructs, i.e., that this periodicity may not necessarily reflect the arrangement of

the H atoms [271]. Lee *et al.* furthermore has been the only group who observed a true saturation of the H uptake and simultaneously obtained the highest coverage under their particular atomic H exposure conditions (which, unfortunately, were not quantified), whereas several similar studies reported continued H-uptake under atomic H exposure, presumably due to H absorption [297, 387, 388, 390]. On the contrary, Kammler and Küppers [297], observed saturation of the β_2 TDS peak assigned to surface-adsorbed H at a coverage of only 0.34 ML (Fig. 27) on atomic H-exposed Cu(111), which is not only significantly smaller than Lee's value of 0.67 ML [271] but even less than the 0.5 ML found by Anger *et al.* after molecular H_2 beam dosage [385].

Fig. 27. Thermal desorption spectra of hydrogen measured after exposing clean Cu(111) surfaces to increasing exposures to H atoms at 79 K. The spectra are stacked according to the applied H fluence (indicated by numbers). 1 ML = $1.77 \times 10^{15} \text{ cm}^{-2}$. The desorption trace emphasized by small filled circles ($\theta_H=0.34$) illustrates the saturated adsorbed layer spectrum. The inset provides a logarithmic representation of the desorption rates. Reproduced with permission from Ref. [297].

A likely origin of this *reduced* saturation coverage under admission of atomic H is the abstraction of surface-adsorbed hydrogen by incoming H atoms in an Eley-Rideal-type mechanism [297, 386, 390]. For the particular exposure conditions [391] of Ref. [297], the probability to abstract surface-adsorbed hydrogen with gas phase atomic H was found to be quite considerable (0.36), i.e., even larger than the initial sticking coefficient of atomic H on the clean Cu(111) surface ($s_0 = 0.22$).

Comparing the experimental conditions of the above studies suggests that hydrogen absorption can be enforced at Cu surfaces below 200 K through large atomic H doses from high-flux sources [297, 387, 390] or mildly accelerated hydrogen ions (18 eV) [388]. Presumably this generates (near-surface) absorbed hydrogen, which desorbs in a characteristic zero-order, non-saturating (so-called ' α ') TDS peak at 200 K (Fig. 27). After elevated exposures the H quantity in this α -peak may exceed the second-order desorption signal of surface-adsorbed H (' β_2 ') [297, 388, 390], which saturates first after moderate atomic H or D exposures [271, 297, 388]. From the population rate of the TDS α peak an absorption probability of $\leq 5\%$ was deduced for atomic H generated with a microwave source [387]. The above interpretations (made in analogy to Ni and Pd surfaces) appear reasonable, although conclusive proof for the H locations assigned to the respective TDS features or for an extended depth range of the H state corresponding to the TDS α feature such as, e.g., for H/Pd(100) and H/Pd(110) with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA [61, 279], has never been provided.

A somewhat surprising feature of the H/Cu(111) system one would possibly not expect from this seemingly innocuous s-metal that does not absorb hydrogen in the

bulk, is an open dispute concerning the preferred location of H atoms near the surface. Despite much theoretical and experimental effort, the relative stabilities of H in chemisorption sites on and in in first subsurface layer sites below Cu(111) remain a subject of debate, especially at low coverages [271, 302, 303, 389, 392-394]. All theoretical treatments of this problem find consistently that for H coverages < 1 ML the subsurface-absorbed H state is considerably less stable than surface-chemisorbed H [295, 300-303]. Hence, H trapping in Cu(111) subsurface sites should be possible only if the surface H layer has a coverage of 1 ML with all energetically preferred fcc sites filled, whereas at coverages below 1 ML the subsurface H would be unstable against returning to the surface [302]. A sizeable energy barrier (~ 1 eV) furthermore prevents the penetration of chemisorbed H atoms into the subsurface of Cu(111) at all coverages up to the observed saturation at 0.67 ML [295, 300, 303]. Due to the difficulty to discriminate these two H states in closest vicinity of the surface, however, the situation has been discussed controversially from the experimental viewpoint.

An HREELS investigation of H/Cu(111) by Lee and Plummer tentatively assigned an energy loss at 115 meV appearing at coverages between 0.5 and 0.67 ML to H in subsurface sites [392]. Due to the strong energetic preference ($0.5 \sim 0.68$ eV) of H chemisorption sites at $\theta < 1$ ML, Nie *et al.* rejected this interpretation and proposed alternatively that the 115 meV HREELS feature reflects an asymmetric vibration mode of *surface* H, which forms by degeneracy lifting of the parallel vibration mode due to H-H interactions at coverages above 0.5 ML [302].

The preferred stability of H atoms in chemisorption versus subsurface sites was challenged again by Luo *et al.*, who monitored small H coverages ($\theta \sim 0.1$ ML) on atomic H-exposed Cu(111) at 210-245 K with *in-situ* HAS and observed that the H atoms seemed to disappear from the surface on a timescale of several 100 seconds as soon as the supply of atomic H was terminated (dotted line in Fig. 28) [393, 394].

Fig. 28. HAS isothermal reflectivity measured at Cu(111) dosed with atomic hydrogen at various surface temperatures. Each curve is normalized to the clean surface value (1.0). The solid lines are simulation curves according to first-order kinetics. Reproduced with permission from Ref. [393].

Eventually, the specular He reflection intensity of the clean Cu(111) surface recovered completely in a process of first-order kinetics, ruling out recombinative H₂ desorption as the origin of the H disappearance [393]. TDS taken after complete restoration of the initial He reflectivity indicated that H was still present on or in the sample and that it desorbed above 250 K as the low coverage ' β_2 ' feature [394] (cf.

Fig. 27). The temperature dependent kinetics of the He reflectivity restoration indicated that this process has a rather large activation barrier of 64.3 ± 1.3 kJ/mol [393], i.e., that it unlikely reflects, e.g., surface H diffusion and trapping at step edges. Luo *et al.* therefore attributed their observations to the transition of surface-adsorbed H atoms into the subsurface.

If true, this would be quite remarkable as it implies that the subsurface sites rather than the adsorption sites on the Cu(111) surface should be the energetically more stable location for H atoms, in direct contradiction to the described theoretical results [295, 300-303]. Apart from the obvious question whether this inconsistency of the H/Cu(111) system can be resolved in the near future, Luo's HAS data clearly highlight the potential merits of a nondestructive *in-situ* detection technique exclusively sensitive to surface hydrogen in elucidating its dynamic behavior.

Cu(100)

The Cu(100) surface saturates at a coverage of 1.0 ML (1.54×10^{15} cm⁻²) under exposure to atomic D. This was determined in two independent investigations via D(³He,p)⁴He NRA [272, 273]. Exposure to a molecular H₂ beam ($E_T = 0.4$ eV), on the other hand, only achieved an uptake of 0.5 ML [385]. In agreement with an earlier HREELS and LEED investigation [395], the atomic hydrogen-saturated Cu(100) surface ($\theta_{\text{sat}} = 1.0$ ML) exhibits a rare p(2×2)-p4g reconstruction, in which the first layer Cu atoms are laterally displaced by 0.23 Å (Fig. 29) [272].

Fig. 29. Model for the $(2 \times 2)p4g$ -D structure on Cu(100). The clock reconstruction of the Cu lattice and a (2×2) Cu unit cell are indicated. The small circles indicate D atoms adsorbed in four-fold-hollow sites (black) and displaced tetrahedral subsurface sites (grey). The experimental results do not reveal which of the displaced subsurface tetrahedral sites are populated with D. Reproduced from Ref. [272] with permission from Elsevier.

In this structure model, which relies on a robust determination of the D adsorption positions by transmission channeling measurements, the first ~ 0.5 ML of D occupy the four-fold hollow sites on an unreconstructed Cu(100) lattice. Additional D atoms ($0.5 < \theta < 1.0$ ML) then populate tetrahedral subsurface interstitial sites, which according to Foss *et al.* is the driving force for the $p(2 \times 2)$ - $p4g$ reconstruction [272]. Walter *et al.* subsequently correlated as many as three additional hydrogen-induced surface reconstruction phases on Cu(100) to absolute D coverages (NRA) that appeared in the range between 0.45 and 1.0 ML and 80-180 K; among these a $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$, a $(4\sqrt{2} \times 2\sqrt{2})R45^\circ$, and a particularly prominent superstructure of so far unidentified periodicity that maximizes at $\theta = 0.65$ ML [273].

The above results [273] supported earlier speculations that the Cu(100) surface tends to reconstruct upon hydrogen adsorption, referring to peculiar anomalies in H_2

TD spectra [385], [395]. D-induced changes of the surface morphology were also manifested by a high density of μm -sized pits visible in SEM micrographs of D-exposed Cu(100), suggesting that high D coverages can apparently enhance the surface diffusion of Cu atoms and thus enable a substantial Cu mass transport [273].

Cu(110)

Although no NRA data of absolute H coverages are reported for Cu(110), we note here that the H coverage saturates at 0.5 ML as determined by calibrated TDS [385, 390] and ion scattering [396, 397]. Atomic H adsorption on Cu(110) at 100 K induces first a (1 $\times$ 3) superstructure at $0.1 < \theta < 0.4$ ML, which transforms into a (1 $\times$ 2) reconstruction as the H coverage increases to 0.5 ML at saturation [398].

Ag(111)

Owing to the completely filled d-band of the noble metal, a substantial activation barrier (1.1 eV) prevents gas phase hydrogen molecules from dissociating on Ag(111) surfaces at room temperature [399]. Lee *et al.* have therefore studied hydrogen chemisorption on Ag(111) after exposure to atomic D, using LEED, HREELS, work function, TDS, and absolute coverage measurements with D($^3\text{He,p}$) ^4He NRA [270]. The H(D) saturation coverage was determined to be 0.6 ± 0.1 ML, where 1 ML corresponds to an atomic density of $1.38 \times 10^{15} \text{ cm}^{-2}$ on Ag(111). The quantitative NRA coverage was used to calibrate the D uptake curve measured by TDS (Fig. 30), which enabled assigning D coverage ranges to the D-induced superstructures observed by LEED [400]. Lee's NRA value for the D saturation coverage is in excellent agreement with quantitative TDS data for H/Ag(111) from Winkler's group ($\theta_{\text{sat}} = 0.65 \pm 0.05$ ML) [401].

Fig. 30. Atomic deuterium coverage on Ag(111) as a function of D₂ exposure (the line is a guide for eyes). Solid circles (•) are from the coverage measurement using D(³He,p)⁴He NRA (Ref. [290]) and open circles (o) are from the integrated D₂ TDS signal calibrated to the absolute coverage. Reproduced from Ref. [417] with permission from APS.

H chemisorption on Ag(111) at 100 K first induces a sharp (2×2) superstructure in the coverage range of 0.25~0.5 ML, followed by a combined (2×2) + (3×3) pattern as the coverage approaches saturation at 0.6 ML [270], resembling the situation on Cu(111) [271]. While the appearance of H-induced superstructures is not uncommon for fcc (111) surfaces (e.g., H/Ni(111) [341], H/Pd(111) [402]), the lack of transformation into a (1×1) structure at saturation seems to be unique to H on Ag(111) and on Cu(111) [271, 403]. Lee *et al.* further note that the intensity of the extra diffraction spots in the H-induced (2×2) and (3×3) superstructures are considerably more intense than those expected to arise solely from an ordered array of H atoms, which lets them consider that the Ag(111) surface may reconstruct upon H chemisorption. This argument is given support by the observation of positive work function changes in proportion to the H coverage, which reach +0.32 eV [270, 400] at H saturation. According to Zhukov *et al.* who find $\Delta\phi = +0.24$ eV at θ_{sat} , this work

function increase corresponds to dipole moments (0.07 Debye) that are unusually large for a H adsorption layer on a metal substrate and might hence be indicative of a surface reconstruction [401]. The latter two $\Delta\phi$ results are at variance with an earlier report of a work function *decrease* upon H adsorption [404].

The H/Ag(111) system shows a peculiar and complex behavior with respect to recombinative H₂ desorption, which occurs at ~185-200 K, corresponding to a desorption activation energy of 8.7 kcal/mol [270]. Lee's TD spectra show nearly symmetric desorption peak shapes indicative of second order kinetics, but the peak maximum shifts to higher temperatures as the initial H coverage increases, which is more common for a process of zero or fractional order kinetics. The presence of two H adsorption phases, i.e., a condensed H island structure in equilibrium with a two dimensional lattice gas (isolated H atoms diffusing on the Ag(111) terraces) has been proposed as an explanation [401]. The suggested formation of well-ordered H-islands accompanied by surface reconstruction is consistent with the H-induced superstructures observed by LEED, and the simultaneous presence of the lattice gas is compatible with the comparatively low saturation coverage (0.6 ML) evidenced by NRA [270] and TDS [401]. Depending on the size and number of the dense H islands relative to the lattice gas area, i.e., on the microscopic surface roughness that is difficult to control (defects or contaminants provide nucleation sites for island formation), the desorption kinetics may either be dominated by desorption from the island rims (half order kinetics) or from the lattice gas (second order kinetics), or contain characteristics from both kinetic regimes in intermediate situations [401]. This argument by Zhukov *et al.* may reconcile the varying shapes and coverage

dependences of the TD spectra that have been reported for the H/Ag(111) system by different groups [270, 401, 404, 405].

Ultrathin Films and (Surface) Alloys

Au/Ir(111), Au/Pt(111), Ag/Pt(111)

A great deal of attention has been paid to the special physics and chemistry of ultra-thin noble metal films and nanostructures deposited on a variety of single-crystalline substrates, because substantial differences in structural, electronic, and chemical properties clearly distinguish these artificial ‘nanomaterials’ from the respective bulk noble metals. Owing to the fully occupied d-band centered far below E_F , H_2 dissociation on Au and Ag single crystal surfaces is inhibited by considerable activation barriers that prevent room temperature adsorption of H_2 [384]. In striking contrast to this general expectation of surface ‘nobility’, Okada *et al.* reported a TDS study, which demonstrated that several (≤ 8) monolayer thin Au films grown at 100 K on an Ir(111) substrate behave surprisingly reactive toward dissociating hydrogen (D_2) molecules at temperatures as low as 100 K [406]. After depositing the Au onto D-precovered instead of clean Ir(111) surfaces, Okada *et al.* furthermore observed an additional low temperature (~ 160 K) D_2 TDS feature which he assigned to a certain amount of D that had become trapped at the Au/Ir interface. This suspect was subsequently corroborated by means of H depth profiling with $^1H(^{15}N, \alpha\gamma)^{12}C$ NRA, which could clearly distinguish between the H adsorbed on the surface of the thin Au films and H located at the Au/Ir interface [274, 407, 408].

Fig. 31. H-uptake curves measured by NRA on the clean (full circles), 4-ML (full diamonds) and 10-ML (open diamonds) Au-covered Ir(111) surfaces under H₂ at 60 K. Au was deposited at 60 K. Open circles denote a D-uptake curve for the D₂ exposure of Ir(111), measured with TDS and taken from Ref. [322]. Reproduced from Ref. [407] with permission from Elsevier.

Fig. 31 shows the NRA-determined H uptake of the clean Ir(111) surface (consistent with earlier TDS data [322]) in comparison to 4 and 10 ML thin Au films on Ir(111) under H₂ exposure at 60 K [407]. Although the Au films are clearly less reactive than the clean Ir(111) substrate, they obviously do adsorb hydrogen after larger H₂ exposures, with strikingly little influence of the Au thickness even up to 10 ML thick films. STM verified that these Au films cover the Ir(111) substrate completely [274, 407]. HD production in TPD after mixed H₂ and D₂ exposures identified the hydrogen adsorption process as dissociative [406]. The energy position, symmetric shape, and relatively narrow width of the high resolution NRA H depth profile for the H₂ exposed 4 ML Au film deposited onto clean Ir(111) in Fig. 32 (a) indicate that H resides on the Au surface, not inside the film volume. The small

additional high energy peak in the H profile resulting from depositing the 4 ML Au film after pre-saturating the Ir(111) substrate with 1 ML H (Fig. 32 (b)) signifies that ~ 0.2 ML H became trapped at the Au/Ir(111) interface [274]. Stopping and straggling of ^{15}N in the Au film reasonably accounts for the energy shift and the width of the interface peak, consistent with the picture that H is located at an atomically sharp interface between Au and Ir; a plausible idea for a junction between two immiscible metals that both do not absorb H in the bulk.

Fig. 32. Resonance excitation curves of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction for 4 ML thick Au/Ir(111) recorded under 10^{-5} Pa H_2 at a ^{15}N incidence angle of 65° from the surface normal. In (a) the Au was deposited onto clean Ir(111), while in (b) the Au film was prepared onto H-saturated Ir(111). Solid curves are fits to (a) one Gaussian form, (b) the sum of two Gaussian forms (dashed lines). Reproduced from Ref. [274] with permission from APS.

The possibility of metastable H binding in octahedral interstitial sites at the Au/Ir(111) interface was further confirmed by DFT total energy calculations [274]. To our knowledge this NRA study currently is the only report of hydrogen trapping at a metal/metal interface. One may compare the situation, e.g., to Ag deposition onto H-covered W(100), in the course of which H is completely desorbed as soon as the

Ag film (which is presumed to grow in islands at room temperature) covers the entire surface [409].

The unusual H_2 dissociation reactivity of the epitaxial Au films on Ir(111) was attributed to localized surface defects, where the half-occupied Au s-band centered at E_F is narrowed due to reduced coordination of the Au atoms [408]. STM images of the Au/Ir(111) system clearly show the presence of localized defects such as Au island edges [274, 407]. In analogy to arguments of the d-band model [384], such localized s-band narrowing leads to reduced repulsion between electrons in the occupied bonding $H_2(\sigma_g)$ molecular orbital and Au states far below E_F and increases attraction between the unoccupied antibonding $H_2(\sigma_u)$ orbital and Au states near E_F [408]. The net effect is a smaller activation energy barrier for H_2 dissociation. To illustrate this concept, DFT calculations at small Au_2-H_2 cluster models have been carried out, demonstrating that (at least in this vastly exaggerated model of a localized defect with obviously minimal s-band width) the H_2 dissociation barrier may even vanish altogether [408]. It is worth mentioning that the d-band model itself is not able to explain the efficient H_2 dissociation on the thin Au films on Ir(111), because paradoxically the d-band center of a Au monolayer on Ir(111) is located even 0.59 eV farther *below* E_F than in case of bulk Au(111), so that the model predicts an even *higher* activation barrier for H_2 dissociation on Au/Ir(111) [410].

In comparison to the highly reactive thin Au films on Ir(111), Ogura *et al.* tested Au and Ag monolayer films on Pt(111) for their activity towards H_2 dissociation [411]. The NRA and TDS study revealed that in striking contrast to the Au/Ir(111) system, the Pt(111) surface became completely *passivated* for the dissociation of molecular

H₂ if covered with either a monolayer of Au or Ag. H adsorption on these Au/Pt(111) and Ag/Pt(111) surfaces was hence possible only through admission of atomic H, which desorbed associatively as H₂ at 120 K from Au/Pt(111) and at 160 K from Ag/Pt(111), with a slight trend of increasing peak temperatures with H coverage for the latter, suggesting that a similar fractional order desorption process from rims of dense H islands is taking place as proposed for H/Ag(111) [401].

Fig. 33. $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ surface resonance excitation curve for 1 ML Ag/Pt(111) after dosage of 1000 L atomic hydrogen. The inset shows the decay of the γ -ray yield as a function of accumulated ion-beam charge

incident on the sample. Reproduced from Ref. [411] with permission from Elsevier.

Fig. 33 shows the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA surface resonance curve for the 1 ML Ag/Pt(111) surface after exposure to 1000 L of partially dissociated H₂ at 90 K. The H saturation coverage derived from the integrated profile area (γ -yield corrected for the decay through ion beam-induced H desorption shown in the inset) amounts to 0.9 ± 0.1 ML with respect to the Pt(111) substrate atomic density (1 ML = $1.50 \times 10^{15} \text{ cm}^{-2}$). This result suggests that the H saturation coverage on the Ag monolayer on Pt(111) is considerably higher than on bulk Ag(111), where it amounts to only 0.6 ML (here: 1 ML = $1.38 \times 10^{15} \text{ cm}^{-2}$) [270], suggesting much higher H densities in the

adsorption layer on the epitaxial Ag film. One may only speculate at this point whether the compressed lattice of the Ag monolayer on the Pt(111) substrate is responsible for this behavior. The slightly reduced H₂ desorption temperature of Ag/Pt(111) (~160-180 K) relative to that of Ag(111) single crystals (~180-200 K) might support the idea of a somewhat destabilized adsorption state owing to increasingly repulsive H-H interactions in the much denser H islands.

On the Au/Pt(111) surface the NRA evaluation of the H coverage produced a value of 0.7 ± 0.1 ML, slightly smaller than the saturation coverage of the clean Pt(111) surface, determined to (0.8 ± 0.1) ML in this study. As H adsorption on Au(111) is endothermic [384], no quantitative comparison to the H saturation coverage on bulk Au(111) can be made in this case. The TPD desorption peak temperature of 120 K matches reasonably with the one on Au(111) (Ref. 51 in [412]).

In their H₂ adsorption/desorption properties the only one monolayer thin Au and Ag films on Pt(111) thus already resemble the (111) surfaces of the respective Au and Ag bulk single crystals [400, 404, 412-414] and in this respect behave indeed drastically differently compared to the Au films on Ir(111), which remain active for H₂ dissociation up to Au thicknesses of at least 10 ML [407]. The surface passivity of the Au and Ag monolayers on Pt(111) also contrasts the unique chemistry displayed by, e.g., the monolayer Ni/Pt(111) surface with respect to cyclohexene (de-)hydrogenation, which differs from both pure Pt(111) and thick Ni films, outlining the potential of bimetallic catalysis [415]. The low reactivity of the Ag/Pt(111) and Au/Pt(111) monolayer systems toward H₂ dissociation observed by Ogura *et al.*, however, is not completely unexpected but in line with predictions of the d-band

model. According to this theory, the position of the metal d-band center with respect to the Fermi level (E_F) is a good indicator of the chemical reactivity of a surface [384, 416]. As the d-band center shifts downward (upward), away from (closer to) E_F , the model predicts that the surface becomes less (more) reactive. The d-band center of Au/Pt(111) is 0.08 eV below that of Au (-3.59 eV), and the d-band center of Ag/Pt(111) is 0.11 eV above that of Ag (-4.30 eV) but still below that of Au [410], so that H_2 molecules are neither expected to dissociate readily on Ag/Pt(111) nor on Au/Pt(111).

Pt(111)-Sn(2×2), Pt(111)-Sn($\sqrt{3}\times\sqrt{3}$)

Motivated by the question whether a chemical modification by substituting surface atoms with heteroelements might alter the H adsorption state on Pt(111), for which delocalization of the H nuclear wavefunction has been discussed [67, 68, 268, 382], Fukutani *et al.* investigated the H adsorption potential on Pt-Sn surface alloys by means of zero-point vibrational analysis using $^1H(^{15}N, \alpha\gamma)^{12}C$ NRA Doppler spectroscopy [417]. Well-ordered Pt-Sn surface alloys of (2×2) and ($\sqrt{3}\times\sqrt{3}$) structures that involve only the topmost surface layer and correspond to Sn coverages of 1/4 and 1/3 ML, respectively, can be prepared in a controlled fashion by Sn deposition onto Pt(111) and annealing at 1000 K [418]. As illustrated in Fig. 34, such alloying substitutes 75% or even all 3-fold hollow adsorption sites that are coordinated by three Pt atoms on clean Pt(111) with Pt_2Sn environments in the Pt(111)-Sn(2×2) and Pt(111)-Sn($\sqrt{3}\times\sqrt{3}$) structures, respectively. As a consequence of Sn-alloying, H_2

dissociation was found to be strongly suppressed so that the surface alloys had to be exposed to atomic H from a partial thermal H₂ dissociation doser in order to create the H adsorption layers [417].

Fig. 34. Structure models of well-ordered Pt-Sn surface alloys: (a) Pt(111)-Sn(2x2) and (b) Pt(111)-Sn($\sqrt{3}\times\sqrt{3}$). Adapted with permission from Ref. [417].

NRA indicated that the H saturation coverage is greatly reduced from 1.0 ML on clean Pt(111) [67] to 0.40 ML on the Pt(111)-Sn(2x2) and 0.42 ML on the Pt(111)-Sn($\sqrt{3}\times\sqrt{3}$) alloys [417]. From the Doppler widths of the nuclear reaction resonance excitation curves measured in surface-normal and 45° inclined incidence, the zero-point energies of the H vibrations in the vertical and in-plane directions were estimated to be 78.2 ± 3.7 and 53.6 ± 5.8 meV on Pt(111)-Sn(2x2), and 72.5 ± 3.7 and 58.5 ± 6.7 meV on Pt(111)-Sn($\sqrt{3}\times\sqrt{3}$), respectively. Compared to the respective zero-point energies of 80.8 ± 3.9 and 62.1 ± 6.0 meV for H on clean Pt(111) these values are only slightly smaller, suggesting that the local H adsorption potential on the Pt-Sn surface alloys does not differ substantially from the one on clean Pt(111). It was concluded that alloying with Sn apparently does not weaken the H-substrate interaction to a large degree, and that the predominant effect of Sn appears to be the introduction of a considerable activation barrier for H₂ dissociation.

Mo_{0.75}Re_{0.25}

Surfaces of transition metal alloys are interesting as their elemental distribution may differ considerably from the bulk composition owing to segregation phenomena. Absolute D coverage measurements on the (100), (110), and (111) surfaces of the bcc Mo_{0.75}Re_{0.25} alloy were performed with D(³He,p)⁴He NRA by Okada *et al.* [275]. Due to different tendencies for elemental segregation, the relative atomic composition of the outermost layers on these alloy surfaces was found to be orientation dependent. While the (100) and (111) surfaces are enriched in Mo, the (110) surface has a bulk-like composition. Only (1×1) LEED patterns were observed on all surfaces upon D₂ exposure, showing no indications for adsorption-induced superstructures at any D coverage. The D saturation coverage on the alloy surfaces was determined to be 2.02 ± 0.10 ML for the (100), 0.99 ± 0.05 ML for the (110), and 2.86 ± 0.24 ML for the (111) orientation. Exposure to atomic D did neither result in a significant increase of the NRA nor of the TDS intensity, so that the possibility of D absorption into the alloy bulk could be dismissed.

The (100) alloy surface contains nearly 100 % Mo atoms, and similar to Mo(100) the D saturation coverage of 2 ML is well consistent with an adsorption structure model based on HREELS [419] and LEED I(V) [420, 421] results, in which D atoms occupy the bridge sites (Fig. 35 (a)). A c(7√2×√2)R45° reconstruction [422, 423] as well as a variety of hydrogen-induced superstructures that form on pure Mo(100) [424, 425], however, do not appear on the Mo_{0.75}Re_{0.25}(100) alloy surface [275]

Fig. 35. Structural models for $\text{Mo}_{0.75}\text{Re}_{0.25}$ (a) (100), (b) (110), and (c) (111) surfaces saturated by D at about 100 K. Saturation coverages correspond to 2, 1, and 3 ML, respectively. Re positions are represented randomly. Adapted from Ref. [275] with permission from Elsevier.

On the $\text{Mo}_{0.75}\text{Re}_{0.25}$ (110) surface the D saturation coverage of 0.99 ML and the (1×1) LEED pattern are the same as the proposed coverage and the observed LEED patterns for H adsorption on the pure Mo(110) [426] and W(110) [427, 428] surfaces. The proposed structural model with D in quasi-trigonal sites is depicted in Fig. 35 (b). H/W(110) has not been evaluated quantitatively, but Iwata et al. observed with ^{15}N NRA that the H coverage on W(110) was (0.7 ± 0.1) times smaller than that on H-saturated W(100). Whether the H coverage on W(100) saturates at 1.5 ML or 2.0 ML is subject of some debate (see W section above), and Iwata *et al.* themselves favored the 2.0 ML hypothesis [83], but if it in fact saturated at 1.5 ML, then Okada's suggestion that the D layer on $\text{Mo}_{0.75}\text{Re}_{0.25}$ (110) at 0.99 ML is isostructural to H-saturated W(110) would be quite consistent $[(0.7 \pm 0.1) \times 1.5 \text{ ML} \approx 1 \text{ ML}]$.

On the $\text{Mo}_{0.75}\text{Re}_{0.25}(111)$ surface the first and second atomic layers are enriched in Mo (nearly 100 %) and Re, respectively. The D saturation coverage of 2.86 ML and the (1×1) LEED pattern are similar to the situation proposed for the isostructural W(111) surface [428, 429], with 3 ML D in bridge sites where they make contact with first layer Mo and second layer Re atoms (Fig. 35 (c)). This structural model is in good agreement with the dominating TPD signal at 233 K that also appears (yet at 205 K and with reduced intensity) on $\text{Mo}_{0.75}\text{Re}_{0.25}(100)$ and has been assigned to Re-rich (i.e., Mo-Re bridge) sites. D desorption from Mo-Mo sites give rise to a TPD signal at a higher temperature (295 K on the (111) and 274 K on the (100) surface) [275].

Pt_{0.5}Ni_{0.5}

Hydrogen adsorption on the (110) and (111) surfaces of PtNi alloy was investigated with quantitative $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA coverage measurements by Fallavier *et al.* [281]. The PtNi alloy shows remarkably different catalytic properties, e.g. with respect to olefin hydrogenation reactions, than the constituting elements [430]. Similar to the above $\text{Mo}_{0.75}\text{Re}_{0.25}$ case, the elemental composition of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ alloy surfaces is orientation dependent: The (110) surface is enriched with 100 % Ni atoms, while the (111) surface contains 88 at.% Pt [281]. The elemental enrichment alternates in the topmost three atomic layers and approaches the bulk composition of the alloy in a slightly damped oscillating fashion. The H coverage on the alloys surfaces was evaluated in the pressure range from 10^{-6} – 10^{-2} Pa H_2 for temperatures between 115 and 400 K. For temperatures above 200 K the coverage dependence exhibited Sievert behavior (θ being proportional to $p(\text{H}_2)^{1/2}$), indicating dissociative adsorption at identical surface sites and the absence of phase transitions.

Below 200 K the coverage dependence on the temperature indicated an ordered overlayer, evidenced by coverage saturation of under 6×10^{-8} mbar H_2 at $1/3$ ML ($1 \text{ ML} = 1.0 \times 10^{15} \text{ cm}^{-2}$) on the Ni-terminated (110) alloy surface, which was assigned to a quasi- (2×6) H phase in analogy to pure Ni(110) [431].

In contrast to Ni(110), however, where the H coverage saturates at 1.5 ML on a (1×2) reconstruction [276, 329], the maximum H coverage on $Pt_{0.5}Ni_{0.5}(110)$ is only 1.0 ML, suggesting that the H-induced pairing-row (1×2) surface reconstruction of Ni(110) may not occur on the PtNi alloy. This situation is reminiscent of the above $Mo_{0.75}Re_{0.25}$ case, where alloying with Re apparently suppressed the formation of an intrinsic and a variety of H-induced superstructures that are observed, e.g., on pure Mo(100) [275]. On the strongly Pt-enriched (111) surface of the PtNi alloy the H saturation coverage is only 0.2 ML ($1 \text{ ML} = 1.64 \times 10^{15} \text{ cm}^{-2}$), i.e. much smaller than on Pt(111) ($1.0 \text{ ML} = 1.50 \times 10^{15} \text{ cm}^{-2}$) [67, 280]. This strong coverage reduction may be related to the compressed PtNi alloy surface lattice constant relative to Pt(111) (1 ML), which may change the electronic surface properties with respect to H and CO adsorption [281]. Alternatively, Ref. [281] speculates that H adsorption on $Pt_{0.5}Ni_{0.5}$ may require surface Ni atoms, the number of which being small ($\sim 12\%$) on the (111) surface due to predominant segregation of Pt.

3.1.3 Semiconductors

Diamond

To our knowledge only a single ^{15}N NRA investigation of hydrogen on diamond single crystal surfaces has been published. Jans *et al.* [432] prepared (100), (110),

and (111) diamond surfaces by chemically treating single crystals in a HNO_3 , HCl , and H_2SO_4 mixture. After transfer into vacuum and evacuation to 10^{-7} mbar, large coverages (several ML) of excess H species were observed on these surfaces. This initial H coverage quickly desorbed under the ^{15}N ion beam to yield more stable H layers of coverages very close to the values expected for ideal mono-hydride termination (H_{th}) of the individual diamond crystallographic planes, i.e., $3.16 \times 10^{15} \text{ cm}^{-2}$ ($0.95 H_{\text{th}}$) on (100), $2.23 \times 10^{15} \text{ cm}^{-2}$ ($0.98 H_{\text{th}}$) on (110), and $1.82 \times 10^{15} \text{ cm}^{-2}$ ($1.06 H_{\text{th}}$) on the (111) surface, respectively. Despite these nearly-ideal termination values, the 'stable' H coverage was found to vary with the ion beam current density and increased after the ion beam was blanked for a period of time, suggesting a dynamic equilibrium of beam-induced H desorption and readsorption from the residual gas.

Jans *et al.* intended to demonstrate the dependence of the nuclear reaction resonance Doppler width on the orientation of the C-H bonds, which are inclined against the ^{15}N ion beam incident along the surface normal direction with angles of 55° for the (100), 35° for the (110), and 0° for the (111) surface, respectively. The measured Doppler width of $14.0 \pm 0.2 \text{ keV}$, however, did not show any significant variation with the crystal orientation and was larger even than the expected value for the fully aligned (111) H surface (13.6 keV). This unfortunate result suggests that the diamond surfaces in Ref. [432] might not have attained their anticipated atomically controlled structures, probably as a consequence of less than ideal surface preparation and/or vacuum conditions during the NRA measurements. The principal possibility to observe the orientation dependent Doppler width of the nuclear reaction resonance for H bound covalently to spatially aligned dangling

bonds on semiconductor surfaces has later been demonstrated by ^{15}N NRA measurements at *in-situ* prepared and UHV-maintained H-terminated Si(111)(1x1)-H surfaces, which are described in the next subsection [67].

A larger body of literature treats H at surfaces of natural and synthetic diamond, which is of great relevance in diamond production by chemical vapor deposition (CVD), as well as for common surface processes such as H-plasma annealing or proton implantation [6, 433]. Since in such situations H is often also found to be absorbed in the diamond bulk or in the subsurface region, this is (briefly) described in Section 3.2.4.

Silicon

The interaction of hydrogen with silicon surfaces has been characterized extensively by a manifold of techniques, driven by the crucial importance of H-terminated silicon surfaces in the fabrication of semiconductor devices and in their reliability physics, as well as out of fundamental interest in covalent H chemisorption on and desorption from semiconductor surfaces. Clean silicon surfaces generally reconstruct in order to lower their surface energy by minimizing the number of dangling bonds that exist in the bulk-truncated structure. Chemisorption bonds with hydrogen atoms remove or rearrange these Si dangling bond states, rendering H-terminated Si surfaces with structures closer to the bulk truncation and with far less reactive properties.

Three characteristics of H-terminated Si surfaces have attracted particular technological and scientific interest: (1) the passivating effect of the hydrophobic H

adlayer that helps preventing the contamination of etch-cleaned Si wafers during handling in ambient conditions between successive stages of semiconductor device production, (2) the strong impact of surface hydrogen on the structure and epitaxial growth behavior of metals [434-436] and semiconductors [437-440] on silicon substrates (surfactant effect), and (3) a giant isotope effect of D vs. H with respect to hot electron-stimulated desorption [441, 442]. For a comprehensive discussion of the latter two phenomena as well as for a detailed presentation of the formation and thermal decomposition mechanisms of the hydrogen adsorption phases on the most stable silicon surface reconstructions consult the excellent review by Oura *et al.* [2].

The above work shall not be duplicated here and we confine ourselves to pointing out that by quantifying the H (D) coverage NRA and ERDA have contributed substantially to establishing our current microscopic understanding of the hydrogen adsorption phases on silicon surfaces. The clarification of the complex Si(111)(7x7) reconstruction [443], the development of surface imaging by STM [444], and the introduction of novel optical high-resolution surface vibrational spectroscopy (Multiple internal reflection (MIR)-FTIR [445]) coincided with early applications of ion beam techniques, i.e., $D(^3\text{He},p)^4\text{He}$ NRA [283, 290], ERDA [252, 259, 260], and $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA [65, 83, 203, 446] to the (quantitative) analysis of hydrogen on well-defined single crystalline surfaces. Although $D(^3\text{He},p)^4\text{He}$ NRA provides no notable depth resolution, its application to quantify the D coverage on Si surfaces is justified by the negligible hydrogen solubility in bulk Si [109]. After the TOF-ERD technique was refined to allow combination with MEIS by Copel and Tromp at IBM

[252, 288, 437], quantitative and highly depth resolved H coverage measurements became also possible with ERD.

The absolute hydrogen coverage values combined with the identification of Si mono-, di-, and trihydride units (see Fig. 37 (a) for their structures on Si(100)) by vibrational fingerprinting with IRAS [447-449] and STM surface imaging [450-453] have provided the key information to characterize the respective adsorption phases. This has been instrumental in assessing the quality of the various H-termination layers on Si surfaces that are obtained by different methods of preparation. Principally, there are two main routes leading to clean and nearly ideally H-terminated Si surfaces: (a) *ex-situ* wet chemical oxidation (H_2O_2) and subsequent etching in aqueous HF solutions [286, 288, 446, 447, 454, 455] and (b) *in-situ* exposure of UHV-cleaned Si surfaces to atomic H (or D) [259, 260, 283, 285, 287, 448-450, 452, 453, 456].

Si(111)

According to IRAS and STM characterizations, ideally smooth and only monohydride-terminated surfaces can be prepared on Si(111) by wet chemical etching in NH_4 buffered HF solutions [454, 457]. The pH of the etching solution is essential to achieve the homogeneous monohydride termination, as treatment in unbuffered dilute HF yields the Si(111) surfaces covered with a microscopically rough layer that contains a mixture of SiH monohydride, SiH_2 dihydride and SiH_3 trihydride species [447]. Alternatively, a monohydride-terminated Si(111)(1x1)-H surface can be produced *in-situ* through atomic H exposure of UHV-cleaned Si(111)(7x7) at 380°C,

which yields a surface condition with less than 5% remaining stacking faults, 1% of point defects, and less than 0.5% contamination [452, 453].

The Si-H bonds on the uniformly monohydride-terminated Si(111)(1x1) are oriented perpendicular to the surface, and subsurface hydrogen is not expected since the H solubility in Si is immeasurably small [109]. The Si(111)(1x1)-H system thus presents an ideal reference system to demonstrate the possibility of zero-point vibration spectroscopy with ^{15}N -H NRA, in which the sensitivity of the Doppler broadening component in the surface resonance excitation curve to the nature of the chemical bonding state of the surface H atoms is exploited [63, 64, 66]. Fukutani *et al.* measured the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonance excitation curves on a H-terminated Si(111) target (prepared *in-situ* by atomic H exposure) using the surface normal (dashed line) and a 40° inclined (solid line) ^{15}N ion incidence geometry (Fig. 36) [67]. For clarity, the normal incidence profile is represented only by its Gaussian fit curve (dashed line in Fig. 36; the original data can be seen in Fig. 3).

Fig. 36. $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ surface resonance excitation curve for Si(111)-(1x1)-H taken at an incidence angle of $\alpha_i = 40^\circ$ with the surface normal (data points and solid line, Gaussian fit). For comparison the Gaussian fit profile recorded at 0° incidence (data in Fig. 3) is shown as the dashed curve. Adapted from Ref. [67].

By deconvoluting the ion beam energy spread (3 keV) and the NR resonance as described in Section 2.1, Fukutani *et al.* obtained the Doppler width parameter δ_D in Eq. (2.7), from which the zero-point vibrational energy of the H atoms in the surface normal direction $E_{H,z}$ could be determined with Eq. (2.8) as 123.4 ± 4.6 meV [67]. This value of the zero-point vibrational energy amounts to almost exactly one half of the first excitation energy of the surface-normal Si-H stretching vibration known from IRAS and HREELS experiments (258 meV) [454], suggesting that the Si-H bond potential in this vibrational mode is reasonably well described by a harmonic oscillator model. As seen in Fig. 36, the resonance curve recorded under the incidence angle of $\alpha_i = 40^\circ$ is significantly narrower compared to the data at normal incidence. The physical reason for this effect is that the vibrational H motion effective for the NR Doppler broadening is the projection of all H vibrational modes in the ion beam incidence direction [64]. At an incidence angle inclined against the surface normal (α_i) the beam thus also probes the H bending vibration mode parallel to the surface ('frustrated translation'), which is known to be softer than the vertical Si-H stretch (corresponding to a first excitation energy of 78 meV for Si(111)(1x1)-H [458, 459]). With $E_{H,x}$ as the zero-point energy of the surface-parallel vibrational mode, the effective variance of the Doppler broadening distribution becomes [67]:

$$\delta_D = \sqrt{\frac{2m_N E_{Res}}{m_H} \left(\frac{\sin^2 \alpha_i}{E_{H,x}} + \frac{\cos^2 \alpha_i}{E_{H,z}} \right)^{-1}} . \quad (3.1)$$

By performing an analog analysis of the 40° incidence resonance curve as described above and using the $E_{H,z}$ value determined there, Fukutani *et al.* obtained $E_{H,x}$ with Eq. (3.1) as 44.6 ± 6.2 meV. This value is again reasonably close to half the

vibrational excitation energy of the Si-H bending mode, suggesting that also this (mainly) surface-parallel motion occurs within a dominantly harmonic potential, as one might expect from this covalently bound surface H adsorption system.

The above study [67] of Si(111)(1x1)-H so far demonstrated the applicability of zero-point vibrational spectroscopy with ^{15}N -H NRA at a well-aligned H adsorption system most clearly. Earlier attempts to do this [446] had apparently failed, from a retrospective viewpoint presumably due to experimental reasons. In Ref. [446] the HF-etched H-terminated Si(111) surfaces were not annealed in vacuum prior to NRA after transferring the samples into the analysis system. NRA then found large quantities (3.5 ML) of volatile H species on the sample surfaces in addition to the expected monohydride termination layer. These weakly adsorbed H-bearing compounds were desorbed by ion beam impact under NRA observation until a stable H coverage of ca. 1 ML was generated in a dynamic equilibrium with H readsorption from the UHV residual gas (10^{-9} mbar range). In order to deplete the H-bearing adsorbates, rather large ^{15}N ion fluences of $5 \times 10^{16} \text{ cm}^{-2}$ had to be administered to the samples before the resonance excitation curves could be recorded on the stable H monolayer. Hartmann *et al.* then observed NRA Doppler widths that were characteristic of Si-H bonds in a disordered layer (with random beam-bond orientations) and showed no dependence at all on the ^{15}N ion incidence angle onto the surface [446]. Although it is not clear whether this disordered Si-H layer was a consequence of the sample preparation or excessive ^{15}N ion irradiation, the results may emphasize again the statements of Section 2.2.5 that great care has to be taken to exclude irradiation damage and contamination effects in the NRA analysis of

especially sensitive surface H systems. In comparison, the ^{15}N ion fluence to record one entire resonance excitation curve from the H-terminated Si(111) prepared *in-situ* by Fukutani *et al.* [67] was only $2 \times 10^{15} \text{ cm}^{-2}$ and the analysis was performed in an UHV system with a base pressure $< 1 \times 10^{-10} \text{ mbar}$ (Section 2.2.2).

Si(100)

Addressing atomic hydrogen exposed Si(100) surfaces first, a series of investigations has shown that the Si(100)(2x1)-H monohydride phase is obtainable either by moderate atomic H (D) exposures of clean Si(100) surfaces at room temperature, [259, 285, 450] by heating the H-saturated Si(100)-(2x1) surface from RT to 600 K [283, 449], or by applying a H saturation dose at 650 K [450]. These ‘recipes’ are based on the fact that the dihydride (SiH_2) and trihydride (SiH_3) species (Fig. 45 (a)), which form at larger exposures after completion of the monohydride phase, desorb above $\sim 600 \text{ K}$ (β_3 and β_2 TDS peaks at $\sim 450 \text{ K}$ and at $\sim 650 \text{ K}$, respectively), whereas the monohydride phase is stable up to $\sim 730 \text{ K}$ (β_1 TDS peak at $\sim 760 \text{ K}$ in Fig. 37 (b)) [460].

In the monohydride phase at room temperature the original dimer row reconstruction and corresponding (2x1) periodicity are conserved and each of the two Si dimer dangling bonds are terminated by a single H atom (Fig. 37 (a)), which corresponds to a H coverage of 1.0 ML [450]. Jiang *et al.* measured the evolution of the deuterium coverage on initially clean Si(100)(2x1) under atomic D exposure at 400 K with $\text{D}(^3\text{He}, \text{p})^4\text{He}$ NRA and characterized the corresponding adsorption phases with LEED (Fig. 38). Subsequent to completion of the monohydride phase the H uptake slows considerably [259, 285] and the surface gradually attains a (1x1)

structure, with exposure and temperature dependent 'saturation' coverages (Table 3) reported as 1.5-1.6 ML [283, 284], 1.7 ± 0.285 ML (RT) [456], 1.6 ± 0.1 ML (400 K) [285], 1.7 ML (100°C) [259], 1.85 ± 0.18 ML (RT) [259], and 1.9 ML ($T_e=210$ K, TDS, containing some SiH_3) [460]. These coverages are slightly smaller than the 2 ML expected for the ideal bulklike (1x1) 'dihydride' structure depicted in Fig. 37 (a), in which the original Si dimer bonds are removed and each surface Si atom holds two H atoms.

Fig. 37. (a) Hydrogen adsorption structures on Si(100): Dihydride-terminated 1x1 phase, monohydride-terminated 2x1 phase, and mono- and dihydride terminated 3x1 phase. Adapted from Ref. [450]. (b) H_2 TDS spectra from Si(100) saturated with atomic H at (a) 630 K, (b) 400 K, and (c) 210 K. Adapted from Ref. [460] with permission from APS.

At 370-400 K an intermediate (3x1) structure evolves from the (2x1) monohydride phase [285, 448, 450], which consists of alternating monohydride and dihydride units (Fig. 37 (a)) and thus corresponds to a H coverage of 1.33 ML. This (3x1) phase, however, does not represent the saturated surface condition even at

400 K as originally suggested on the basis of IR spectroscopy [448]. Instead, Jiang's data in Fig. 38 show that the intermediate (3x1) phase degrades under further D uptake and slowly converts into the (1x1) structure upon prolonged D exposure [285].

Fig. 38. Evolution of the absolute deuterium coverage measured with $^3\text{He}(\text{D},\text{p})^4\text{He}$ NRA and the corresponding adsorption phases (LEED) on Si(100) under atomic D exposure in 2×10^{-6} Torr D_2 gas at 400 K. Adapted from Ref. [304] with permission from APS.

As noted above, the H saturation coverage in the (1x1) phase was found to be consistently larger than 1.33 ML by several groups, indicating that the $(3 \times 1) \rightarrow (1 \times 1)$ transformation is not due to a simple increase of disorder in the (3x1) phase [448] but that it reflects a continued surface etching process, in which the number of SiH_2 species increases gradually as the coverage approaches the ideal dihydride termination [285, 450, 460]. Since the formation of higher hydride species involves cleavage of the Si-Si dimer bonds in the 2x1 reconstruction, their presence

introduces a form of microscopic surface roughness on monohydride-terminated Si(100)-(2x1) that can disrupt the homoepitaxial growth of Si on Si(100) substrates when the H coverage exceeds one monolayer [437].

The tendency to form higher hydrides as well as the pronouncedly larger etching rate in the (111) direction relative to (100) also affect the quality of wet chemically etched Si(100) surfaces. Whereas etching in NH_4F buffered HF solutions produces ideally smooth and only monohydride-terminated surfaces on Si(111) [454], the same treatment renders Si(100) surfaces covered by several hydride species (SiH , SiH_2 , and SiH_3) [288, 447]. Nonetheless, this mixed hydride termination layer is hydrophobic and effectively protects Si(100) wafers from recontamination in ambient conditions; therefore the HF etching procedure is widely applied in semiconductor industry [461]. The resulting absolute H coverage in the passivating H-termination layer on HF-etched Si(100) had nonetheless remained obscure for quite some time until Wilde *et al.* determined it as 1.3 ± 0.1 ML with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA [286] (cf. Fig. 39 (a) in the next subsection). The value is remnant of the H-(3x1) phase described above and quite consistent with Chabal's IRAS observation [447] that predominantly SiH mono- and SiH_2 dihydrides form under the NH_4F -buffered HF etching with only a minor fraction of SiH_3 units.

$Si_{1-x}Ge_x(100)$

In analogy to Si(100), HF etching treatments are also commonly applied procedures to hydrogen-passivate SiGe alloy surfaces in the fabrication of high performance SiGe/Ge/SiGe heterostructure devices through epitaxial growth techniques [462]. The resulting H coverages and the stability of the H-terminating layers on $Si_{1-x}Ge_x$ alloys in ambient conditions as a function of the Ge content were characterized with $^1H(^{15}N, \alpha\gamma)^{12}C$ NRA after HF-etching and air-to-vacuum transfer [286]. The hydrogen coverages on HF-etched $Si_{1-x}Ge_x$ surfaces ($x=0, 0.30, 0.60, 0.82$) were determined from the integrated NRA surface resonance excitation curves after correcting the data for the ion irradiation-induced H decay, which showed different kinetics for the individual samples. The results are summarized in Fig. 39.

Fig. 39. (a) Surface hydrogen coverage on HF-etched $Si_{1-x}Ge_x(100)$ alloys of different Ge content determined with ^{15}N NRA. (b), (c): H-coverage decay under ^{15}N -ion irradiation on (b) HF-etched $Si_{0.40}Ge_{0.60}$ and on (c) pure Si(100). A double exponential decay function (solid line) is necessary to reproduce the initially fast and subsequently much slower

H depletion on the $Si_{0.40}Ge_{0.60}$ alloy (b), whereas a single exponential decay is observed on Si(100) (c). Adapted with permission from Ref. [286].

As-etched $\text{Si}_{0.7}\text{Ge}_{0.3}$ was found to expose a similar initial H-coverage (1.2 ± 0.1 ML) as pure Si(100) (1.3 ± 0.1 ML), but the alloys of higher Ge contents had strongly increased H coverages that approached 2 ML at $x=0.60$ and even exceeded 3 ML at $x=0.82$ (Fig. 39 (a)). In addition to these large H coverages on the Ge-rich SiGe alloys, the Doppler width of their respective surface resonance profiles was significantly broadened and the ^{15}N -ion-induced desorption kinetics of the surface H atoms showed a second, initially rapid decay channel (Fig. 39 (b)) that was neither observed on pure Si(100) (Fig. 39 (c)) nor on $\text{Si}_{0.7}\text{Ge}_{0.3}$.

Together, these observations were interpreted in terms of H-rich contaminants (most likely hydrocarbons from the laboratory air) that repopulate the surfaces of the Ge-rich alloys ($x=0.60, 0.82$) within minutes after removal from the HF etching solution and thus increase the NRA Doppler broadening width owing to their stiffer (C-H, O-H) vibrational stretching modes compared to those of the Si-H_n surface species [286]. The observation that the resistance of HF-etched $\text{Si}_{1-x}\text{Ge}_x$ alloys against recontamination in air apparently reduces drastically at higher Ge contents was in agreement with the practical experience from MBE production that the H-passivation layers become increasingly unstable at Ge contents above 60%. Although the H-coverage on the $\text{Si}_{0.7}\text{Ge}_{0.3}$ alloy was similar as on pure Si(100) right after the HF etching, it gradually increased over a duration of one week in air from 1.2 to 1.6 ML and also the vibrational Doppler width increased from initially 9.8 to 11.2 keV, suggesting that a slight recontamination of the $\text{Si}_{0.7}\text{Ge}_{0.3}$ surface occurs during air storage [286]. On HF-etched pure Si(100), on the other hand, no significant changes of the H coverage nor of the Doppler width were observed during 167 hours in air

within the experimental accuracy, consistent with the well-known rather stable properties of H-terminated Si(100). One should note, however, that despite the apparent integrity of the H-termination layer a complete passivation of the surface in air cannot be deduced from the NRA data alone, as a very slow but nonetheless noticeable process of surface oxidation is known to occur, which inserts O atoms into Si-backbonds but leaves the terminating H-layer intact [455].

The above study exemplifies that although the ^{15}N -H NRA technique is principally insensitive to the chemical oxidation state of ^1H , a distinction of well-passivated SiGe surfaces terminated exclusively by hydrides of Si and Ge from those partially covered by contaminating adsorbates can be made if the information on the total H coverage, on the H zero-point vibrational width, and on the ^{15}N ion-induced H-decay kinetics are considered in combination. The fact that the Doppler broadening of the surface resonance curves in NRA reflects the vibrational nature of the surface H species and thus bears a certain degree of chemical information was pointed out as early as 1986 by Zinke-Allmang *et al.* [63, 64]. Presumably due to the scarcity of well-defined H-surface target systems and the rather limited resolution with respect to differences in vibrational frequency (ω_{vib}), however, this potential NRA application has rarely found analytical use [66, 67, 286, 446].

By applying Eq. (2.8) in the harmonic approximation ($E_{\text{H}} \approx \frac{1}{2} \hbar \omega_{\text{vib}}$) the Doppler broadening parameter (δ_{D}) for different chemically bound H species can be estimated from respective vibrational excitation energies, and the resulting width (FWHM) of the NRA surface resonance profiles (ΔE_{tot}) follows from Eq. (2.10) for $z = 0$. Assuming that the vibrational amplitude is fully aligned in the ^{15}N ion incidence

direction (for a disordered surface layer a reducing factor of ~ 0.7 ($=1/\sqrt{2}$) enters from integration over all possible bond-beam angles between 0 and 90°), ΔE_{tot} values of 13.1 keV for Si-H ($\hbar\omega_{\text{vib}} = 2100 \text{ cm}^{-1}$), 14.7 keV for C-H ($\hbar\omega_{\text{vib}} = \sim 2700 \text{ cm}^{-1}$), and 16.5 keV for O-H ($\hbar\omega_{\text{vib}} = \sim 3500 \text{ cm}^{-1}$) species result for an incident ion beam energy spread of $\Delta E_B = 3 \text{ keV}$. Experimentally ΔE_{tot} is easily determined with an accuracy of $\sim < 0.5 \text{ keV}$, thus in the present example [286] the Si-H_n surface species were clearly distinguishable from C-H or O-H contaminants.

3.1.4 Insulators

Owing to the electrostatic charging problem that affects bulk samples of insulating materials under ion or electron probing beams, the preparation and characterization of single crystalline insulator surfaces is inherently difficult with standard techniques of surface analysis. Much progress in the Surface Science of metal oxides has been achieved after methods of charge compensation for bulk samples were introduced [463]. Later, especially the establishment of preparation routes for thin epitaxial oxide films on metal substrates has very significantly expanded the range of well-ordered metal oxides that can be studied by Surface Science techniques, which propelled the field much further [464]. Some oxides (TiO₂, ZnO, SrTiO₃, etc.) also develop a certain bulk or surface conductivity in presence of impurities (hydrogen being discussed as one of them [38]) or oxygen vacancies that form by annealing in UHV, and hence permit surface analysis with charged particle probes. The interaction with hydrogen or water can rather dramatically change the chemical and physical properties of oxide surfaces; surface hydroxylation, reconstruction, metallization, hydrophilicity, hydrogen incorporation into the bulk or

subsurface region, and induction of electrical conductivity are prominent examples of the possible effects. These phenomena have tremendous technological importance for heterogeneous catalysis, photocatalysis, self-cleaning and anti-fogging coating materials, electronic and photonic devices, and sensor applications. Accordingly, the subject has received considerable attention from the Surface Science community and is documented in excellent reviews [3, 294, 465, 466].

Nevertheless, compared to the wealth of knowledge on the hydrogen behavior on metal and semiconductor surfaces described in the preceding sections, there is still a striking lack of quantitative information on the hydrogen coverage on single crystalline oxide surfaces under well-defined conditions in the literature. Most of the existing knowledge on surface hydroxyl on oxides stems from vibrational spectroscopy (HREELS, IRAS) and XPS, where OH is identified by a characteristic shoulder in the bulk oxide O 2p signal at a ~ 1.5 eV higher binding energy. To our best knowledge, only two quantitative ^{15}N NRA evaluations of hydrogen interactions with single crystalline oxide surfaces have been published so far.

ZnO(10 $\bar{1}$ 0)

The hydrogen content on the surface, in the subsurface region, and in the bulk of hydrothermally grown ZnO single crystals of different surface orientations (pure Zn-terminated polar Zn(0001), pure O-terminated polar ZnO(000 $\bar{1}$), and mixed (Zn and O) terminated non-polar ZnO(10 $\bar{1}$ 0)) was studied with ^{15}N NRA, comparing pristine samples to those after *in-situ* exposure to atomic hydrogen or water vapor [291]. The structural details of these ZnO surfaces and their behavior towards H adsorption are comprehensively reviewed by Wöll [294]. Traeger *et al.* determined native bulk H

concentrations of (0.02–0.04) at.% in the above ZnO samples, which did not depend on their surface orientation [291]. A roughly 10 times larger H amount (up to 0.17 at. %) was detected in the ZnO subsurface region in 10 nm depth. A fraction of this subsurface H could reversibly be removed by heating to 550 °C and subsequently be reloaded with atomic H dosed at room temperature, yet ~0.1 at.% always stably remained (heating above 550 °C was avoided to prevent formation of O-vacancies).

For the mixed-terminated nonpolar ZnO(10 $\bar{1}$ 0) surface the H coverage and H uptake into the near surface region under atomic H dosage was studied in more detail. The same saturation H coverage was found to result reproducibly on ZnO(10 $\bar{1}$ 0) either from surface hydroxylation with a dose of $1\text{--}2\times 10^{-8}$ mbar H₂O vapor at 130–200°C or by atomic H exposure at 30–100°C. After applying the same H₂O exposure ($1\text{--}2\times 10^{-8}$ mbar, 30 min) to the freshly cleaned ZnO(10 $\bar{1}$ 0) surface at room temperature (25°C), the saturated amount of surface H was found to be twice as large (Fig. 40 (a)). Using a calibrated γ -detection system, these discrete H coverage conditions were found to correspond to about 80% of the H densities expected for ideal termination layers with H equivalents of 1 and 2 ML, respectively [291]. The 1 ML structure (Fig. 40 (b)) contains one H atom per surface unit cell (5.9×10^{14} cm⁻²) bound in an OH group and is metallic [467]). The 2 ML H structure (Fig. 40 (c)) holds an equivalent of one partially dissociated H₂O molecule per surface unit cell, i.e., one OH group and an additional Zn-H unit, which are stabilized by intralayer hydrogen bonds [468]].

Fig. 40. (a) $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonance excitation curves of $\text{ZnO}(10\bar{1}0)$ surfaces saturated with H_2O at 25 °C (gray) and 200 °C (black). (b) Structure model of the $\text{ZnO}(10\bar{1}0)\text{-H}$ surface [467]. (c) Structure model for the half-dissociated $\text{H}_2\text{O}/\text{ZnO}(10\bar{1}0)$ surface. Adapted from Refs. [291, 467, 468].

Traeger *et al.* rationalized the significant deficiency of the ^{15}N NRA-observed H coverages relative to the ideal 1 ML or 2 ML termination layers on $\text{Zn}(10\bar{1}0)$ by crystal imperfections (evidenced by a less than 10 nm small coherent scattering domain size in HAS) [291], which may account for a surface defect density around $\sim 10\%$. Although no further comments were offered, the γ -yield curves in Ref. [291] appear to be uncorrected for ion beam-induced H-loss that is expected to occur to some degree even under the low ^{15}N beam fluxes applied (< 20 nA of $^{15}\text{N}^{2+}$ in a ~ 3.5 mm² beam spot), which might also in part explain smaller than ideal H coverages derived from the yield curve integrals (cf. Section 2.2.5).

The saturation of the surface H peak under atomic H admission above room temperature was evidenced in Fig. 41 (a) by the identical height of the γ -yield curves. The high energy tail in the surface resonance peak developing under increasing atomic H dosage indicated a gradual H incorporation into the $\text{ZnO}(10\bar{1}0)$ subsurface

region. A close inspection of the NRA profiles in Fig. 41 (a) also revealed that the surface peak maximum continuously shifted to higher energy (up to 4 keV after 50 min H-loading). In order to separate the signal contributions from H on the surface and in the subsurface region, Traeger *et al.* convolved parameterized error function H concentration profiles (Fig. 41 (b)) (assuming an in-diffusion model under constant H-supply through the H-saturated surface) with the NRA instrumental function (a total width of 17 keV was derived from the surface peak of the sample before H-loading), until the excitation curves (solid lines in Fig. 41 (a)) were adequately reproduced. The analysis revealed that H-loading for 20 min and 50 min increased the H content in the first ZnO double layer below the surface relative to the H surface layer density from the native content ($\sim 1\%$) to 2.7% and 4.7%, respectively.

Fig. 41. (a) $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ excitation curves for ZnO(10 $\bar{1}$ 0) surfaces exposed to various doses of atomic H above room temperature. (b) Model H depth distributions that reproduce the data (solid lines in (a)) by convolution with the NRA instrumental function. Adapted from Ref. [291] with permission from APS.

The study highlights the potential of ^{15}N NRA to reveal details of the H behavior in closest vicinity of oxide surfaces that are of high potential value, e.g., for the elucidation of many open questions regarding the role of hydrogen in sensor action and catalytic reactivity of ZnO surfaces in contact with H_2 gas or water (vapor). At the same time the present case also illustrates the difficulties associated with the quantification of the surface H coverage when the subsurface region contains significant amounts of hydrogen, since these two H-states cannot be resolved within the surface resonance peak width. This problem resembles the situation of H near surfaces of H-absorbing metals, which is discussed in Section 3.2.

The case of zinc oxide is special in this respect, since appreciable amounts hydrogen have also be found in the bulk of crystalline ZnO. The relation of these hydrogen impurities to the electrical and optical properties of zinc oxide (ZnO) has attracted considerable interest, because H could be demonstrated to be a source of *n*-conductivity in ZnO [38-40, 469-472], which precludes its application, e.g. as a dielectric in electronic devices. Since IR-active as well as ‘invisible’ (i.e., Raman-active) hydrogen states were found to coexist in ZnO [39], the total hydrogen concentration could not be revealed by either of the optical techniques alone (cf. Section 3.2.5.1). This has motivated several further ion beam studies including NRA [470, 473, 474] and positron annihilation spectroscopy (PAS) at ZnO nanowires [473] and electrochemically hydrogen-charged single crystals [474].

As a final remark, we notice a substantial shift (~ 30 keV) of the surface peak positions in the NRA excitation curves of Figs. 40 (a) and 41 (a) from the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ resonance energy (6.385 MeV), which Ref. [291] left uncommented. It

is not clear to us, whether this shift results from a slightly miscalibrated accelerator energy, a floating potential sample stage (the entire sample compartment appears to be electrically insulated from the accelerator for the convenience of accurate ion beam charge integration in the NRA apparatus of Ref. [291]), or whether it might possibly reflect a more general complication for the NRA analysis of single crystalline bulk insulators (of which there are still only very few to date) due to charging of the target under the ion beam.

SrTiO₃(001)

Takeyasu et al. recently applied $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA to investigate the interaction of hydrogen with SrTiO₃(001) prepared in two different controlled conditions with respect to the surface electron density [289]. The group had previously demonstrated the possibility to deliberately manipulate the SrTiO₃(001) surface electron density by selectively introducing oxygen-vacancies through energetic electron irradiation [475] (high-temperature vacuum annealing also generates O-vacancies on SrTiO₃ surfaces but affects the bulk as well). O-vacancies modify the surface electronic structure of SrTiO₃(001) by introducing a Ti 3d state in the band gap (induced gap state, IGS), which is observable at 1.3 eV below E_F in the UV photoemission spectrum. Oxygen (O₂) adsorption (10 L at room temperature) on an oxygen-deficient (OD) surface, on the other hand, was shown to passivate these vacancies to produce nearly-vacancy-free (NVF) SrTiO₃(001), where the Ti 3d state (IGS) is completely quenched.

In their ^{15}N NRA study [289], Takeyasu et al. quantified the amount of hydrogen on such (NVF) and (OD) SrTiO₃(001) surfaces that adsorbed upon room temperature

exposures to either only molecular (H_2) or to a mixture of molecular and atomic hydrogen ($H+H_2$) and characterized the surface electronic structure alterations concomitant with hydrogen adsorption by UPS. Fig. 42 depicts the $^1H(^{15}N, \alpha\gamma)^{12}C$ NRA hydrogen profiles obtained from the NVF and OD surfaces after applying large hydrogen exposures ($5 \times 10^4 \sim 1 \times 10^5$ L) that saturated the H-induced changes in the UP spectra (described below).

Fig. 42. $^1H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction profiles taken at room temperature for the nearly-vacancy-free (NVF) $SrTiO_3(001)$ surface, the NVF surface exposed to 5×10^4 L H_2 (NVF: H_2), the NVF surface exposed to 1×10^5 L $H+H_2$ (NVF: $H+H_2$), and the oxygen-deficient $SrTiO_3(001)$ surface exposed to 1×10^5 L H_2 (OD: H_2). Reproduced from Ref. [289] with permission from AIP.

As seen in Fig. 42, all NRA profiles maintained Gaussian-shapes centered at $E_R = 6.385$ MeV, i.e., neither before nor after the hydrogen exposures did the subsurface region of $SrTiO_3(001)$ contain any measureable H concentrations, so that the respective surface H coverages could readily be evaluated from the resonance curve

integrals. The NVF surface held a small initial H coverage of $(2.2 \pm 0.4) \times 10^{14} \text{ cm}^{-2}$. The source and nature of this H remained unclear, but it was suspected that H_2 residual gas adsorbed and bound strongly to defects. The NRA data in Fig. 42 showed that molecular H_2 evidently did not adsorb on the near-stoichiometric $\text{SrTiO}_3(001)$ surface without O-vacancies (NVF: H_2), whereas the partially dissociated $\text{H}+\text{H}_2$ gas caused a substantial increase of the H coverage by $(3.1 \pm 0.8) \times 10^{14} \text{ cm}^{-2}$ (NVF: $\text{H}+\text{H}_2$). On the OD surface, molecular H_2 led to a moderate H coverage increase by $(0.9 \pm 0.7) \times 10^{14} \text{ cm}^{-2}$ (OD: H_2).

Complementary UPS data evidenced that the $\text{H}+\text{H}_2$ adsorption on the NVF surface induced novel Ti 3d gap state density, which corresponded to about one third of the initial IGS intensity of the OD surface. The latter had an estimated O-vacancy density of $1 \times 10^{14} \text{ cm}^{-2}$, and was produced by irradiating NVF $\text{SrTiO}_3(001)$ with an electron dose of $5 \times 10^{18} \text{ cm}^{-2}$ at an energy of 1500 eV [289]. Contrary to the effect of atomic H adsorption on the NVF surface to generate new IGS, H_2 adsorption on OD $\text{SrTiO}_3(001)$ partially reduced the IGS density on that surface to about half of its initial value. By taking the absolute H coverage, the in-gap state photoemission intensity, and the H-induced work function changes into account, Takeyasu et al. estimated that hydrogen is positively ($\text{H}^{\sim 0.3+}$) and negatively (H^-) charged on the nearly-vacancy-free and oxygen-deficient surfaces, respectively, clearly demonstrating its amphoteric character.

3.2 Absorbed Hydrogen

Prior to reviewing NRA applications to hydrogen absorbed in the near-surface region of (mainly single crystalline) materials, we provide a minimum physical background on the hydrogen absorption phenomenon at metal surfaces, describe briefly a few common experimental practices in hydrogen absorption studies, and introduce the type and benefit of the information that NRA can contribute therein. This will allow describing results from individual materials more consisely in the following Sections (3.2.3.1-4).

3.2.1 General aspects of hydrogen absorption at metal surfaces

a) Energetics of surface and absorbed H states: In hydrogen-absorbing metals, one can distinguish three characteristic hydrogen atom locations that differ in terms of the metal-hydrogen interaction strength: sites on the surface, in the first subsurface layer, and in the bulk. On metal surfaces, hollow sites are often (but not always, cf. Section 3.1) the most stable locations for chemisorbed hydrogen. Bulk-dissolved H atoms usually prefer octahedral interstitial sites in fcc and hcp metals, and tetrahedral interstitials in bcc metals [27]. In general, hydrogen atoms are considerably more strongly chemisorbed (E_{ads}) at the relatively low-coordinated surface metal atoms than they are dissolved in bulk interstitial sites (H solution enthalpy $\Delta H_s \gg E_{\text{ads}}$) [299]. First-layer subsurface sites provide a special environment for absorbed H atoms that differs both from the surface chemisorption as well as from the bulk interstitial sites [301, 304, 476, 477]. In metals, Thomas-Fermi screening by conduction electrons rapidly restores the bulk electronic structure

within a very short distance from the surface, yet at least the first one or two atomic layers are distinguished from surface and from bulk sites, both electronically (by reduced bandwidth and slight d-band center shifts) as well as geometrically (by particular interlayer separations (relaxations) that deviate from the bulk lattice parameter) [476, 478-480]. As a result, hydrogen in first-layer subsurface sites often assumes an energetically intermediate position (E_{ss}) between the most stable chemisorbed and the much more weakly bound bulk dissolved state [299], i.e., $\Delta H_s > E_{ss} > E_{ads}$. This principal energetic position of H in first-layer subsurface sites prevails regardless of whether H absorption in the metal is exothermic or endothermic [301, 304]. Even for certain metals with endothermic H dissolution in the bulk (such as Cu(111)), the possibility of H stabilization in first-layer subsurface sites through strong repulsive interactions with surface hydrogen at large coverages has been suggested theoretically [303].

The content of bulk-dissolved hydrogen in H-absorbing metals can vary widely over a large concentration range and even nominally clean single crystals may contain residual H impurities in the bulk. At low concentrations, H atoms exist within the host metal lattice in solid solution. At elevated H levels, a phase separation in certain metals causes precipitation of hydride grains in the solid solution matrix when the concentration limit of the latter phase is exceeded. The H_2 pressure- and temperature-dependent equilibrium H contents in the dilute solid solution and in the concentrated hydride are described by material-specific metal-hydrogen phase diagrams [26]. Within the two-phase coexistence regime the average bulk H content corresponds to $c_{avg} = V_\alpha c_\alpha^* + V_\beta c_\beta^*$, where c_α^* and c_β^* are the phase boundary

concentrations and V_α and V_β the volume fractions of the solid solution (α) and hydride (β) phases, respectively.

b) Equilibrium hydrogen depth distribution and temperature-induced changes:

The hydrogen depth distribution in the near-surface region of H-absorbing metals depends sensitively on the particular experimental history of any given sample, especially on the conditions (H_2 pressure and temperature) during preceding H_2 gas exposures and/or annealing treatments. Before addressing the outcome of typical absorption experiments we describe the equilibrium H distribution in a H-containing single crystal in UHV, where additional H uptake from the gas phase is negligible.

For $p(H_2) \approx 0$, the relative thermal equilibrium population of surface, subsurface, and bulk sites by H atoms, i.e., their depth distribution, is a readily predictable function of the sample temperature. At low temperatures the sizeable enthalpy difference ($\Delta H_s^b = \Delta H_s - E_{ads} \gg 0$) between the surface chemisorption and bulk dissolution states stabilizes hydrogen on the surface (analog arguments apply to the surface/subsurface and subsurface/bulk site population ratios, for which separate equilibria can be considered on the basis of E_{ads} , E_{ss} , and ΔH_s). We describe only the surface/bulk case here. When the temperature is raised, the gain in configurational entropy, $\Delta S_s^b = k_B \ln[b!/(n!(b-n)!)] \approx k_B \ln(b/n)$, associated with distributing n surface (or analog: subsurface) H atoms into a much larger number of bulk interstitial sites (b) will eventually turn the free energy difference between H in bulk and surface sites, $\Delta G_s^b = \Delta H_s^b - T\Delta S_s^b$ negative, so that initially surface-adsorbed H may migrate into the bulk through diffusion. When this change of sign in ΔG_s^b occurs at a temperature prior to the onset of thermal desorption, bulk dissolution of surface H is

the result of heating a H-covered crystal in UHV [62, 481]. This is the case for metals with large negative H solution enthalpies such as Ti ($\Delta H_s = -0.47$ eV/H [26]) and Zr ($\Delta H_s = -0.567$ eV/H [482], α -phase values). Here, the strong tendency of surface-adsorbed hydrogen to dissolve into the bulk upon heating lets the standard TDS experiment devised to reveal the H chemisorption energy fail completely due to lacking H_2 desorption [62, 483, 484]. Care is then required not to mistake such observations for the absence of surface hydrogen. On the other hand, if H absorption is only weakly exothermic (such as in Pd, $\Delta H_s = -0.1$ eV/H, α -phase [26]), the free energy contribution $T\Delta S_s$ from the even larger entropy gain by releasing the surface H atoms into the vacuum rather than into the metal bulk (the entropy difference between these two final states corresponds to the entropy of H dissolution (e.g., $\Delta S_s = -7k_B$ for Pd [27])) dominates over the small negative H solution enthalpy, thus favoring desorption over bulk absorption. For this reason the TDS technique is successfully applied to Pd as well as to the many transition metals that absorb H endothermically (positive ΔH_s).

c) Hydrogen absorption experiments: In typical Surface Science hydrogen absorption studies, initially clean single crystals are exposed to H_2 gas at relatively low (exposure) temperatures (T_e) so that dissociative H adsorption more or less spontaneously saturates the energetically strongly favored chemisorption sites, before H incorporation into the metal interior takes place on a slower timescale. The detailed microscopic H_2 absorption mechanism at such H-saturated surfaces is still subject of ongoing research [279] and its discussion goes beyond the scope of this review. In general, the result of such low-temperature H_2 exposures is the

simultaneous presence of *surface-adsorbed* and (potentially multiple) *absorbed* hydrogen states, where H may populate subsurface sites and/or bulk interstitials, the latter potentially in solid solution as well as in hydride phases. The amount of absorbed hydrogen and its depth-dependent distribution among these absorbed states are very difficult to predict quantitatively, and have been found to vary strongly with the metal and the H₂ exposure conditions (H₂ pressure, time, and temperature, T_e) [61, 62, 279, 485]. Often the H₂ exposures and hence the absorbed H quantities are too small to fully establish the equilibrium between the applied H₂ gas pressure and bulk-absorbed H throughout the entire single crystal (i.e., the H₂ dosage is terminated before the H-uptake saturates), so that H concentration gradients can remain between the near-surface region and the deeper bulk. A common observation is that the near-surface H depth distribution extends into larger depths when T_e is increased, which can be qualitatively understood because the diffusion of absorbed H into the bulk is thermally activated and becomes increasingly favored entropically at elevated temperatures. Upon H absorption at low T_e , hydride may nucleate just underneath the surface, producing a near-surface hydride with steep concentration gradients into the bulk. If thermodynamically favorable, hydride may also nucleate homogeneously in the metal bulk.

3.2.2 NRA observation of absorbed hydrogen

The main experimental strategies to characterize adsorbed and absorbed hydrogen states with ¹⁵N NRA can be classified into two procedures: (i) The H probing depth is scanned at a constant target temperature. If performed at sufficiently low temperatures where neither thermal H diffusion nor the NRA

measurement perturb the hydrogen profile, this delivers 'static' visualizations of the H depth distribution. (ii) The ^{15}N energy is fixed to selectively observe H at a particular probing depth while either the target temperature is varied or the evolution of the H concentration in the selected depth is monitored as a function of time. This allows capturing 'dynamical' aspects of the H behavior, such as thermally driven H redistribution processes between the surface and the bulk, or H uptake kinetics on or underneath H_2 -exposed surfaces in absorption experiments.

(i) In H-depth profiling at constant temperature, surface hydrogen (always present at low temperatures) gives rise to the nearly-Gaussian shaped γ -peak at E_R (Fig. 4 (a) and Section 3.1). The NRA measurement of bulk-absorbed hydrogen at $E_i \geq E_s$ (Fig. 4 (b)) will assess the areal average bulk H content (c_{avg} in the hydride/solid solution coexistence region) at the depth selected by E_i , provided that the hydride grains are much smaller than the analyzing ^{15}N ion beam spot on the target surface. The outstanding advantage of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA in hydrogen absorption studies lies in its unique ability to reveal the hydrogen concentration-depth distribution and thereby to identify the absorbed H states, i.e., H in first layer subsurface sites, in bulk solid solution, and in bulk or near-surface hydrides). With reference to metal-H phase diagram data, NRA thus allows for direct observations of hydride nucleation phenomena in the near-surface region (Sections 3.2.3.1-4).

In addition to low-temperature hydrogen absorption studies at metal single crystals, non-uniform near-surface H depth distributions may also prevail in a variety of other pure and homogeneous host materials, such as in the case of the gradual hydration of mineral surfaces (Section 3.2.5.1), where the bulk diffusion of absorbed

hydrogen species is rather slow. H-enriched or H-depleted near-surface layers may further arise from the interaction of absorbed hydrogen with lattice imperfections and impurities that result, e.g., from a modification of the near-surface region through an external treatment such as ion implantation or polishing (cf. Sections 3.2.2.5 and 3.2.2.6). Here, H-profiling with ^{15}N NRA can be useful to evaluate the depth extension of the affected region.

Hydrogen in first-layer subsurface sites is located in a very shallow depth (d) not more than about 1 Å beneath the substrate surface atoms. Thus, in surface-normal ^{15}N incidence the NRA signal of H in first-layer subsurface sites is shifted relative to E_R by only a very small energy increment $\Delta E = d \cdot S$, which amounts to ~ 0.2 keV for Ti ($S = 2.335$ keV/nm) and ~ 0.4 keV for Pd ($S = 3.90$ keV/nm). Since on otherwise clean metal surfaces H can stably occupy first-layer subsurface sites only at relatively low temperatures in coexistence with a larger quantity of surface chemisorbed hydrogen ($E_{SS} > E_{ads}$), the H occupation of subsurface sites will merely add surplus γ -yield to the resonance profile of surface H so close to E_R , that neither the center position nor the width of the excitation curve change markedly within the experimental accuracy. The sizeable width of the Doppler-broadened surface resonance (ca. 8-10 keV on metals) and the finite ^{15}N stopping power ($2\sim 4$ keV/nm) thus principally make the resolution of H in first-layer subsurface-sites from surface hydrogen very difficult, even for ^{15}N NRA at 6.385 MeV. Adopting strongly grazing ^{15}N ion incidence geometries is an effective way to increase the near-surface NRA depth resolution in the top 1-2 nm, as demonstrated for H in Pd nanoparticles (Sect. 3.2.3.8) and at ultra-shallow metal/Si(111) interfaces (Sect. 3.3.2). So far, however, the ultimate distinction

between *surface-adsorbed* and coexisting H *absorbed in first-layer subsurface sites* by means of ^{15}N NRA has remained an unaccomplished challenge.

(ii) Through its unique ability to detect hydrogen at a selected depth while the temperature of a previously H-exposed sample is varied, ^{15}N NRA can evaluate the thermal stability of surface and absorbed hydrogen states against redistribution by diffusion and/or desorption. This is suited in particular to observe *in-situ* thermally induced H redistribution between surface-adsorbed and bulk-dissolved states, as the free energy balance for H occupation of surface and bulk sites shifts as a function of temperature. As noted in Section 3.2.1, diffusion of surface-adsorbed H into the bulk may occur when H-covered surfaces of H-absorbing materials are heated in vacuum (such as in common TDS measurements), or, conversely, residual bulk-dissolved hydrogen can segregate onto the (initially H-depleted) surface when a H-containing crystal is quenched from a high annealing temperature in vacuum (Sections 3.2.3.1-2) [62, 486].

The same type of ^{15}N NRA measurement (monitoring H at a fixed depth while T is varied) is also useful in hydrogen absorption studies in combination with TDS. When surface-chemisorbed and absorbed hydrogen species coexist and give rise to multiple TDS states, it may not be immediately apparent which TDS signals originate from surface hydrogen and which represent(s) the absorbed H state(s). As illustrated at the example of Pd(100) in Sect. 3.2.3.3, ^{15}N NRA achieves unambiguous identifications of individual TDS features by correlating the selectively monitored temperature-dependent signatures of surface and absorbed H species with the TDS trace [61, 62, 279].

Examples for the monitoring of surface hydrogen uptake processes at H₂-exposed metals have been described in Section 3.1 (Figs. 16, 26, 30). The H-uptake into the entire near-surface region of Zr(10 $\bar{1}$ 0) has been studied with D(³He,p)⁴He NRA (Fig. 49). With ¹⁵N NRA it is furthermore possible to reveal the uptake kinetics at H₂-exposed single crystal surfaces in a selected narrow depth region, although no systematic studies have been published yet to our knowledge.

We would like to add one comment on terminology. Most experimental Surface Science studies related to absorbed hydrogen have been conducted without depth resolving detection methods so that the actual H distribution below the surface often remained unclarified. This situation has produced the vague but frequently encountered term '*subsurface hydrogen*', which has been used synonymously to address H in first layer subsurface sites as well as to denote H that is distributed over a wider region below the surface, although these circumstances are evidently rather different (Section 3.2.1). We will avoid the ambiguous '*subsurface hydrogen*' label here altogether and prefer to speak more generally of *absorbed* hydrogen whenever its location below the surface cannot be specified, as no potentially unjustified surface vicinity is implied. Since ¹⁵N NRA at 6.385 MeV can quantify and locate absorbed H with a precision of a few nm beneath the surface, we will use the more specific definitions of 'H in first-layer subsurface sites' and 'bulk-absorbed H states', which include 'H in solid solution' as well as 'near-surface' and 'bulk hydrides'.

3.2.3 Metals

3.2.3.1 Titanium (0001)

a) As-cleaned Ti(0001)

As an example for the distinction between surface-adsorbed and bulk-absorbed hydrogen with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA we present the excitation curve from a Ti(0001) single crystal that had been cleaned by sputtering and annealing at 970 K and was allowed to cool to room temperature in UHV (Fig. 43) [62]. The perfectly symmetric Gaussian resonance profile centered at 6.385 MeV was indicative of surface H and the small and constant γ -yield at ^{15}N energies above 6.40 MeV showed the presence of H below the surface that exhibited no H concentration gradient within the investigated depth.

Fig. 43. NRA γ -yield curve of Ti(0001) single crystal recorded in UHV at $T=300$ K after cleaning by sputtering/annealing. The line through the experimental data points is a fit to a Gaussian and an error function-like step profile representing hydrogen on the surface and in the bulk,

respectively. The γ -yield averaged between 7-17 nm depth (1.4 cts/ μC) corresponds to a bulk H concentration of 500 ppm. Arrow: Ion energy used for probing surface-H in the experiments of Figs. 44 and 45. Adapted from Ref. [62].

The resonance peak integral quantified the surface H coverage to 0.5 ML (1 ML = $1.33 \times 10^{15} \text{ cm}^{-2}$ on Ti(0001)) and the low γ -yield plateau of $1.39 \pm 0.35 \text{ cts/C}$ reflected

a H impurity concentration of ~ 500 ppm in the topmost 17 nm. Although only a shallow region was analyzed, it could be concluded that this H impurity content extended homogeneously throughout the entire crystal specimen, since it had been annealed repeatedly at 970 K in UHV so that any remaining concentration gradients of absorbed H were deemed unlikely as they should have leveled out by diffusion. The existence of a large reservoir of bulk-absorbed H was corroborated by intense H_2 desorption that evolved during UHV annealing of the single crystal. The TD spectrum in Fig. 44 evidenced this bulk-dissolved H release by the exponentially growing H_2 desorption rate above 700 K, which (at 900 K) exceeded the intensity expected for a monolayer of surface-adsorbed H by several orders of magnitude. From the temperature dependence of this H_2 release, an activation energy equivalent to the H solution enthalpy in α -Ti ($\Delta H_s = -0.47$ eV/H [26]) was deduced [62].

Fig. 44. H_2 thermal desorption spectrum of a H-saturated Ti(0001) single crystal (12000 L H_2 at 120 K) compared to the temperature dependence of the NRA signal of surface hydrogen ($\theta_H = 0.5$ ML at 200 K). The dashed line indicates the H surface occupation expected for thermal equilibrium with the Ti bulk for an adsorption energy of -1.05 eV/H. Adapted from Ref. [62].

Remarkably, the TDS trace in Fig. 44 detected only spurious H₂ desorption signals below 600 K, although the Ti(0001) surface was prepared for the TDS measurement with a large H coverage (saturated with $\theta = 1.3$ ML H at 120 K, including some H in the subsurface region, cf. Fig. 46). For comparison, Fig. 44 shows the temperature-dependent ¹⁵N NRA γ -yield (blue squares) obtained in a separate experiment by directly probing the surface H coverage (at a slightly off-resonant ¹⁵N energy of 6.391 MeV, arrow in Fig. 43), while the sample prepared with an initial surface H coverage of 0.5 ML was heated incrementally in UHV [62]. The surface H was found to be approximately stable between 200 K and 300 K, above which it vanished gradually in a broad decay up to 500 K. These combined TDS/NRA data clearly demonstrate the tendency of chemisorbed H atoms to penetrate below the Ti(0001) surface upon heating in vacuum - rather than to desorb -, and to escape out of the NRA depth detection window by diffusing into the deeper bulk.

Selective hydrogen surface coverage monitoring with ¹⁵N NRA was also applied to observe the segregation of the bulk-dissolved hydrogen to the strongly binding sites on the Ti(0001) surface, while the Ti single crystal (containing ~500 ppm H in the bulk) was rapidly quenched to below room temperature after flash-heating to >900 K in UHV (Fig. 45). This 'resurfacing' of bulk-dissolved H was considered to be the major source of surface hydrogen detected in the NRA H-profile of Fig. 43, as even under different UHV background pressures a very reproducible H coverage of 0.5 ML was observed under the particular heating/quenching conditions and the bulk H content of the Ti(0001) specimen of Ref. [62], which could not be explained only by H₂ readsorption from the residual gas. As described in Sect. 3.2.1, this H

redistribution between the bulk and the surface results from a shift in the free energy balance that favors hydrogen surface site occupation over bulk-dissolution at low temperatures.

Fig. 45. Rapid recovery of the H-NRA signal on the Ti(0001) surface in UHV upon cooling a Ti single crystal containing 500 ppm H in the bulk after flash-annealing to 923 K. The acquisition time for each data point is 100 s. Within the first 200 s, the H coverage rapidly saturates at 0.5 ML (40 cts/ μ C at 6.3912 MeV, arrow in Fig. 43). Reproduced with permission from Ref. [62].

The verification of this ‘resurfacing’ effect with NRA showcased that remaining traces of bulk-dissolved hydrogen will pose serious impediments to the preparation of ideally clean Ti surfaces by UHV sputtering/annealing cycles unless all H is completely removed from the bulk. This is an important concern for accurate geometric structure determinations of Ti surfaces, because adsorbed H is known to very strongly affect the interlayer relaxations at the Ti(0001) surface [487, 488]. Thus, together with the possibility of H₂ adsorption from the UHV residual gas on the highly reactive clean Ti(0001) surface, the segregation tendency of bulk-dissolved H aggravates the difficulty to perform, e.g., LEED I(V) measurements under well-

controlled (especially zero) H coverage conditions. Since the H coverage on Ti cannot be evaluated by TDS due to the described propensity of surface H to diffuse into the bulk upon heating, ^{15}N NRA in combination with LEED may be the only experimental routes available to establish a quantitative correlation between the H coverage and the Ti(0001) surface interlayer relaxations.

b) H_2 -exposed Ti(0001)

$^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA has also been applied to investigate low-temperature H_2 adsorption and absorption at Ti(0001). In Fig. 46 we present the γ -yield curve of a Ti(0001) single crystal surface that was exposed to large dose of 12000 L H_2 at 120 K, which saturated the H uptake [62]. The profile shows a clear asymmetric broadening on the high energy side and the resonance peak center is shifted from the surface position to a depth of about 1 nm, indicating that in addition to H-saturating the surface sites the large H_2 exposure had caused H absorption into shallow depths (< 10 nm) below the surface. The total hydrogen uptake deduced from the profile integral was $(1.3 \pm 0.1 \text{ ML})$. Obviously, the absorbed H is not resolved from the surface hydrogen signal, so that neither the surface saturation coverage nor the amount of absorbed H atoms could be specified with certainty in this situation. The shifted peak maximum and the asymmetry of the H profile, however, indicate that the absorbed H atoms were clearly not confined only to first-layer subsurface sites, but that they must have been distributed over several tens of atomic layers below the surface, likely with a concentration gradient into the depth.

This somewhat extended H depth distribution is remarkable because at 120 K the thermal diffusion of H in bulk titanium is essentially frozen ($D = D_0 \cdot \exp(-E_{\text{diff}}/k_{\text{B}}T)$ with

$D_0 = 3.64 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $E_{\text{diff}} = 0.53 \text{ eV}$, $L_D = (D \cdot \Delta t)^{1/2} = 1.4 \times 10^{-4} \text{ nm}$ in $\Delta t = 1000 \text{ s}$), so that any absorbed H is expected to remain in closest vicinity of the single crystal surface, i.e., not to escape from the first few subsurface layers. The origin of the observed slight low-temperature in-diffusion has remained unclear. It was verified that the NRA measurement did not perturb the H depth profile, leaving tunneling diffusion, altered H diffusion properties in the near-surface region, or energy dissipation in the absorption and potential hydride nucleation processes as possible tentative explanations. Fig. 46 thus illustrates the unique possibility to study such so far rarely investigated phenomena with highly depth-resolving ^{15}N NRA.

Fig. 46. ^{15}N NRA γ -yield curve obtained from a H-saturated Ti(0001) single crystal surface (exposed to 12000 L H_2 at 120 K). The solid line is a guide to the eye. Reproduced from Ref. [62].

The potential of ^{15}N NRA to reveal temperature-dependent hydride nucleation processes in the near-surface region with nanometer resolution is exemplified in Fig. 47, which displays two H profiles of a Ti(0001) single crystal that had been exposed

to a large dose (12000 L) of partially dissociated hydrogen gas ($H + H_2$) at 200 K and 250 K [84]. A thin (~ 10 nm) H-rich layer with an average H-concentration of about 10 atomic % was found below the Ti(0001) surface after the exposure at 200 K, whereas in addition to some H accumulation below the surface a wider H plateau reaching more than 40 nm deep into the bulk resulted at 250 K. This is clearly indicative of a temperature dependent transition from near-surface to bulk hydride nucleation. In Ti the low concentration ($\ll 1\%$ H) solid solution α -phase has hcp structure and is in equilibrium with γ -Ti below room temperature, a phase of fcc structure and a composition close to Ti-dihydride (TiH_2) [26]. In notable contrast to Pd (Sect. 3.2.3.3), the H_2 exposure at 200 K *saturated* the H uptake into the only ~ 10 nm wide near-surface layer of Ti(0001). This suggests that the near-surface hydride of Ti exhibits self-limiting growth behavior at low temperatures. Apparently this limitation is lifted at 250 K, presumably due to a higher diffusion mobility of the absorbed H.

Fig. 47. ^{15}N NRA excitation curves of H/Ti(0001) taken after atomic H dosage (12000L H_2) at (a) 200 K and (b) 250 K. Reproduced with permission from Ref. [84].

3.2.3.2 Zirconium (0001), (10 $\bar{1}$ 0)

Hydrogen absorption in Zr is even more exothermic ($\Delta H_s = -0.567$ eV/H) [482]) than in Ti, and the tendency to dissolve surface-adsorbed hydrogen into the bulk (Sect. 3.2.2) is so strong, that even under the extreme heating rates ($>10^{10}$ K/s) of laser-induced thermal desorption experiments only a tiny fraction ($\sim 1\%$) of an initially adsorbed H coverage desorbs, whereas the dominant part migrates below the surface [484, 489-491]. This precludes meaningful TDS measurements at Zr surfaces [62, 483, 484] and thus hampers determining, e.g., the H chemisorption energy and also the verification of the H₂ exposure that saturates the surface H coverage under any given temperature and H₂ pressure conditions, an otherwise trivial task for TDS.

A possible solution for this problem has been proposed by Norton and coworkers [483, 484, 486, 492, 493]. They measured the D-uptake into the entire near-surface region of a D₂-exposed Zr(10 $\bar{1}$ 0) single crystal with D(³He,p)⁴He NRA (no depth resolution in the top 500 nm) and correlated the obtained uptake curve (Fig. 48) with corresponding SSIMS data, which exclusively monitor the surface hydrogen [484]. This figure shows that for proper relative axis scaling, the SSIMS H⁺ yield and the NRA D signal are strictly proportional in the initial H₂ (D₂) exposure regime up to the saturation point of the SSIMS data, so that the quantitative NRA information on the D coverage can be used to calibrate the SSIMS signal. The SSIMS H⁺ yield uptake terminates after a H₂ exposure of ~ 1 L, indicating saturation of the surface chemisorption layer, whereas the NRA D signal grows further due to continued D-uptake into the Zr bulk [484]. The combined data thus rather accurately identify the exposure regime where surface-adsorption saturates and quantitatively reveal the

saturation coverage. These experiments permitted determining the initial sticking coefficients ($s_0 = 0.38 \pm 0.16$ for Zr(0001) and $s_0 = 1.0, 0.71$, and 0.51 at 100 K, 293 K, and 370 K, respectively, for Zr($10\bar{1}0$)) and that the hydrogen saturation coverages on these surfaces are 0.77 ML for Zr(0001) and 1.0 ML for Zr($10\bar{1}0$)) [483, 484]. This information had remained entirely elusive in a previous study [494], where the tendency of surface hydrogen to dissolve into the bulk during the TDS heating ramp was not realized and the resulting small desorption signals were misinterpreted as a low sticking probability [483].

Fig. 48. Comparison of the hydrogen uptake at the Zr($10\bar{1}0$) surface measured by $D(^3\text{He},p)^4\text{He}$ NRA (square symbols and fitting curve) and SSIMS (small circles) at 293 K. Reproduced from Ref. [484].

Norton's group also established a similar 'calibration' of work function changes against absolute coverages via $D(^3\text{He},p)^4\text{He}$ NRA during adsorption and H-induced reconstruction of H (D) on Pd(110), and thereby contributed significantly to the

clarification of the surface adsorption structure. These work function measurements identified the H₂ TDS ' α_2 ' desorption feature at 220 K related to the lifting of the H-induced (1x2) pairing-row reconstruction of Pd(110) as a surface-adsorbed species [492, 493].

Norton et al. also investigated the exposure temperature dependence of D adsorption and absorption at Zr surfaces with D(³He,p)⁴He NRA. Fig. 49 shows the initial D uptake on a D₂ exposed Zr(10 $\bar{1}$ 0) surface [484] at different temperatures. Due to the limited depth resolution, the data quantify the total D uptake within the top ~500 nm of the sample.

Fig. 49. Uptake of hydrogen at the Zr(10 $\bar{1}$ 0) surface measured by D(³He,p)⁴H NRA at 100 K (circles), 293 K (squares) and 370 K (triangles). The lines through the data points are polynomial fitting curves. Reproduced with permission from Ref. [484].

At 100 K the D uptake saturates rapidly at a density of $9.1 \times 10^{14} \text{ cm}^{-2}$ corresponding to a surface coverage of 1 ML ($9.04 \times 10^{14} \text{ cm}^{-2}$), suggesting that the energy barrier for the penetration into the bulk cannot be overcome at the low temperature, so that D remains confined to the deep chemisorption potentials on the surface [484]. At 293 K a continuous D uptake exceeding the monolayer equivalent is observed during the first 10 L of exposure, the excess being most likely due to the build-up of a D concentration below the surface. At 370 K, the D diffusion into the bulk ($L_D = 11 \text{ }\mu\text{m}$ in 100 s) has apparently become so effective that a reduced stationary surface D coverage and a D concentration in the $\text{D}(\text{}^3\text{He,p})\text{}^4\text{He}$ detection region result, which even combined are smaller than the monolayer density. These $\text{D}(\text{}^3\text{He,p})\text{}^4\text{He}$ NRA data demonstrate the strong effect of temperature on the D_2 transport across the Zr surface during absorption, yet no statements about the relative D concentrations on the surface and in the subsurface region can be made due to the lack of depth resolution. Effective D_2 'sticking coefficients' on the $\text{Zr}(10\bar{1}0)$ surface were determined from the slopes of the uptake curves in the initial exposure range [484]. Note that for 293 K and 370 K such coefficients make no distinction between D surface adsorption and absorption into a $\sim 500 \text{ nm}$ deep region.

Norton's group also presented a detailed analysis of segregation kinetics of bulk-dissolved hydrogen onto $\text{Zr}(0001)$ and $\text{Zr}(10\bar{1}0)$ surfaces, again in an experiment that monitored the surface H coverage with NRA-calibrated SSIMS [486]. Fig. 50 (a) shows the evolution of hydrogen on these surfaces as the single crystals containing a few ppm of H in the bulk were heated between room temperature and 400°C at 1°C/s . At first, a non-equilibrium H distribution with an almost empty surface was

prepared by rapidly quenching the heated crystals from 650 °C to room temperature. Upon slow heating, the H coverage increased first as the bulk diffusion rate rose exponentially, allowing H segregation onto the surface up to ~ 0.2 - 0.4 ML (depending on the bulk H content). At higher temperatures desegregation diminished the surface coverage again, as entropy drove the H atoms back into the bulk, so that the curves ran through a maximum. The onset of segregation at 80 °C on Zr($10\bar{1}0$) was lower than that on Zr(0001) (150 °C), since the H bulk diffusion along the $\langle 10\bar{1}0 \rangle$ direction is faster than along $\langle 0001 \rangle$, presumably as a consequence of the almost two-fold reduced atomic density in these layers relative to the close packed Zr(0001)

basal plane [486].

Fig. 50. (a) Surface segregation of hydrogen on Zr(0001) and Zr($10\bar{1}0$) measured with NRA-calibrated SSIMS during linear heating (1°C s^{-1}). (b) Arrhenius plots of the H- yield vs. $1/T$ on Zr(0001) and Zr($10\bar{1}0$). A linear relationship is observed from 300 to 410 °C on Zr(0001) and from 260 to 380 °C on Zr($10\bar{1}0$). The heats of segregation were derived from these linear portions. Reproduced with permission from Ref. [486].

The above experiment was performed at a slow heating rate so that establishment of thermal equilibrium between the surface and bulk sites could be confirmed in the high temperature decay part of Fig. 50 (a), where bulk diffusion was sufficiently fast as not to kinetically control the H redistribution. The Arrhenius plot of the high temperature coverage decay shown in Fig. 50 (b) yielded the expected linear relationship, from which the energy difference between sites in the bulk and on the surfaces, i.e., the heat of H segregation, could be determined as 10.1 kcal/mol for Zr(0001) and 10.7 kcal/mol for Zr($10\bar{1}0$), respectively [486]. Thus, with reference to the known ΔH_s , such NRA-calibrated SSIMS measurements permit the experimental determination of the H chemisorption energy on strongly exothermic H absorbing metals, which cannot be achieved with TDS. In principle, this should also be possible through a careful evaluation of the surface/bulk occupation equilibrium with ^{15}N NRA, as suggested by the experiments in Figs. 44 and 45 for H/Ti(0001) [62].

3.2.3.3 Palladium(100)

To demonstrate the unambiguous identification of H_2 TDS features in the case of the simultaneous presence of surface-chemisorbed and absorbed hydrogen species with ^{15}N NRA we consider the H_2 TDS trace in Fig. 51, measured at a Pd(100) surface after dosing a mixture of molecular and atomic hydrogen at 100 K [61, 62]. (Atomic H was used as a means to accelerate the H uptake below the surface since the H_2 absorption probability at Pd(100) is rather small ($\sim 10^{-3}$) at 100 K [495].) Two H_2 desorption signals with peak temperatures of 185 K and 330 K were seen. The characteristically sharp low-temperature (so-called α_1) desorption feature at 185 K

has been observed in numerous previous TDS studies of low-index Pd surfaces [61, 279, 402, 495-499] and was attributed to `subsurface` hydrogen [495], on the basis of its peculiar desorption kinetics (close to zero or fractional orders at not too large populations) and due to the facts that its integrated intensity may exceed the desorption signal of surface-adsorbed H (the rapidly saturating feature at 330 K) after large exposures but does nonetheless not saturate, and that it does not induce notable work function changes. While all this certainly has been compelling *indirect* evidence for an absorbed H species, its nature and location below the surface could not be assessed any further.

Fig. 51. H_2 thermal-desorption spectrum of Pd(100) exposed to 300 L $H+H_2$ at 100 K compared with temperature-dependent NRA signals of surface ($z=0$ nm) and near-surface absorbed ($z=6$ nm) hydrogen on/in Pd(100). Reproduced from Ref. [62].

The NRA γ -yield curve of Pd(100) obtained after identical exposure conditions as in the above TDS experiment (Fig. 52) exhibited the dominant Gaussian peak at 6.385 MeV characteristic of surface-adsorbed hydrogen with an integrated area corresponding to a full monolayer of H atoms (Pd(100): 1 ML = $1.32 \times 10^{15} \text{ cm}^{-2}$).

Saturation at 1.0 ML met expectations from the large exposure (300 L H₂) [499], and this H coverage agreed quantitatively with an earlier ERD determination calibrated against D(³He,p)⁴He NRA [258]. In the saturated (1×1) phase on Pd(100) hydrogen chemisorbs in fourfold hollow sites at a height of 0.3 Å above the Pd surface layer as clarified by transmission ion channeling [258] and confirmed by low energy recoil scattering [500], which directly probed the hydrogen-exposed surface and thus avoided possible errors in transmission channeling due to surface relaxations. The latter possibility had been a non-trivial concern for Pd(100) since H adsorption gives rise to a large (4.7 %) first layer outward expansion [501], attributed to strong s-d hybridization between H and surface Pd atoms that weakens the Pd back bonds to the second layer [476, 479, 502].

Fig. 52. NRA γ -yield curve of Pd(100) after exposure to 300 L H+H₂ at 100 K. Sample temperature during NRA: <150 K. The line through the data is a guide for the eye. The incident ¹⁵N ion energy is converted into a probing depth scale (upper abscissa) with the stopping power of 6.4 MeV ¹⁵N in Pd ($dE/dz = 3.90$ keV/nm). Reproduced from Ref. [62].

In addition to the surface peak of chemisorbed hydrogen the NRA profile in Fig. 52 also showed a broad γ -yield distribution between 6.39 and 6.41 MeV. This

revealed the presence of absorbed hydrogen, which was distributed within a few nanometer wide region below the Pd(100) surface [61]. Quantification of the absorbed H content yielded an areal average of 2.6 % of the Pd atomic density. This suggested that the very small H solubility in the solid solution phase of the Pd-H system (the terminal H concentration is only 12.3 ppm at 100 K) [503] was exceeded and that a few grains of Pd hydride (containing ~65 at. % H) [504-506] had precipitated in a shallow region below the surface. Hence, the NRA H profile revealed that the absorbed hydrogen here again was clearly not confined only to the first layer subsurface sites but that it rather corresponded to a *near-surface hydride* phase [61, 279]. Its assignment to the TDS α_1 state is described in the following.

By measuring the NRA signals at fixed ^{15}N ion energies that selectively probed the near-surface hydride and surface-adsorbed H at depths of 6 nm and 0 nm, respectively, while incrementally raising the sample temperature, the thermal stability of the absorbed and the chemisorbed H species were evaluated individually. The obtained NRA signals were superimposed with the TDS trace of the hydrogen-exposed Pd(100) surface in Fig. 51, where they are seen to decay sharply at temperatures that coincide exactly with the peak positions of the two dominant H_2 desorption features at 185 K and 330 K [62]. This experiment convincingly assigned the former (α_1) feature to thermal decomposition of the *near-surface hydride* and the latter to recombinative desorption of chemisorbed surface hydrogen. This direct and unambiguous identification of TDS desorption signals by non-destructive, highly depth-resolved, and temperature-selective monitoring of the H density on or below the surface represents one of the strongest advantages of ^{15}N NRA in the

characterization of H states in the near-surface region of hydrogen-absorbing materials.

The revelation of the H₂ exposure temperature (T_e) dependence of near-surface hydrogen profiles through ¹⁵N NRA is exemplified by comparing the excitation curves of Fig. 52 and Fig. 53 (a). For the latter, 300 L H₂ were dosed onto the Pd(100) surface at 160 K (at 3×10^{-6} Pa). The γ -yield profile in Fig. 53 (a) displays the saturated resonance peak due to surface-adsorbed H (1 ML coverage) and an additional intensity plateau of (28 ± 1) cts/ μ C height extending to at least 16 nm below the surface, indicative of an absorbed H concentration of $7.1 \times 10^{20} \text{ cm}^{-3}$, or 1 % of the Pd atomic density. Together with the associated TDS spectrum (Fig. 53 (b)), this NRA H profile corroborated a previous tentative assignment of the TDS α_2 feature to bulk-absorbed hydrogen. The TDS α_2 feature is clearly different from the α_1 peak in Fig. 51 as it shows a long high temperature tail and a higher peak maximum position, which, moreover, shifted to even higher temperatures when the T_e was raised. This suggested bulk diffusion-controlled H₂ desorption [495], a conjecture here clearly confirmed by ¹⁵N NRA through the larger depth extension of the H distribution in Fig. 53 (a) relative to that in Fig. 52.

Fig. 53. (a) NRA depth profile of H/Pd(100) at $T < 160$ K under 3×10^{-6} Pa H_2 . (b) Post-NRA H_2 -TDS (linear heating rate 2 K/s). Total H_2 dosage: 300 L. Reproduced with permission from Ref. [61].

By extrapolating the H_2 plateau pressures in the solid-solution/hydride coexistence region of the Pd-H phase diagram to low temperatures and comparing with isotherm data at the Pd solid solution phase boundary [503], one realizes that the absorbed H concentration in the near-surface NRA depth profiles (~ 1 -2.6 at. %) in Figs. 52 and 53 exceed the H solubility limits of the Pd solid solution phase (12 ppm at 100 K and 570 ppm at 160 K). This indicates that Pd hydride has precipitated in the solid solution phase matrix in both cases. According to the Pd-H phase diagram [505] Pd hydride contains ~ 65 at. % H under the low temperature conditions of the present experiments, whereas the terminal solid solution phase concentrations (12 and 570 ppm at 100 K and 160 K, respectively) do not or just barely exceed the NRA sensitivity (~ 400 ppm for Pd). This suggests that almost all (98 %) absorbed H atoms detected in the NRA profiles of Figs. 52 and 53 are contained in hydride grains.

In the Pd solid solution phase the H diffusion coefficient $D = D_0 \cdot \exp(E_{\text{diff}}/k_B T)$ ($D_0 = 42.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $E_{\text{diff}} = 0.13 \text{ eV}$ at $T < 220 \text{ K}$) [507] translates into diffusion lengths ($L_D = (D\Delta t)^{1/2}$; $\Delta t = 100 \text{ s}$) of 340 nm at 100 K and 5 μm at 160 K. Compared to this, the depth extensions of the hydride-containing regions in Figs. 52 and 53 are considerably shorter [28, 29, 61, 508]. In Pd hydride the fcc lattice is expanded by 3.3% from 3.89 to 4.02 Å, which slows the H diffusion as the jump distance between adjacent octahedral interstitial sites elongates. Also the number of vacant interstitial sites reduces strongly due to the much larger H content in the hydride [25, 28, 29]. The elastic H-H interaction, which is repulsive in the solid solution phase but attractive in the expanded lattice of Pd hydride, further promotes localization of absorbed H atoms in growing hydride grains [27, 28]. These factors may provide a qualitative explanation for the reduced extension of the observed hydride distributions compared to the H diffusion length in the solid solution phase [61]. The depth extension of the hydride distribution obtained by H_2 exposure of Pd(100) at 160 K (Fig. 53) is evidently larger than that formed in the absorption experiment at 100 K (Fig. 52). Similar as in recent observations of H_2 -absorption at Pd(110) [279], this may be ascribed qualitatively to strongly temperature sensitive hydride nucleation underneath the surface, as the absorbed H can diffuse larger distances at higher temperatures and may give rise to hydride nucleation in more extended regions below the surface.

3.2.3.4 $\text{Pd}_{70}\text{Au}_{30}(110)$

Ogura et al. reported a combined NRA and TDS investigation of the low-temperature H_2 absorption at a single crystalline $\text{Pd}_{70}\text{Au}_{30}(110)$ alloy surface [485].

Due to their expanded lattice compared to pure Pd, Pd-Au alloys exhibit increased dilute phase H solubility at a given H₂ pressure (a more negative ΔH_s) and they do not precipitate a hydride phase above 298 K if the Au content exceeds ~17% [509, 510]. As mentioned in Sect. 3.1.2, alloys are interesting also because their surface elemental composition may deviate significantly from the bulk stoichiometry due to segregation effects. Ogura et al. found that through variation of the UHV annealing temperature (400 – 900 K) for the ion sputter-cleaned single crystal, the surface layer composition of Pd₇₀Au₃₀(110) can be adjusted to contain between 40 and 90% Au, and that a surface Au coverage of ~90% is obtained by annealing at 700 K [485]. H₂ TD spectra of such a 700 K-annealed strongly Au-enriched Pd₇₀Au₃₀(110) surface are shown in Fig. 54 (a) after exposure to 100 L H₂ at various temperatures between 105 and 180 K. All H₂ TDS traces showed a broad main desorption feature at 240 K with a small shoulder at 360 K. While the amount of desorbed hydrogen at 105 K was very small (corresponding to a coverage of 0.1 ML (1 ML = 8.8×10^{14} cm⁻²) with reference to the H₂ TDS intensity of a H-saturated Pd(110) surface [279, 511]), it increased steadily with the temperature during H₂ exposure above 120 K and assumed quite substantial values of several (>8) MLs at 180 K as shown in the inset. This suggested that at 105 K H adsorbed only on the few remaining Pd atoms in the surface layer (~10%), whereas larger H quantities appeared to have been incorporated into the alloy interior at temperatures above 120 K.

Fig. 54. (a) TD spectra from a $\text{Pd}_{70}\text{Au}_{30}(110)$ surface annealed at 700 K exposed to 100 L H_2 at various temperatures. The inset shows the amount of desorbed hydrogen in ML units as a function of sample temperature during H_2 exposure. (b) NRA yield curves from $\text{Pd}_{70}\text{Au}_{30}(110)$ after exposure to 1000 L H_2 at 120 (circles), 140 (triangles), and 180 K (squares). The inset shows the γ -yield curve of 140 K enlarged near the surface. Solid and dashed lines are Gaussian and sigmoid components, respectively. Reproduced with permission from Ref. [485].

This conjecture was corroborated by the ^{15}N NRA H profiles in Fig. 54 (b), obtained after exposing the alloy surface of the same composition to 1000 L H_2 at 120, 140, and 180 K. The NRA profiles clearly confirmed that hydrogen absorption had occurred in the probed region < 30 nm deep below the surface, evidencing accumulation regions in 0-12 nm and plateau-like features at larger depths. All profiles showed maximum H content near but not right at the surface. The decomposition of the 140 K profile into a Gaussian peak and a sigmoid component reflecting absorbed H shown in the inset revealed that the H distribution peaked at a depth of (0.8 ± 0.2) nm, clearly indicating H accumulation below the surface. A surface H coverage smaller than 0.1 ML was deduced from the data, quite consistent with the quantity of TDS-detected H_2 after exposure at 105 K, supporting the interpretation that the surface-adsorption of hydrogen remains rather limited.

Contrary to the increasing amount of H₂ desorbing in TDS (Fig. 54 (a)), the average concentration of H absorbed in the 12-30 nm deep alloy region evaluated with ¹⁵N NRA decreased at higher exposure temperatures, from an average of 2.7 at. % at 120 K, to 1.2 at.% at 140 K, and 0.3 at.% at 180 K. This apparent contradiction was qualitatively reconciled by the fact that the depth distribution of the absorbed H is expected to extend into increasingly larger depths by entropy-driven diffusion into the bulk at higher H₂-exposure temperatures [485]. The noticeably non-uniform depth distribution of the absorbed hydrogen was tentatively attributed to possible Pd-Au alloy composition fluctuations below the surface, since the Au segregation process creates Pd-enriched layers below the surface [512], and the H solubility in Pd-Au alloy is known to vary with the alloy composition [510, 513, 514].

3.2.3.5 Hydrogen trapping at internal defects and surfaces

The research reviewed so far has focused on (low-temperature) H₂ absorption studies at (more or less perfect) metal single crystal surfaces and on the direct and depth-resolved ¹⁵N NRA observation of variations in the hydrogen gas/surface/bulk population equilibrium elicited by changes of the thermodynamic boundary conditions (temperature or H₂ pressure). Methodically closely related are NRA investigations of the thermally induced redistribution of bulk-absorbed hydrogen between various kinds of H trapping sites that may exist in the *interior* of metals. Such studies aim at evaluating the bonding strength of hydrogen as it interacts with immobilizing entities in the metal host lattice such as implanted heteroatoms,

radiation defects, vacancies, vacancy-solute complexes, crystalline precipitates, and in particular with the interior surfaces of gas (He, D₂, H₂) bubbles (voids) that are suspected as a cause of blistering and embrittlement [122, 515-518].

In order to experimentally distinguish internal hydrogen redistribution processes from desorption through the surface, initial hydrogen and trap site distributions that differ largely in their depth location (on the order of several micrometers) can be prepared by energy-controlled ion implantation, so that even the very limited depth resolution of $D(^3\text{He},p)^4\text{He}$ NRA suffices to provide information on the hydrogen relocation behavior [122, 517, 518]. This technique is illustrated in Fig. 55 (a), which shows the $D(^3\text{He},p)^4\text{He}$ nuclear reaction cross section as a function of depth in beryllium for incident 500 keV ^3He together with the TRIM-calculated implantation ranges of 10 keV H and 15 keV He ions, which were used in high doses to generate gas bubbles as traps for D in about 0.1 μm depth below the surface [122]. After implanting 60 keV D into a deeper range at 20 °C (a smaller dose that does not create bubbles), the NRA proton yield from the $D(^3\text{He},p)^4\text{He}$ reaction was monitored while the sample temperature was ramped linearly to 600 °C.

It is seen in Fig. 55 (b) that between 440 and 480 °C the D was removed by desorption from the Be sample implanted with D only. When H or He had been implanted in addition, the NRA yield increased instead as soon as the implanted D became mobile when it detached from its own implantation-induced defects near 400 °C, because the D relocated to the bubble defects near the surface where the $D(^3\text{He},p)^4\text{He}$ cross section is larger. At yet higher temperatures of 550 °C (pre-implanted H) or even 600 °C (pre-implanted He), D was then thermally released from

the near-surface traps and desorbed. These data demonstrated a significantly stronger interaction of D with the gas bubbles than with the lattice defects generated by its own implantation. The interaction energy difference between H bound to He bubbles and H at D-implantation-induced defects can be extracted from the NRA redistribution data [122, 517].

Fig. 55. (a) Calculated concentration versus depth for the H, He, and D implants used in the internal redistribution experiment in beryllium. Also shown is the $\text{D}(^3\text{He},\text{p})^4\text{He}$ cross section for 500 keV ^3He and how it decreases with depth due to the ^3He energy loss. (b) NRA yield during temperature ramping at 2°C/min. The yield increase near 450°C occurs when D migrates from its implanted depth to the H or He nearer the surface where the NRA cross section is larger. Reproduced with permission from Ref. [122].

Similar investigations of D interaction with implanted He have been performed for a series of metals including Al, Fe, Ni, Mo, Pd, Ta, stainless steel, and Inconel [516, 517]. Including evaluations of near-surface H (D) depth distributions by NRA and ERDA [519, 520], this line of research has remained highly active to the present day, in part motivated by the importance to understand the mechanisms of deuterium

retention and tritium inventory in plasma facing components of fusion-energy devices (JT-60, JET, ITER, etc.), where the proper material selection is a top engineering priority. To give just one example of an important result, a substantial suppression of near-surface D retention in tungsten under fusion-relevant conditions by small additions of He to the plasma has recently been discovered by $D(^3\text{He},p)^4\text{He}$ NRA and TDS measurements [515]. In conjunction with microstructure characterization by TEM [521] it was suggested that this effect of He results from reduced blistering and the formation of a network of He nanobubbles underneath the surface that may effectively interrupt the D transport from the surface region into the bulk [522].

Hydrogen trap generation by ion implantation in combination with NRA analysis has also been used to investigate the H-absorption and release kinetics between the metal interior and the gas phase, which has enormous fundamental importance for hydrogen storage, purification, sensors, and catalysis [508, 516, 523-526]. Similar to penetration studies [527-529], such experiments aimed to extract information on the relative energy levels of H atoms in the metal interior, on the surface, in the gas phase, and on the kinetic barriers between them. A presentation of the extensive research in this area and of the proposed kinetic models is beyond the scope of the present article. For earlier reviews of the NRA contribution to this field in conjunction with the implantation technique see Myers et al. [517, 518].

As a representative example we refer to the deuterium uptake/release kinetics at a clean (polycrystalline) palladium surface monitored by means of $D(^3\text{He},p)^4\text{He}$ NRA after introducing bubble traps into a shallow average depth (56 nm) below the

surface by implantating a large dose ($4 \times 10^{16} \text{ cm}^{-2}$) of 15 keV He [516]. The He traps confined the major amount of absorbed D to a shallow depth region where the $\text{D}({}^3\text{He},\text{p}){}^4\text{He}$ nuclear reaction cross section is approximately constant, and thus allowed observing the equilibration kinetics of D between these He traps and the gas phase during D_2 ($10^{-9} - 10^{-5}$ Torr, 1 Torr = 133 Pa) absorption as well as during D_2 release upon evacuation.

Such data are shown in Fig. 56 as (a) D uptake and (c) D release curves. An analysis of the initial uptake and release rates as well as of the equilibrium trap populations determined the energetic positions of D bound to the He traps (-0.29 eV relative to D in solid solution) and in recombination sites (at least 0.15 eV less strongly bound than D in low coverage chemisorption sites) [516]. Besides ensuring full visibility to $\text{D}({}^3\text{He},\text{p}){}^4\text{He}$ NRA, a further advantage of restricting the major D uptake to a shallow depth region was that the distance of the He traps from the surface was short enough to exclude that the uptake/release kinetics were limited by bulk diffusion. This was verified by Fig. 56 (b), which shows that the experimental D uptake rate was much smaller than an upper ('bulk permeation rate') limit estimated from the H diffusion rate in the Pd solid solution phase, and also by Fig. 56 (c), where the D-release is much slower than calculated for bulk-diffusion limited desorption. Thus, the kinetics of the D uptake into and of the release from the near-surface He traps were concluded to be limited by surface processes, and indeed showed the expected linear dependence on the D_2 pressure (Fig. 56 (b)). Owing to the $\sim 10^4$ times shorter diffusion length involved, this result was no contradiction to the fact that the macroscopic equilibration kinetics of H_2 gas with clean Pd single crystals were

observed to be controlled by bulk diffusion, showing a characteristic $p^{1/2}$ dependence of the initial uptake rate [508, 516].

Fig. 56. (a) Uptake of D into Pd monitored by $D(^3\text{He}, p)^4\text{He}$ NRA after D_2 enters the chamber at $t = 0$. The closed and open circles show data for D_2 gas pressures of 5.3×10^{-6} and 5.3×10^{-7} Pa, respectively.

(b) Initial D-uptake rate vs. gas pressure (closed circles). The rate of impingement on the surface from the D_2 gas and the bulk transport-limited uptake rate are shown by the two solid lines.

(c) Areal density of D vs. time during release after equilibrating at pressures of 5.3×10^{-7} Pa (open circles) and 5.3×10^{-5} Pa (closed circles). The curve shows the calculated D release when surface processes are not rate limiting. The time scale begins when the D_2 gas

was pumped from the chamber. Adapted from Ref. [516].

Fig. 56 (b) also showed that the population of the He traps by gas phase D₂ proceeded quite efficiently with a sticking probability of 0.2-0.4 (compare the D-uptake rate (closed circles) with the impingement rate). This probability is several orders of magnitude higher than reported in typical low pressure H₂ absorption studies at Pd single crystals ($\sim 10^{-3}$ - 10^{-2}) [61, 279, 495, 496]. Since surface defects such as steps and vacancies are well known to enhance H₂ dissociation on metal surfaces [364, 365, 530, 531] and are suspected to be sites of high absorption rate [279, 402, 495] this observation hints at the possibility that the generality of the results in Ref. [516] regarding the energy position of the recombination sites is limited to surfaces damaged by ion implantation.

3.2.3.6 Modified surface layers

Hydrogen uptake and release kinetics into and from bare metals [525, 526] are extremely sensitive to surface modifications, and much research effort has been devoted to clarify the influence of native oxides [166, 532], hydrides [533], metallic overlayers [534, 535], implanted heteroatoms [516, 517, 532] (including hydrogen itself [515, 536, 537]), as well as surface processing (e.g., polishing) [537]. A prominent application of NRA has been to reveal the near-surface H-depth distributions resulting from either the modification process itself or after hydrogen uptake through the modified surface. Similarly, near-surface hydrogen depletion layers resulting from vacuum annealing of titanium hydrides have been analyzed by ERD [538]. The thin native oxide layers formed on metal surfaces in air are frequently

found to suppress the hydrogen uptake into the bulk material. On H-loaded samples this is manifested as a depletion layer near the surface, where the absorbed H concentration shows a depression that relates to the content of dissolved oxygen, as exemplified by ^{15}N H profiles from polycrystalline Nb foils [166]. Rauch and coworkers demonstrated by H profiling with ^{15}N NRA that such inhibition of H absorption from H_2 gas at oxide-passivated Ti surfaces can be circumvented even without removing the surface oxide layer through the implantation of low energy (<5 keV) Pd ions [532]. Enhancements of the H uptake in Nb and Ta foils by coating with Pd are also reported [534, 535]. Here, the origin of the improved H uptake is threefold, as Pd (1) prevents oxidation of the surface, (2) enables efficient H_2 dissociation, and (3) lowers the energy of the surface adsorption state and thereby reduces the energy barrier for the transition of H atoms into the bulk [525, 534, 535]. Owing to this unique property combination, thin Pd films are widely employed as capping layers in oxidation-sensitive hydrogen absorbing metallic thin film devices such as metal gas sensors and switchable mirrors [32, 33, 539-543].

Recent developments in ion beam analysis include the application of strongly focused beams that allow for the detection of lateral elemental concentration differences within the surface plane of a specimen. Combined with the high depth-resolving powers of ^{15}N NRA or ERD these micro-beam techniques enable three-dimensional evaluations of the H concentration distribution in the surface-near region on a micrometer scale [537, 544-553]. An example is given in Figs. 57-58, where the laterally and in-depth H distribution in mechanically polished and H-implanted Ti samples is revealed by combined ^{15}N NRA and micro-ERD

measurements [537]. The conventional near-surface ^{15}N NRA H profile in Fig. 57 shows the areal averaged in-depth H distribution. A ~ 70 nm wide layer in ~ 220 nm depth holds a high H concentration (~ 50 a.%) as a result of the implantation ($6 \times 10^{17} \text{ H}_2^+/\text{cm}^2$ at 25 keV/amu). Furthermore a broad H distribution is seen in which the concentration gradually decreases from close to 60 at.% near the surface to below 10 at.% in the bulk at depths above 330 nm. This broad structure originates from H incorporation during the polishing process, which is in good agreement with earlier ERD observations of Mizuno et al. [554].

Fig. 57. ^{15}N NRA depth profile of H in a mechanically polished Ti sample implanted with a fluence of $6 \times 10^{17} \text{ H}/\text{cm}^2$. An implantation peak at ~ 230 nm is seen on a broad H distribution in a near-surface H-enriched layer. Reproduced from Ref. [537].

As indicated in Fig. 57, four depth regions ((a): 0-100 nm, (b): 101-180 nm, (c): 181-280 nm, (d): >281 nm) were assigned, for which in-plane H concentration distribution maps were obtained with micro-ERD by scanning a focused 16 MeV Si^{5+} ion beam of 3 μm diameter across the sample at an incidence angle of 70° relative to the surface normal. This resulted in a lateral resolution of 10 μm (X, beam direction)

x 3 μm (Y) sized pixels [537]. In each depth region the lateral H concentration distribution was evaluated in 32 x 64 pixel maps, corresponding to a scan area of $\sim 300 \times 250 \mu\text{m}^2$. The obtained concentration maps in Fig. 58 (implantation dose: $1 \times 10^{17} \text{ cm}^{-2}$) clearly reveal lateral concentration gradients in the in-plane H-distributions. The inhomogeneity is particularly pronounced near the depth region of the hydrogen implant [537]. Similar laterally inhomogeneous H distributions were previously observed at surfaces of a H-implanted titanium alloy [536] and of a titanium sheet under bending stress [555], the latter revealing the redistribution of implanted hydrogen due to the mechanical deformation (Gorsky effect). Complementary X-ray diffraction data and SEM images gave evidence that the laterally inhomogeneous H distributions arise from the non-uniform nucleation of titanium hydride [536, 537].

Fig. 58. Depth dependent in-homogeneities of the in-plane H distribution on a mechanically polished and H-implanted (1×10^{17} H/cm²) Ti surface determined by micro-ERD. H-distribution maps in depths of (a) 0 – 100 nm; (b) 101 – 180 nm; (c) 181-280 nm and (d) >280 nm. Reproduced from Ref. [537].

A recent two-dimensional and depth-resolved analysis of H distributions in the plane of fracture surfaces of amorphous glassy alloys by ¹⁵N NRA is also reported [551]. In contrast to ordinary crystalline alloys, where hydrogen bubble formation at grain boundaries may cause embrittlement, the fatigue mechanism of ductile Zr- and Pd-based bulk glassy alloys (BGAs) is discussed as being due to extreme hardening and embrittlement at the tip of fatigue cracks [556]. Since the alloys retain their glassy structure without nucleating a crystalline phase near the fracture tip,

hardening by hydrogen was considered a possible explanation. Previous H depth profiling measurements by conventional ^{15}N NRA near the crack tip of a fatigue fractured BGA surface showed a slight enhancement of the H concentration in comparison to an impact-fractured surface (which displays the average bulk composition that includes 1 at. % H), supporting the hypothesis of hydrogen involvement in the fracture mechanism [556]. The conclusion remained preliminary though, as the ^{15}N ion beam (3 mm diameter) irradiated both fatigue fractured and impact fractured area simultaneously.

A verification of the result at higher spatial resolution succeeded recently by utilizing a focused ^{15}N ion beam (rectangular profile of $17 \times 30 \mu\text{m}^2$ area) in conjunction with optical microscopy, which could selectively confine the NRA analysis region to either the fatigue fractured tip or the impact fractured surface area [551]. The thumbnail pattern corresponding to the fatigue-fractured region is seen in the upper left corner of the $\text{Zr}_{50}\text{Cu}_{37}\text{Al}_{10}\text{Pd}_3$ fracture surface as indicated by the white dashed line in the optical micrograph (Fig. 59 (a)). The in-plane hydrogen concentration distribution was evaluated by scanning the sample under the focused ^{15}N ion beam in $150 \mu\text{m}$ increments within the analyzed $3 \times 3 \text{ mm}^2$ area (white square in (a)) and recording the NRA γ -yield at each position. For a shallow probing depth of 2.5 nm below the surface, Fig. 59 (b) shows that the H concentration in the fatigue-fractured region (A) is very substantial (exceeding 50 at.%) and significantly higher than in the central bulk region (C).

Fig. 59. (a) Optical microscope image and (b) ^{15}N NRA-determined in-plane H distribution in 2.5 nm depth on a fatigue-fractured surface of $\text{Zr}_{50}\text{Cu}_{37}\text{Al}_{10}\text{Pd}_3$ glassy alloy. The fatigue-fractured region is encircled by a white dashed line in (a). The NRA H-distribution map (b) shows that it corresponds to a region of increased H content closely below the surface (region A). Reproduced from Ref. [551].

In a probing depth of 8 nm still a similar relative in-plane H concentration contrast was observed, while in 20 nm depth the H concentration was nearly uniform, which is consistent with an conventional area-integrated H depth profile showing that the H enrichment over the bulk concentration (1 at. %) is limited to only the top 20 nm [551]. These spatially-resolved H profiling results thus support the suspect that the fatigue fracture of the glassy alloys correlates with high local H concentrations near the crack tips. Several open questions, such as the origin of the hydrogen accumulation in the vicinity of the crack tip and in the outer circumference region (B), as well as the distribution of other elements, however, remain subject to further investigation.

3.2.3.7 *Thin films and superlattices*

Several groups have invested substantial effort in elucidating the effects of finite size and interfacial strain on the hydrogen behavior in thin metallic films [540, 557-560] and metal/metal superlattices [561-572]. Pundt and Kirchheim offer a comprehensive review of the subject [573]. With respect to the influence of hydrogen absorption on the host metal's material properties, H-concentration dependent variations of the magnetic coupling in metallic superlattices [562, 567, 568] as well as H-driven metal/insulator transitions allowing to fabricate thin films with switchable optical properties [32, 33, 539-543, 574-577] have been in the center of attention. To highlight the contribution of ^{15}N NRA in this line of research, we illustrate examples of H concentration and distribution measurements in thin film systems, going from simple metallic layers on rigid substrates to more complex clamped thin films and finally to metallic superlattices. From the viewpoint of hydrogen, the most frequently encountered phenomenon is a pronounced variation of the H solubility in the near interfacial regions of the thin films, giving rise to notable changes in the pressure-composition phase diagrams compared to the respective bulk metals [557, 558, 567, 570, 571, 578].

Fig. 60 (a) displays ^{15}N NRA hydrogen depth profiles of a thin (140 nm) Pd-capped Nb film grown by MBE onto an Al_2O_3 substrate after hydrogen loading at 200°C under different external H_2 pressures [557]. The H concentration information obtained from the central Nb plateau region of the profiles was used to construct the equilibrium phase diagram for the thin film system. Open and filled circle symbols denote data points of two consecutive ^{15}N energy scans, verifying that the

system had reached equilibrium conditions. The main observation was that the film showed considerably reduced hydrogen solubility compared to bulk Nb. Further characteristic changes in the pressure-concentration (H/Nb) phase diagram (Fig. 60 (b)) compared to that of bulk Nb were sloped isotherms in the solid solution/hydride coexistence region and increased solubility in the low concentration solid solution phase of the thin film. This behavior has been attributed to a reduction of the attractive H-H interaction in the concentrated Nb hydride phase due to the epitaxial clamping of the films by the substrate, since the rigid interfacial locking to the Al_2O_3 hinders the lattice expansion of the Nb film upon hydrogen absorption [557, 558].

Fig. 60. (a) ^{15}N hydrogen depth profiles for a 140 nm Nb film on an Al_2O_3 substrate after in-situ hydrogen charging under different H_2 pressures at a temperature of 200°C . The film structure is illustrated on top of the figure. The small rectangle on the left represents a Pd cap layer. (b) Solubility curve for the Nb film (circles) at $T = 200^\circ\text{C}$ compared with those of bulk Nb (solid line) and an extrapolation of Sievert's law to higher H-concentrations (dotted line). Reproduced from Ref. [557].

As an example of *mutual* interfacial strain effects in stacked metal layers on the H solubility we show in Fig. 61 ^{15}N NRA H depth profiles of a 45 nm thin Hf sheet sandwiched between two epitaxial Nb films before and after H charging [579]. In this system the clamped Hf layer represents the component of higher hydrogen affinity, i.e., the more negative H solution enthalpy [580]. In addition to a thin H rich surface layer, the depth profiles reveal H accumulation at the upper metal/metal interface and a small native H concentration in the Nb layer, presumably due to incorporation of H surface impurities during layer deposition. LEED investigations of the Hf lattice structure at early stages of the deposition show a high amount of distortion in the first 5 nm from the interface presumably due to the misfit between the Nb (bcc) and the Hf(hcp) lattices, which may explain the interfacial H accumulation by trapping at the lattice distortions.

Fig. 61. ^{15}N NRA H depth profiles of a Nb-Hf-Nb multilayer before (open circles) and after (filled circles) hydrogen charging. The thickness of the Hf layer is 45 nm. Reproduced from Ref. [579].

Most obvious, however, is the strong increase of the H concentration in the Hf layer after electrolytic hydrogen charging. Despite this substantial hydrogenation, the atomic H/Hf ratio in the clamped Hf layer does not attain the value of 1.63

expected for the bulk Hf- δ phase, indicating again a reduced H solubility compared to the bulk material. Furthermore, the H distribution is seen to extend below the bottom Hf/Nb interface, i.e. the H solubility in the Nb is locally strongly increased over the bulk value near the interface. Both effects are ascribed to mutual interfacial strain exerted between the two metals due to their interface-locked lattices. Clamping of the Hf film to the rigid Nb substrate causes compressive strain in the Hf layer that hinders its lattice expansion during H absorption, resulting in overall reduced H solubility in the Hf layer [557, 558]. On the other hand, upon H loading the expanding Hf lattice exerts tensile stress on the Nb layers adjacent to the interface, expanding the Nb lattice locally, which in turn increases the H solubility in the Nb substrate near the interfaces [558, 579]. Similar clamping-related alterations of the H solubility in interfacial regions revealed by ^{15}N NRA measurements are also reported for Nb layers sandwiched between Cu films [571, 581] as well as in thin films of Nb and V due to interfacial interactions with the respective substrates [560, 569, 582, 583] and for Pd-capped Mg films [578].

The groups of Hjörvarsson and Zabel extended these investigations to bimetallic *superlattices*, which are open to structural analysis by X-ray diffraction [167, 563, 565, 566, 572]. In such multilayer stacks of two alternating metals the hydrogen potential (i.e., ΔH_s) is modulated periodically. The amplitude of the modulation depends on the hydrogen solubility difference between the two metals and the period is determined by the respective layer thicknesses [563, 567]. Analog to the interfacial clamping effects described above, the average hydrogen solubility can thus be adjusted by the selection of the metal combination in the superlattice and by

variation of the respective layer thicknesses, which may be as small as only a few atomic distances. A well-studied weakly modulated system both in terms of the H solubility difference and similar lattice parameters is Nb-Ta. On the other hand, sandwiching, e.g., vanadium into either Fe/V or Mo/V superlattices achieves a very strong modulation of the H potential (the ΔH_s difference is as large as ~ 0.6 eV/H), and the resulting interfacial strain can be switched from compressive (Fe/V) to tensile (Mo/V) [167, 562-564, 569].

^{15}N NRA H profiles of H-loaded Fe/V systems of different periodicities are shown in Fig. 62 (a). It is seen that the H concentration reduced strongly at shorter periods (Λ_1 , i.e., thinner layers) of the superlattice, where the proportion of the Fe/V interfacial region in the respective V layers was large [564]. As illustrated in Fig. 62 (b), the H-depletion was explained by destabilization of hydrogen in the interfacial regions of the V layers adjacent to the Fe interlayers owing to lattice strain and interfacial charge transfer [167, 563, 564]. Clarifications of the interfacial structure in the V layers after H loading to H/V=0.5 by XRD (avg. lattice expansion 4.5%) [565] and EXAFS (5.1%) [561] were in good agreement. A similar interfacial charge transfer effect deduced from average ^{15}N NRA H concentration measurements was also reported for $\text{Mo}_x\text{V}_{1-x}/\text{V}$ superlattices [167, 584]. Contrary to Hjörvarsson and Zabel's reasoning that interfacial strain and charge transfer are the origin of the reduced H-solubility [167, 563, 567], Pundt et al. suggested based on 3-dimensional atom probe measurements that the modulation of the near-interfacial H potential results from a partial intermixing of the two metals near the interfaces. [585]

Fig. 62. (a) ^{15}N NRA hydrogen depth profile of a Fe/V multilayer superlattice on an MgO substrate hydrogenated at 150°C in 2100 Torr H_2 . The superlattice periodicities are $\Lambda_1 = 1.8$ nm, $\Lambda_2 = 3.1$ nm, and $\Lambda_3 = 4.4$ nm. The normalized yield is proportional to the H/V ratio. (b) Schematic view of the potential seen by a diffusing H atom in the Fe/V superlattice. The shadowed areas are the iron layers surrounding the vanadium, which is 10 ML in the upper and 6 ML thick in the lower panel of (b), respectively. In the upper panel of (b) the energy difference between monolayers 3 and 4 from the interface is 97(5) meV. E_{min} in the lower panel is 87(6) meV higher than in the upper panel. Reproduced from Ref. [564].

Much attention has been paid to the drastic optical property changes that certain rare-earth metal thin films display during their reversible metal-to-insulator phase transitions upon hydrogenation, which may find applications as energy-saving smart windows that change between reflective and transparent properties on demand. Griessen and coworkers demonstrated first that the optically reflective (metallic $\alpha\text{-YH}_x$ and YH_2) or transparent (insulating YH_3 trihydride) phases of thin yttrium films on glass substrates can reversibly be interchanged by controlling the external H_2 pressure [32, 33, 539, 541]. ^{15}N NRA depth profiling was used here to verify that the optical transmission variations indeed correlated to changes of the H concentration

in the thin films, for which the YH_x phase transition points apparently showed little differences to those of bulk yttrium [586]. These results were later substantiated by spatially resolved ERD measurements at Y films to which H was only locally supplied through Pd caps that were separated by a H_2 -impermeable Y_2O_3 surface oxide layer as illustrated in Fig. 63 (a) [587, 588]. After hydrogenation the H concentrations in lateral sections of different optical transparency were analyzed by ERD using a 0.1-mm diameter beam, which again confirmed that these regions corresponded to the respective YH_x phases of the bulk Y-H system and that the boundaries between them were comparatively sharp (Fig. 63 (b)) [587, 588].

Fig. 63. (a) Schematic illustration of the Y-film on a glass substrate as well as an optical photograph of the sample after a few weeks of H loading at 373 K. The different YH_x phases (α , β , γ) can be recognized in the photograph. Adapted from Ref.[601].

(b) Results of an ERD line scan (squares) on a H-loaded double diffusion sample (Y film on glass; region between the Pd caps in (a)). The solid lines represent an optical transmission measurement along the same line. Both the red (R) and blue (B) signals of the used 3-CCD camera are shown. Adapted from Ref. [602].

A few years later Mg alloys [542, 543] were proposed for hydrogen storage and switchable mirror applications operable at room temperature. Pure Mg has a very favorable H storage capacity of 7.6 mass % in its ionic hydride MgH_2 , however, the strongly exothermic H bonding ($\Delta H_s = -0.37$ eV/H) [27, 589] implies an impracticably low equilibrium H_2 pressure at room temperature (10^{-3} mbar) that precludes its application in devices relying on quick reversible H loading and release. As MgH_2 is in addition almost impermeable to H_2 , it can passivate the metal against further H uptake near the H_2 exposed surface [533, 590]. Hydrogen destabilization through alloying [542, 543, 576, 591] and/or elastic effects due to interfacial clamping [578] was shown to be effective in improving the hydrogenation equilibrium, yet Pd capping layers are still required to prevent surface oxidation and to catalyze H_2 dissociation. Currently, efforts are undertaken to improve the reproducibility of the mirror switching process [592, 593] and the durability of the film systems in ambient conditions [594-596]. The amplitude of the transmittance change of the switchable layers degrades during hydrogenation/dehydrogenation cycling and the devices finally attain an irreversible half-mirror state [574, 592]. The degradation apparently relates to the tendency of alloy formation between Pd and Mg at the cap layer/alloy interface, causing interdiffusion of the two metals that enables oxidation of Mg at the surface [574].

A recent ion beam analysis study combining RBS, ERD, and ^{15}N NRA has provided insight into the degradation mechanism of such a switchable mirror alloy film system consisting of Pd-capped Mg-rich $\text{Mg}_{3.3}\text{Ni}$ alloy on a diamond-like carbon (DLC)/glass substrate [597]. RBS data demonstrated clearly that Mg segregates into the

interface between the Pd cap and the Mg-Ni alloy, and the total number of atoms above the DLC substrate increased after many switching repetitions when the system approached the half mirror state near the end of its life cycle (Fig. 64 (a)) [597]. The NRA depth profile obtained in this investigation (Fig. 64 (b)) evidenced that this effect is due to strong permanent H incorporation into the Pd/Mg interfacial region [597]. Together, the data support the conclusion that the formation of Mg hydride and oxide compounds into the Mg enriched region at the Pd cap/alloy interface increasingly impedes the switching performance by blocking the hydrogen transport.

Fig. 64. (a) Light ($\lambda = 670$ nm) switching behavior of a Pd-capped $\text{Mg}_{3.3}\text{Ni}$ thin film as a function of the switching cycles by alternating hydrogenation and dehydrogenation.

(b) ^{15}N NRA H profile taken on an 'old' Pd-capped $\text{Mg}_{3.3}\text{Ni}$ film (after many switching cycles). The corresponding H concentrations in Pd and in $\text{Mg}_{3.3}\text{Ni}$ are indicated on the right hand side. Adapted from Ref. [597].

Qualitatively similar conclusions on the hindering effect of MgH_2 layers in the Pd/Mg interfacial region on the hydrogenation kinetics of Pd-capped Mg-based multilayers intended for hydrogen storing applications were recently drawn from combined by X-ray diffraction and neutron reflectivity measurements [598]. The above degradation problem in Mg-based switchable mirrors is closely related to the strong tendency for interdiffusion at interfaces between Pd and Mg, which readily form alloys. Interfacial alloying has very recently been pointed out as the dominant factor responsible for the considerable destabilization of hydrogen in Pd-capped MgH_2 [599], rather than the elastic strain effects due to interfacial clamping assumed previously [578]. The above examples clearly illustrate that in order to understand the behavior of hydrogen in multilayer systems it is necessary to reveal the in-depth distribution of all constituting elements, including that of hydrogen, and therefore highlight the valuable contribution of non-destructive H profiling by ^{15}N NRA.

3.2.3.8 Nanoparticles

Nanoparticles may exhibit size-dependent properties that can differ drastically from that of the corresponding bulk metals. A common observation with respect to hydrogen absorption in Pd nanoparticles made by volumetric pressure-composition analysis is a narrowed coexistence region of the solid solution and hydride phases in the H-Pd phase diagram, implying increased solubility in the low concentration solid solution phase and reduced solubility in the hydride, as well as a lowering of the critical temperature [573, 600-602]. In addition, the pressure-composition isotherms show sloped intervals instead of the flat equilibrium pressure plateau characteristic for the bulk metal, and a strong hysteresis upon absorption/desorption cycling is

observed [603]. Although the phenomena are still not completely understood [573], the most widely accepted explanation has been the hypothesis that H binds into particular subsurface sites that are presumed to stabilize hydrogen more strongly than regular bulk interstitial sites (cf. Section 3.2.1) [602]. Owing to the large surface to volume ratio of nanoparticles, surface and subsurface sites can comprise very significant atomic fractions of the H-binding sites in these particles, amounting to, e.g., 40 or even 75 % of all atoms in the particle if the size is decreased from 5 nm to 2 nm [602].

Finely dispersed palladium particles on oxide supports are widely utilized industrial catalysts for olefin hydrogenation reactions [604], and Pd-absorbed hydrogen has long been suspected to play a role in the catalytic reaction. Model catalysts [605] consisting of UHV deposited nanometer-sized Pd crystallites on a thin alumina film [606, 607] have shown increased reactivity for ethene hydrogenation compared to Pd(111) single crystals [608, 609]. This was tentatively attributed to particle-absorbed hydrogen as TDS gave evidence for a weakly bound H state that only existed in the latter but not in the single crystal [610, 611]. The unambiguous confirmation that low-pressure ($<2 \times 10^{-3}$ Pa) H absorption inside such oxide-supported Pd nanocrystals does indeed take place was achieved via high resolution depth profiling with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA in grazing ion incidence (75° relative to the surface normal) [59, 612], which matched the 3.9-fold enhanced depth resolution (Eq. (2.15)) to the small size (5-10 nm width and 2 nm height) of the Pd nanocrystals [607, 613] and thereby succeeded in a straightforward discrimination between surface-adsorbed and volume-absorbed hydrogen in the nano-sized particles [60].

Fig. 65. NRA γ -yield curves of 5.85 Å Pd/Al₂O₃/NiAl(110) at 90 K for H₂ pressures of a) 2×10^{-5} Pa, b) 6×10^{-4} Pa, c) 2×10^{-3} Pa at 75° grazing ion incidence. Profile (a) shows data of two consecutive scans (filled and open circles) demonstrating the reproducibility of the measurement. The filled Gaussian curves indicate surface-adsorbed H. The open curves symbolize γ -yield from H in the interior of the Pd-particles. Inset: grazing incidence geometry and Pd-nanocrystal morphology (schematic). Reproduced from Ref. [60].

Fig. 65 schematically shows the particle morphology, the adopted NRA geometry, and three hydrogen depth profiles obtained for the Pd nanocrystals under H₂ pressures between 2×10^{-5} and 2×10^{-3} Pa at 90 K. The profiles are asymmetrically broadened on the high energy side in addition to the symmetric ~ 10 keV wide signal of surface hydrogen (shaded Gaussian shapes centered at E_R) [61, 62, 67], clearly revealing a substantial amount of absorbed H (open Gaussian-shaped curves) that increases with the applied H₂ pressure. Near the resonance energy the height of the profiles saturates quickly below 2×10^{-4} Pa reflecting the saturation of the surface-adsorbed hydrogen states on the nanocrystals, whereas the absorbed H species

remains pressure-dependent. For the given particle size, a rather large average H/Pd ratio of up to 0.8 was obtained, consistent with previous TDS results [610]. Panel (a) of Fig. 65 contains two data sets of consecutively recorded depth profiles, demonstrating that the NRA measurement is non-destructive and reproducible. The data also show that equilibration of the H-concentration inside the nanocrystals with the surrounding H₂ gas phase has taken place; an observation in full agreement with recent synchrotron XAFS results, which demonstrated that the Pd lattice expansion upon H uptake saturates very rapidly (on a microsecond time scale at room temperature) [614].

The dominant advantage of the highly depth-resolved analysis is the ability to separate the NRA signal of the particle-absorbed H from that of the surface hydrogen. At ¹⁵N energies above 6.399 MeV (arrow in Panel (b) of Fig. 65), surface H remains excluded from detection, allowing for the selective monitoring of the H content in the interior of the particles. In turn, the distinction of surface-H from absorbed H at the resonance energy is not quite as strict, since the NRA γ -yield also contains a significant contribution from H absorbed closely below the surface, although the surface hydrogen signal still dominates at lower H₂ pressures. An individual evaluation of the thermal stabilities of the particle-absorbed hydrogen and of the (predominantly) surface-adsorbed H could hence be performed by monitoring the respective NRA signals at 6.399 MeV and 6.385 MeV in a constant H₂ background pressure while the sample was heated incrementally. The results in Fig. 66 demonstrate that the particle-absorbed H is more weakly bound (the signal decays at lower temperatures, i.e., 200-300 K) than the surface-adsorbed H (decay between

300-450 K), thereby confirming general expectations (surface-H is the most strongly bound H species, cf. Section 3.2.1.2) and the interpretation by Morkel et al. that the catalytically reactive low-temperature TDS states (200-300 K) indeed represent nanoparticle-absorbed hydrogen [610, 611].

Fig. 66. Temperature dependent NRA signals of surface ($E=6.385$ MeV, 1.5×10^{-3} Pa H_2) and Pd-absorbed H ($E=6.399$ MeV, 9×10^{-5} Pa H_2) in alumina-supported Pd crystallites. The dashed line indicates the small background (10 cts/ μ C) at $E=6.399$ MeV (arrow in Fig. 65) due to energy-shifted surface H signal. Reproduced from Ref. [60].

The van't Hoff analysis of the temperature-dependent equilibrium H concentration inside the Pd nanocrystals for the dilute regime of $H/Pd < 0.20$ revealed that the H solution enthalpy of (-0.28 ± 0.02) eV/H [60], is 2-3 fold increased relative to bulk Pd [27]. This result is quite consistent with the extended H concentration range of the solid solution phase in nanoparticles as observed by volumetric pressure-composition analysis [573, 600-602] and X-ray diffraction studies [603, 614-616]. The depth-resolved NRA analysis, on the other hand, indicates that this particular property of the nanocrystals is not a consequence of preferential hydrogen binding into first-layer subsurface sites [573, 600-602], which even at the

enhanced depth resolution of the above experiment remain almost indistinguishable from surface sites, so that predominant subsurface site occupation should result in much narrower NRA profiles than those seen in Fig. 65. A more or less homogeneous H distribution within the interior of the nanoparticles appears to be most consistent with the observed depth profiles [60], which is also in line with X-ray diffraction [616] and X-ray absorption data that show a continuous lattice expansion throughout the entire particles [614]. These results suggest that the *volume* of the small crystallites rather than their immediate surface vicinity provides enhanced H solubility compared to bulk Pd. It is speculated that this effect is due to free boundary surfaces of the nanoparticles, as unlike agglomerated grains in macroscopic bulk material they do not experience a spatial obstruction of their lattice expansion upon H absorption [60, 616].

The question of possible catalytic activity of the nanoparticle-absorbed hydrogen suggested by evidence from TDS [608-611] was subsequently addressed by combining ^{15}N NRA measurements of H-absorption at alumina-supported Pd nanocrystals with molecular beam reactive scattering experiments that monitored the hydrogenation of butene (C_4H_8) to butane (C_4H_{10}) at comparable Pd/ Fe_3O_4 model catalysts under identical pressure/temperature conditions [617]. A very similar H_2 pressure dependence of the nanoparticle-absorbed hydrogen state occupation and the butane production rate was observed. NRA thus helped substantiating the long-standing suspect that hydrogen absorbed inside the Pd-nanocrystals is indeed an essential ingredient for the catalytic olefin hydrogenation reaction on oxide supported nanoparticles [617].

Fig. 67. NRA γ -yield curves demonstrating the change of the H distribution in the Pd/Al₂O₃/NiAl(110) model catalyst under the cis-2-butene conversion conditions (260 K, 4×10^{-6} mbar H₂) induced by successive carbon depositions. Reproduced from Ref. [617].

Interestingly, the hydrogenation reactivity was found to be unstable on clean Pd nanoparticles, whereas slightly carbon-contaminated Pd crystallites showed sustained catalytic hydrogenation reactivity. This promotion of hydrogenation reactivity was striking in the sense that carbon is commonly known as a catalyst poison. The observation could be explained qualitatively, however, by an enhancement of the replenishing rate of Pd-absorbed hydrogen through the carbon impurities, which are mainly located underneath the nanoparticle surface near the crystal edges. Rather than blocking H adsorption sites on the large crystal facets, carbon only energetically destabilizes the surface-adsorbed hydrogen state and thereby reduces the energy barrier for its transition from the surface into the interior of the nanocrystals, which accelerates the H uptake. This interpretation was based on ¹⁵N NRA H profiles recorded under hydrogenation reaction conditions (260

K, 4×10^{-6} mbar H_2) for clean and carbon-contaminated Pd nanocrystals, on which the deposited C coverage was stepwise increased (Fig. 67) [617]. The data demonstrate the H coverage depletion on the nanoparticle surface as a consequence of the carbon deposition at the reaction temperature. At 90 K, however, the H surface coverage on the C-contaminated Pd nanocrystals was found to be fully restored, in line with the hypothesis that carbon only destabilizes but does not block surface-H. The proposed facilitation of hydrogen absorption into Pd nanocrystals in presence of subsurface carbon has meanwhile found theoretical confirmation [618-620].

3.2.4 Semiconductors: H in thin films

Pure and crystalline semiconductors generally have only very little hydrogen solubility [109]. However, the microelectronic industry fabricates semiconductor thin films for integrated circuit devices, optoelectronics, solar cells, sensors, displays, etc. on an enormous scale, and these materials are often not single crystalline. Widely applied film growth techniques such as chemical vapor deposition (CVD) employ H-containing gaseous precursors such as H_2 , methane (CH_4), acetylene (C_2H_2), silanes (SiH_4 and Si_2H_6), and ammonia (NH_3). Residual hydrogen is therefore a very common observation in the produced films. Here, H interacts dominantly with bulk defects, such as vacancies, grain boundaries, heteroatoms (dopants and impurities), and surfaces. Since the purity, defect concentration, and microstructure of the films depend sensitively on the synthesis conditions, their H content can vary widely in a range from a few ppm to several atomic percent [621]. The incorporated hydrogen strongly influences the electrical and optical properties of the materials and therefore their performance in devices. In amorphous silicon, for example, hydrogen

is introduced deliberately to passivate dangling bonds, which eliminates electrically active states from the band gap and thereby enables application of the material in solid state detectors and solar cells.

The characterization of the H content in thin semiconducting films is thus of high technological interest, and ^{15}N NRA (as well as ERD) has found wide applications to materials such as hydrogenated amorphous silicon [203, 622-629], silicon carbide [630-632], silicon nitride [110, 633-636], BCN [637], CVD diamond [255, 621, 638, 639] and diamond-like carbon films [634]. Notable phenomena include, e.g., the sensitivity of the H bonding states in amorphous silicon to elastic stress [622]. Myers et al. studied hydrogen interactions with dopants and radiation-induced defects in Mg-doped p-type gallium nitride (GaN) with $\text{D}({}^3\text{He,p}){}^4\text{He}$ NRA by monitoring the kinetics of isotopic exchange against H after D incorporation [640]. In this context most ^{15}N NRA investigations focused on determining the average H content in the semiconductor films in order to draw indirect conclusions on the microstructure. Since these studies seldom had explicit relation to hydrogen at surfaces or interfaces, we only provide the above references here and refrain from detailed descriptions.

We would like to mention, however, the important role of NRA as a calibration reference for the optical hydrogen analysis of thin film semiconductor materials (as well as of insulators, cf. Sect. 3.2.5.1) with vibrational spectroscopy. Infrared absorption and Raman spectroscopy readily identify H species in different chemical environments through their specific vibrational fingerprints. In many IR-transparent materials linear correlations have been found between the IR absorption or Raman scattering intensities of H-related vibrational bands and the absolute volume

hydrogen concentrations that were determined with NRA [55, 622]. With NRA as a reference, calibration relations could thus be established that allowed measuring average bulk H concentrations quantitatively with the highly convenient optical techniques [622, 640-642].

To illustrate that also the depth-resolving powers of ^{15}N NRA can be beneficial in the hydrogen analysis of thin semiconducting films, Fig. 68 displays H depth profiles of CVD grown diamond films of various thicknesses [643]. In addition to the large H concentration (7.5–8 %) in the film volume evidenced by the plateau region of the thickest film, a H-rich surface layer was observed on all samples.

Fig. 68. ^{15}N NRA hydrogen depth profiles of the three samples of ultra-nanocrystalline diamond films of 95, 600, and 820 nm thickness on Si(100) substrates. From Ref. [643].

Apparently this layer formed already at the beginning of the deposition process and grew outward as the film thickness increased. The authors revealed with vibrational spectroscopy (FT-IRAS) that this surface layer contained a large fraction of sp^3

hybridized CH₂ groups and accordingly concluded that surface stabilization by hydrogen is an important factor in the CVD growth of diamond. The large H concentration in the film volume was attributed to the formation of an amorphous carbon matrix that embeds diamond nanocrystals [643].

The surface interaction of crystalline diamond with hydrogen and its possible induction of electrical conductivity has also been investigated with a variety of ion beam analysis techniques that include ¹⁵N NRA [432, 433, 644, 645] and high-resolution ERD [255, 638, 639]. Kimura et. al addressed the debated possibility of H subsurface site occupation at CVD diamond surfaces with high-resolution ERD H profiling and could indeed confirm a small amount of H buried in a region less than 1 nm deep below the surface [255].

3.2.5 Insulators

3.2.5.1 *H in near-surface regions of oxides and minerals*

¹⁵N NRA has found numerous applications in the analysis of water and hydroxyl (OH) in the near-surface region of oxides and silicates. Central research interests encompass the chemical modification of glass surfaces by leaching in aqueous environments [646-648], related to moist air and pollution-induced weathering of glass that causes, e.g., the decay of historic stained glass windows in European churches [649, 650], the non-destructive chemical analysis of archaeological and historical artifacts [78, 79, 651-654], the surface hydration kinetics of silicates in Portland cement relevant to concrete technology [655-657], as well as the quantitation of the water content in minerals and gemstones that are important

parameters in the geochemistry of the Earth's mantle materials [641, 642, 658-663]. According to Doremus' theory [664-666] water penetrates into the surface of aluminosilicates and replaces network modifying Na, Ca, and Al ions against protons in exchange processes such as:

A common observation in leached glasses and minerals thus is a near-surface region that is depleted in Na, Ca, etc., but enriched with H. Through revealing the hydrogen depth distribution, ^{15}N NRA hydrogen profiling allows assessing the thickness of the erosion layer. Fig. 69 shows exemplarily a typical ^{15}N NRA depth profile of an aluminosilicate exposed to air and water vapor [649] that evidences hydration up to a depth of $\sim 0.4 \mu\text{m}$ with an average H concentration of $1.2 \times 10^{22} \text{ cm}^{-3}$, as well as a much thinner hydrogen-rich surface layer. Trocellier et al. applied three resonant nuclear reactions ($^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$, $^{23}\text{Na}(p, \alpha\gamma)^{20}\text{Ne}$, and $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$) to study the leaching of lime-soda glasses by deionized water through monitoring Na, Al and H [646]. Mäder et al. analyzed the corrosion of a potash-lime glass of medieval composition (60 wt% SiO_2 , 25 wt% CaO , 15 wt% K_2O) leached in 0.1 N HCl at room temperature and cross-correlated the depth extension of the hydrated layer derived from H profiling with ^{15}N NRA to the Ca/K/Si composition information obtained from PIXE and PIGE measurements with a 4 MeV proton beam. The authors observed that the ratio of the Si PIXE/PIGE signals increased linearly with the thickness of the leached layer in the range of 0-5 μm but saturated at thicker corrosion layers. They consequently suggested to use this information as a rough indicator for the presence

of an eroded surface layer [653, 654], which enables a quick distinction between a thin surface-hydration layer from a deeply bulk corroded sample condition in objects of historical value by a simple non-destructive measurement.

Fig. 69. A typical NRA hydrogen concentration profile measured with ¹⁵N NRA in an aluminosilicate sample exposed to air and water vapor. Characteristics of the profile include the hydration depth (0.4 mm), the equilibrium hydration concentration (1.2×10^{22}

atoms cm⁻³) and a H-rich surface layer. From Ref. [649].

Compared to leaching of amorphous glass, the water diffusion in crystalline quartz is many orders of magnitude slower and studies of the hydration process had long been limited to temperatures above 500°C. Dersch and Rauch extended the observation regime to a lower temperature range of 60 to 200°C by using hydrothermal treatments, i.e., by heating the quartz samples with a certain quantity of H₂O (or H₂¹⁸O) in an autoclave for several days, and analyzed the resulting near-surface H and ¹⁸O diffusion profiles with the ¹H(¹⁵N,αγ)¹²C and ¹⁸O(p,α)¹⁵N nuclear reactions [78, 79, 652]. Examples are shown in Fig. 70. The observed H depth profiles were well reproduced by error function shaped concentration distributions:

$$c(x, t) = c_0 \cdot \operatorname{erfc} \left(\frac{x}{2\sqrt{D_{eff}t}} \right) + c_i, \quad (3.3)$$

where x : depth, c_0 : concentration at depth zero, c_i : intrinsic (bulk) concentration, t : treatment time. Note that D_{eff} is an effective diffusion-reaction rate (not merely a diffusion coefficient), since the hydration process includes the reaction of H_2O with the SiO_2 lattice, according to [664]:

From the temperature dependence of D_{eff} Dersch and Rauch determined the activation energy for the hydration process and obtained a common value of 60 kJ/mol for various samples of natural and synthetic quartz [652]. The absolute D_{eff} value was found to depend also on the bulk H concentration c_i and on the angle of the surface with the c-axis of the quartz crystals, indicating an orientation dependence of the diffusion process. The bulk concentrations were found to vary between 10 and 100 at. ppm for synthetic and up to 500 at. ppm for natural quartz specimen [79]. On the basis of the common activation energy for synthetic and prehistoric quartz artifacts, a universal hydration mechanism was suggested [651]. Indeed, modeling H-diffusion profiles with Eq. (3.3) for an average ambient temperature of 10°C gave good agreement with NRA H profiles of hydration layers obtained from natural, age-dated quartz specimen, confirming that the same form of quartz hydration kinetics also applies in natural environments [652]. The evaluation of the hydration layer thickness (defined as the depth where the H concentration attains half the value of depth zero) was thus proposed as a versatile and non-destructive method for the age determination of quartz crystals in geological material or in historical artifacts [79]. Based on the water mobility in SiO_2 and the

NRA-accessible probing depth range, this ^{15}N NRA 'quartz hydration dating' technique allows for the specification of hydration periods between 100 to more than 10,000 years with an accuracy of 35% to 20% depending on the sample material [79, 80].

Fig. 70. Comparison of ^{15}N NRA H profiles of quartz samples exposed for different times to a hydrothermal treatment at 200 °C in 1.56 MPa H_2O vapor showing progressive hydration of the near-surface region. From Ref. [79].

Similarly, observing hydrated surface layers that form on tricalcium silicate with time-resolved ^{15}N NRA was pointed out as a possibility to investigate the hydration kinetics of Portland cement at a suitable model system [655-657]. The study established that during an induction period in the first few hours, the hydrogen diffusion is controlled by an only 10–20 nm thin surface layer, which poses high demands on the ^{15}N beam energy resolution (on the order of 10 keV or less) to be observed [656]. Lanford's group studied the fracture mechanism of glass under mechanical stress and moisture exposure by monitoring the diffusion of water into silica glass with ^{15}N NRA while simultaneously applying a hydrothermal treatment at several temperatures and mechanical stress [650]. It was found that at low temperatures the stress affected the kinetics of the water uptake, while at high

temperatures the applied stress influences the glass-water reaction equilibrium [650]. The above examples illustrate the versatility of NRA to investigate the response of a given sample material in terms of its internal H distribution to changes of external conditions, based on the non-destructive nature of the measurement.

3.2.5.2 Hydrogen redistribution in electrochromic multilayers

Wagner et al. applied ^{15}N NRA to monitor *in-situ* the proton transport occurring under different operational conditions in electrochromic multilayer systems [81, 82]. These optical devices are all-solid-state film structures on glass substrates, in which an active layer of electrochromic WO_3 , a storage layer (WO_3) or anodically coloring electrochromic material (NiO_x), and a solid electrolyte (here: Ta_2O_5) placed between these two layers are sandwiched between two electrodes, such as illustrated in Fig. 71.

Fig. 71. Configuration of the electrochromic mirror system. Reproduced from Ref. [81].

Indium tin oxide (ITO) is used as a transparent and conductive electrode adjacent to the glass. The outermost Al layer serves simultaneously as the counter electrode (anode) and as the metallic reflector. The reflectance, absorbance, or transmittance of the optical device can thus be controlled by applying an external voltage to the outer electrodes, typically in the order of 1 V. Reflectance measurements with a He-Ne laser and a photodiode detector established that the reflectivity of the above

system changes from 10% to 70% when the external voltage is varied between +2 to -1.5 V. To the human eye, the system appears dark blue in the low-reflectance region, whereas at $U \leq 0$ V it has a metallic luster.

The absorbance change results from the electrochromic effect that has been discussed in relation to the following red/ox reactions: WO_3 is a cathodically coloring electrochromic material which varies between transparent and blue during the transition of the W^{6+} (transparent) oxidation state to W^{5+} (blue) [667] in the reaction [668]:

The electrochromism of the anodic coloration of NiO_x is due to the reaction of Ni^{2+} (transparent) to Ni^{3+} (colored) according to [669]:

Wagner et al. visualized the actual proton transport involved in these reactions by means of NRA via $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$. Figs. 72 (a) and (b) show H profiles of the above optical system (Fig. 71) under application of different voltages, with the 0 V profile displayed as a reference. For simplicity, only the H/W ratio is given on the ordinate. No H is detected in the Al layer (except for a surface peak) and the slight H concentration at the ITO/glass substrate boundary is due to a thin SiO_2 layer on the glass serving as an alkali diffusion barrier. The H content in the NiO_x is smaller than in WO_3 and corresponds to $x = 1.5$ as judged from RBS [81]. The H concentration in $\text{Ta}_2\text{O}_5/\text{WO}_3$ is very high, and exceeds that of single Ta_2O_5 or WO_3 layers without the NiO_x/Al overlayer structure [670].

Fig. 72. (a) ^{15}N NRA H concentration profile of the electrochromic system at $U = +1.8\text{ V}$ (Reflectivity state: dark blue) and the reference profile. (b) H concentration profile of the electrochromic system at $U = -1.5\text{ V}$ (Reflectivity state: strongly bleached) and the reference profile. Reproduced From Ref. [81].

As seen in Fig. 72 (a), a voltage of +1.8 V applied to the Al electrode (corresponding to the dark state of the system) causes a strong depletion of the H concentration (c_{H}) in the NiO_x layer and enhances c_{H} in the Ta₂O₅ near the Ta₂O₅/WO₃ interface. In addition the H concentration is decreased in the WO₃ and increased in the ITO layer. The integral amount of H in the system has not changed, and the direction of the H transport is in accordance with the expectation that the H⁺ ions are shifted towards the negative ITO electrode. NRA also verified that short-circuiting (0 V) the device reversibly restores the original H distribution without hysteresis in the H transport and no H loss from the system. For negative voltages (-1.5 V, Fig. 72 (b)), the H distribution is drastically altered in the opposite direction, i.e., c_{H} increases in the NiO_x layer at the outer interface, while it decreases in the Ta₂O₅ layer and very strongly in the WO₃ and ITO layers. As expected, the H displacement is directed towards the (negative) Al electrode. A loss of H is also

noticed in Fig. 72 (b), which is attributed to the large negative voltage that has been outside the permitted range for this electrochromic system and is suspected to cause H desorption through micro-pores of the Al film [81].

By demonstrating that the H concentration in NiO_x is smaller in the colored state than in the bleached condition, the NRA results confirmed that the optical changes in the electrochromic system agree with reaction (3.6). Apparently, the H^+ ions are sufficiently mobile to be noticeably redistributed between the NiO_x , Ta_2O_5 , WO_3 , and ITO layers through external electric field application. An increase of the H/W ratio associated with the colored state of the WO_3 layer according to reaction (3.5), however, could not be observed [81].

3.2.5.3 *Hydrogen in ultrathin dielectric films on silicon*

The detection of residual hydrogen in ultrathin dielectric films of metal-oxide-semiconductor (MOS) capacitors and gate insulating layers of field-effect transistors (MOSFETs) is one of the most prominent ^{15}N NRA applications in industry-related research. In view of the nanometer scale of the thin layers and the small H impurity concentrations in MOS devices, these NRA applications are challenging with respect to depth resolution and sensitivity. The dominant motivation to investigate hydrogen in stacked dielectric layers with NRA is that the H interaction with the respective interfaces is believed to very significantly affect the electrical device characteristics. Especially the problem of potentially hydrogen-related degradation of the SiO_2/Si interface is recognized as a highly relevant reliability concern in semiconductor device technology, which will be given particular attention in Section 3.3.1. Here, we first introduce general aspects of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA hydrogen analysis in ultrathin

dielectric films on Si substrates, focusing primarily on the H concentration and its distribution in various materials, on the influence of the NRA measurement on this distribution and the analytical value of this effect, and on the possibility to study in-situ the impact of processing treatments on the H distribution by exploiting the non-destructive virtues of NRA. The literature contains a sizeable body of NRA investigations of hydrogen in the traditional silicon oxide on silicon (SiO_2/Si) [107, 160, 161, 671-676] [677-682], in buried SiO_2 layers in $\text{Si}/\text{SiO}_2/\text{Si}$ structures [683, 684], in silicon nitride (SiN) [634, 636, 685, 686], and in silicon oxynitrides (SiO_xN_y) [687-691].

a) Hydrogen distribution in SiO_2/Si

The hydrogen (deuterium) content [677, 692] and distribution [107] [161, 678, 680] in SiO_2 films of various thickness on $\text{Si}(100)$ wafers has been studied by several groups. H concentrations in the order of (10^{18} - 10^{19} cm^{-3}) in the volume of the SiO_2 layers have been found, corresponding to areal H densities in the order of $\sim 10^{13-14}$ cm^{-2} if the concentration is integrated over the oxide thickness (typically several tens of nanometers). Similar H concentrations were detected in buried SiO_2 layers of $\text{Si}/\text{SiO}_2/\text{Si}$ structures [684]. The depth-resolving ^{15}N NRA measurements revealed in addition that the H distribution within the oxide is not necessarily uniform, but that hydrogen tends to accumulate not exactly at but in a region extending over a few nm of the oxide in front of the interface [107, 160, 161, 671, 673, 675-678, 680, 681]. Fig. 73 (a) illustrates this situation at the example of three ^{15}N NRA H depth profiles of wet oxidized $\text{Si}(100)$ specimens bearing SiO_2 films with thicknesses of 19.0, 30.0, and 41.5 nm [680].

Fig. 73. (a) NRA H-profiles for three SiO₂ films on Si(100) with thicknesses of (i) 19.0 nm, (ii) 30.0 nm, and (iii) 41.5 nm. Interface positions are indicated by dashed vertical lines. (b) Center positions of the NRA-determined near SiO₂/Si interfacial H distributions compared to the optically obtained SiO₂ film thickness. From Ref. [680].

Fig. 73 (b) indicates that the centroid of this peak follows the interface position but is separated from it by a small offset of a few nm. This H localization behavior has been attributed to the near-interfacial SiO₂ structure, where a large number of strain and sub-oxide [693] related defects provide preferential binding sites for hydrogen species [694]. The strained interfacial region results from the reduction of the Si atom number density by a factor of ~ 2 in the abrupt transition from crystalline Si to amorphous SiO₂.

b) ¹⁵N-induced H accumulation near the SiO₂/Si interface

It is necessary at this point to recognize a characteristic influence of the NRA depth profiling on the H distribution in thin dielectric layers on Si substrates. As first

reported by Briere et al. [160] and later observed in many similar studies [636, 680, 681, 685, 686, 695-697], the ^{15}N ion irradiation can cause a noticeable redistribution of hydrogen in the analyzed targets that leads to a pile-up of H in the near-interfacial (SiO_2/Si) accumulation region. As the Si substrate is generally H-free, the relocating hydrogen can originate from any region above the SiO_2/Si interface that contains H, such as the silicon oxide (or oxynitride) film volume, hydroxylated or H-contaminated surface layers on uncapped dielectric films, an interface layer formed with a capping electrode material (such as in $\text{Al}/\text{SiO}_2/\text{Si}$) [698], or the volume of a H-rich material covering the oxide (such as in $\text{SiN}/\text{SiO}_2/\text{Si}$ [686], or $\text{SiO}_2/a\text{-Si:H}/\text{SiO}_2/\text{Si}$ [697]) stacks.

As illustrated in Fig. 74, the redistribution phenomenon is imagined to result from H release in such H-rich layers due to local H-bond cleavage by ion beam generated secondary electrons (and holes), followed by diffusion of the mobilized H species through the dielectric towards the SiO_2/Si interfacial region, where a fraction of them binds to the available H trap sites. Many details of the process (the bond-breaking mechanism, the chemical identity and charge state of the diffusing H species, the nature of the near-interfacial trap sites, etc.) are still unknown. Nonetheless, the effective H accumulation cross section (determined through NRA measurements of the near-interfacial pile-up kinetics described below) is in the order of $10^{-16} \sim 10^{-15} \text{ cm}^2$ which points towards an electron-induced rather than nuclear collision-related origin of the relocation [680, 686].

Fig. 74. Schematic illustration of the H relocation process under the NRA ion beam. Interaction of beam-generated secondary electrons with H bound in surface-near layers releases mobile H species that migrate through the MOS structure and may accumulate in near SiO₂/Si interfacial trap sites.

The H redistribution is observed at room temperature as well as in liquid nitrogen cooled targets [107]. The phenomenon is furthermore not specific to ^{15}N NRA. High-resolution ERD measurements with 400 keV C^+ ions at ultrathin SiO₂ films on Si(100) have reported a similar near-interfacial H accumulation effect [699], supporting the notion that the process is driven by secondary electrons, which are universally released upon energetic ion beam impact on insulating materials (cf. Section 2.2.5). Hydrogen accumulation at SiO₂/Si interfaces as a consequence of electron injection into Al/SiO₂/Si MOS structures has also been reported in SIMS studies [700, 701], but due to the destructive nature of the latter technique no assesment can be made as how far the observed H distributions are characteristic of the native samples and how strongly they may be distorted by artifacts from the sputtering analysis.

Due to the ion beam-induced H relocation the NRA depth profiles such as those in Fig. 73 do not reflect the initial H distribution of the unperturbed sample but display some additional hydrogen in the near-interfacial accumulation region that has piled up during acquisition of the profile. The H accumulation in the near-interfacial region typically saturates after application of moderate ($<10^{16} \text{ cm}^{-2}$) ^{15}N

ion doses (cf. Fig. 75 (b)) [702]. Prior to the state of pileup saturation the application of different ^{15}N ion exposures will lead to variations in the near-interfacial accumulation peak amplitude. Fig. 75 (a) exemplarily shows two H profiles recorded subsequently with the beam in the same sampling area of a 25 nm SiO_2/Si stack capped by a thin (10 nm) H-rich SiN layer [686], thus comparing an early stage of the H redistribution process with the situation after H uptake saturation. The initially smaller H content in the SiO_2/Si interfacial region compared to the one obtained after saturation is evident. In addition, the H concentration in the SiN layer clearly reduces in the course of the measurements. Apparently, the H loss in the SiN film is larger than the H gain in the SiO_2/Si interfacial region and in the SiO_2 volume combined, suggesting that besides H relocation from SiN towards the SiO_2/Si interface the NRA ion irradiation also causes desorption of mobilized H species from this near-surface layer.

Fig. 75. (a) NRA H depth profiles of SiN/SiO₂ stacks in an early stage and after saturation of the beam-induced H-redistribution. (b) H-uptake as a function of the cumulative ^{15}N ion dose observed in the near SiO₂/Si interfacial accumulation region (probing depth: 32 nm, arrow in (a)). From Ref. [46] with permission from ECS.

Depth-resolving $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA can directly visualize the progressing H accumulation in the near-interfacial region of SiO_2/Si . To this end the evolution of the near-interfacial H concentration is probed selectively as a function of the cumulative ^{15}N ion dose with the incident ^{15}N ion energy fixed to the maximum of the interfacial pile-up peak position. This procedure is exemplified in Fig. 75 (b), which shows the H uptake in the SiO_2/Si interfacial region of the above $\text{SiN}/\text{SiO}_2/\text{Si}(100)$ stack in a probing depth of ~ 32 nm (arrow in Fig. 75 (a)). The data indicate that the near-interfacial H concentration is initially very small and that the uptake tends to saturate at a ^{15}N ion fluence well below 10^{16} cm^{-2} .

The authors have found empirically in a large number of investigations of different dielectric materials that the ion beam-induced H uptake in the SiO_2/Si interfacial region is rather well described by a function of the type:

$$[H](\Phi_N) = [H_0] + [H_\infty] * [1 - \exp(-\sigma_p \Phi_N)]. \quad (3.7)$$

Here, $[H](\Phi_N)$ is the NRA γ -signal proportional to the near-interfacial H concentration after a given ^{15}N ion fluence (Φ_N) [ions/cm^2] has impinged on the sample, $[H_0]$ is its initial value, $[H_\infty]$ is the signal increase due to H relocation after uptake saturation, and σ_p is an effective H redistribution ('pile-up') cross section that characterizes the uptake rate.

Evaluating the near-interfacial H accumulation kinetics by fitting experimental NRA pile-up curves to relation (3.7) provides highly useful analytical information as the specific H uptake parameters ($[H_0]$, $[H_\infty]$, and σ_p) can depend rather sensitively on the analyzed material. Evidently, by performing pile-up measurements in

different depth locations one can establish the original H distribution in the SiO₂ layer from the obtained $[H_0]$ values. If the H uptake in the accumulation region is not limited by the supply from the H-rich 'reservoir' layer above the dielectric film, the saturation value ($[H_0] + [H_\infty]$) may be considered to reflect the density of available H trapping sites in the near-interfacial oxide region, which can hence be evaluated. Finally, σ_p , the effective kinetic rate constant of the near-interfacial H pile up provides information on the mobility of hydrogen species diffusing in the MOS structure. Examples for the evaluation of the material-specific mobility of H impurities by means of NRA in conjunction with electrical measurements as a highly versatile analytical tool in device reliability research will be presented in Section 3.3.1.

c) Effect of H₂ FGA

Although the SiO₂/Si interface is atomically sharp, a small number of Si dangling bonds (trivalent Si defects backbonded to the Si crystal, Si₃≡Si·, so-called P_b centers) remains, which due to their radical character act as electrical charge traps and are thus highly undesirable for the device performance and reliability. In order to H-passivate these interfacial P_b centers the semiconductor industry deliberately introduces hydrogen into the MOS structures by subjecting the fabricated devices to a so-called forming gas annealing (FGA) process in a H₂ containing atmosphere (typical are several % H₂ diluted in N₂ and temperatures around 400°C). This treatment is known to reduce the interface state density by 1-2 orders of magnitude and dramatically improves the electrical device characteristics [703-705]. Electron

spin resonance (ESR) has confirmed that H₂ FGA eliminates the paramagnetic P_b states according to reaction (3.8) [703, 705]:

The influence of H₂ forming gas annealing on the hydrogen distribution near SiO₂/Si interfaces was also studied by *in situ* ¹H(¹⁵N,αγ)¹²C nuclear reaction analysis [680]. The results are summarized in Fig. 76.

Fig. 76. (a) Effect of H₂ annealing (FGA) on the H distribution in 41.5-nm-thick SiO₂ on Si(100). (i) As-oxidized sample prior to FGA, (ii) after annealing in 260 mbar H₂ at 400 °C for 40 min, and (iii) after heating the FGA-treated sample in vacuum to 540 °C. For clarity, trace (iii) is vertically shifted by an offset of -2 cts/ μC . (b) Thermal stability of the H₂ FGA-introduced H in the near-interfacial region upon heating in vacuum for 60 s to the given temperatures. From Ref. [680] with permission from AIP.

The H depth profile (ii) in Fig. 76 (a) evidences a dramatically enhanced H content in a 41.5 nm thick thermal SiO₂ film on Si(100) after the sample was annealed inside the NRA vacuum system for 40 min in 260 mbar H₂ gas at 400°C. After this anneal the

sample had no air contact prior to the subsequent NRA analysis. The total amount, average areal density, and volume concentration of H incorporated into the ca. 8 nm wide near-interfacial oxide region were found in the orders of $(1-3) \times 10^{14} \text{ cm}^{-2}$, $>5 \times 10^{12} \text{ cm}^{-2}$, and $\sim 1.2 \times 10^{20} \text{ cm}^{-3}$, respectively. These figures greatly exceeded the interfacial P_b center density ($1 \times 10^{12} \text{ cm}^{-2}$) and were also far larger than the native H concentration in the bulk ($1.5 \times 10^{19} \text{ cm}^{-3}$) and in the interfacial region of the wet-grown SiO_2 dielectric.

The result was interpreted as to demonstrate that the near-interfacial oxide apparently contained a very substantial number of hydrogen trap sites that became populated during the FGA process [680]. By selectively probing the H content in the near-interfacial region it was verified that the *in-situ* FGA treatment incorporated hydrogen directly into the accumulation region near the SiO_2/Si interface. Any ion beam induced H redistribution that would cause further H uptake in this region as initially observed in the as-oxidized SiO_2 film sample without FGA (profile (i) in Fig. 76 (a)) did not take place. This suggested that all available trap sites in the near-interfacial SiO_2 had been H-saturated during the FGA treatment. Fig. 76 (b) illustrates the selective NRA monitoring of the H content in the interfacial region of the FGA-treated sample while the specimen was heated incrementally in vacuum. This experiment established that the FGA-introduced H was rather stable and did not tend to desorb below 430°C . The depth profile taken after the heating step to 540°C ((iii) in Fig. 76 (a)) indicated that the small quantity of remaining H in the interfacial region was even stronger bound than H on the surface of the SiO_2 film, which was almost completely removed at this temperature.

d) High-k dielectrics

The profound interest in hydrogen impurities in insulating thin films extends further to the rapidly developing field of novel gate dielectrics [706]. The aggressive down-scaling of device dimensions in Si-based MOSFET technology has spurred an evolution of alternative gate dielectric materials as a replacement for the conventional SiO₂. As the gate dielectric thicknesses approached the order of 1 nm or less, excessive leakage current by direct electron tunneling through the SiO₂ gate oxide reached intolerable levels. Novel high dielectric constant (high-k) materials were devised to overcome this limitation by allowing for physically thicker films that reduce the leakage current, while still maintaining the necessary MOSFET capacity. Thus hafnium oxide (HfO₂) [707], hafnium silicates ((SiO₂)_x(HfO₂)_(1-x)) [210, 708-710], and other high-k materials (such as Al₂O₃ [711]) have been proposed as alternative gate dielectrics, and their H content was assessed with NRA (among other techniques).

Hafnium silicate films ('HfSiO') were found to contain much higher H impurity levels than the bulk regions of thermally grown SiO₂, exceeding the H concentration of the latter (10^{18} - 10^{19} cm⁻³) [675, 676, 680, 692] by more than 2 orders of magnitude (10^{21} - 10^{22} cm⁻³) [210, 709]. Driemeier and coworkers observed with D(³He,p)⁴He NRA that the total D content in HfSiO dielectrics on Si increased linearly with the film thickness [708], concluding that the hydrogen is preferentially built into the bulk of the HfSiO films. This finding was corroborated directly by depth-resolved H profiling via ¹H(¹⁵N, $\alpha\gamma$)¹²C NRA [210]. The H distribution in HfSiO thus differs from that in HfO₂/Si thin film structures, where H mainly incorporates close to the HfO₂

surfaces [707, 708, 712], and also contrasts SiO₂/Si structures, where H accumulates mainly in the SiO₂/Si interfacial region as described above (Fig. 73) [677, 680].

Based on a strongly reduced D uptake during D₂ FGA after a pre-annealing treatment in O₂ gas and backed by DFT calculations which demonstrated that oxygen defect sites in hafnium silicates can stabilize hydrogen, it was concluded that H mainly interacts with O deficiencies in the HfSiO films, which were assumed to result from the MOCVD deposition process [210, 708, 709, 712]. Presumably related to similar fabrication techniques such as reactive sputtering and CVD from H-containing precursors, much larger H impurity levels than in thermal SiO₂ layers have also been found in other novel dielectric films, such as CVD-silica grown from SiH₄ and O₂ [713]. As also revealed through NRA, the ion implantation-induced damage of amorphous SiO₂ films (used, e.g., for the synthesis of Si, Ge, or Sn nanocrystals in an SiO₂ matrix) and the subsequent interaction of the generated defects with atmospheric moisture can present a major source of hydrogen impurities in dielectric layers [714].

While the above investigations demonstrate the versatility of ¹H(¹⁵N,αγ)¹²C NRA to characterize the H content and distribution in novel insulating thin film materials, a clear correlation between the H impurity concentration and the electrical characteristics of MOSFET devices employing these high-k dielectrics has yet to be established. This appears to present a highly challenging task, given that the very large H concentrations found in these films outnumber the intrinsic SiO₂/Si interfacial defect density by yet two additional orders of magnitude compared to devices based on traditional silicon oxide. At least for the conventional SiO₂ dielectric,

$^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA has contributed substantially to clarifying several influences that hydrogen impurities in MOS structures can take on the device reliability [46, 715, 716], which is discussed in the following chapter (Section 3.3.1).

3.3 *Interfacial H*

3.3.1 *H at MOS interfaces and its relation to device reliability*

The previous section has introduced hydrogen as a common impurity in the oxide dielectrics of MOS structures. Electrical device characterization has lead to the suspicion that such residual hydrogen can critically affect the device reliability when it interacts with the SiO₂/Si interface, where it appears to play an ambivalent role in the passivation and regeneration of electrically active defects [703-705, 717-721]. On one hand, hydrogen has the described beneficial effect to passivate the SiO₂/Si interfacial P_b centers [694, 703, 705, 717] and is thus deliberately introduced in device fabrication through FGA (reaction (3.8)). On the other hand, diffusible H species in the MOS structure are suspected to cause SiO₂/Si interface degradation by extracting the terminating H atoms from the interfacial Si dangling bonds, which reactivates the charge trapping P_b centers. This notion grounds on electrical evidence for interface degradation under conditions that favor the production of diffusible atomic H species: heat (which reverses reaction (3.8)) [704], exposure to atomic H [718], H₂ FGA at elevated temperatures [719], as well as injection of hot carriers into the gate oxide such as those generated by ionizing radiation under bias [698, 700, 701, 722, 723] or through high electric fields (> 6 - 20 MV/cm) [724] that cause Fowler-Nordheim (F-N) tunneling current through the dielectric.

A second device degradation phenomenon that involves P_b center depassivation under the alleged influence of diffusible 'hydrogenous' species near the Si/SiO₂ interface occurs under low electric fields (< 6 MeV/cm) and is known as negative bias temperature instability (NBTI) [45, 720, 721, 724, 725]. NBTI poses a serious

reliability concern and primarily affects p-channel MOSFETs stressed at negative gate voltages and typical temperatures of 100-250°C. The degradation is manifested through interface trap (D_{it}) generation and the build up of fixed (positive) charges in the gate oxide, which reduce the transconductance and the absolute drain current and detrimentally increase the threshold voltage (V_T). Also here the suspect that hydrogen is involved has initially been based primarily on circumstantial evidence, such as the greater NBTI susceptibility of wet as opposed to dry gate oxides (i.e., SiO_2 films grown by Si oxidation with steam instead of O_2 as oxidant) [725], or the generally enhanced NBTI affinity of silicon oxynitride (SiN_xO_y) based devices, since nitrogen incorporation into SiO_2 increases the H content in the dielectric [720].

The first direct experimental support for the hypothesis that the attack of the H-passivated SiO_2/Si interface by diffusible H species in the gate dielectric is the cause of the electrical degradation has been provided through ^{15}N NRA investigations in conjunction with electrical device characterization, which evidenced a clear correlation between H impurity redistribution in MOS structures and electrical device degradation [45, 681, 685, 686, 689, 691, 698, 715].

Buchanan et al. were the first to apply ^{15}N NRA H depth profiling together with electrical measurements to prove that electrical degradation upon hot-carrier injection into MOS capacitors, which generates interfacial defects, is linked to the redistribution of hydrogen impurities in the device [698]. Internal photoemission under applied electric fields between 0 and 6.5 MV/cm was used to inject hot electrons from the Al cathode (14 nm thick) into the SiO_2 dielectric (~90 nm) of large Al-gate capacitors. As evidenced by the NRA H depth profiles in Fig. 77 (a), a

hydrogen-rich layer ($\sim 10^{15}$ atoms/cm²) at the Al/SiO₂ interface was found to serve as the source of diffusive hydrogen during the hot-electron stress. For large electron fluences a small fraction of the hydrogen released from this layer was found to be retrapped near the Si/SiO₂ interface, indicated by the characteristic H accumulation peak in ~ 1000 Å depth. The buildup of hydrogen at the Si/SiO₂ interface exhibited an electric field threshold at -1 MV/cm, consistent with the onset of electron heating in SiO₂. The electron fluence dependent H buildup at the Si/SiO₂ interface is shown in Fig. 77 (b) for both positive (V_G^+) and negative (V_G^-) gate voltages in dry and wet oxide dielectrics.

Fig. 77. (a) NRA H depth profiles of Al(140 Å)/SiO₂(900 Å)/Si MOS capacitors prior to and after injection of an electron fluence of 1 C/cm² using internal photoemission from the Al gate at a field of ~ 4.2 MV/cm. In the injected sample note the decrease in the hydrogen amount at the Al/SiO₂ interface, and the appearance of a peak at a depth of 1020 Å, corresponding to H at the Si/SiO₂ interface. (b) Dependence of Si/SiO₂ interface hydrogen on the injected electron fluence at oxide fields >3 MV/cm. Data are shown for both positive V_G^+ and negative V_G^- gate bias for both wet and dry oxides. Reproduced from Ref. [698] with permission from AIP.

In “wet” SiO₂ films with deliberately introduced excess hydrogen (through H₂O exposure), the H buildup rate was seen to be significantly greater than that found in the “dry” (as oxidized) films. During electron injection, hydrogen redistribution was also confirmed via the deactivation of boron dopant in the silicon substrate, suggesting that the interface-attacking species was atomic H, since molecular H₂ did not show such reactive behavior [698]. The generation rates of interface states, neutral electron traps, and anomalous positive charge were found to increase with increasing H buildup in the substrate and with the initial H concentration in the film. This allowed for the conclusion that the generation of interfacial defects is preceded by the hot-electron-induced release and transport of atomic hydrogen and that the chemical reaction of this species within the metal-oxide-semiconductor structure generates electrically active defects.

Also with respect to NBTI degradation, the combination of ¹⁵N NRA and electrical characterization succeeded in confirming that the application of negative bias temperature stress (NBTS) on poly-Si/SiO₂/Si MOS diodes causes increased H densities near the SiO₂/Si interface [45, 681]. Liu et al. measured the H-concentration in the near-interfacial region of the 25 nm SiO₂ dielectric of MOS diodes before and after application of NBTS at -5 MV/cm and zero-bias temperature stress (ZBTS) at 0 MV/cm. Some samples received an additional POA treatment (post-oxidation anneal at 1000°C in an N₂ ambient).

The electrical capacitance-voltage (CV) data (Fig. 78 (a)) indicated that only NBTS caused CV curve distortions characteristic of interface state generation and positive oxide-fixed charge, whereas the ZBTS-treated and pristine samples exhibited ideal

MOS capacitor CV curves, which emphasized the critical importance of bias rather than temperature for the degradation. The POA treatment obviously alleviated the detrimental NBTS effects. Fig. 78 (b) shows corresponding NRA evaluations of the SiO_2/Si near-interfacial H content. Evidently, the near-interfacial H concentrations followed the same trend as the degree of stress-induced electrical degradation, which is pronounced for NBTS but insignificant after ZBTS. POA was seen to strongly suppress the local H accumulation under NBTS and to slightly reduce the H content near the SiO_2/Si interface in the pristine diodes.

Fig. 78. (a) CV curves of poly-Si/SiO₂/Si diodes before and after application of ZBTS (0 MV/cm) and NBTS (-5 MV/cm) at 360°C for 6 h in vacuum. Panels ii) and i) refer to samples with and without a POA (post-oxidation anneal at 1000°C in N₂) treatment of the oxide layer, respectively. (b) Comparison of the NRA-determined H content in the SiO₂/Si near-interfacial region of the samples with and without POA for different stress conditions). Reproduced from Ref.[681].

The above investigation strongly corroborated the correlation between NBTI and H in the SiO₂/Si near-interfacial region and suggested further that the enhanced stability versus NBTS of POA-treated diodes may be connected to a reduced H

content in this critical region of the device structure [45, 681]. A number of related ^{15}N NRA H profiling studies combined with electrical characterizations performed by the authors' group clearly linked the hydrogen content and its mobility to reliability degradation in several types of MOS devices [45, 685, 686, 689, 691, 715]. The consistently observed failure pattern was that mobile H species originating in upper sections of the device structures approach the SiO_2/Si interface, where their accumulation may cause electrical degradation [46]. Liu et al. hence suggested that achieving control of the H impurity transport in MOS structures is an important key to improve the device reliability [46, 690, 691], for which the visualization of H relocation processes with ^{15}N NRA is an essential and highly effective tool.

Fig. 79 exemplifies the NRA evaluation of the H impurity mobility in two different SiN layers on SiO_2/Si , which model the liner material in split-gate type FLASH EEPROMs (Electrically Erasable Programmable Read-Only Memory, a type of non-volatile memory). Their structure is illustrated in Fig. 79 (a) [686] (the NRA sample structure and a corresponding H depth profile are depicted in Fig. 75 (a)). Panel (i) of Fig. 79 (b) displays the ^{15}N ion beam-induced reduction of the H content in the H-rich SiN layers due to H relocation and desorption. The associated H pile-up kinetics in the SiO_2/Si interfacial regions are shown in Panel (ii). Obviously both the H decay in the SiN layer and the near-interfacial H uptake were considerably faster for P-SiN (produced by plasma-deposition) than in LP-SiN (fabricated by low pressure CVD). Solid lines in Panel (b) of Fig. 79 are fits of the data to Eq. (3.7), which revealed that the effective interfacial H pile-up cross section σ_p was 5 times larger in the oxide dielectric covered by P-SiN than in that underneath LP-SiN [686].

Fig. 79. (a) Schematic illustration of the split-gate type FLASH EEPROM memory cell structure. Hydrogen impurities are considered to diffuse from the BPSG region through the SiN liner film into the tunnel oxide dielectric. (b) NRA ion beam-induced H-decay in the SiN films (i) and concomitant H-uptake in the SiO_2/Si near-interfacial region (ii) of $\text{SiN}(10 \text{ nm})/\text{SiO}_2(25 \text{ nm})/\text{Si}$ model structures for two different types of SiN. Reproduced from Ref. [686].

Since the initial H content in the SiN films and hence the hydrogen mobilization probability as well as the oxide below the two films were identical, the σ_p values could be regarded to reflect the respective H permeabilities of the SiN materials. Electrical characterization revealed that the memory cells using LP-SiN liner exhibited an overall drastically enhanced performance compared to those under P-SiN liner, manifested as increased program/erase (P/E) endurance, higher resistance against F-N stress, and strongly reduced interface state density generation upon charge injection. This ^{15}N NRA study demonstrated that the P/E endurance of split-gate type FLASH memory cells is strongly influenced by the hydrogen permeability of the liner SiN, and hence suggested a possible route to improve the device reliability by

choosing a liner material that can reduce the diffusion of H-impurities into the tunnel dielectric [686].

The secondary electron generation in SiO₂ films under ¹⁵N ion irradiation resembles the hot carrier injection conditions encountered in MOS dielectrics. The evaluation of the trend to NRA-induced redistribution of hydrogen impurities can therefore also provide valuable information on the tendency of H species in a given device structure to potentially relocate to the SiO₂/Si interfacial region and concomitantly cause electrical degradation. This concept has been followed in a series of ¹⁵N NRA studies by Liu et al. [636, 685, 689-691, 715], which among other findings led to the discovery of an ultrathin (< 1 nm) silicon oxynitride layer of Si₂N₂O-like stoichiometry on the surface of N₂-annealed SiN films that can bind hydrogen very stably with respect to thermal desorption (above 1050°C) and to ion beam-induced relocation [636]. Liu et al. consequently suggested incorporating an ideal Si₂N₂O-like layer (without mobile H) as a hydrogen diffusion barrier in front of the SiO₂/Si interface as a structural means to enhance the MOS device reliability, since the trapping of diffusing H species in this H-retaining layer can be expected to protect the interface from the approach by mobile H species [46, 715, 716].

3.3.2 H at metal/silicon interfaces

Hydrogen situated at interfaces between metals and semiconductors has been discussed as the origin of Schottky barrier height variations in metal/silicon contacts [726-729]. Mönch and coworkers observed a significant alteration of the Schottky barrier height in lead contacts fabricated by Pb deposition onto H-terminated

Si(111)(1x1) surfaces in contrast to the Pb contacts formed with bare Si(111)(7x7) surfaces. The effect was attributed to an interfacial electric dipole layer constituted by the slightly polarized covalent Si-H bonds that were assumed to remain intact at the Pb/Si interface [726, 728]. Consistent with this model, the different orientation of the interfacial C-H bond dipole was found to induce barrier height changes of the opposite sign in metal contacts on H-terminated diamond [727, 730]. On the contrary, no difference in the Schottky barrier heights resulted from the room temperature formation of Ag contacts on bare and H-terminated Si(111) surfaces [730], which was ascribed to hydrogen loss from the Si(111) surface upon Ag deposition. Hydrogen is nonetheless known to strongly influence the morphology of Ag overlayers grown on this substrate [435, 731-733], and the possibility of H existing at Ag-Si(111) interfaces has been discussed controversially [734-737]. Similarly, the epitaxial growth mode of Au on the H-terminated Si(111)(1x1) surface as opposed to bare Au/Si(111)(7x7) has been subject of some debate, although both groups assumed that H would be desorbed upon Au deposition [738, 739]. These issues prompted Fukutani and coworkers to investigate the possible existence of hydrogen atoms at a variety of metal/silicon interfaces (Cu/Si(111) and Ag/Si(111) [42, 43], Pb/Si(111) [42, 43, 59], and Au/Si(111) [612]) by means of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA, exploiting the non-destructive character and the high depth resolution advantage of the technique.

The first papers [42, 43] addressed the stability problem of interfacial hydrogen in various metal/Si systems and investigated the temperature-dependent growth mode of the metals on the H-terminated Si(111) surface. Fig. 80 (a) shows NRA

excitation curves for the H-terminated Si(111)(1x1) surface (*in-situ* prepared by atomic H exposure of Si(111)(7x7) at 380°C and desorbing excessive di- and trihydride species (SiH₂, SiH₃) at 430°C in UHV [453]) before (trace (i)) and after deposition of 45 Å Pb at 360 K (trace (ii)) and at 110 K (trace (iii)), respectively. The latter two NRA profiles maintained the integrated γ -yield of the bare H-terminated Si(111)(1x1) substrate, indicating that the initial H coverage was fully conserved in the system after Pb deposition at both temperatures. Trace (iii) has the shape of a single Gaussian feature with a broadened width (FWHM = 21.3 ± 1.2 keV) and its center is shifted by 10.3 ± 0.4 keV relative to the resonance energy. Judged from the ¹⁵N stopping power in Pb at 6.385 MeV and the ion beam incidence along the surface normal, this shift corresponds to a mean H atom depth of 44.4 Å.

Fig. 80. (a) γ -ray yield profiles from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction as a function of the incident ¹⁵N beam energy taken after Pb deposition onto Si(111)(1x1)-H. (i) Si(111)(1x1)-H before Pb deposition, (ii) Pb deposition of 45 Å at 360 K, and (iii) Pb deposition of 45 Å at 110 K. Solid curves are fits to a Gaussian form [a sum of two Gaussian forms for (ii)]. (b) Schematic figures of Pb growth on Si(111)(1x1)-H at substrate temperatures of 360 K (left panel) and 110 K (right panel). Black dots denote H atoms. Adapted from Ref. [760] with permission.

The results are therefore fully consistent with the interpretation that at 110 K Pb grows in a uniform overlayer on the H-terminated Si(111)(1x1) substrate without intermixing with Si or disrupting the interfacial H atoms, which are considered to be confined in an atomically sharp interface layer as illustrated in the right panel of Fig. 80 (b). For Pb deposition above room temperature (360 K, trace (ii)), the NRA profile splits into two Gaussian-shaped components; a surface peak containing 0.63 ± 0.1 ML H and a broadened (FWHM = 24.0 ± 8.5 keV) and energy shifted (23.5 ± 3.5 keV vs. E_R) peak, containing 0.41 ± 0.17 ML H. The energy shift of the latter feature corresponds to an average H depth of 101 Å, suggesting that ~40% of the H is buried under ~10 nm high Pb islands, between which ~60% of the open substrate surface is exposed to the vacuum as schematically depicted in the left panel of Fig. 80 (b).

The NRA results in Fig. 80 thus positively confirmed the conjecture from the Schottky barrier measurements [726, 728] on the existence of stable H atoms at the Pb/H/Si(111)(1x1) interface and revealed in addition that the Pb growth mode on H-terminated Si(111)(1x1) apparently changes from a layer-by-layer fashion at 110 K to an island forming mode at 360 K. The latter result may be related to the unique tendency of Pb to form islands with flat tops, uniform height, and high aspect ratios on Si(111) surfaces that are driven by quantum effects in their electronic structure, although most of such observations have been made for Pb films grown onto bare Si(111)(7x7) substrates [740-743]. A comparison to the island structure that would be obtained on H-terminated Si(111)(1x1) or Si(111) (7x7) appears to be an interesting task for the future.

Similarly, a more recent evaluation of the current-voltage characteristics of Mg/p-Si(111)-H Schottky diodes grown at 190 K on H-terminated Si(111) [729] revealed that the barrier height in the as-deposited condition exceeded the value predicted from the concepts of electronegativity and metal induced gap states (MIGS) for Mg and Si, by an amount (~ 0.36 eV) in very close agreement to the change of the homogeneous Schottky barrier height that is expected to result when a monolayer of H atoms is present at the interface (0.35 eV) [728]. Annealing to room temperature reduced this initially increased barrier height by 0.15 eV and increased the inhomogeneity of the interface, suggesting that the H atoms initially residing at the metal/Si interface were desorbed upon warming and that formation of a Mg₂Si silicide interface layer was taking place [729]. The authors invited the verification of these hypotheses by means of NRA.

The NRA study of Fig. 80 [42, 43] clearly proved the possibility that H interfacial atoms can prevail at least up to 360 K after Pb depositions onto the H-terminated Si(111)(1x1) surface, yet the interface structure still remained obscure. In order to shed light into this matter, Fukutani and coworkers investigated in detail the initial stages of low-temperature Pb growth on Si(111)(1x1)-H, using a strongly grazing ion incidence geometry for the detection of the interfacial hydrogen, and thereby achieved the best resolved distinction of Pb film thickness variations (in the sub-monolayer regime) that has presently been realized with $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA [59]. The NRA profiles shown in Fig. 81 (a) were recorded at a ^{15}N incidence angle of $\alpha_i = 80^\circ$ with respect to the surface normal. It is seen that the center positions of the resonance peaks due to the Si(111)-terminating H layer shifted to higher energies

and that the profiles broadened continuously as the amount of lead (deposited at 110 K) was increased, whereas at all Pb coverages the original H-coverage (1.01 ± 0.07 ML) was fully maintained. As discussed in the previous examples, the peak center shifts reflect the energy loss of the ^{15}N ions as they intersect the respective Pb overlayers before reaching the H buried at the Pb/H/Si(111) interface.

Fig. 81. (a) γ -ray intensity profile of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction as a function of the incident ^{15}N beam energy taken for the Si(111)(1x1)-H surface before Pb deposition (triangles) and after Pb deposition of 0.37 nm (filled circles) and 1.11 nm (open circles) at 110 K. Solid and dashed curves are fits of the spectra to a

Gaussian form. (b) Relation between the Pb thickness estimated from the shift of the NRA spectra (including additional data for 0.2 nm Pb) and the deposited amount measured by the quartz oscillator. Solid line is a fit to a linear relation. (c) Side view of the schematic model for the initial adsorption of Pb on Si(111)(1x1)-H at 110 K. Filled, open, and shaded circles denote H, Si, and Pb atoms, respectively. Reproduced from Ref. [48] with permission from AIP.

The linear dependence of this energy shift on the deposited Pb thickness is displayed in Fig. 81 (b). Clearly, even *submonolayer* changes of the Pb layer thickness as small as 0.1 nm are discernible by distinctly different energy shifts, highlighting the excellent depth resolving capability of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA in grazing incidence [59]. It can further be observed in Fig. 81 (b) that the first ~ 0.1 nm of deposited Pb did not lead to any appreciable shift of the NRA profile, which the authors tentatively attributed to an interface structure in which the Pb atoms partially reside at a similar height within the plane of the H-adlayer on the Si substrate, so that the first ~ 0.5 ML of Pb atoms have a reduced shading effect on the ^{15}N ion beam at the grazing incidence. The suggested interfacial model structure is schematically illustrated in Fig. 81 (c). Fukutani et al. demonstrated further that when H exists only at the metal overlayer/Si interface or on openly exposed H-terminated Si-substrate surface, the energy shift (ΔE_c) of the experimental NRA profile center will always be strictly proportional to the *average* thickness (h) of the deposited Pb layer (i.e., $\Delta E_c = S \cdot h / \cos \alpha_i$, even if the film grows in form of three-dimensional islands (S : stopping power) [59].

As a final result, the spectral width of the NRA profiles for the Pb-covered samples (circles in Fig. 81 (a)) was observed to consistently exceed the broadening obtained from convolving the profile of the H-terminated Si(111) surface before Pb deposition (triangles in Fig. 81 (a)), which contained all experimental energy broadenings, i.e., resonance width, beam spread, Doppler broadening, and any possible roughness of the Si(111) surface) with an additional Gaussian component to reflect the ^{15}N ion straggling in the Pb overlayers, when this latter component was

based on an estimation of the straggling cross section derived by Rud et al. [106]. The deviation increased with the Pb thickness and could thus neither be accounted for by assuming morphological roughness of the Pb/Si interface (intermixing of Pb and Si was further excluded by the low experimental temperature) nor height variations of the overlayer (ascribing the experimental spectral widths to the latter would have required the unreasonable assumption of surface roughness in excess of the actual Pb film thickness). As a byproduct, this high-resolution study thus pointed out the possibility that the Rud theory might underestimate the straggling cross section of 6.4 MeV ^{15}N in Pb [59] (cf. Section 2.1.4).

It should be noted that the extremely acute sensitivity to overlayer thickness variations in the work above became possible by virtue of three combined favorable properties of the particular Pb/H/Si(111) system: Apparently H is much more stable at the Pb/Si(111) interface rather than (1) either on the surface of the top Pb layer or (2) in the volume of the Pb film, and (3) the Pb-Si interaction is significantly weaker than the Si-H bond. These conditions ensured that the original density and location of the Si-terminating H-adlayer is preserved during the overgrowth by the Pb film and that assuming the H distribution to remain confined to a single layer at an atomically sharp Pb/H/Si(111) interface was justified. The position shifts of the NRA profile centers could thus be determined with sufficient numerical accuracy and be interpreted as the effective Pb overlayer thickness retarding the ^{15}N ion beam. Any possible solution of H in the metal film or in potentially forming metal-silicide compounds, any degradation of the abrupt interface structure by reactive metal-silicon interdiffusion, or H adsorption on the surface of the growing overlayer that

may occur in other metal/Si systems would seriously hamper a straightforward analysis such as the one above. An example for such a more complicated (yet far more common) situation is presented by the NRA profiles measured in normal incidence at a thin (35 Å) amorphous Si film deposited onto H-terminated Si(001) [203]. Here, the energy-shifted signal component of the interfacial hydrogen could not be resolved from the simultaneously present signal of H adsorbed on the surface of the α -Si layer (and from possibly remaining H traces within the α -Si film), and the experimental energy shift of the unresolved profile amounted to only about one half of the value expected from the α -Si film thickness for the case that H existed only at the α -Si/H:Si(001) interface [203].

Addressing now the Ag/Si(111)(1x1)-H system, Fig. 82 (a) shows NRA excitation profiles for H-terminated Si(111)(1x1) surfaces covered by Ag deposits of 39 Å (trace (i)) and 70 Å (trace (ii)) prepared at 360 K [43]. Compared to the original resonance profile of the H-terminated substrate (dashed curve), the H coverage was obviously strongly reduced, i.e. to 0.25 ± 0.03 ML and 0.15 ± 0.02 ML for the 39 and 70 Å thick Ag films, respectively. As H desorbs from Ag(111) surfaces at 190 K [270], the remaining H was concluded to be present on uncovered patches of the Si substrate between Ag islands rather than on the surface of these islands. This situation is modeled in the left panel of Fig. 82 (c). The inferred islanding growth mode of Ag on H-terminated Si(111)(1x1) and the estimated island height were in good agreement with results obtained with various surface imaging techniques [435, 731-733]. To explain the remaining H on the open Si substrate surface between the Ag islands Fukutani et al. conjectured that isolated Ag atoms diffused over the H-termination layer without

disrupting it, causing H detachment from the interface only upon aggregation into Ag islands. Exactly this scenario has recently been confirmed by first-principles calculations [734, 735] and synchrotron based photoemission spectroscopy that evidenced the formation of direct Ag-Si chemical interactions and a concomitant decrease of a Si-H bond related spectral feature [736]. In line with the unaltered Schottky barrier height of Ag/Si contacts on bare and H-terminated Si(111) surfaces [730], the above results thus consistently support the hypothesis that the preadsorbed Si-terminating H atoms are replaced by deposited Ag at room temperature.

Fig. 82. (a) γ -ray yield profiles from the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ nuclear reaction as a function of the incident ^{15}N beam energy taken for Ag deposition onto Si(111)(1x1)-H with coverages of (i) 39 Å and (ii) 70 Å at a sample temperature of 360 K. Solid curves are fits to a Gaussian form and the broken curve denotes the profile for Si(111)(1x1)-H. (b) γ -ray yield profiles from the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ nuclear reaction as a function of the incident ^{15}N beam energy taken for Ag deposition onto Si(111)(1x1)-H with coverages of (i) 33 Å and (ii) 67 Å at a sample temperature of 110 K. (iii) Intensity profile taken after annealing the sample corresponding to (ii) at 300 K. Solid curves are fits to a sum of two Gaussian forms and the broken curve denotes the profile for

Si(111)(1x1)-H. (c) Schematic figures of Ag growth on Si(111)(1x1)-H at temperatures of 360 K (left) and 110 K (right). Black dots denote H atoms. Adopted from Ref. [760].

Analog NRA measurements after Ag deposition onto Si(111)(1x1)-H at 110 K demonstrated that this behavior changes at low temperature [43]. As seen in Fig. 82 (b), the single surface peak in the NRA profile of the H-terminated Si(111) substrate decreased strongly as before, but at the same time a second component emerged that intensified and separated farther from the surface H signal as the Ag coverage was increased from 33 Å (profile (i)) to 67 Å (profile (ii)), clearly suggesting the presence of H at the Ag/Si interface. The initial H coverage was almost completely preserved in this condition. The center positions of the interface components coincided quite precisely with the respective deposited Ag thicknesses, suggesting that closed Ag films had formed at $T=110$ K, with some H (ca. 0.25 ML) residing on their surface, as illustrated on the right hand side of Fig. 82 (c). The NRA profile (iii) measured after warming to 300 K indicated by the almost complete loss of the higher energy signal component that the interfacial H was only stable at low temperatures, whereas the surface-H appeared to remain. Although no definite conclusion could be reached on which surface the H actually resided, it was suggested that the originally closed Ag film had transformed into an island structure upon annealing, which partially re-exposed the still H-covered Si surface, whereas H was expected to desorb from the Ag surface at 300 K [43].

Qualitatively similar results as for Ag/Si(111)(1x1)-H were obtained also for Cu deposition onto Si(111)(1x1)-H [43]. Cu deposition at 360 K resulted in a very substantial reduction of the H coverage without any evidence for a buried H

component (only 0.13 ML remained for either 19 Å or 31 Å Cu), whereas $\sim 0.19 \text{ ML} \pm 0.04$ of interfacial H could be observed at 110 K underneath an apparently closed Cu film of 60 Å in addition to $\sim 0.29 \pm 0.04$ ML of surface hydrogen. Nonetheless, about one half of the original H-coverage was found to be desorbed after Cu deposition even at 110 K. In summarizing the chemical trend of the H atom stability at metal/Si(111)(1x1) surfaces revealed in this NRA study, Fukutani et al. noted that the Pb/Si(111) interface apparently provides a stable environment for interfacial hydrogen even at room temperature, whereas Ag and Cu interact increasingly strongly with the Si substrate, expelling H from the metal/Si bonds at room temperature and only weakly stabilizing them at 110 K.

Even stronger interfacial metal/Si interactions occur during the growth of Au on Si(111) surfaces. At room temperature, Au-silicide surface layers are produced by the out-diffusion of Si atoms onto the surface of the Au film, when the Au film thickness exceeds 0.5 ML [744, 745]. This reactive Si segregation is substantially suppressed at low temperatures (173 K), where closed Au films grow on both Si(111)(7x7) and Si(100) [746]. H-termination of Si(111) has been proposed to change the room temperature growth of Au from a layer-by-layer fashion on bare Si(111)(7x7) to island formation on H-terminated Si(111)(1x1). In contrast, even at thicknesses as low as 2 Å closed Au films were observed by STM on Si(111)(1x1)-H [747]. On the basis of the known reactive Au/Si interaction, both studies assumed but could not prove with the available methods that desorption of H occurred upon Au deposition. On the other hand, other authors claimed the possibility of H prevalence at Au/Si

interfaces such as those formed on amorphous Si [748] or on H-terminated Si(100) [738].

Wilde and Fukutani therefore addressed the controversial hydrogen stability and the growth mode during the low-temperature Au/Si interface formation on H-terminated Si(111)(1x1) by means of high-resolution $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA [612]. Fig. 83 displays the NRA resonance excitation curve measured in strongly grazing ion incidence ($\alpha_i=80^\circ$) at the H-terminated Si(111)(1x1) surface before and after the deposition of 4.1 Å Au at a low temperature of 110 K, where the reactive Au-Si segregation could safely be ruled out.

Fig. 83. Grazing-incidence ^{15}N NRA profiles of the Si(111)(1x1)-H surface before and after deposition of 4.1 Å Au at 110 K. The energy shift $\Delta E_{if} = 9.4$ keV expected for H located at the Au/Si interface is indicated. Reproduced from Ref. [612].

The reduced integral γ -yield of the post-deposition NRA profile indicated that evidently a fraction of the H-termination layer was lost upon arrival of the Au atoms, yet $\sim 70\%$ of the original H coverage was still preserved. Relative to the excitation

curve of the bare H-terminated Si(111)-substrate the peak maximum of the post-deposition NRA profile was shifted by ($\Delta E = 0.8 \pm 0.3$) keV to higher energy and the spectral width had increased from (10.3 ± 0.3) keV to (12.5 ± 0.6) keV due to energy loss and straggling of the ^{15}N ions transecting the Au deposit before their reaction with H atoms. This energy shift was substantially smaller than the energy loss expected for the hypothetical situation that the remaining H was located in a single atomic layer at the Au/Si interface, where it would appear shaded by the Au overlayer (thickness $h = 4.1 \text{ \AA}$) by an effective ^{15}N ion trajectory length $z = h/\cos\alpha_i = 2.41 \text{ nm}$ and should thus give rise to an energy shift of $\Delta E_{\text{if}} = S \cdot h/\cos\alpha_i = 9.4 \text{ keV}$ (cf. Fig. 2). Dominant hydrogen prevalence at the Au/Si interface after Au deposition onto H-terminated Si(111)(1x1) could therefore conclusively be ruled out even for the low deposition temperature of 110 K [612].

In order to further elucidate the low-temperature growth mode of Au on H-terminated Si(111)(1x1), the authors performed simulations of the NR resonance excitation curve for all conceivable hydrogen depth distributions and Au overlayer morphologies that were compatible with the deposited Au film thickness and the observed H coverage, and compared the resulting energy shift in the simulated NRA profile with the experimentally observed value [612]. For H on top of a layer-by-layer growing film (Frank-van-der-Merwe growth mode: $4.1 \text{ \AA}$ Au (1.78ML in the lattice spacing of Au(111)) correspond to a closed Au monolayer with flat terraces of monoatomic step height nucleating in the second layer) resulted in an energy shift (0.4 keV) even smaller than the experimental one (0.8 keV). As such a surface morphology thus apparently did not offer sufficient surface roughness to account for

the experimental energy shift, a layer-by-layer growth mode of Au on H-terminated Si(111)(1x1) at 110 K could be excluded. On the other hand, Stranski-Krastanov-type (SK) nucleation of ~ 6 nm small 3-dimensional islands on top of a H-covered closed Au wetting layer appeared equally compatible with the measured NRA profile as did Vollmer-Weber (VW) growth of 5–8 layers high and ~ 7 –15 nm wide Au islands with uninterrupted H-terminated Si(111)(1x1) substrate patches between them.

The information on the H location in addition to the total coverage gained from grazing incidence NRA further allowed the authors to discuss interesting aspects of the H behavior during the Au film growth in both of the two conceivable epitaxial scenarios. In case of SK growth, H remaining on the Au wetting layer would imply a stabilization of H atoms on a Au surface at 110 K, which is not observed for Au(111) single crystals. The situation of Au/Si(111) might thus resemble the peculiar hydrogen adsorption properties of thin Au films such as those on Ir(111) substrates [274, 407, 408] (cf. Section 3.1.2). On the other hand, if VW island growth left the H-passivation layer on the Si surface between the 3-dimensional islands intact, the Au atoms impinging on the open terraces should be able to diffuse over the terminating H layer without disrupting the Si-H bonds, whereas H would be desorbed upon merging of the Au adatoms into islands [612].

Exactly this latter interpretation of the above NRA measurements has recently received support from first principles calculations of Au atom diffusion dynamics on H-terminated Si(111)(1x1) surfaces. Lee and Hwang found that at moderate temperatures far below the onset of H desorption from Si (450°C), isolated Au atoms can diffuse on the H-terminated Si surface by reversibly inserting into and emerging

from the Si-H bonds without disrupting the latter, forming intermediate linear Si-Au-H units [749]. The overall activation energy for this diffusion-reaction pathway was predicted to be 0.5 eV, implying that the Au adatom mobility is much smaller than, e.g., that of Ag adatoms (0.14 eV) [734, 735] on Si(111)(1x1)-H, which Lee and Hwang presume to diffuse above the H-termination layer without insertion into the Si-H bonds [749]. Similar to the case of Ag/Si(111) [735], their calculations also predicted the liberation of H atoms from the Au/Si(111) interface upon agglomeration of the Au atoms into clusters [749]. In agreement with the above NRA results [612], the H atoms were shown to be energetically more stable on the Au cluster surface rather than at the Au/Si interface. The Au-surface H bonding interaction varies as a function of the Au cluster size and H coverage but is generally very weak, so that the H atoms easily recombine and desorb without a significant activation barrier [749], which is consistent with the NRA-observed substantial H loss caused by Au island formation on Si(111)(1x1)-H even at 110 K [612].

3.3.3 H at metal-insulator interfaces:

Cr₂O₃/(Cr110)

The investigations reviewed so far have already showcased the versatility of ¹⁵N NRA to observe hydrogen at buried interfaces. For hydrogen trapped at metal/silicon interfaces, the interpretation of the NRA profiles has greatly been aided by the fact that the H solubility in the Si substrate as well as in the metals selected for deposition was extremely small, i.e., well below the NRA detection limit. Thus, only H at the metal/Si interface and on the sample surface had to be considered. In the

case of metal/oxide interfaces this situation can be more complicated. As shown in Section 3.2, certain metals are prone to dissolve H in the bulk and many metal oxides can contain sizeable proton concentrations. In principle, hydrogen may thus be located directly at as well as in the material volume on either side of the interface. The following ^{15}N NRA studies of H distributions near metal/oxide interfaces will exemplify that the actual H behavior is not always easily anticipated, and that one may encounter actually H-free interfaces, H-trapping interfaces, as well as interfaces where H accumulates on either the oxide or on the metal side. Among the phenomena that make H localization at metal/oxide interfaces potentially interesting we mention the possibility that interfacial hydrogen may destabilize the metal/oxide adherence and thus lead to loss of surface protecting films, or the role that hydroxyl impurities appear to play in reducing the strength of passivating oxide films to resist metal corrosion [750, 751].

Hjörvarsson et al. investigated the possibility of H trapping at a structurally highly-defined metal/insulator interface between a layer of Cr metal of excellent crystalline quality and its oxide, $\alpha\text{-Cr}_2\text{O}_3$, grown epitaxially by *in-situ* oxidation under control with X-ray reflectivity measurements [752]. This $\alpha\text{-Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ interface was almost atomically flat; its roughness (rms) did not exceed 0.2 – 0.3 nm. A single-crystal like Nb film on a sapphire (Al_2O_3) substrate was chosen to serve simultaneously as a high quality epitaxial buffer layer for the Cr(110) film growth and as an indicator for the successful H uptake by the system upon later hydrogenation. The $\alpha\text{-Cr}_2\text{O}_3(0001)$ layer was further protected from hydroxylation in ambient atmosphere through an additional thin Cr overlayer, which was allowed to oxidize

naturally as to provide a passivating surface film. Thickness and crystalline quality of all layers were carefully characterized with RBS and X-ray reflectivity measurements. The hydrogen affinity at the lower α -Cr₂O₃/Cr(110) metal/oxide interface in the resulting Cr₂O₃(0001)/Cr(110)/Cr₂O₃(0001)/Cr(110)/Nb(110)/Al₂O₃(11 $\bar{2}$ 0) multilayer structure was finally evaluated by measuring the H distribution with ¹⁵N NRA after hydrogenation under 10⁵ Pa of purified H₂ at 573 K [752].

Fig. 84. Normalized γ -yield from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction as a function of the incident ^{15}N ion energy. The hydrogen concentration is proportional to the normalized yield, and corresponds to a H/Nb atomic ratio of 0.65 ± 0.03 . A schematic illustration of the sample structure is included for clarity. The dotted horizontal line is the natural background, giving the definition of zero concentration in the measurements. Ox denotes the chromium oxide region. Reproduced with permission from Ref. [752].

The obtained H depth profile is shown together with the schematic sample structure in Fig. 84. The large and confirmed saturated H content in the Nb film corresponded to the atomic ratio of $x = 0.65 \pm 0.03$ as in the ordered β -phase of NbH_x, indicating that hydrogen had successfully penetrated all layers of the sample system,

i.e., that the $\text{Cr}_2\text{O}_3/\text{Cr}$ layers did not present H diffusion barriers. The integrated intensity of the smaller H peak in the surface region corresponded to roughly one monolayer of H equivalent [752]. The dashed line at 4 counts/ μC marks the natural background of the γ -detection system, defining the sensitivity limit of the measurement. The H concentration at the lower $\text{Cr}_2\text{O}_3/\text{Cr}$ interface did not exceed this detection limit and was thus estimated to be smaller than 1% of a monolayer. The authors hence concluded that the highly crystalline $\alpha\text{-Cr}_2\text{O}_3/\text{Cr}$ metal/oxide interface did apparently not provide a suitable (electronic) structure to stabilize hydrogen, but noted that structurally less coherent interfaces with higher defect densities may offer energetically favorable trapping sites for hydrogen [752].

$\text{Al}_2\text{O}_3/\text{Al}_{0.065}\text{W}_{0.935}\text{-alloy}$

The question of possible H binding into metal-insulator interfaces raised above is closely related to the distribution and behavior of hydrogen impurities in thin alumina films formed by anodic oxidation of aluminum and its alloys. Water penetration into the oxide films had long been suspected to be the cause for the loss of dielectric strength of such barrier layers. In one of the first H profiling applications of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ NRA, Lanford indeed proved as early as 1980 the hydrogen inclusion into anodic alumina films [753]. A more recent NRA investigation of the H impurity behavior in Al-6.5 at.% W alloy during anodic oxidation reported increased H concentrations near the alloy/anodic oxide interface, amounting to $\sim 2 \times 10^{15}$ H atoms cm^{-2} , whereas the bulk of the anodic oxide films contained $\sim 0.1\text{-}0.3$ at. % hydrogen [754]. This was the first report of H accumulation at an aluminum-alloy/anodic film interface. Accidentally, the magnetron sputtering produced Al-W

alloys used in this study contained up to 0.5 at. % H. This raised the question whether the source of the incorporated H in the oxide films and of that accumulated at the alloy/oxide interfaces might originate from the aqueous electrolyte or from H impurities that diffused from the bulk of the alloys to the interface during the anodic oxidation [754].

Anodically oxidized Zr-Nb alloy

The possibility that metal-dissolved hydrogen diffuses and localizes near metal-oxide interfaces during anodic oxidation was elegantly demonstrated with ^{15}N NRA by Khatamian for the anodization of Zr-Nb alloys [755]. This is exemplified by the H profiles of Zr-2.5Nb alloy (2.5 wt. % Nb 10 wt. ppm H) in Fig. 85, which clearly display hydrogen accumulation peaks on the metal side of the respective interfaces to oxide layers of various thicknesses that were grown by different anodizing potentials.

Fig. 85. Hydrogen profiles of a set of low-H Zr-2.5Nb samples anodized in KOH at different applied potentials and 1 mA cm^{-2} current density. The vertical lines mark the depth at which the oxygen signal starts

decreasing from a plateau level in the oxide measured by SAM (Scanning Auger Microprobe). From Ref. [755].

The source of the accumulated hydrogen was identified as bulk-dissolved H in the alloy rather than H from the electrolyte [756]. The H peak position below the oxide and the accumulated H amount followed the interface position in a strictly linear fashion. This behavior was the same for low (10 wt. ppm) as well as higher (150 wt. ppm) H concentrations in the alloy bulk. The H quantity below the metal/oxide interface increased somewhat with the H content in the alloy bulk but was clearly not proportional to it. The amount of H trapped below the interface also increased with the applied anodizing potential, i.e., with the longer time required to grow thicker oxides. The sub-interfacial H profiles were very stable at room temperature but first increased further in height and width (towards the alloy bulk) upon moderate annealing of the anodized specimen at 400-500 K. Upon prolonged annealing the H peaks first saturated and then started to decrease, and became entirely depleted by annealing at higher temperatures (e.g., 673 K) for short periods (~5 min). Khatamian attributed his observations to trapping of hydrogen in the strained sub-interfacial region, where the metal lattice had been expanded due to the presence of the superficial oxide [755]. He assumed that H in the bulk of the alloy became mobile during moderate annealing and started populating the trap sites in the stressed sub-oxide region until all sites were filled. He reasoned further that as the heating process continued, the stressed lattice beneath the oxide layer gradually annealed, so that the hydrogen in the region moved back into the alloy. The disappearance of the H peak upon annealing at elevated temperatures was ascribed to much faster stress relief in the region.

To test the alternative hypothesis that H may have been trapped at alloy-dissolved oxygen (which had been the tentative explanation for the sub-interfacial H accumulation prior to the study [756]), Khatamian implanted first oxygen (~ 6 at.% O) and then hydrogen into the same depth region ($0.32 \mu\text{m}$) of unoxidized Zr-2.5Nb alloy. Zr and its Nb-alloys have a high solubility for oxygen, so that *oxide precipitates* would only form above an O concentration of 30 at. % [757]. The expected (TRIM-calculated) depth distributions of the implanted oxygen and hydrogen are compared to the actually measured ^{15}N NRA H profile in Fig. 86.

Fig. 86. Oxygen and hydrogen profiles of a low-H Zr-2.5Nb sample implanted with oxygen and subsequently implanted with hydrogen at room temperature. The position of the expected hydrogen profile, based on previous hydrogen implantations at lower temperatures, is also shown. Reproduced from Ref. [755].

Contrary to the calculation, the actual hydrogen distribution showed accumulation just beneath the (naturally oxidized) surface at a shallow depth of $0.06 \mu\text{m}$, but a minimum (0.08 at.% H) in the O-implanted region (around $0.32 \mu\text{m}$), suggesting that the H interaction with *dissolved* oxygen in the Zr-Nb alloys was in fact repulsive [755].

Through this experiment Khatamian showed convincingly that dissolved O was not responsible for the H trapping beneath the Zr-Nb alloy-oxide interfaces seen in Fig. 85. The apparently repulsive O-H interaction observed here for the Zr-Nb alloys thus closely resembles the reduced H solubility found in surface layers of naturally oxidized Ti and Ti alloys [166, 532] (Section 3.2.3.6).

4. Conclusions

We hope to have presented a clear picture of the potential of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA to contribute invaluable to the analysis of hydrogen at surfaces and interfaces. Due to its virtues of detecting hydrogen quantitatively, highly depth-resolved, and non-destructively, $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA has proven instrumental in elucidating the static and dynamical behavior of hydrogen at surfaces and interfaces in a wide variety of processes and materials.

Resonant $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA at 6.385 MeV determines surface H coverages with a sensitivity in the order of $\sim 10^{13} \text{ cm}^{-2}$ ($\sim 1\%$ of a monolayer) and H volume concentrations with a typical detection limit of $\sim 10^{18} \text{ cm}^{-3}$ ($\sim 100 \text{ at. ppm}$). For surface-normal ^{15}N ion incidence on the analyzed target the near-surface depth resolution is $2\sim 5 \text{ nm}$, which can easily be enhanced to below 1 nm by adopting a surface-grazing incidence geometry. Especially in combination with standard surface science techniques for *in-situ* preparation and characterization $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA is very well suited to hydrogen analysis at atomically controlled surfaces and nanostructured interfaces.

By quantifying the hydrogen coverage NRA has helped substantially to establish our current microscopic understanding of the hydrogen behavior in adsorption phases on an appreciable number of single crystal surfaces (Section 3.1, Table 2). $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA is the only experimental technique to determine the zero-point vibrational energy of surface-adsorbed H atoms as a function of the azimuthal angle [67], i.e., it delivers the real space vibrational amplitude of the adsorbed H atoms.

The nanometer-scale discrimination between surface-adsorbed and absorbed H is a particularly important capability of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA that can provide valuable insight, e.g., into hydrogen ingress processes into materials, relevant to mineral hydration dating [79] or the observation of hydride nucleation in the near-surface region of H-absorbing metals (Section 3.2.3) [61, 84, 279]. In high-resolution mode the potential to detect submonolayer thickness variations of adlayers [59] and for the distinction of surface-adsorbed from volume-absorbed hydrogen in nanocrystalline materials have been demonstrated [60]. The combination with TDS allows for unambiguous identifications of thermal desorption features and for the depth-resolved assessment of the thermal stability of adsorbed and absorbed hydrogen states against desorption and diffusion [61, 62, 279].

Its nondestructive nature and high depth resolution also make $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA the ideal method to detect hydrogen buried at intact interfaces, allowing to study hydrogen trapping at metal/semiconductor interfaces (Section 3.3.2), to track hydrogen transport phenomena in stacked thin film systems [81], to reveal non-homogeneous hydrogen distributions and interface accumulation in clamped metal thin films (Section 3.2.3.7), etc. In directly visualizing hydrogen redistribution processes between interfaces of MOS structures under conditions relevant to electrical degradation (Section 3.3.1) $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA has made invaluable contributions to device reliability research [46].

Recent developments include micro-beam applications for the three-dimensional mapping of hydrogen distributions in the surface region of materials [551, 552] as well as NRA measurements under atmospheric pressure conditions [212]. As future

perspectives we mention the remaining challenge to achieve the ultimate distinction of hydrogen in surface chemisorption and first-layer subsurface sites. This may be realized by applying $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA in a strongly grazing incidence geometry on large single crystal targets. Such measurements may help clarifying the peculiar chemical reactivity of subsurface hydrogen in catalytic hydrogenation reactions of co-adsorbed hydrocarbon molecules [48, 358-360] or finally resolving the long-standing controversy about the exact location preference of H atoms at the Cu(111) surface [302, 393, 394]. Also the quantification of the hydroxyl coverage at single-crystalline oxide surfaces is worth exploring further.

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5. Appendix A

Stopping cross sections for ^{15}N in elemental targets

Note that two stopping cross section notations are in equally common use:

(1) $\varepsilon = 1/N (dE/dz)$ [$\text{eV cm}^2/10^{15}$ atoms], where N is the number density of the material in [atoms/cm^3]. This notation is convenient to calculate the energy loss in a layer of target atoms. The other definition is:

(2) $\varepsilon = 1/\rho (dE/dz)$ [$\text{MeV}/(\text{mg/cm}^2)$], with ρ being the mass density [g/cm^3] of the material.

To calculate the stopping power $S = (dE/dz)$ in [keV/nm] from the above stopping cross sections, either

- multiply ε [$\text{eV cm}^2/10^{15}$ atoms] by the number density N [cm^{-3}] and divide by 10^{25} ,
or
- multiply ε [$\text{MeV}/(\text{mg/cm}^2)$] by the mass density ρ [g/cm^3] and divide by 10.

Table A-1. Stopping cross sections (ε) of ^{15}N in elemental targets at 6.385 and 13.35 MeV. Data reproduced from Ref. [124].

Element	Atomic number	Density [g cm^{-3}]	ε at 6.385 MeV [$\text{MeV}/(\text{mg cm}^{-2})$]	ε at 13.35 MeV [$\text{MeV}/(\text{mg cm}^{-2})$]
H	1		28.38	21.66
He	2		11.48	9.233
Li	3	0.54	8.514	7.399
Be	4	1.82	7.693	7.055
B	5	2.47	8.307	7.227
C	6	3.52	8.453	7.397
N	7		8.537	7.112
O	8		7.965	6.923
F	9		6.915	6.266
Ne	10		6.747	6.198
Na	11	1.01	6.987	6.442

Element	Atomic number	Density [g cm ⁻³]	ϵ at 6.385 MeV [MeV/(mg cm ⁻²)]	ϵ at 13.35 MeV [MeV/(mg cm ⁻²)]
Mg	12	1.74	6.535	6.022
Al	13	2.70	5.858	5.556
Si	14	2.33	6.242	5.677
P	15	1.82	6.055	5.458
S	16	2.07	5.820	4.924
Cl	17		6.162	5.222
Ar	18		5.416	4.834
K	19	0.91	6.133	5.456
Ca	20	1.53	5.978	5.354
Sc	21	2.99	5.613	4.872
Ti	22	4.51	5.178	4.737
V	23	6.09	5.263	4.566
Cr	24	7.19	4.825	4.477
Mn	25	7.47	4.550	4.264
Fe	26	7.87	4.531	4.261
Co	27	8.9	4.243	4.037
Ni	28	8.91	4.160	4.116
Cu	29	8.93	3.776	3.814
Zn	30	7.13	3.797	3.783
Ga	31	5.91	3.606	3.537
Ge	32	5.32	3.547	3.593
As	33	5.77	3.501	3.417
Se	34	4.81	3.321	3.319
Br	35		3.422	3.646
Kr	36		3.434	3.340
Rb	37	1.63	3.783	3.570
Sr	38	2.58	3.749	3.431
Y	39	4.48	3.669	3.404
Zr	40	6.51	3.704	3.405
Nb	41	8.58	3.828	3.601
No	42	10.22	3.440	3.249
Tc	43	11.5	3.455	3.302
Ru	44	12.36	3.431	3.271
Rh	45	12.42	3.332	3.211
Pd	46	12.00	3.244	3.169
Ag	47	10.5	3.187	3.032
Cd	48	8.65	3.082	2.998
In	49	7.29	3.066	2.984
Sn	50	5.76	2.985	2.855
Sb	51	6.69	2.955	2.866
Te	52	6.25	2.932	2.782
I	53		2.947	2.859
Xe	54		2.894	2.825
Cs	55	1.99	3.151	2.994
Ba	56	3.59	3.037	2.891
La	57	6.17	3.083	2.866

Element	Atomic number	Density [g cm ⁻³]	ϵ at 6.385 MeV [MeV/(mg cm ⁻²)]	ϵ at 13.35 MeV [MeV/(mg cm ⁻²)]
Ce	58	6.77	2.729	2.732
Pr	59	6.78	2.859	2.828
Nd	60	7.00	2.753	2.731
Pm	61		2.755	2.709
Sm	62	7.54	2.844	2.809
Eu	63	5.25	2.523	2.613
Gd	64	7.89	2.541	2.541
Tb	65	8.27	2.441	2.503
Dy	66	8.53	2.405	2.477
Ho	67	8.80	2.181	2.308
Er	68	9.04	2.327	2.413
Tm	69	9.32	2.165	2.276
Yb	70	6.97	2.164	2.207
Lu	71	9.84	2.094	2.184
Hf	72	13.2	2.060	2.157
Ta	73	16.66	2.092	2.191
W	74	19.25	2.083	2.083
Re	75	21.03	2.062	2.137
Os	76	22.58	2.025	2.101
Ir	77	22.55	1.981	2.082
Pt	78	21.47	1.917	2.015
Au	79	19.28	2.022	2.043
Hg	80	14.26	1.949	2.000
Tl	81	11.87	1.984	2.017
Pb	82	11.34	2.042	2.022
Bi	83	9.8	2.134	2.077
Po	84	9.24	2.097	2.090
At	85		2.122	2.113
Rn	86		2.030	2.025
Fr	87		2.088	2.021
Ra	88	5	2.129	2.040
Ac	89		2.217	2.110
Th	90	11.2	2.117	2.035
Pa	91	15.4	2.207	2.090
U	92	18.7	1.948	1.962

6. Appendix B

Elastic recoil detection (ERD)

a. Principles

The most basic and conventional arrangement for ERD analysis of thick solid targets is the reflection geometry illustrated in Fig. B-1. A primary beam of projectile ions (mass M_1 , energy E_1) incident at a small (near-grazing) angle with the target surface (θ_1) recoils atoms out of the sample into a laboratory angle $\theta_r < 90^\circ$. According to the kinematics of elastic nuclear collisions (energy and momentum conservation), the energy of the recoiled particles (E_r) depends as follows on M_1 , E_1 , and θ_r , and thus provides information on their atomic masses (M_r):

$$E_r = E_1 \cdot \left[\frac{4M_1M_r}{(M_1 + M_r)^2} \cos^2\theta_r \right] = E_1 \cdot K_r \quad . \quad (\text{B.1})$$

K_r is called the kinematic factor for recoiling. A silicon surface barrier detector (SSBD) is typically used to analyze the energy distribution of these recoiled elements. A thin absorber (or range) foil (often a few μm of Mylar or rolled metal) placed in front of the detector lets hydrogen isotopes penetrate due to their small stopping powers, but fully retains the scattered primary ions and heavier recoils. Target tilt angles (measured between the surface normal and the beam direction) of 75° or larger ($\theta_1 < 15^\circ$) and recoil angles (θ_r) around 30° are the most common settings.

The energy spectra of the recoiled particles are converted into respective depth profiles by taking into account the stopping energy losses of both the incident

projectile ion and of the recoiled atoms along their trajectories into and out of the target, respectively. At a depth d normal from the surface, the incident projectile energy has decreased from E_1 to E_1' and recoiling transfers the energy $E_2' = K_r E_1'$ to the recoiled target atom, which reduces to E_2 on the recoil's way to the surface (Fig. B-1). For recoiling in shallow depths, the principally energy-dependent stopping powers of the projectile (S_1) and the recoils (S_r) can reasonably be assumed as constants (*surface approximation*), which combine into an effective target stopping power $S_{\text{eff}} = K_r \cdot S_1(E_1)/\sin\theta_1 + S_r(K_r E_1)/\sin\theta_2$, so that $E_2(d) = K_r \cdot E_1 - d \cdot S_{\text{eff}}$. Obtaining the final detection energy (E_d) requires calculating the additional energy loss of the recoils in the range foil by means of a slab analysis, in which the foil is divided into a set of equally thin layers for which the stopping power of the recoils is reasonably assumed as constant at their respective energy [193, 240].

Fig. B-1. Schematic illustration of the conventional ERDA recoiling and detection geometry, defining the laboratory angles of recoil (θ_r), incidence (θ_1), and exit (θ_2), as well as the

projectile (M_1) and recoil particle (M_r) energies (E_1 , E_2 , respectively). Only the light hydrogen isotopes (H and D) can pass through the range foil and are counted by the SSBD with a final detection energy E_d .

b. Sensitivity

The sensitivity of ERD measurements for a given target element is principally determined by the differential recoil cross section, σ_r [barn sr⁻¹] (1 barn = 10⁻²⁴ cm²). In the laboratory frame, this recoil cross section is again only a function of the recoil angle (θ_r), of the projectile energy (E_1), and of the atomic numbers and masses of the projectile (Z_1 , M_1) and the recoiled target atoms (Z_r , M_r):

$$\sigma_r = \left(\frac{Z_1 Z_r e^2}{2E_1} \right)^2 \left(\frac{M_1}{M_r} + 1 \right)^2 \frac{1}{\cos^3 \theta_r} \quad . \quad (B.2)$$

This Rutherford recoil cross section applies as long as the repulsive interaction between the colliding nuclei is adequately described by a pure Coulomb potential. This is a reasonable assumption for projectile velocities in the order of (~ 1 -2 MeV/amu)^{1/2}, which are therefore frequently employed conditions for quantitative and standard-free ERD measurements. In routinely used ERD of H and D with ⁴He beams, significant deviations of the ¹H(⁴He,¹H)⁴He [235, 262, 758-763] and D(⁴He,D)⁴He [235, 342, 758, 759, 763, 764] scattering cross sections from the Rutherford values require attention at ⁴He energies already above 1 MeV. The D(⁴He,D)⁴He cross section furthermore has a ~ 60 -70 keV wide (FWHM) and strongly θ_r -dependent [193, 235, 342, 759, 764] resonance at 2.135 $\pm$ 0.01 MeV, which corresponds to the first excited nuclear level of ⁶Li [758].

The recoil cross section decreases strongly with the projectile's energy ($\sigma_r \sim 1/E_1^2$) and shows a prominent dependence on the nuclear charge of the latter (Z_1 in Eq. (B. 2)). For hydrogen recoiling by heavy projectiles ($M_1 \gg M_r$) at a constant E_1 and in the approximation $M_1 \approx 2Z_1$, σ_r increases very significantly with Z_1 ($\sigma_r \sim Z_1^4$), which promises substantial gains in sensitivity through the use of large Z projectiles. This is exploited as one major advantage in ERD with heavy ion projectiles (**HI**ERD). In practice, the ratio (E_1/M_1) is often kept approximately constant in the ~ 1 -2 MeV/amu range to ensure Rutherford scattering behavior, so effectively a Z_1^2 dependence of σ_r applies when different projectiles are to be compared. The Z_r/M_r ratio is nearly the same ($\sim 1/2$) for all elements except H, where it is unity. Hence HI^{ERD} offers an approximately constant sensitivity for all recoiled elements with the exception of H, for which it is relatively enhanced by a factor of 4. The requirements, advantages, and limitations of hydrogen analysis by HI^{ERD} are discussed in detail by Dollinger et al. [765, 766] and Davies et al. [200, 248].

c. Depth resolution

The depth resolution in ERDA is generally expressed as $\Delta d = \Delta E_d / S_{\text{eff}}$, where ΔE_d is the total spread in the detected recoil energy. As explained in Refs. [193, 222, 238, 767-770], several factors enter ΔE_d : (1) Energy (typically $\Delta E_1/E_1 \sim 10^{-3}$) and angular spread of the projectiles (negligible for well-collimated beams), (2) geometrical spread caused by the finite beam spot and detector solid angle ('kinematic broadening'), (3) straggling and multiple scattering in the target [221, 222, 263, 771], (4) Doppler broadening (negligible), (5) energy straggling in and inhomogeneities of the absorber foil, and (6) energy resolution of the detection system.

Straggling and multiscattering of projectile and recoil in the target are sizeable contributions to ΔE_d . Small incidence angles with the target surface (θ_1) make better use of the higher stopping power of the heavier projectile relative to that of the lighter recoils, so that the ERD depth resolution can be optimized by adjusting the recoil geometry within the limit $\theta_r = \theta_1 + \theta_2$ (Fig. B-1) [771, 772]. The near-surface resolution of H ERD, e.g. in amorphous Si with a 3 MeV ^4He beam, thus improves significantly from 75 to 22 nm when θ_1 and θ_r are decreased from 12.5° and 23° to 4.5° and 15° , respectively [235] (Table 2). The small angles crucially demand high precision with respect to the sample position and recoil geometry (on the order of 0.1 mm and 0.1° , respectively) and samples with smooth surfaces are a strict requirement [266, 267].

The geometric recoil energy spread, also addressed as ‘kinematic broadening’, is another sizeable and inevitable resolution limiting factor in ERD. The size of the beam spot on the target and the detector slit dimensions define the recoil geometry less than ideally and allow that target atoms recoiled into slightly different directions $\Delta\theta_r$ reach the detector, which according to Eq. (B.1) implies a difference in recoil energy. The resulting geometric energy spread ΔE_r can be approximated as $\Delta E_r/E_r = 2\tan\theta_r \Delta\theta_r$ [235, 238, 250, 254, 765, 768, 769].

In conventional range foil/SSBD setups the dominating resolution-limiting factors are the energy straggling of the recoil in the (typically several μm thick) range foil and the energy resolution of the detector itself (~ 15 keV for standard silicon surface-barrier detectors). Hence, detector quality and the thickness, homogeneity, and uniformity of the range foil are highly important. Mylar and other organic polymers

are popular absorber foils because films with uniform thickness free of pinholes can easily be obtained and straggling is relatively weak in these low Z materials. Conventional ERD setups with absorber foils typically achieve some 10 nm depth resolution near the surface and a sensitivity ~ 0.1 at.% in H depth profiling (Table 2) [234, 235, 758, 772]. Mainly due to elimination of the range foil and better timing-resolution compared to the energy resolution of standard SSBD's, about one order of increased depth resolution is realized in TOF-ERD [193, 244, 773, 774]. In high resolution ERD applications with magnetic or electrostatic spectrometers that avoid the most prominent energy spreads (namely range foil straggling and SSBD detector resolution) of the conventional ERD setup altogether, the geometric energy spread prevails as the dominant resolution-limiting factor, and it is then essential to correct for the kinematic broadening with focusing ion optics in order to realize high depth resolution [238, 249, 250, 765].

d. Advanced detection systems

Several improved detection systems have been developed to enhance the ERD depth resolution and to become able to distinguish recoiled elements of very small mass differences, such as H, D, B C, N, and O. One such device is the ΔE -E telescope, in which the recoils deposit only a small portion of their energy (ΔE) upon transmitting a first thin absorber foil, before they are fully stopped in a second detector that measures their remaining energy [768, 769, 775, 776]. The sum of the two energies gives the total recoil energy and provides the depth information. ΔE is proportional to the stopping power of the transmitting particle, so that different recoil species can be identified through their mass (more precisely Z_R) even if they

have the same kinetic energy. Since their principle is still based on energy loss in transmitted foils, ΔE -E detectors do not offer a particularly enhanced depth resolution, but they tolerate large acceptance angles, so that high sensitivity measurements can be performed, and several recoil species can be detected simultaneously [257, 776]. This is particularly useful for the ERD analysis of hydrogen isotopes, when several of these species are present in a target at the same time [257, 776-778].

Also time-of-flight (TOF) spectrometers [244, 773, 774], E x B filters [256, 779-781], or sophisticated electrostatic [238, 253, 782] and magnetic [239, 247, 249, 250, 254, 783-785] spectrographs with position sensitive detectors (PSDs) in the analyzer focal plane have been devised for the purposes of rejecting scattered projectiles and highly resolved mass-dispersive energy analysis of the recoils. These instruments identify recoils of individual masses by virtue of measuring either their velocity, momentum, electric or magnetic rigidity, respectively. In addition to determining the total energy, i.e., providing depth information, these advanced detection systems can achieve sub-nanometer depth resolution for H isotopes near surfaces, provided that kinematical broadening is corrected for [238, 247, 249, 253, 255].

7. References

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