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SURFACE ANALYSIS AND HYDROGEN PERMATION MEASUREMENTS FOR SUPER-PERMEATING MEMBRANE MATERIALS— C. -S. Wong, R. D. Kolasinski, and J. A. Whaley (Sandia National Laboratories)

OBJECTIVE

The goal of this work is to characterize hydrogen-surface interactions and surface-to-bulk transport mechanisms associated with super-permeable membranes. On the upstream side of a super-permeable membrane, a low energy plasma is used to implant hydrogen ions beneath a thin oxide layer (potentially as thin as 1 monolayer.) The integrity of the oxide layer is critical as it must be relied upon to prevent hydrogen recombination and release. The opposite situation is true at the downstream surface, where fast recombination is needed to ensure adequate throughput of hydrogen gas. The goal of this work is to investigate the sensitivity of hydrogen transport to these surface conditions. Because of their relevance to super-permeation, we focus our efforts on understanding the effects on Group V metals (Nb, V, and Ta.) We will use a combination of surface analysis techniques and hydrogen permeation measurements to decipher the relevant mechanisms.

SUMMARY

In this report, we summarize preliminary surface characterization results for Nb surfaces, using low energy ion scattering, direct recoil spectrometry, and Auger electron spectroscopy. While most surface analysis tools cannot detect hydrogen, the low energy ion beam techniques described here are among the few techniques that are directly sensitive to it. For this study, we examined chemisorption using both molecular and atomic hydrogen (using an heated tungsten capillary to dissociate the hydrogen.) To complement these results, we have been performing ex-situ spectroscopic ellipsometry as a means of detecting the surface oxide.

PROGRESS AND STATUS

Surface Characterization

We characterized a clean reference niobium surface using low energy ion scattering (LEIS) techniques and Auger electron spectroscopy (AES). For these measurements, a 7-mm diameter polycrystalline niobium foil sample was prepared. The sample surface was first cleaned with successive ultrasonic baths of methanol and isopropanol, followed by rinsing in deionized water. Afterward the Nb sample was transferred into our ultra-high vacuum system (5×10^{-10} Torr for LEIS and 6×10^{-9} Torr for AES), where it was then sputtered cleaned using the 3 keV Ne^+.

Our low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) measurements for the niobium sample were obtained with an angle-resolved ion energy spectrometer (ARIES). The experimental apparatus for ARIES has been described in detail in several references [1–6], so we provide just a short summary here. A mass separated 3 keV Ne^+ beam was produced using a Colutron source. The beam was shaped and then steered with ion optics through an aperture into the primary measurement chamber. The chamber had a base pressure of 5×10^{-10} Torr, primarily due to residual H2(g). During operation of the ion beam, the pressure of the measurement chamber was maintained at 3×10^{-8} Torr by differential pumping. Hydrogen dosing of the sample was performed by introducing either atomic or molecular hydrogen into the chamber through a leak valve, until the chamber pressure increased to 2×10^{-7} Torr.

Ion energy spectra of the niobium surface for the different three hydrogen environments are presented in Fig. 1 for angles of incidence in the range $69° \leqslant \alpha \leqslant 84°$. We adopt the standard notation that X(QS) indicates a detected Ne+ that has undergone quasi-single scattering from a surface atom of species X, while X(R) indicates a detected X+ that has been recoiled by the incident Ne+. These spectra reveal that the surface composition is primarily niobium and hydrogen, with trace amounts of oxygen. As expected, the hydrogen peak increases when either molecular or atomic hydrogen are introduced into the chamber. However, it is notable that the hydrogen peak is identical in both cases. This indicates that molecular hydrogen is readily dissociated and adsorbed onto the niobium.

The ion energy spectra also reveal finer details. Firstly, the presence of hydrogen alters the shape of the Nb peaks. When hydrogen is added to the surface, the primary Nb(QS) peak undergoes a slight shift to lower energies, likely due to blocking and shadowing by the hydrogen. Secondly, the Nb(DS) peak is found to be suppressed by increasing the surface hydrogen. The Nb(DS) peak, which sits on the high energy shoulder of the Nb(QS) peak, corresponds to Ne+ with trajectories that have undergone two θ/2-collisions with Nb atoms. A final and less critical detail is the increase in scattered and recoiled oxygen for the atomic hydrogen dosing as compared to the molecular hydrogen dosing. This likely was caused by out gassing from the heated capillary used to dissociate the molecular hydrogen. To ensure that the peaks in the ion energy spectra are being attributed to the correct scattering and recoil processes, we constructed a scattering circles map, as described in Ref. 1. This map, which is presented in Fig. 2, was generated by obtaining ion energy spectra for scattering angles in the range $20^\circ \leqslant \theta \leqslant 90^\circ$, while α was fixed at 84°. The radial coordinate of the map corresponds to the square root of the normalized ion energy, while the polar coordinate corresponds to the scattering angle θ. Lighter regions in the map correspond to larger scattering and recoil intensities. These lighter regions are expected to trace out circles, which have been computed and overlaid on the map. The strong agreement between the overlaid circles and the underlying scattering and recoil intensity profile suggest that scattering and recoiling of the Nb, O, and H is sufficient to describe the obtained spectra.

Lastly, we performed Auger electron spectroscopy on the niobium sample. AES complements LEIS and DRS, as it has higher sensitivity to other surface impurities, in particular carbon. The obtained spectrum, shown in Fig. 3, has niobium peaks that are consistent with the literature. The spectrum also reveals the presence of oxygen and carbon, which indicate that perhaps more substantial sputter cleaning is required to fully remove adsorbates from the surface.

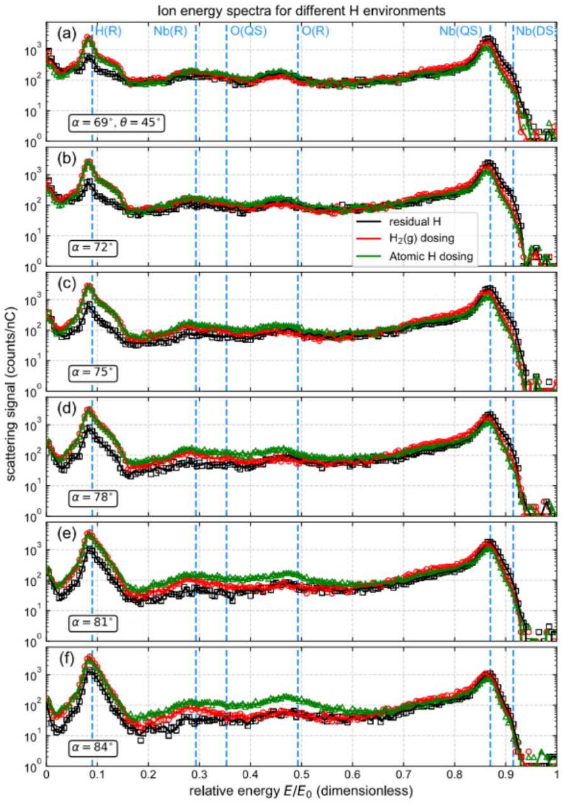

Figure 1. Ion energy specta for 3 keV $Ne^+ \rightarrow Nb$ at angles of incidence $69^\circ \leqslant \alpha \leqslant 84^\circ$. These spectra were taken for the sample in three different hydrogen environments: residual hydrogen (black squares), H_2(g) dosing (red circles), and atomic H dosing (green triangles). Most prominent are the Nb(QS) and H(R) peaks, which correspond to Ne^+ scattering off a Nb atom and H+ recoiled by an incident Ne^+, respectively.

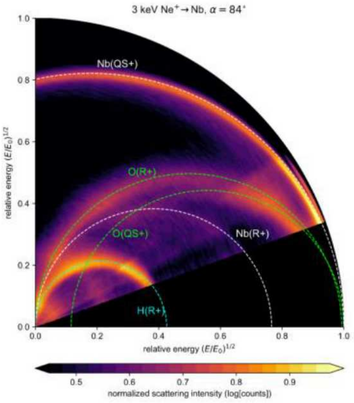

Figure 2. Scattering circle for the niobium sample for residual H conditions. The angle of incidence for this measurement was α = 84◦. These data provide confidence in attributing the scattering and recoil peaks in Fig.1 to niobium, hydrogen, and oxygen.

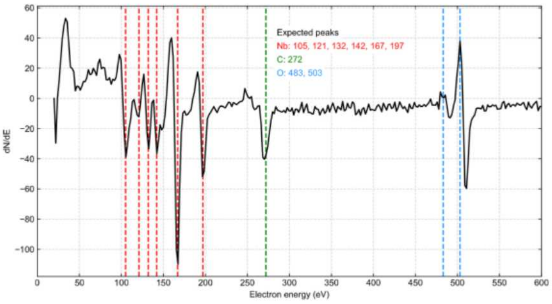

Figure 3. Auger electron spectroscopy of the clean niobium sample after sputter cleaning. The positions of the expected Auger peaks are given by the colored dotted lines (red for niobium, green for carbon, and blue for oxygen). The niobium peaks align extremely well with those from the literature, while the presence of oxygen and carbon were also detected.

SUMMARY AND OUTLOOK

To build upon these preliminary results, additional surface characterization will be performed in a more representative plasma environment. We are working to set up in-situ spectroscopic ellipsometry measurements to study oxide sputtering and growth during low energy D_2 plasma exposure. Spectroscopic ellipsometry relies on reflecting a beam of elliptically polarized light from a surface. A detector is then used to determine how the polarization state of the reflected light has changed. This general approach can provide nanometer resolution measurements of oxide growth on semiconductor surfaces. We recently had success in developing a similar system for examination of tungsten nanostructure growth upon exposure to He plasmas. Applying this same approach to Nb, V, and Ta surfaces could provide a means of directly determining the oxide thickness as a function of plasma fluence, providing key information needed to assess the robustness of the oxide layer.

In addition, we have been working with the other national laboratories on a hydrogen permeation benchmarking exercise. Four labs agreed to participate in the effort, including Idaho National Laboratory (INL), Savannah River (SRNL), Oak Ridge (ORNL), as well as Sandia National Laboratories. In addition, Pacific Northwest National Laboratory and Los Alamos agreed to participate in an advisory capacity. As model system for comparison between laboratories, we will start with polycrystalline Ni. To begin with, Ni does not form a hydride and has a relatively high permeability. In addition, chemisorbed O is reduced in a H environment. This mitigates concerns about oxide growth affecting dissociation and recombination at the surface. Furthermore, there seems to be reasonable consistency in the literature database for H diffusion and permeation in Ni over a wide temperature range. To ensure that we are working within conditions that would be accessible to most instruments, will consider a temperature range of 100 - 500 °C to start. Post-mortem depth profiling using Auger / X-ray photoelectron spectroscopy will be used to quantify the thickness of any oxides that have grown on the membrane surfaces.

ACKNOWLEDGEMENTS

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