1 **Analysis of hydrogen adsorption and surface binding configuration on**
2 **tungsten using direct recoil spectrometry**

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9 **Abstract** – In this work, we apply low energy ion beam analysis to examine directly how the
10 adsorbed hydrogen concentration and binding configuration on W(100) depend on temperature. We
11 exposed the tungsten surface to fluxes of both atomic and molecular H and D. We then probed the H
12 isotopes adsorbed along different crystal directions using 1-2 keV Ne⁺ ions. At saturation coverage, H
13 occupies two-fold bridge sites on W(100) at 25 °C. The H coverage dramatically changes the behavior
14 of channeled ions, as does reconstruction of the surface W atoms. For the exposure conditions
15 examined here, we find that surface sites remain populated with H until the surface temperature
16 reaches 200 °C. After this point, we observe H rapidly desorbing until only a residual concentration
17 remains at 450 °C. Development of an efficient atomistic model that accurately reproduces the
18 experimental ion energy spectra and azimuthal variation of recoiled H is underway.

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35 **I. Introduction**

36 Adsorption, recombination, and exchange of hydrogen isotopes on surfaces are of fundamental
37 interest from the perspective of fuel recycling from plasma-facing materials in magnetic fusion
38 devices. The atomic-scale details of these processes are difficult to resolve experimentally, largely
39 because most surface analysis techniques cannot detect adsorbed hydrogen. Two exceptions include
40 low energy ion scattering (LEIS) and direct recoil spectrometry (DRS), both of which provide direct
41 information on the adsorbed hydrogen configuration on surfaces, as well as binding energies and
42 exchange kinetics. Such insight complements ongoing fundamental atomic-scale modeling efforts (e.g.
43 density functional theory or molecular dynamics) that focus on simulating the complex chemical
44 effects that occur when surfaces are exposed to high flux plasmas. Experiments are needed to test
45 these models, thereby motivating further refinements to interatomic potentials and other simulation
46 inputs.

47 Both LEIS and DRS are forms of low energy ion beam analysis which provide both composition
48 and structural information, with high surface-specificity (< 1 nm sampling depth.) In terms of the
49 underlying physics, these techniques bear many similarities to their higher energy counterparts,
50 Rutherford backscattering spectrometry and elastic recoil detection. We refer the reader to several
51 excellent reviews [1,2] for further details. In our prior work, we used LEIS and DRS to study the
52 hydrogen binding configuration along open channels on the W(100) crystal plane [3]. While we were
53 able to identify definitively two-fold bridge sites as the preferred binding site for complete coverage
54 of the W surface with hydrogen, the details of the binding configuration at lower coverage were still
55 unclear. Furthermore, the equilibrium surface coverage as a function of temperature was left
56 unaddressed in our prior work. While this could be inferred from the H evolved from the surface
57 during thermal desorption, DRS provides a direct measure. This coverage dependence is somewhat
58 complicated due to reconstruction of the surface as the adsorbed H desorbs, where W surface atoms
59 are displaced out of ideal bulk-terminated sites.

60 With the above concerns in mind, we address the temperature/coverage effects in greater detail in
61 the present study. We use ion focusing along surface channels as a sensitive means of determining the

hydrogen concentration present on the surface. To calibrate this process, we dosed the surface with molecular hydrogen (^1H) and deuterium (^2H), and measured the recoiled adsorbate signals as a function of temperature under a variety of conditions, with the eventual goal of comparing our results with recently-developed models of surface adsorption/recombination kinetics [4]. For comparison, we also performed a single set of measurements to study the adsorption of atomic D.

To complement our experimental results, we are developing a molecular dynamics (MD) model to simulate H migration on the W(100) surface. The use of MD allows for the inclusion of more sophisticated potentials and provides a more realistic calculation of interatomic forces than possible with the binary collision approximation models that are frequently used as inputs to recycling calculations. For the purpose of modeling the LEIS/DRS experiments, an MD framework to directly simulate Ne^+ scattering on the crystal surface is also under development.

II. Experiment

Our scattering experiments were performed using an ion energy spectrometer, which has been previously described in Ref. 5. Briefly, the system includes an ion source that produces mass-separated beams through electron bombardment of inert gases. Scattered or recoiled particles are detected with a hemispherical analyzer (50 mm radius) with a 2° acceptance angle. For this set of measurements, we used beams of low energy (1 keV and 2 keV) Ne^+ ions to characterize a 7 mm diameter, 1 mm thick W single crystal (MaTecK GmbH) that had been polished and aligned to within 0.1° of the (001) plane. We secured the crystal with Ta wire along its outer circumference to a button-style heater and an isolating sapphire disc. A well-ordered, clean sample surface could be achieved through repeated cycles of sputtering with 2 keV Ne^+ ions at grazing incidence followed by heating to 450°C . The Ne^+ ion beam (100 nA current) could be focused to a 0.5 mm spot, which was then rastered over a $2\text{ mm} \times 2\text{ mm}$ area, producing an incident flux of $1.5 \times 10^{13}\text{ cm}^{-2}\text{s}^{-1}$. The raster amplitude was adjusted with incidence angle to maintain a constant spot size and flux on the sample surface. To verify that the low flux from the Ne^+ analysis beam did not damage the surface, we frequently compared with a set of measurements that were performed shortly after the pristine crystal

88 was inserted into our vacuum system. The scans were identical, suggesting that the beam had a
89 negligible effect on the surface structure.

90 The concentration of hydrogen isotopes on the W crystal surface could be controlled by varying
91 the surface temperature or the incident flux of hydrogen isotopes. For the purposes of dosing, we
92 introduced the hydrogen through a tungsten capillary (1 mm inner diameter) into our vacuum system.
93 The tungsten capillary could be heated by electron bombardment to 1700 °C to assure 100%
94 dissociation of the effusing hydrogen flux [6], thus allowing us to dose with either atomic or
95 molecular species. The atomic state of the flux from our doser was confirmed by examining D
96 adsorption on an Al(100) single crystal cooled with liquid nitrogen to -160 °C. In contrast to W, prior
97 measurements indicate a very low sticking coefficient ($< 10^{-4}$) for D₂ on Al(100), whereas atomic D
98 has a high sticking coefficient (0.6 ± 0.1) [7]. Exposure of our Al crystal to atomic D rapidly
99 increased the height of the associated recoil peak, whereas D₂ exposure produced no observable
100 difference.

101 The key geometrical parameters for this set of experiments are illustrated in Fig. 1(a), including
102 the angle of incidence of the analysis beam (α), the azimuth on the W(100) surface (ϕ), and
103 observation angle (θ). Recall that the energies of the scattered and recoiled particles are used to
104 identify species present on the surface. Fig. 1(b) shows ion energy spectra for 2 keV Ne⁺ → W(100)
105 in cases where the surface is exposed to background gases present within the vacuum system only as
106 well as during exposure to D₂(g). Note that we have normalized all energies relative to that of the
107 incident beam (E_0). Within the two spectra, three prominent peaks are readily visible, corresponding
108 to H, D, and W present on the surface. The vertical lines indicate the theoretical positions for these
109 peaks, calculated using classical kinematics and ignoring any inelastic energy loss mechanisms. Based
110 on calculations using the binary collision code MARLOWE [8], the smaller peak centered at
111 $E/E_0 \approx 0.75$ is attributed to a more complex scattering process involving multiple collisions of Ne⁺
112 ions with the H layer and W substrate. Even when the surface is not dosed, a peak associated with
113 recoiled H is still present, which we attribute to dissociative chemisorption of residual H₂(g) in our
114 vacuum system. Hydrogen dissolved within the W lattice may also diffuse to the surface, although

115 this is expected to be only a minor contribution to the H surface concentration at room temperature.

116 Using D₂ as the exposure gas helps to circumvent this issue.

117 Once the surface was exposed to D₂(g), the H signal diminished rapidly and the W signal
118 decreased slightly. We systematically tested different molecular fluxes to the surface, finding that
119 saturation coverage at 25 °C could be assured with a partial pressure of 3.0×10^{-7} Torr. This
120 concentration depends on a dynamic equilibrium dictated by the arrival rate of H₂(g), the sticking and
121 reflection coefficients, as well as the desorption rate due to recombination. One key concern is that the
122 incident ion beam used for our measurements also contributes to desorption. To minimize this effect,
123 we ensured that the exposure flux produced an arrival rate of H₂(g) at the surface that much higher
124 than that of the incident Ne⁺ ions. Based on the kinetic theory of gases, the aforementioned partial
125 pressure of 3.0×10^{-7} Torr corresponds to a flux of 3.0×10^{14} D₂ cm⁻²s⁻¹, or a factor of 20 higher than the
126 ion arrival rate at the surface. In practice, because the angular distribution of emitted particles is
127 highly peaked along the capillary centerline, the arrival rate of D at the sample surface is much higher
128 than estimated above.

129 We were able to calculate the chemisorbed concentrations of H and D by integrating the area
130 under each peak and correcting the result for the recoil cross-sections for each species. For 2 keV Ne⁺
131 and a laboratory recoil angle of $\theta=25^\circ$, the relevant cross-sections are: 5.93×10^{-2} Å²/sr (H) and
132 2.96×10^{-2} Å²/sr (D). These values were calculated using the Biersack-Haggmark approximation for
133 the scattering integrals and assuming a ZBL interatomic potential [9]. Assuming that the dosed case
134 shown in Fig. 1(b) corresponds to saturation, the H coverage is 6%, with the remaining D comprising
135 94% of the total. Note that this analysis assumes that the surface H and D occupy the same adsorption
136 sites.

137 **III. Coverage as a function of temperature**

138 To understand the coverage dependence as a function of temperature better, we performed a
139 systematic series of controlled adsorption experiments, in a manner similar to the procedures specified
140 in Ref. 4. This involved rapidly heating the crystal to 450 °C while exposing the sample to different

fluxes of deuterium or protium. In each case, the sample was held at 450 °C for 30 min and then allowed to cool at a linear rate of 7.1 °C/min. (This corresponds to a 1 hr cooling time from 450 °C to room temperature.) The observed concentrations during adsorption were found to be independent of the cooling rate up to 14.2 °C/min. During the entire process, we monitored the recoiled peak height corresponding to hydrogen isotopes adsorbed on the surface. We obtained all measurements using a 2 keV Ne⁺ beam at an incidence angle of $\alpha=80^\circ$ to probe the hydrogen present along <100> surface directions.

In Fig. 2, we show recoil signals from D adsorbed on the W(100) surface as the temperature is slowly cooled from 450 °C using the procedure described above. In case (a), three different D exposure pressures are considered, ranging over an order of magnitude between 7.4×10^{-8} Torr to 1.1×10^{-6} Torr. To aid in the interpretation of the data, we rendered the adsorption isobars as Arrhenius plots. In addition, we assumed that once the surface temperature declined below 100 °C, the surface was saturated with D, hence the isobars were normalized to this saturation condition. Keep in mind that the sampling depth of our analysis beam at oblique incidence is < 1 nm, hence all signals shown here correspond to D present on the surface. Regardless of the exposure pressure, the same basic adsorption curve shape is evident. In the Arrhenius coordinates, the quantity adsorbed follows a nearly linear dependence at temperatures greater than 300 °C. Afterward, the slope of the isobar decreases until it reaches a constant level for $T < 150$ °C. As shown in case (a), modifying the exposure pressure offsets the adsorption profile along the $1/T$ axis without affecting its slope.

It was also of interest to determine whether dosing the samples with atomic D versus D₂ would produce any appreciable difference in the quantity adsorbed on the surface. Adsorption curves for both cases are shown in Fig. 2(b). We could not discern an appreciable difference within the error of our experiment. We also noted a slight offset between chemisorption of H₂ vs. D₂ on the surface, but the difference was very slight and within the experimental error.

IV. Variation of binding configuration as a function of temperature

For single crystal surfaces, it is possible to use LEIS and DRS to gain detailed information about the surface structure. The main effect exploited here is surface channeling. At grazing angles of incidence, the energy of the incoming Ne^+ particles perpendicular to the sample surface is very small, enabling the tungsten substrate atoms to gently deflect them along open channels on the crystal surface. For W(100), the predominant channels are along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, as illustrated by the shaded regions in Fig. 3. Ion focusing increases the likelihood of collisions between the incident Ne^+ and any adsorbed hydrogen isotopes bound along a given channel. Hence, enhanced signals from recoiled hydrogen would be observed along surface channels containing hydrogen, thereby enabling a definitive identification of the binding configuration. More details on the use of surface channeling to study adsorbed H may be found in Ref. 3.

To aid in our analysis of the adsorbed H layer, we monitored the recoiled H peak height over a wide range of incidence angles (α) and azimuths (ϕ). These data are compiled into the maps depicted in Fig. 4. To examine the binding configuration as a function of temperature (and surface H coverage), we considered four different temperatures between 25 °C and 350 °C, as shown in cases (a-d). All of the maps were acquired at an observation angle of $\theta=45^\circ$ using 1 keV Ne^+ ; in each case we exposed the surface to a H_2 partial pressure of 3×10^{-7} Torr. Immediately evident in each map is the presence of distinct hydrogen recoil structures along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions that repeat every 90° , annotated respectively by “A” and “B” in Fig. 4. The slight variability in the repeating pattern with azimuth is due to a small misalignment of the crystal surface normal with respect to the incident beam.

The saturation coverage case at 25 °C depicted in Fig. 4(a) is nearly identical to our prior observations [3], with the same distinct hydrogen recoil patterns aligned along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. This pattern provides clear evidence of adsorbed H residing in 2-fold (bridge) sites on the W(100) surface at 25 °C at saturation coverage. Had the hydrogen been residing in other high symmetry surface sites (such as four-fold hollow or top), local maxima in recoiled hydrogen intensity would not be observed along both the $\langle 100 \rangle$ and $\langle 110 \rangle$ azimuths. In addition, prior low energy electron diffraction (LEED) measurements provide compelling evidence that at 25 °C, the W surface

atoms on the (100) plane reside in a 1×1 configuration when saturated with hydrogen [10,11]. (Note that this notation indicates the basic translation vectors that describe the surface superstructure.) This configuration is illustrated in Fig. 3(a), and corresponds to 2 H/W (or $2\times 10^{15}\text{ H/cm}^2$). Note that the dashed line in this figure indicates the surface unit cell.

Our previous analysis [3] did not reveal the definitive binding configuration at partial coverage. In the present study, the carefully controlled H dosing and systematic examination of coverage with temperature provide an opportunity for further analysis. While the relative positions of the adsorbed H cannot be detected directly with LEED, such measurements provide valuable insight into the W(100) substrate configuration at different hydrogen isotope coverages [10,11]. At room temperature, the clean W(100) surface is in a simple 1×1 configuration, with the W atoms residing close to their bulk lattice sites (aside from a small relaxation between the first few atomic layers.) As hydrogen isotopes adsorb, the substrate reconstructs to form a $c(2\times 2)+\text{H}$ structure. Here the W surface atoms displace laterally by $0.2\text{ \AA}$ toward the hydrogen adatoms, as depicted in Fig. 3(b). Finally, as the surface approaches saturation, it reverts back to a 1×1 phase, as shown in Fig. 3(a).

The positions of the tungsten surface atoms are crucial, as they affect both the adsorbed hydrogen configuration as well as how ions are scattered along the surface. In the reconstructed configuration, the surface channels along $\langle 100 \rangle$ directions narrow by $0.4\text{ \AA}$ (by 13 %). At $150\text{ }^\circ\text{C}$, the intensity patterns along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions still persist, indicating that bridge sites are still preferred, even at somewhat lower coverage. The H recoil patterns, however, subtend a smaller azimuthal range than is evident in the saturation coverage case. This behavior is consistent with narrowing of the surface channels on the reconstructed surface. At $250\text{ }^\circ\text{C}$ and higher, the same basic recoil pattern persists, thereby confirming that H remains in bridge sites even at low coverage.

V. Future Model Development

While the analysis discussed here provides support for bridge site occupation for all levels of H coverage on W(100), a more compelling case can be made through computational modeling of surface collisions. Because grazing incidence angles are used to probe the tungsten surface, the incident ions

interact with many surface atoms at once. In this sense, MD is a better computational approach to simulate this than binary collision models. While MD simulations are often considered impractical for simulating scattering, simplifying assumptions (as discussed by Danailov et al. [12]) can be incorporated to make the problem more tractable. We are developing simulations of ion scattering at grazing incidence along $\langle 100 \rangle$ and $\langle 110 \rangle$ surface channels that involve varying the amount of H present to match the measured surface coverage.

A key starting point for this work involves the evaluation of interatomic potentials for incorporation into MD simulations. Since most potentials are optimized to reproduce bulk properties, surface properties may not be well represented. Such problems aside, we do not foresee any insurmountable obstacles to applying MD techniques to the scattering analyses presented here. The coupling of such experiments and models provides a promising avenue for simulating atomic-scale phenomena of interest to ITER and other plasma devices, and will be presented in future publications.

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253 **Figure Captions**

254 FIG. 1: (a) Illustration of the geometry of the scattering experiments showing definitions of the polar
255 (α), azimuthal (ϕ), and observation (θ) angles. (b) Ion energy spectra for scattered Ne and recoiled H
256 and D from the W(100) surface. Dashed lines correspond to calculated elastic scattering and recoil
257 energies for the indicated surface species.

258 FIG. 2: Adsorption profiles for hydrogen isotopes on W(100). Case (a) shows the dependence on D₂(g)
259 exposure pressure, whereas case (b) compares adsorption of different isotopes and illustrates the
260 effect of dosing with atomic species.

261 FIG. 3: Hydrogen configuration on W(100) at (a) saturation coverage, and (b) partial coverage. Large
262 markers indicate W surface atoms, small markers indicate adsorbed H. Prominent channeling
263 directions are indicated by the shaded regions, and the surface unit cell is indicated by the dashed line.

264 FIG. 4: Ion scattering maps depicting H recoiled from the W(100) surface, for four different surface
265 temperatures. Experimental conditions: H₂(g) partial pressure of 3×10^{-7} Torr; $\theta = 45^\circ$.

Figure

Fig. 1

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Fig. 2

Figure

Fig. 3

Fig. 4