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Analysis of hydrogen adsorption and surface binding configuration on tungsten using direct recoil spectroscopy

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

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PSI-21 keywords: ion-surface collisions, hydrogen recycling, hydrogen adsorption, molecular dynamics simulations, tungsten

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I. Introduction

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

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

With the above concerns in mind, we address the temperature/coverage effects in greater detail in 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 both atomic and molecular H and D, and measured the recoiled adsorbate signals as a function of temperature under a variety of conditions, with the goal of comparing our results with recently-developed models of surface adsorption/recombination kinetics [4].

To complement our experimental results, we are developing an 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 (BCA) models that are frequently used as inputs to recycling codes. For the purpose of modeling the LEIS/DRS experiments, we also developed an MD framework to simulate Ne^+ scattering on the crystal surface.

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 dia., 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) was rastered over a 2 mm × 2 mm area, producing an incident flux of 1.5×10^{13} $cm^{-2}s^{-1}$. The raster amplitude was adjusted with incidence angle to maintain a constant spot size and flux on the sample surface.

The concentration of hydrogen isotopes on the W crystal surface could be controlled by varying the surface temperature or the incident flux of hydrogen isotopes. For the purposes of dosing, we introduced the hydrogen through a 1 mm ID tungsten capillary into our vacuum system. The tungsten capillary could be heated by electron bombardment to 1700 °C to allow for complete dissociation of the effusing hydrogen flux, thus allowing us to dose with either atomic or molecular species.

The key geometrical parameters for this set of experiments are illustrated in Fig. 1(a), including the angle of incidence of the analysis beam (α), the azimuth on the W(100) surface (ϕ), and observation angle (θ). Recall that the energies of the scattered and recoiled particles are used to identify species present on the surface. Consider Fig. 1(b), which shows ion energy spectra for 2 keV Ne+ → W(100) in cases where the surface is exposed to background gases present within the vacuum system only, as well as during exposure to D_2(g). Note that we have normalized all energies relative to that of the incident beam (E_0). Within the two spectra, three prominent peaks are readily visible, corresponding to H, D, and W present on the surface. The vertical lines indicate the theoretical positions for these peaks, calculated using classical kinematics and ignoring any inelastic energy loss mechanisms. Even when the surface is not dosed, a peak associated with recoiled H is still present, which we attribute to dissociative chemisorption of residual H_2(g) present in our vacuum system. Hydrogen in dissolved within the W lattice may also diffuse to the surface, although this is expected to be only a minor contribution to the H surface concentration.

Once the surface was exposed to D_2(g), the signals associated with W and H rapidly diminished. We systematically tested different molecular fluxes to the surface, finding that saturation coverage at 25 °C could be assured with a partial pressure of 3.0×10^{-7} torr. This concentration depends on a dynamic equilibrium dictated by the arrival rate of H_2(g), the sticking and reflection coefficients, as well as the desorption rate due recombination. One key concern is that the incident ion beam used for our measurements also contributes to desorption. To minimize this effect, we ensured that the exposure flux produced an arrival rate of H_2(g) at the surface was much higher than that of the incident Ne^+ ions. Based on the kinetic theory of gases, the aforementioned partial pressure of 3.0×10^{-7} torr corresponds to a flux of 3.0×10^{14} D_2 $cm^{-2}s^{-1}$, or a factor of 20 higher than the ion arrival rate at

the surface. In practice, because the gas is directed toward the sample through a W capillary, its arrival rate at the sample surface is much higher.

We were able to calculate the chemisorbed concentrations of H and D by integrating the area under each peak and correcting the result for the recoil cross-sections for each species. For 2 keV Ne^+ and a laboratory recoil angle of θ=25°, the relevant cross-sections are: 5.93×10^{-2} Å^2/sr (H) and 2.96×10^{-2} Å^2/sr (D). Assuming that the dosed case shown in Fig. 1(b) corresponds to a saturation coverage of hydrogen isotopes, the H coverage is 6%, with the remaining D comprising 94% of the total.

III. Coverage as a function of temperature

To better understand the coverage dependence as a function of temperature, we performed a systematic series of controlled adsorption experiments, in a manner similar to the procedures specified in Ref. [4]. This involved rapidly heating the crystal to 450 °C while exposing the sample to different fluxes of deuterium or hydrogen. 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. 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 α=80° to probe the hydrogen present along the <100> surface direction.

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), different D exposure pressures are considered, ranging over an order of magnitude between $p=7.4\times10^{-8}$ torr to 1.1×10^{-6} torr. To aid in the interpretation of the data, we render the adsorption curves as Arrhenius plots. In addition, we assume that once the surface temperature declined below 100 °C the surface was saturated with H or D, hence the curves 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 H present on the surface. Regardless of the exposure pressure, the same basic adsorption curve shape is evident. In the Arrhenius coordinates, the adsorbed concentrations follow a nearly linear dependence until the

temperature approaches 300 °C. Afterward, the adsorption rate slows 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 if dosing the samples with atomic D versus D_2 would produce any appreciable result in the adsorbed concentrations 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 H_2 and D_2 adsorption on the surface, but the difference was very slight and still within the error of our experiment. This indicates that any dependence of adsorption on isotope is rather modest.

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 structure of surfaces. 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 the <100> and <110> directions, as illustrated by the shaded regions in Fig. 3. Ion focusing increases the likelihood of collisions between the incident Ne^+ and any adsorbed H 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 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 θ=45° 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 the <100> and <110> 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 described in Ref. [1], with the same distinct hydrogen recoil patterns aligned along the <100> and <110> 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 other high symmetry surface sites (such as four-fold hollow or top), recoiled hydrogen would not be observed along both the <100> and <110> 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 [7,8]. This configuration is illustrated in Fig. 3(a), and corresponds to 2 H/W (or 2×10^{15} H/cm^2). Note that the dashed line in this figure indicates the surface unit cell.

Our previous analysis described in Ref. [1] 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 provided an opportunity for further analysis.) The surface behavior under these conditions becomes more complex, as the aforementioned LEED measurements indicate that the W surface atoms displace laterally by 0.2 Å to form a $c(2\times2)$+H surface reconstruction, as depicted in Fig. 3(b). 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 the <100> directions narrow by 0.4 Å (by 13 %). While the positions of the W surface atoms can easily be detected by LEED, the relative positions of the H adatoms cannot be determined with this approach.

At 150 °C, the intensity patterns along the <100> and <110> directions still persist, indicating that bridge sites are still preferred, even at 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 °C and higher, the same basic recoil pattern persists, thereby confirming that H remains in bridge sites even at low coverage.

V. Model Development and Summary

While the analysis discussed presented here provides support for bridge site occupation for all 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. The computational approach that most closely simulates this is molecular dynamics (MD). While MD simulations are often considered impractical for simulating scattering, simplifying assumptions (as discussed in Ref. [9]) can be readily incorporated to make the problem more tractable. Using LAMMPS, we are developing simulations of ion scattering at grazing incidence along the <100> and <110> surface channels, while 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 an promising avenue for validating models of atomic-scale phenomenon of interest to ITER and beyond.

VI. Acknowledgements

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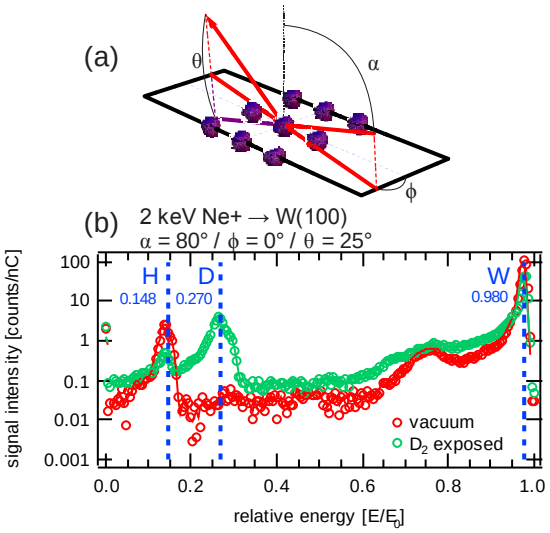
Figure Captions

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

FIG. 2: Adsorption profiles for hydrogen isotopes on W(100). Case (a) shows the dependence on D_2(g) exposure pressure, whereas case (b) compares adsorption of different isotopes and illustrates the effect of dosing with atomic species.

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

FIG. 4: Ion scattering maps depicting H recoiled from the W(100) surface, for four different surface temperatures. Experimental conditions: H_2(g) partial pressure of 3×10^{-7} torr; θ=45°.



239

240 FIG. 1

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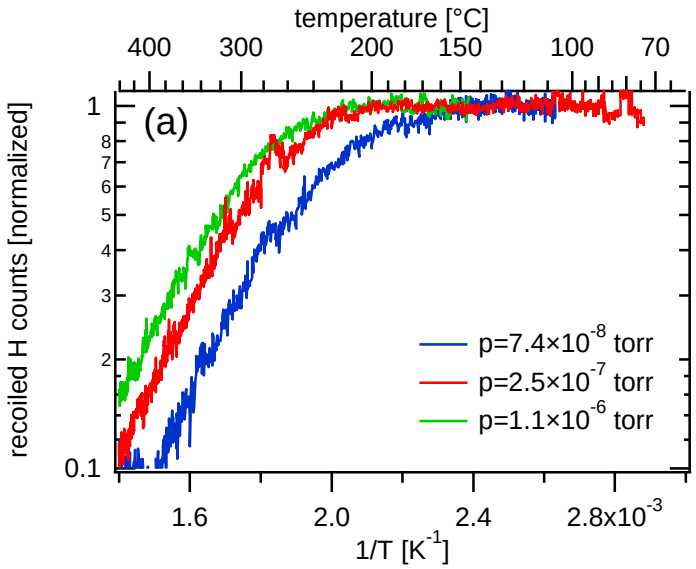
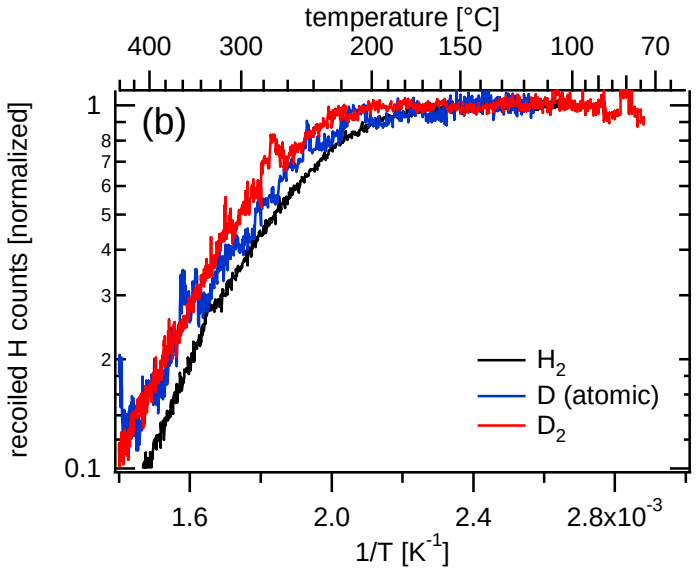


242



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244 FIG. 2

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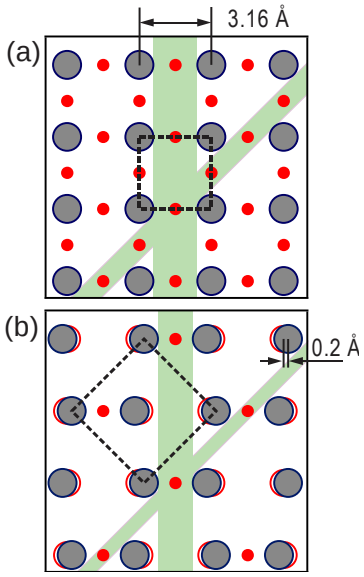

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247 FIG. 3

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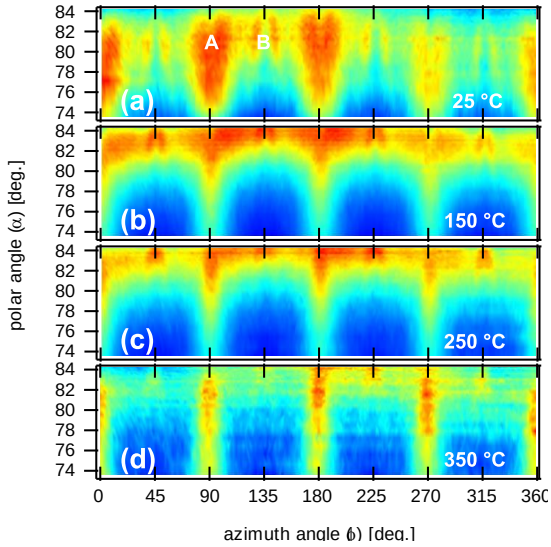
A
B
(a)
25 °C
(b)
150 °C
(c)
250 °C
(d)
350 °C
polar angle (α) [deg.]
azimuth angle (φ) [deg.]
84
82
80
78
76
74
0
45
90
135
180
225
270
315
360

249

250 FIG. 4