Advanced Techniques for Characterization of Ion Beam Modified Materials

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ABSTRACT

Understanding the mechanisms of damage formation in materials irradiated with energetic ions is essential for the field of ion-beam materials modification and engineering. Utilizing incident ions, electrons, photons, and positrons, various analysis techniques, including Rutherford backscattering spectrometry (RBS), electron RBS, Raman spectroscopy, high-resolution X-ray diffraction, small-angle X-ray scattering, and positron annihilation spectroscopy, are routinely used or gaining increasing attention in characterizing ion beam modified materials. The distinctive information, recent developments, and some perspectives in these techniques are reviewed. Applications of these techniques are discussed to demonstrate their unique ability for studying ion-solid interactions and the corresponding radiation effects in modified depths ranging from a few nm to a few tens of μm , and to provide information on electronic structure of the materials, defect configuration and concentration, as well as phase stability, amorphization and recrystallization processes. Such knowledge contributes to our fundamental understanding over a wide range of extreme conditions essential for enhancing material performance and also for design and synthesis of new materials to address a broad variety of future energy applications.

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Key words

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1. Introduction

The use of ion beams over a broad range of energies to synthesize and modify materials has evolved over the past several decades. Ion beam modification of materials is well established as a unique tool to shape and design materials at different length scales with controlled modification of electrical, optical, structural, mechanical and chemical properties for a wide range of research and applications, including advanced electro-optical devices, engineered nanostructures, nuclear materials, and space exploration [1-18]. Recent examples include swift heavy ion irradiation at oblique incidence to produce graphitic nanostripes on the surface of silicon carbides (SiC) as a result of silicon sublimation induced by intensive electronic energy deposition along the ions path [1]. This finding might offer new possibilities for defect-engineering dielectric materials. Ion beam surface nanopatterning depends on instabilities caused by erosion of the surface. Recent work suggests that the dynamics of a semiconductor surface nanopatterned by normal incidence ion beam sputtering is a time-dependent process that slows down with sputtering time, which should open new perspectives for understanding surface-morphology changes [2]. Ion beams can also be utilized to shape metallic nanoparticles embedded in a dielectric matrix [3] or to transform materials at the nanoscale but over large thicknesses [4]. Response of nuclear materials to neutron irradiation in harsh reactor environments can be studied via accelerated ion beam irradiation experiments. In the framework of research on radiation tolerant materials for next generation fission and fusion reactors, nanocrystalline materials have demonstrated great potential because grain boundaries act as very efficient defect and impurity traps [5-8]. In order to understand the mechanisms of irradiation-induced defect production, volume swelling and phase stability that may occur in structural materials over their service lifetime, ion irradiation combined with computational studies were conducted in oxides, carbides and metals [9-18].

Understanding the mechanisms of damage formation in materials as a result of energy deposition is essential for the field of ion-beam materials modification and engineering [1-18]. The interaction of energetic particles with solids results in energy loss to both atomic nuclei and electrons in the solid. While it is known that the ratio of energy transfer to electronic and atomic structures depends on the ion velocity, the energy regimes are commonly classified by particle energy. The corresponding response of materials can be divided into three principal regimes. At low ion energies ($E < 0.5$ MeV) where the modification depth is close to the surface (well below half of a micrometer in most cases), the transfer of energy to atomic nuclei (nuclear energy loss) dominates, leading to the displacement of atoms via elastic collisions between atomic nuclei in ballistic collision cascades. At intermediate ion energies ($0.5 < E < 50$ MeV) where nuclear and electronic energy losses are both significant, the coupled energy deposition processes can lead to additive [8, 19], synergetic [20] or competitive effects [20-22] on defect production and damage recovery processes that affect disorder accumulation and microstructure evolution. At high energies typical of swift heavy ions ($E > 50$ MeV) where the penetration depth can be beyond a few tens of μm (such as with GeV ions), electronic energy loss dominates, leading to intense localized thermal spikes that can cause damage production [19], track formation [4, 23] or damage recovery [11]. This article reviews a number of techniques used to characterize materials modified by ions in the low, intermediate and high-energy regimes.

Advances in ion beam modification and their applications benefit from our knowledge obtained from various characterization techniques. Utilizing different types of probing particles (ions, electrons, photons, and positrons), a wide range of characterization techniques is available. High-energy light ions, such as MeV hydrogen and helium ions, are commonly used, based on elastic and inelastic scattering processes, to probe the composition and obtain elemental depth profiles in the near-surface layer of solids (up to a few micrometers). Similar to the high-energy probing ions, high-energy electrons have recently been utilized to determine elemental profiles in the surface region of materials (up to a few tens of nanometers) and provide information on their electronic structure. Interaction of X-ray photons with solids can give rise to several scattering phenomena. In crystalline materials, owing to the atomic long-

range order, diffraction of X-rays at high angles gives information on the crystallographic structure and on the strain/stress state of the materials. At low angles (i.e. from the critical angle for total reflection to a few degrees), scattering of X-rays allows studying material modifications [23] that exhibit electronic density changes on nanometer length scales such as thin film superlattices, nanostructures, multi-phase compounds and extended defects; information including nano-object size, shape and spatial correlation, interface depth location and roughness is thus accessible. Positrons are positively charged particles that are very sensitive to free volumes in materials; annihilation of a positron with its antiparticle leads to the emission of two gamma rays that contain information of the nature of vacancy-type defects in materials. Other microstructure analysis techniques, such as transmission electron microscopy (TEM) and atom-probe tomography (APT) [15-18], are also powerful tools for investigating irradiation-induced microstructural changes. They offer insights into mechanisms of damage evolution with a resolution hardly unmatched by other experimental techniques. TEM with *in situ* ion irradiation [17, 18 and references therein] allows the direct observation of microstructure evolution under ion bombardment that provides invaluable insights into the atomistic processes to validate modeling predictions, which in turn can elucidate the underlying mechanisms seen in the microscope. While TEM and APT techniques have been effectively utilized to characterize ion beam modified materials, this review draws attention to some recent advances in analysis techniques of Rutherford backscattering spectrometry (RBS), electron Rutherford backscattering spectrometry (eRBS), Raman spectroscopy, high-resolution X-ray diffraction (HRXRD), small-angle X-ray scattering (SAXS), and positron annihilation spectroscopy (PAS). The insights provided from these techniques have significantly contributed to our fundamental understanding over a wide range of extreme conditions essential for enhancing material performance and for design and synthesis of new materials to address a broad range of future energy applications.

2. Advanced Techniques in Characterization of Ion Beam Modified Materials

A: Rutherford backscattering spectrometry

Rutherford backscattering spectrometry derives its name from Lord Ernest Rutherford who in 1911 was the first to present the concept of atoms having a positively charged nucleus. It is perhaps the most conventional ion beam analysis method, in which light ions penetrate a sample and are elastically backscattered from target nuclei and subsequently detected, yielding information on the mass and depth of the target atoms. In this ion

Fig. 1 Damage depth distributions from the fits of the McChasy code [27] to RBS/C spectra recorded on c-ZrO₂ crystals irradiated with 4 MeV Au²⁺ ions at indicated fluences (cm⁻²) at 80 K.

scattering technique, the elemental information is obtained from the mass-dependent energy transfer from a collision. The depth information obtainable from RBS is based on stopping power concept, *i.e.*, inelastic energy loss during ion-solid interactions. Ion channeling (RBS/C) for ions incident parallel to a low index crystal axis is utilized to determine structural imperfection of crystalline materials. If a crystal contains defects (displaced lattice atoms), the minimum yield will increase as a result of direct backscattering and dechanneling of the ions due to the interaction with the displaced atoms. The dechanneling mechanisms depend on the type of defects, impurities, dislocations, and local strain/lattice distortion, which are characteristic between the displacements and the lattice atoms [24]. Besides very sensitive to detect displacement atoms, RBS/C technique can also differentiate impurities on interstitial or on substitutional sites. While the elemental composition and film thickness are characterized by RBS at random directions, irradiation-induced damage in crystalline samples can be determined by RBS/C along a major channeling direction [24-27].

For data analysis of RBS/C spectra, iterative procedures are typically applied to separate the backscattered dechanneled probing ions from those that are backscattered from the displaced atoms. Iterative procedures with improved accuracy and self-consistency are reported to quantitatively analyze disorder profiles from the RBS channeling measurements [25, 26] or to improve energy-depth conversion with correction for reduced stopping powers along channeling direction [25] in monocrystalline solids.

While the dechanneling analysis based on iterative procedures works well for relatively low-energy ion-irradiated samples, it is inapplicable for a deeper damage region ($> \sim 1\mu\text{m}$). The RBS technique has been advanced with the development of simulation codes employed for data analysis to reveal detailed information contained in the ion channeling spectra. A Monte Carlo CHAnneling SYmulation (McChasy) code [27] can, however, determine the damage profile produced by high-energy ions that is too deep to be analyzed by the iterative methods of the dechannelling analysis [25,26]. The McChasy code can also be used to analyze multi-elemental targets, where an overlap of numerous elemental contributions renders standard depth profile analysis difficult [27]. Moreover, it is possible in the McChasy simulation to distinguish between randomly displaced atoms and long-range extended defects, such as dislocations. Hence, complex defect structures can be nominally characterized by the relative contribution from displaced atoms and extended defects without going into structural details. The McChasy code can be operated on a personal computer and evaluation of a typical spectrum can be performed in a few hours. Another widely used computer code, the Dechanneling In Crystals And Defect Analysis (DICADA) code, based on a discontinuous model of dechannelling [24] where uncorrelated displaced lattice atoms are assumed, can be employed to explore the existence of point defects, clusters of point defects, and/or amorphous zones. DICADA1 and 2 are respectively developed for elementary crystals containing point defects, dislocations and stacking faults and for compound crystals containing two different kinds of point defects with two different configurations of uncorrelated displaced lattice atoms. The DICADA codes have been recently applied to understand the response of various covalent and ionic-covalent semiconductors to swift heavy ion irradiation [28].

Recent advances in RBS and RBS/C include the study of ion beam induced surface and interface engineering [29], of the role of electronic energy loss on ion beam modification of materials [20, 22, 30, 31] and radiation research on ion irradiation damage evolution from cryogenic temperatures to elevated temperatures [28, 30]. For example, yttria-stabilized cubic zirconia (YSZ or c-ZrO_2), as a material widely used for electronic, space, and nuclear applications, was irradiated with 4 MeV Au^{2+} ions from liquid nitrogen temperature (80 K) to 1073 K. Several characterization techniques, such as RBS/C and XRD

(see Section D), were used to monitor the disordering process including defect production, strain buildup, and dislocation formation, and to identify the microstructural changes. Typical damage depth profiles obtained from the fitting using the McChasy code of the RBS/C spectra corresponding to c-ZrO₂ crystals irradiated at 80 K are shown in **Fig.1**. Damage profiles at this cryogenic temperature appear similar to those obtained at higher temperatures [30]. The fact that the fluence ($\sim 10^{15}$ cm⁻²) at which the disorder level significantly increases is the same as that for crystals subjected to room-temperature irradiation indicates that defect mobility is identical at both temperatures.

B. Electron Rutherford backscattering spectrometry

For ion-induced surface modification, determination of the composition with nm depth resolution, as well as isotope sensitivity and high spatial resolution, is highly desired. A recently developed technique, electron Rutherford backscattering spectrometry [32-34], has demonstrated its analytical power that is complementary to other surface analysis techniques, including RBS, medium energy ion scattering (MEIS), X-ray photoemission spectroscopy (XPS), and secondary ion mass spectrometry (SIMS).

The eRBS technique, based on high-energy (from 5 to 40 keV) electron scattering, can be used to probe depth profile of a sample surface region from

very thin (a few nm) to relative thick layers (a few tens of nm, depending on the incoming energy and geometry), and provide information on the electronic structure of the layer [32,33]. The main features of the eRBS technique are the use of elastic cross-sections and kinematic factors as in RBS and inelastic electron mean free paths (IMFP) as in photoemission. While the separation of the elements is accomplished as in RBS by calculating the recoil energies of electrons backscattered from target nuclei

Fig. 2 Spectra (triangles) taken using probing electrons at 25 keV from a Ta sample implanted with 10 keV O to ion fluence of (a) 1×10^{17} cm⁻² and (b) 5×10^{17} cm⁻². Detailed scattering geometry and data analysis can be found in Ref. [33]

(the energy transfer from an electron to a nucleus assuming a collision between free particles is in the order of the atomic binding energies in the case of eRBS), the intensity of the elastic peaks is proportional to the elastic scattering cross-section of each atomic species and their concentration. As in RBS, the atomic composition and thickness of the surface region can, therefore, be quantitatively determined from the energy position of the elastic scattering peaks characteristic of each element in the sample. The stoichiometry of the film can be determined with an accuracy of 5-10%. In contrast to RBS, only the trajectories without any inelastic events (i.e., electronic excitations) are used for the compositional analysis. As the intensity of an elastic peak depends on both the element concentration and the IMFP, the corresponding depth profiling is done in a similar way as in XPS. Electrons that have scattered inelastically as well as elastically contain information on the electronic structure. Since the small recoil energy losses from the e-beam energies are far below the displacement energies to create irradiation-induced defects and the electronic excitations resulting from the modest current densities (typically at $\sim 25 \mu\text{A cm}^{-2}$) are usually too low to cause sample decomposition, eRBS can also be applied to investigate irradiation-induced or thermally-activated self-diffusion within the surface region or at the interfaces [34].

One example of an eRBS application is a study of the electronic structure and elemental composition of O-implanted Ta films [33] used for the fabrication of memristor devices [35]. Memristors based on tantalum oxides rely on the

Fig. 3 Energy loss spectra taken using probing electrons at 25 keV for Ta, O implanted Ta samples, and Ta_2O_5 . All elastic peaks are normalized to equal area, and the curves are offset vertically for clarity purpose. Electronic structure of Ta (peaked at 21 eV marked by the long dashed line) and Ta_2O_5 (from 10 to 60 eV with characteristic “shoulders” from 15 to 30 eV) are shown by the bottom and the top curves. The O elastic peak (short dashed line) is visible near 4.5eV. [33]

facts that Ta₂O₅ is highly resistive due to its large band gap (~4.5eV), and sub-stoichiometric tantalum oxides are much more conductive due to much smaller or no band gaps. eRBS with electron energies ranging from 5 to 40 keV was utilized to investigate Ta films implanted with 10 keV O ions to different ion fluences [33]. The inelastic mean free path and hence the probing depth at these electron energies are of the same order as the range of the implanted ions. As shown in **Fig. 2**, with 25 keV probing electrons, the main elastic peak at zero energy loss corresponds to electrons scattered from Ta atoms, and the weaker peak, separated from the main peak by 2.7 eV, is due to electrons scattered from O atoms. The composition of the films was determined directly from elastically scattered electrons, with the angle and energy dependence of scattering providing additional information about the depth distribution of the implanted oxygen. Electronic structure of the films can be derived from inelastic electron scattering, and the measurement of this energy loss features from the inelastic processes is also termed as reflection electron energy loss spectroscopy (REELS). As shown in **Fig. 3** with a 40 keV electron beam along the surface normal, fingerprints of the electronic structure besides the oxygen peak were recorded. *Inspection of the O elastic peak as marked by the short-dashed line, a tiny peak (due to surface oxidation) and a strong peak for the Ta and Ta₂O₅ samples, respectively. Moreover, the intensity increase with the increase of O fluences in the implanted samples is evident.* Implantation with increasing O fluence up to 5×10¹⁷ cm⁻² dramatically suppresses the signal from the metallic Ta phase at ~ 21 eV. In addition, a shoulder due to the formation of Ta₂O₅ appears in the region from 15 to 30 eV and its intensity becomes more pronounced with increasing O fluence. The trace of the Ta metal plasmon peak at the highest implantation fluence indicates that part of the loss spectrum originates from larger depths than the maximum implantation range of 10 keV O ions. An onset of a continuous broad distribution near 4.5 eV observed in both **Figs. 2** and **3** is due to electrons scattered elastically from Ta and additional electronic excitation with the minimum energy loss in Ta₂O₅ set by the band gap of 4.5 eV.

C. Raman Spectroscopy

Raman spectroscopy is known to be sensitive to the nature of chemical bonds in solids and is used to observe vibrational, rotational, and other low-frequency modes in a solid. The technique relies on inelastic scattering of a monochromatic light. As a result of the interaction of the laser light with molecular vibrations, phonons or other excitations, the energy of the laser photons can be shifted up or down, which then contains information about the vibrational modes in the sample. Raman spectroscopy has been increasingly applied for the structural characterization of ion-beam modified materials, such as in carbides [36-38] and oxides [39-42]. More recently, micro-Raman spectroscopy has been used to characterize the damage created over the entire ion range [36, 41, 42] to provide new information on quantification of the damage and structure modification as a function of depth, and on enlightenment of possible synergistic effects due to both nuclear and electronic energy deposition to the materials [31].

Utilizing complementary analytical techniques described in this article (RBS and XRD) and electron microscopy techniques [15,16], Raman spectroscopy studies have revealed ion-induced structural modifications (defects, distortion of bonds, fluorite phase transformation and amorphization) in binary oxides, such as zirconia [40], ceria and urania [41], and more complex oxides, such as pyrochlores [39, 43]. In nanocrystalline monoclinic ZrO_2 thin films, Raman spectroscopy has been utilized to characterize the structural changes and phase evolution as a function of increasing fluence induced by the swift heavy ion irradiation [40], and the result indicates that such highly ionizing irradiation of 1.33 GeV ^{238}U with an electronic energy loss of 52.2 keV nm^{-1} can induce full amorphization at a fluence of $1 \times 10^{13} \text{ cm}^{-2}$ without any intermediate transformation to other zirconia polymorphs. In pyrochlore materials, as potential matrices for nuclear waste disposal, the chemical composition has a strong effect on the character and energetics of the type of structural modifications that can be obtained under irradiation [39,43]. A review of detailed Raman studies of $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore response to irradiation has revealed a consistent behavior that high-dose irradiation results in the amorphous state in Ti-rich pyrochlores as the final phase whereas the disordered, defect-fluorite structure is the stable phase under the same conditions in Zr-rich pyrochlores [39].

Raman spectroscopy has often been implemented in a geometry where the direction of the laser beam aligns with that of the ion beam (i.e., normal to the sample surface). Such conventional use of Raman spectroscopy does not allow probing depths exceeding several micrometers and especially does not provide quantitative analysis at a fixed damage level.

Recent developments have shown that micro-Raman can be employed to quantify the damage in the wake of energetic ions from the

Fig. 4 Raman line scan of a He irradiated UO_2 sample (25 MeV , $1.6 \times 10^{16} \text{ cm}^{-2}$) and the corresponding SEM cross-section image. A SRIM-predicted depth profile of energy deposited by the He ions is included. The dashed lines show the correspondence between grain boundaries and sharp peaks in the Raman intensity [41].

surface of a crystal to the depth at which the ions come to rest (tens of micrometers) by analyzing thin cross sections of irradiated bulk samples [36, 38, 41, 42]. Such cross-sectional approach provides several salient outcomes, such as distinctive effects of nuclear and electronic mechanisms resulting from the ion slowing down processes and information regarding the final structure of ion-irradiated materials along the ion path. Micro-Raman experiments have been performed on cross sections of 6H-SiC crystals irradiated with heavy ions of both low and intermediate energies [36]. The results have revealed that while ballistic collisions lead to the amorphization of the surface region of samples under 900 keV I irradiation where the nuclear stopping power is significant, the ionization effect in the surface region under 36 MeV W irradiation where electronic stopping power prevails does little to the crystalline structure and amorphization occurs only at the end of the ion path.

One of the recent developments includes an *in situ* Raman setup coupled with a cyclotron accelerator developed at CEMHTI laboratory (Orléans, France) that allows direct monitoring of the irradiation-induced changes in solid samples and at solid/fluid interfaces in real time [41, 42]. Uranium dioxide (UO_2) is currently the standard fuel used in light water reactors, and its response to ion irradiation is of great interest for the nuclear industry. Utilizing this unique capability, *in situ* Raman measurements

were carried out to probe ion beam irradiation-induced damage and their in-depth profiles on a UO_2 sample under 25 and 45 MeV He^{2+} cyclotron beam irradiation (under reducing Ar/H_2 atmosphere) to a fluence of $1.6 \times 10^{16} \text{ cm}^{-2}$ [41, 42]. The depth profile of 25 MeV implanted He was estimated using the stopping and range of ions in matter (SRIM) code (<http://www.srim.org/>), as shown in **Fig. 4** (white solid line). The 2D color map of 776 Raman spectra recorded with 633 nm of He-Ne excitation laser in **Fig. 4** clearly shows the most prominent characteristic feature of UO_2 (T_{2g} Raman-active mode) appearing at 445 cm^{-1} , one additional peak at 550 cm^{-1} corresponding to imperfections at grain boundaries, and a triplet of the defect peaks resulting from He irradiation appearing in the $500\text{--}700 \text{ cm}^{-1}$. The in-depth distribution of these three defect bands at 530, 575, and 635 cm^{-1} inside the sample exhibits a clear increase of the damage from the surface up to the depth of the implanted He, and the high-resolution mapping reveals the spatial evolution of the defect bands. In addition, kinetic evolution of the triplet can be well described by a simple direct-impact model with a constant annealing rate, in agreement with results from a X-ray diffraction study in alpha-irradiated urania [44].

In carbon materials, mechanical properties can be improved and the synthesis of new phases can be induced by introducing controlled amounts of

lattice damage, such as by ion modification. Quantifying defects is essential to both fundamental understanding and practical applications. In graphene, this is a key step toward the understanding of the limits to its ultimate electron mobility [45]. Raman spectroscopy has demonstrated, as shown in **Fig.**

5, its unique power to quantify defects (point defects in the sp^2 carbon lattice) and disorder (one-dimensional defects with respect to the

Fig. 5 Raman spectra of five Ar^+ bombarded single layer graphene under excitation energy of 2.41 eV (wave length of 514.5 nm). The Ar^+ (90 keV) implantation was performed with a large incident angle of 45° with respect to the surface normal, and ion fluence ranges from $1 \times 10^{11} \text{ cm}^{-2}$ to $1 \times 10^{15} \text{ cm}^{-2}$ [45].

crystallite size). Single layer graphene (SLG) samples were irradiated using 90 keV Ar^+ ions. A large incident angle of 45° with respect to the surface normal was applied to create single and double vacancies in the graphene lattice. Ion fluence ranging from $1 \times 10^{11} \text{ cm}^{-2}$ to $1 \times 10^{15} \text{ cm}^{-2}$ were utilized to create defects with average distance, L_D , varying from 24 nm (one defect per 4×10^5 C atoms) to 2 nm (one defect per 4 C atoms), respectively. The D peak at $\sim 1350 \text{ cm}^{-1}$ is due to the breathing modes of six-atom rings and requires a defect for its activation, and the G peak at $\sim 1580 \text{ cm}^{-1}$ is due to the high frequency E_{2g} Raman allowed optical phonon at the Brillouin zone center. The 2D and 2D' peaks are the second order of the D and D' peak, respectively. With increasing irradiation fluence, a significant increase in the D peak intensity and decrease in the 2D peak intensity are observed in **Fig. 5**, reflecting the evolution of the electronic band structure. This suggests structural evolution from graphene to graphite, to nanocrystalline graphite, and to the onset of the low sp^3 amorphous carbon [45]. The loss of sharp second order features in the Raman spectrum obtained from the $L_D = 2 \text{ nm}$ is an evidence for the latter.

D. X-ray based techniques

In the past decade, there has been a renewed interest for X-ray based techniques to investigate ion-beam-induced modifications of materials. Two main advanced techniques, HRXRD and SAXS that both combine state-of-the-art experimentation and simulation approaches, have clearly demonstrated their potential in this field. HRXRD can be employed to measure the strain in strain-engineered materials for enhanced physical properties [46, 47], and to examine correlation between strain/stress and disorder in materials subjected to ion irradiation [30, 48]. SAXS allows characterization of density changes on the nanoscale associated with irradiation-induced microstructural transformations, such as formation of extended defect [50], modification of nanoparticle shape [49,51], and creation of ion tracks [23, 52]. A brief description of both techniques is presented below, and some recent results are discussed to illustrate their analytical power.

D.1. High-resolution X-ray diffraction

Basic research on ion-beam-induced modifications of materials is frequently conducted on model, single-crystalline bulk materials or high-quality epitaxial layers for which advanced, dedicated characterization techniques are required. The use of high-resolution XRD allows an accurate study of ion-beam-induced modifications of materials in such model materials. High-resolution can be achieved on laboratory equipment with suitable primary optics (mainly X-ray mirrors and multiple reflection monochromators) that provide an intense and monochromatic X-ray beam. In addition, the diffracted X-rays can be spatially or angularly discriminated using a narrow slit or a crystal analyzer in front of the detector, respectively, thereby allowing to achieve a series of so-called coupled omega-2theta scans. The recording of reciprocal space maps (RSMs) provides a two-dimensional distribution of the scattered intensity in the vicinity of a Bragg reflection. The use of position sensitive detectors, instead of a slit- or analyzer-based detection system, dramatically reduces the counting times [53].

To extract the maximum information from these measurements, simulation of the experimental data is possible, which gives access to strain and disorder depth profiles. Recently, a new computer program, implementing the dynamical theory of XRD for distorted crystals, was developed to fit HRXRD experimental curves recorded on irradiated single-crystalline ceramics, such as cubic zirconia (c-ZrO₂) [30] and SiC [54], and can be applied to both metals and semiconductors. In this simulation approach, the irradiated layer is divided into lamellae that are characterized by given strain and disorder (*i.e.* static Debye-Waller) levels.

B-spline (*i.e.* piecewise third degree polynomials) functions are used to describe

Fig. 6 HRXRD patterns (dots) recorded in the vicinity of the (400) reflection for c-ZrO₂ crystals irradiated with 4 MeV Au²⁺ ions at 80 K. From bottom to top, curves correspond to the virgin crystal and crystals irradiated at fluences of 5×10^{12} , 10^{13} , 2.5×10^{13} , 10^{14} , 2×10^{14} , 10^{15} , 5×10^{15} cm⁻². Solid (black) lines are the best fits. Curves are shifted vertically for clarity purposes.

both strain and disorder depth profiles, which ensures that the solutions are continuous and do not display unphysical oscillatory behavior. The resolution of the diffractometer is taken into account by convolving the calculated curve with a pseudo-Voigt function (i.e. the linear combination of a Lorentzian and a Gaussian function) whose shape is adjusted such that the peak corresponding to pristine crystals is correctly reproduced. The generalized simulated annealing (GSA) algorithm is used to rapidly and efficiently obtain best-fit simulations. In brief, the GSA algorithm is a global optimization approach based on random variations (with decreasing amplitude on the basis of an artificial decreasing temperature) of the parameters entering the model to be optimized until an equilibrium state, i.e. the best solution, is reached. It mimics the motion of atoms observed during the annealing of materials.

Numerous studies of radiation effects in ceramic oxides, such as c-ZrO₂, have been undertaken. Together with other complementary techniques, such as RBS (see **Sect. A**) and TEM [15], HRXRD was utilized to study irradiation effects in c-ZrO₂ single-crystals irradiated with 4 MeV Au²⁺ ions over a broad

Fig. 7 Strain (a) and disorder (b) depth distributions corresponding to simulation of XRD curves presented in Fig. 6 (the same color code). From bottom to top, curves correspond to fluences of 5×10^{12} , 10^{13} , 2.5×10^{13} , 10^{14} , 2×10^{14} , 10^{15} , 5×10^{15} cm⁻². The dashed line refers to a region near the surface where the very high disorder level prevents quantitative assessment of the strain level.

range of fluences and temperatures. An example of XRD spectra and the corresponding simulations for crystals irradiated at 80 K is presented in **Fig. 6**. The peak at high diffraction angle originates from the undamaged part of the crystal, and its position corresponds to the theoretical Bragg angle of the (004) reflection. After irradiation, an additional peak at lower angle is observed, indicating that tensile strain is induced by ion-induced damage in the irradiated area. The position of this additional peak moves towards lower angles with increasing fluence, which clearly suggests an increase in the tensile strain. Interference fringes between the Bragg peak and the additional peak indicate the existence of a strain gradient,

whose shape can be recovered by the simulation of the diffraction curve. The strain and disorder depth profiles obtained from the fitting are displayed in **Fig. 7**. It is readily observed that both strain (**Fig. 7(a)**) and disorder (**Fig. 7(b)**) distributions broaden with increasing fluence and concurrently their maximum level also increases. The shape of the disorder profiles is comparable to that of profiles obtained by RBS/C, as shown in **Fig. 1**. By monitoring the maximum strain and disorder levels with fluence, it is possible to determine damage accumulation kinetics, such as those obtained from RBS/C experiments [30]). In the case of zirconia [30], analysis of the kinetics indicates that, independent of the irradiation temperature, the material adapts its microstructure to sustain the radiation damage: the defect structure changes from small isolated point defect clusters to dislocations loops and, finally, to an intricate network of dislocations. Furthermore, elastic strain associated with defect clusters formed in the primary stage of the irradiation process does not seem to trigger the observed subsequent microstructural transformations.

Implantation-induced effects in ion-doped semiconductors have also been investigated using HRXRD, for instance in Fe-implanted SiC to form a diluted magnetic semiconductor [55] or in Eu-implanted GaN for optoelectronic applications [48]. In the latter case, it was shown that nanocrystallization (i.e. the fragmentation of the single crystal into nanocrystals) at the surface of implanted samples was triggered by defect diffusion towards the surface due to the high strain levels in the buried regions. Elastic strain or elastic energy was also shown to have a dramatic influence on the amorphization process of irradiated SiC. In fact, combining molecular dynamics (MD) simulations and HRXRD experiments, it was demonstrated that the elastic energy associated with the presence of point defect clusters formed in the early stage of irradiation promotes defect clustering and thus accelerates the amorphization process. [54].

D.2. Small-angle X-ray scattering

Scattering of X-rays or neutrons into small angles (typically between 0.1° and 10°) is originated by density fluctuations on nanometer length scales and is commonly used to obtain information on the size, shape and spatial arrangement of ensembles of nanometer-sized objects. As a consequence, SAXS is a

technique particularly well suited for the study of ion irradiation induced tracks. Indeed, these columnar ‘cylindrical’ objects are often characterized by a change in density with respect to the surrounding matrix and they sample a large volume of matter. If generated in an accelerator, an ensemble of ion tracks comprises parallel almost identical nano-sized objects with stochastic spatial arrangement and negligible overlap at low irradiation fluences (in the order of 10^{11} cm^{-2}). As a result, the observed scattering from typically $\sim 10^7$ ion tracks is representative of the individual track structure averaging out fluctuations on an atomic level. SAXS was already used successfully in early 1980’s to measure ion tracks in mica and polymer materials [56]. The following examples highlight its ability to resolve structural details difficult or impossible to attain with other techniques.

The characterization of ion tracks in amorphous materials is very challenging as most techniques are not sensitive enough to measure the subtle density changes that often characterize the tracks in these materials. In amorphous SiO_2 for example, where ion tracks have long been studied using chemical etching, only recently details on the track structure were discovered by SAXS [23]. The track radial density distribution was found to be that of a core-shell cylinder with an under-dense core and an over-dense shell compared to that of un-irradiated material [23]. As an example, Fig. 8 shows a schematic of the scattering geometry and a typical scattering image (a), and extracted scattering intensities together

Fig. 8 (a) Schematic of the SAXS measurement geometry and SAXS detector image of ion tracks in amorphous SiO_2 , typical of a core shell cylinder. (b) Angular distribution of the scattering intensity of ion tracks in amorphous SiO_2 generated by irradiation with 185 and 27 MeV Au ions (symbols) and corresponding fits with the core shell model (solid lines) [23]. (c) Density distribution extracted from the fit to the SAXS data from tracks generated by 185 MeV Au ions (solid line). The dotted line shows the density distribution from MD simulations for these irradiation conditions.

1 with the corresponding fits to the core shell model (b), the latter clearly confirming the dependence of the
2 track dimensions on the irradiation energy [23]. A track radial density distribution corresponding to the
3 fitted parameters is shown in (c) together with the density distribution extracted from MD simulations for
4 the same irradiation energy. The simulations reproduce the core shell structure with strikingly similar
5 dimensions. The core-shell track structure was pivotal in explaining a process by which metallic
6 nanoparticles are elongated by swift heavy ion irradiation [51,57]. In amorphous Si and Ge, where ion
7 tracks were inferred from macroscopic plastic deformation observed after high fluence swift heavy ion
8 irradiation, SAXS measurements provided clear evidence for their existence and also revealed core shell
9 track structures [4,58]. In Ge, single ion tracks additionally consist of bow tie shaped voids [4], which
10 form the precursors for the observed porosity at higher irradiation fluences.

11 In addition to the materials described above, tracks in amorphous metallic alloys are characterized
12 by a cylinder of constant density different from that of the surrounding material with a density change of
13 less than 0.1% [59]. Combining SAXS with simultaneously performed wide-angle X-ray scattering
14 measurements, it was shown that the existence of the ion tracks enhances the recrystallization of the
15 amorphous metallic alloys consistent with a melt-quench process during ion track formation different
16 from that operational during the production of the metal [60].

17 A number of crystalline materials form amorphous track structures. While such tracks are
18 generally observable by TEM [63], SAXS enables to determine the average track radii with Angstrom
19 precision. In natural quartz and apatite, an increase in the track radius of about 1Å/100°C with increasing
20 irradiation temperature was resolved [61]. The technique is also well suited to study the annealing kinetics
21 of such ion tracks using *in situ* and *ex situ* annealing experiments, as recently demonstrated for natural
22 apatite [62]. Radial re-crystallisation with an activation energy similar to that obtained from etching
23 experiments was observed. Furthermore, the tracks show a density difference of about 1% compared to
24 the crystalline matrix in agreement with MD simulations.

25 In quartz, the density difference of the amorphous tracks amounts to ~ 2%, significantly different
26 from values of up to 15% reported for ‘unconstrained’ amorphous SiO₂ [63]. The track radii determined

by SAXS are generally smaller than those measured by RBS/C originating from a defective halo around the amorphous track core that has no appreciable density difference yet leads to de-channelling [57, 63]. This highlights the fact that SAXS often provides complementary information to other techniques.

E. Positron annihilation spectroscopy

Positron annihilation spectroscopy is an effective method for the investigation of open volume structures in materials [63]. In particular, PAS has been widely applied to study ion beam induced vacancy-type (point or clustered) defects in metals and semiconductors, [64-69]. Positrons implanted into a sample can get trapped in and localize at neutral and negative vacancies due to the missing positive ion core. The trapping of positrons at these defects is observed as well-defined changes in the positron-electron annihilation radiation, i.e., as an increase of the positron lifetime and a narrowing of the momentum distribution of the annihilating positron-electron pair (Doppler broadening). The combination of experimental techniques with theoretical calculations provides means to deduce both the identities (sublattice, decoration by impurities) and the concentrations of the vacancies [64]. In the majority of ion beam damage studies with positrons, a variable-energy slow positron beam is employed. As the implantation energy and hence the depth distribution of the positrons can be controlled, this approach allows studying irradiation damage in thin films as well as the depth profile of ion implantation-induced damage up to a few microns from the material surface. Performing positron lifetime experiments with a slow positron beam is complicated and access to such experiments is limited [64], hence the vast majority of the studies are performed by measuring the Doppler broadening of the 511-keV positron-electron annihilation radiation peak. The shape of the spectrum is typically described with two parameters, S and W. The low-momentum parameter S is the fraction of counts in the central region of the peak, whereas W corresponds to the fraction of counts in the wing areas on both sides of the peak, making it more sensitive to highly localized core electrons. Typically, an increase in the value of S indicates an increase in open volume defects in the depth being probed. The value of W is more dependent on the type of atoms surrounding the annihilation site.

In order to illustrate the sensitivity of the PAS technique, **Fig. 9** shows recent results obtained in ion beam damaged zinc oxide (ZnO), which is considered as an alternative to gallium nitride for use in optoelectronic devices. In this figure, positron annihilation data (S parameter) are plotted as a function of positron implantation depth. The region of constant S extends up to about 10 keV in the thin film samples (grown by molecular beam epitaxy) [70] and provides the characteristic value of the ZnO layer. This corresponds to a layer thickness of ~ 500 nm, as the positrons probe the material to a depth corresponding to double of the mean implantation depth (the decrease of the S parameter at higher energies is due to the increasing fraction of positrons annihilating in the sapphire substrate, for which the characteristic S parameter is roughly $S = 0.41$). The high S parameter values at low implantation energies (less than 5 keV) characterize the positron surface state and the diffusion of positrons into the surface. It is clearly seen that the S parameter characteristic of the thin film increases with the 2 MeV O^+ irradiation fluence, albeit it is already above the ZnO lattice value in the as-grown sample. Detailed analysis of the S and W parameters (see Fig. 2 in Ref. [70]) shows that the increase in S parameter is due to Zn vacancies for the lower fluence, but clustering of Zn and O vacancies takes place in the higher-fluence irradiated material [70]. In the He and Li implanted samples (bulk ZnO crystals grown by the hydrothermal method) [65], the S parameter increases strongly after the initial decrease when moving away from the sample surface. This increase corresponds to the strong damage near the projected range ($1.9 \mu\text{m}$) of the 840-keV Li^+ and 680-keV He^+ ions. It is important to note that the positron implantation profile is roughly twice as wide as the mean implantation depth, causing the maximum of the S parameter profile to emerge at mean implantation depths less than $1 \mu\text{m}$. Moreover,

Fig. 9 S parameter as a function of positron implantation energy and mean penetration depth in ion-irradiated ZnO samples. The dashed line shows the S parameter characteristic to the ZnO lattice. The data are adapted from Refs. [65] and [70].

1 detailed analysis shows that the elevated S parameter is due to strong clustering of multiple Zn and O
2 vacancies.

3 Measurements with two high-purity Ge detectors in coincidence dramatically improve the peak-
4 to-background ratio of the Doppler-broadened annihilation peak, and hence provide access to the details
5 of the positron-electron momentum distribution [64]. In the above examples, these kinds of measurements
6 allowed to clearly distinguish between isolated Zn vacancies and vacancy clusters with varying numbers
7 of Zn and O vacancies. In particular, by performing additional electrical measurements, it was possible to
8 conclude that the Zn vacancies introduced in the irradiation act as dominant compensating centers on n-
9 type conductivity and eventually cause electrical isolation if the original doping level is moderate [70],
10 while vacancy clusters are mostly electrically inactive. This powerful method of detailed defect
11 identification has been recently used for a range of materials. The identification of $V_{In}-nV_N$ complexes in
12 InN [71], Li- and H-related defects in ZnO [72], analysis of E-center-Ge complexes in SiGe [73], and
13 shedding light on the vacancy clusters in SiC [74] serve as good examples. On the metal side the
14 emphasis has been on studying vacancy-induced precipitation of impurities and alloy elements, such as
15 Cu in Fe or Mg in Al [75] .

16 **3. Perspectives**

17 This review draws attention to some recent advances in characterization techniques using
18 electrons, ions, photons, and positrons to investigate ion beam modified materials. The insights provided
19 from the techniques, including RBS, eRBS, Raman spectroscopy, HRXRD, SAXS, and PAS, have
20 contributed significantly to our fundamental understanding over a wide range of conditions essential for
21 enhancing material performance and also for design and synthesis of new materials to address a broad
22 range of future technologies and applications. To better characterize ion beam induced effects in
23 materials, to get the most comprehensive understanding of the physical mechanisms at the origin of these
24 effects, and to address new, challenging issues, further developments in the characterization techniques
25 and data analysis are required.

Advances in characterization techniques follow the development of the instrumentation. For ion channeling experiments, a new methodology has been recently proposed based on the use of position sensitive detectors for fast recording of RBS/C angular scans. The corresponding 2D channeling patterns can be used to evaluate the disorder and calculate the strain state of thin films with high depth resolution. Monte Carlo simulations performed with dedicated codes [76] allow an accurate determination of the strain even in some challenging cases where the angular shift [between the minima of the angular scans of the pristine and strained materials](#) is close to 0° . This method was first successfully used to determine the strain of different as-grown GaN-based heterostructures close to lattice-matched conditions [77]. Its applicability to irradiated materials was very recently demonstrated in irradiated c-ZrO₂ single crystals that were previously characterized by HRXRD. This newly developed eRBS technique is based on relatively simple equipment and has the potential to be integrated in a scanning electron microscope (SEM) where the use of a focused electron beam would enable laterally resolved analysis [32]. For PAS experiments, technical development is driven towards pump-probe methods to allow advanced sample state manipulation eventually with pump-probe capability of light, bias, magnetic field, temperature, and pressure and to enable systematic and selectively sensitive studies in materials with complex crystalline order [\[64\]](#).

Advance in characterization techniques also follows the development of theoretical models and interpretation of the techniques. Since the simulation of HRXRD data is based on a phenomenological description of the defective crystal, no direct information is provided on nature of the defects and their density. To overcome this limitation, a new approach must be implemented where the actual crystal structure is described using the elastic strain fields of individual defects, obtained from elasticity theory or atomistic computations. The most important challenge in describing the structure of an actual single crystal with macroscopic dimensions is the huge computing power that is required. The latest developments in parallel computing now make this task conceivable. Similarly, future improvements in modelling of the SAXS data [from ion tracks](#) using Monte Carlo methods that include [density](#) variations along the track axis will provide an important step to a more accurate characterization of the track

structure using this technique. This is, for example, desirable to quantify track fragmentation during annealing observed in olivine [78] and to characterize the track structure near the formation threshold. Detailed interpretation of experimental PAS data in systems where the 3D periodicity is broken, namely surfaces and interfaces between crystalline solids, as well as nanocrystalline or amorphous systems, requires further development of theoretical methods. In particular, the description of positron states, thermalization, and trapping in these kinds of materials are not well established.

Combined studies of characterization with advanced computational approaches always strengthen the research effort. The computational work, which can be conducted at different time and length scales, provides underlying physics and interpretation of experimental findings [8, 11, 23, 54, 64, 74]. One example is the recrystallization phenomenon occurring in damaged SiC upon swift heavy ion irradiation: this process was first observed by RBS/C and then well supported by the results from MD simulations [11]. Another example in SiC is given by a recent work where vacancy-type defects observed by PAS were identified by performing electronic structure calculations [74]. A more integrated approach, computational-guided experiments, can also be realized. One [demonstrated](#) example is a recent work of amorphization process of SiC [54], where the analysis of experimental [and simulated](#) XRD patterns allows the interplay between disorder, swelling and defect energy.

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