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The influence of ion irradiation on hydrogen chemisorption and diffusion on gadolinium surfaces

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ABSTRACT

The role of irradiation induced surface defects on the chemisorption process of hydrogen and inward penetration of chemisorbed H atoms was studied on sputtered, with 4.5 keV Ar + ions and on annealed gadolinium surfaces. A combination of Direct Recoil Spectrometry (DRS) and Contact Potential Difference (CPD) enabled to distinct between topmost surface and subsurface processes. Simulations of irradiation-induced defects, which assume two types of defects-vacancies due to sputtering and Frenkel pairs, taking account of the annealing processes occurring at different temperatures, have reasonably reproduced the experimental Ar scattering peaks in the DR spectra. It has been concluded that the presence of surface defects has a significant effect on the binding energies of the chemisorbed hydrogen, resulting in hydrogen trapping on the surface and affects the surface to subsurface inward penetration process.

1. Introduction

Metal-hydrogen systems are of interest from both a theoretical and a practical point of view. They can be utilized for energy-storage systems, in hydrogen sensor applications and in catalysis. Some of the rare earth hydrides can also be used for switchable optical devises, where their optical properties can change between metallic to transparent, depending on the hydrogen load [1,2]. Due to their chemical reactivity, some of the rare-earths are used as surrogates for actinides corrosion studies [3], avoiding the need for expensive experimental and safety set-ups. The rare-earth metals have also a scientific interest due to their highly localized 4f electrons and some extraordinary electronic and surface magnetic properties.

The initial stage of the massive hydrogen reaction is by hydride nucleation and growth on the surface and different families of hydride precipitates were identified and correlated with different types of defects at the oxide and oxide-metal interface [3–6]. Recently, it has been also found that hydroxyl groups adsorbed on the gadolinium oxide surface impede the dissociative chemisorption of hydrogen and inhibit this reaction [7]. Understanding and controlling the surface characteristics is therefore essential in order to understand and control the initial interactions of hydrogen with metals and alloys.

In order to avoid the formation of a native oxide and its influence on the hydrogen interaction with metallic surfaces, ultrahigh vacuum (UHV) conditions have to be employed. Hydrogen adsorption on evaporated thin films of Gd (0001) using angle resolved photoemission and scanning tunneling microscopy (STM) revealed that hydrogen adsorption on gadolinium is a dissociative chemisorption process that occurs on the surface and that hydrogen atoms tend to form islands and alter the surface electronic structure [8]. Hydrogen adsorption starts at crystallographic surface imperfections, which form the initial nucleation centers of the hydrides. In the system of evaporated Gd layers on top of W(110), oriented (0001) Gd islands are formed and elastic strain in the Gd islands can also influence the hydride nucleation [8–11]. Li [8] also compared the sticking coefficient and chemisorption of hydrogen on the Gd surface at 120 K and at room temperature and attributed the differences to the possibility of hydrogen diffusion

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into the bulk.

Sputtering with Ar^+ ions in the keV range is commonly used to clean the surface during experiments and can also be used to mimic radiation effects and damage at the surface of nuclear materials, influencing the corrosion behavior (see for example Refs. [12–14]). The objective of the present work was to study the influence of radiation damage, as inflicted by Ar^+ ions irradiation, on hydrogen adsorption and trapping on Gd surfaces, at room temperature and below.

Direct recoil spectrometry (DRS) was applied to monitor hydrogen adsorption in the range 140–473 K. A Kelvin probe, measuring contact potential difference (CPD) was used to evaluate surface work function (WF) changes due to hydrogen exposure. This combination enables the distinction between topmost surface and subsurface processes.

The sample on which the experiments was performed was polycrystalline Gd, probably containing some bulk oxygen (surface oxygen under the detection limit of AES and the more sensitive DRS) so the processes and calculated values might be somewhat quantitatively affected by its presence. Since the measurements are relative, i.e. sputtered vs. annealed, the effect of surface defects and the principle processes are, in our opinion, not significantly affected by them.

2. Experimental

The experiments were performed in an ultra-high-vacuum (UHV) system, pumped by turbo-molecular and titanium sublimation pumps to a base pressure of ~2×10^{-10} Torr. The pressure is monitored by a Bayard-Alpert type ionization gauge and a quadrupole residual gas analyzer (RGA). The direct recoil spectrometry (DRS) is based on grazing irradiation of the surface with a pulsed beam of 3 keV Ar^+ ions (at 15° to the surface) and time of flight (TOF) measurements of the surface atoms and ions, which are recoiled in a forward direction at the same angle, following the direct collision inflicted by the impinging primary ions (it is common to indicate the scattering angle with respect to the incident angle – therefore the scattering angle is 30°). A channel electron multiplier detector, which is sensitive to both ions and fast neutrals, is mounted on a long drifting tube at the opposite direction. Typical ion current densities used are ~0.1 nA/mm^2 and a DR spectrum can be collected with a total ion dose of $<10^{-3}$ ions/surface atom, so the technique can be considered as nondestructive. The main characteristics of this technique are topmost surface sensitivity and detection of light atomic masses, including hydrogen [15–18]. The system also contains standard surface analysis instrumentation for AES and XPS and a Kelvin Probe for contact-potential-difference (CPD) measurements.

Sputter cleaning of the sample surface is performed by a rastered, differentially pumped, Ar^+ ion gun with an energy range up to 5 keV and current of about 2 μA/cm^2, located at 30° to the surface. This ion gun was also used to induce radiation damage at the sample surface.

The polycrystalline Gd sample (Goodfellow 99.9%, ~1 cm^2 area, 1 mm thick) was gradually polished using diamond past, down to 1 μm roughness, cleaned in distilled water and ethanol and then attached by spot-welding to two Ta wires, which are connected to copper feedthrough rods on the manipulator. The sample can be cooled down to ~140 K, by dipping the copper rods in liquid nitrogen and heated up to ~1000 K by driving an electric current through the wires. The sample temperature was monitored by a Chromel–Alumel (type K) thermocouple spot-welded to the sample back.

The Gd sample surface was continually sputtered at room temperature for 24 h with 4.5 keV Ar^+ ions, in order to obtain a steady state and spatially uniform roughness of the surface. Scanning electron microscope (SEM) micrographs, taken after prolonged sputtering, revealed the formation of relatively flat facets on the surface, as depicted in Fig. 1.

Annealing of the surface was performed at 673 K for 30 min. The radiation damage was induced by irradiation of the annealed sample with 4.5 keV Ar^+ ions for different doses and sample temperatures. The ion dose was evaluated by measuring the sample current during irradiation. In order to improve accuracy and overcome the secondary electron emission, the sample was biased at +100 V during current measurements to recollect those electrons.

Two kinds of experiments were performed:

1) Radiation damage measurement

The radiation damage was monitored by the decrease of the DR Ar(SS) peak.

The polycrystalline gadolinium metal was bombarded uniformly (starting from an annealed surface) at various temperatures, by 4.5 keV argon ions, impinged the surface at 30°. The flux of the argon ions during irradiation was held constant at an average value of 7.4×10^{12} ion/s/cm^2. At each temperature and for short periods of time (50sec each), DR spectra were taken and were used to probe the surface as a function of time.

2) Hydrogen adsorption measurements

For each adsorption experiment, measurements were taken on an annealed and on a sputtered surface, in order to evaluate the net contribution of radiation damage. In order to equalize the initial conditions during hydrogen exposure and rule out the difference in surface damage due to ion irradiation at different temperature, all the radiation damages for the adsorption experiments were performed by sputtering at room temperature to 1.8×10^{16} ions/cm^2, before lowering the sample temperature for hydrogen exposure.

3. Results and discussion

3.1. Analyzing radiation induced damage at the Gd surface

3.1.1. DRS results

DR spectra from clean Gd surface, presenting the forward scattered Ar(SS), as a function of the 4.5 keV ion irradiation dose is presented in Fig. 2. As the radiation damage to the surface increases

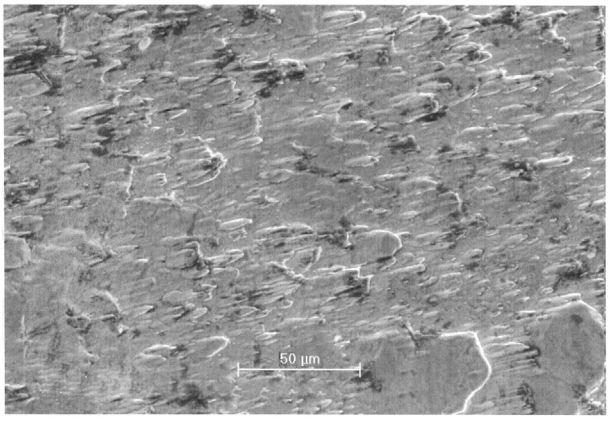

Fig. 1. SEM micrograph of the gadolinium surface after a prolonged sputtering, depicting the steady state features developed at the surface.