

Low energy ion scattering characterization of materials for hydrogen applications

R.D. Kolasinski, L.E. Klebanoff, V. Stavila, J.L. White, J.A. Whaley, M.D. Allendorf, and D.A. Buchenauer

rkolasi@sandia.gov

Sandia National Laboratories, Livermore, CA 94550 USA

Hydrogen-surface interactions are relevant to many technologies, including solid storage for fuel cell electric vehicles [1], hydrogen energy infrastructure [2], and plasma-facing materials for magnetic fusion [3]. Detecting hydrogen is notoriously difficult for most surface analysis techniques. Chemisorbed hydrogen, for example, is invisible to x-ray photoelectron or Auger electron spectroscopies, and only subtly affects low energy electron diffraction patterns. Often changes in the substrate structure (e.g. reconstruction) overwhelm the comparatively smaller effect that hydrogen has on the detected signal. As a result, most of our understanding of the behavior of hydrogen on surfaces has been acquired through indirect methods, including temperature programmed desorption, work-function, and electron energy loss measurements. In contrast to electron- and photon-based spectroscopies, element (and isotope) specific detection of hydrogen on surfaces is a unique strength of low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS). The full potential of these techniques for hydrogen applications has yet to be fully realized, partly because the complexity of the ions-surface interaction makes the scattering result difficult to interpret. In this report, we explore recent progress in several aspects of characterizing hydrogen chemisorption with LEIS and DRS.

We first consider how to precisely identify sites for hydrogen chemisorption. With conventional ion scattering measurements, one would use shadow cone analysis to determine atomic positions. This approach is at best qualitative and effective only for simple surface geometries. For surfaces containing adsorbates, LEIS/DRS spectra will contain contributions from additional collision sequences that may overlap with the main features of interest. De-convolving these effects remains a considerable challenge. One way to address this complexity is to map scattered ion fluxes over a large angular sector. This provides a far more comprehensive data set in comparison to conventional LEIS, where typically only a small number of orientations are considered (e.g. azimuthal rotations of the crystal surface at fixed angle of incidence.) Consider, for example, Fig. 1 which shows a scattering map revealing the local atomic structure of the W(110) surface. In this case, we have rendered the map in real space to illustrate how atom positions are related to the scattered ion intensities. Particularly at grazing incidence, scattering features quickly morph into different patterns with slight changes in the incidence angle. Scattering maps clarify how these features are related to each other.

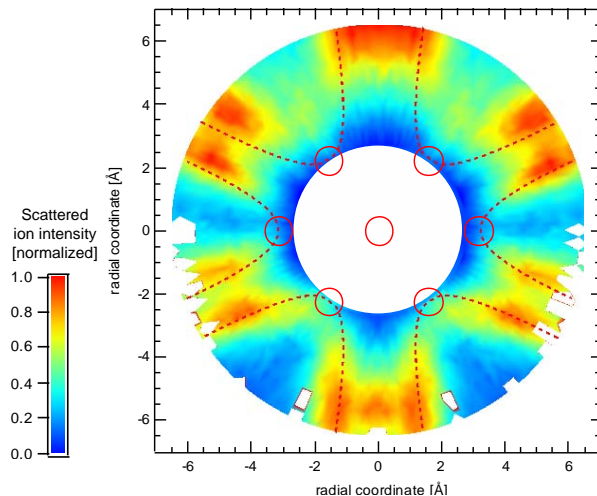


Fig. 1: LEIS map showing scattered ion intensities from the W(110) surface.

hydrogen intensity can be measured with DRS. To determine the exact bond length between the hydrogen and the neighboring substrate atoms, we relied on detailed comparisons between our experiments and computational models. It is important to keep in mind that at grazing incidence, the binary collision approximation breaks down, and the incident ions interact with an extended region of the surface. Hence, to accurately reproduce the scattering physics, we developed a molecular dynamics model; quantitative comparisons with experiments enable the height of the hydrogen above the surface to be determined to within $\pm 0.1 \text{ \AA}$ [4,5].

How hydrogen diffuses along surfaces is a process that is fundamental to hydrogen recombination and desorption. The prevailing approach for measuring surface diffusion, laser-induced desorption spectroscopy (LIDS), has considerable limitations. Because it involves local, rapid laser heating of the surface to remove chemisorbed hydrogen, LIDS can cause damage (including melting) of the substrate for materials with low melting temperatures. Recently, we have demonstrated the feasibility of an alternate approach that uses LEIS to measure surface diffusion. The basic experimental procedure includes first dosing the surface with hydrogen and then using a low energy ion beam to rapidly clear a well-defined region of the surface. We then use DRS to directly monitor the rate at which H from the surrounding area repopulates the cleared region of the surface. We have successfully demonstrated the feasibility of this approach for the Mg(0001) single crystal surface.

Finally, we have also studied hydrogen chemisorption on and desorption from practical metal hydride powders relevant to fuel cell electric vehicles. For this purpose we considered both Ni-doped Mg powder and Ti-doped NaAlH_4 materials. These powders were prepared in an inert glove box environment, pressed into soft metal foils (In and Pb alloy), and loaded into a clean transfer cylinder. This enabled us to characterize the surface impurities of the as-prepared material without adventitious contamination from air exposure. Given the considerable barrier to H_2 adsorption for most light metals, we used a heated tungsten capillary doser to expose the surface to an atomic H beam. This enabled us to examine both uptake of molecular and atomic hydrogen, and to decipher how dopants accelerate H chemisorption (and uptake.) In Fig. 2(a), we show the surface

In this work, we apply the aforementioned mapping techniques to determine the hydrogen binding configuration on several tungsten and beryllium crystal planes. These materials will comprise the plasma-facing surfaces of the ITER magnetic fusion experiment under construction at the Cadarache facility in southern France. The atomic-scale details provided by LEIS and DRS provide a valuable test of detailed models of recycling at the plasma-surface interface. Here we consider surface channeling of ions at grazing incidence. If hydrogen is present within open surface channels, an enhancement in the recoiled

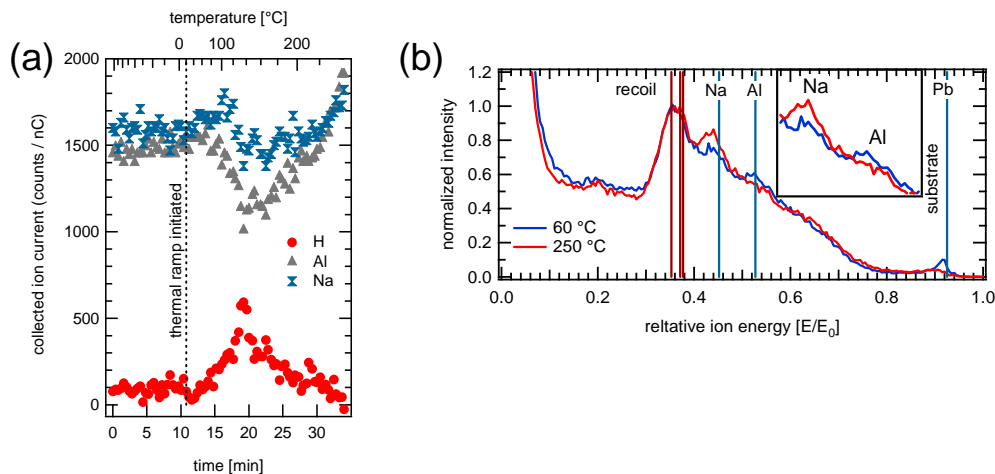


Fig. 2: (a) LEIS/DRS data showing variation of surface composition of TiCl_3 -doped NaAlH_4 during heating. (b) Ion energy spectrum confirming enrichment of Na (or depletion of Al) when heated. Measurements acquired using a 2 keV Ne^+ analysis beam with an electrostatic analyzer.

composition evolution of NaAlH_4 doped with 2% mol. TiCl_3 during in-situ thermal desorption. Here, H recoils are detected by DRS, whereas the Al and Na surface concentrations are simultaneously measured using LEIS. As illustrated by the ion energy spectrum in Fig. 2(b), the Na concentration at the surface appears to increase at higher temperatures. This could be due to segregation of Na to the surface, or perhaps due to release of volatile AlH_x species during heating.

The advancements represented by the aforementioned experiments offer the potential to study hydrogen-surface interactions with much greater fidelity. We foresee no insurmountable obstacles to applying these techniques other materials systems where hydrogen effects are of importance.

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