Solid State Ionics 263 (2014) 39–45

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Water chemisorption on a sputter deposited uranium dioxide film — Effect of defects

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ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 17 March 2014
Accepted 6 May 2014
Available online 2 June 2014

Keywords:
UO_2
Adsorption kinetics
Dissociation
Chemisorption, Surface defects
Hydrogen bonds

ABSTRACT

The characteristics of water vapor chemisorptions on stoichiometric and on sputtered reduced UO_2 thin film surfaces, obtained by the reactive sputter deposition technique, were studied by utilizing direct recoil spectrometry and X-ray photoelectron spectroscopy over a temperature range of 300–500 K. It seems that dissociative chemisorption takes place on both types of surfaces but surface coverage and adsorption rates are different. For the stoichiometric surface, DRS results indicate that water partially dissociate on this surface up to 350 K, probably on sparse defect sites. On the other hand, the kinetics of water dissociation fragments (H, O, OH) on the defected surface displayed a complex behavior, caused by the healing effect of surface defects, being temperature dependent. A modified water chemisorption model is proposed, assuming dense clusters of hydroxyls with a mix of perpendicular and tilted O–H bonds formed on the UO_{2-x} sputtered surface. Perpendicular isolated hydroxyls are assumed to be predominant on UO_2 stoichiometric surface.

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1. Introduction

Uranium dioxide (UO_2) is used mainly as fuel for nuclear reactors and in the manufacturing of radioisotopes. Therefore, numerous studies have been conducted on UO_2 surface structure and reactions; see, for example, the comprehensive review provided by Idriss [1].

The two main corrosion threats to UO_2 are moisture and oxygen. Moisture is mostly effective under atmospheric conditions (endless supply), and its reactivity can be further increased by radiation damage and radiolysis during long term storage. The enhanced oxidation and hydrogen formation can lead to a pressure buildup, and eventually a threat of breaching the storage container and a release of radioactive materials. Therefore, the safe disposal of UO_2 spent fuel is crucial to environmental safety.

Water vapor adsorption on oxidized (UO_{2+x}) vs. reduced (UO_{2-x}) single crystal surfaces had been studied earlier by Stultz [2] and Senanayake et al. [3] utilizing temperature programmed desorption (TPD), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). Stultz observed significant amount of D_2 desorption after 1 L (1 Langmuir $= 10^{-6}$ Torr × sec) D_2O exposure at 400 K, from a sputtered UO_2 (100) surface, while an annealed surface did not desorb measurable quantities. Annealing experiments indicated that even before water exposure, oxygen segregates from the bulk at 700 K, to heal surface defects. It was also found [3] that the amount of H_2 desorption after H_2O adsorption on a UO_2 (111) sputtered surface is related to both surface and subsurface reduction and coverage. Both studies [2,3] suggested that at room temperature (RT), water interacts weakly with the UO_2 surface inducing molecular adsorption on stoichiometric oxide single crystal surfaces, and dissociates over defective surfaces. Senanayake et al. also investigated the formation of defects [4] and D_2O interactions [5] on UO_2 thin film surfaces using high resolution XPS (HRXPS). Using synchrotron light, new U 4f lines were identified on the sputtered surface at 95 K and 300 K. These lines were attributed to intermediate oxidation states of U^{2+} and U^{3+}. Senanayake et al. proposed that following water exposure at 300 K, desorption of H_2 from a UO_2 defective surface is partially due to surface and subsurface H–H recombination. An experimental and theoretical study by Alexandrov et al. of the interaction of water vapor with the surface of actinide dioxides [6], determined coverage-dependent adsorption enthalpies and demonstrate a mixed molecular and dissociative structure for the first hydration layer. Their results also show a correlation between the magnitude of the anhydrous surface energy and the water adsorption enthalpy. DFT calculations show the atomic structure and the roll of hydrogen bonding on the configuration of the adsorbed water and hydroxyl ions on top of the oxide. Tan et al. [7] predicted the energies and structures associated with surface hydroxide groups on the (100), (110) and (111) surfaces of UO_2 and PuO_2 and also calculated a defected (100) surface with adsorbed hydroxides to be the most stable surface.

In the present study, the characteristics of water vapor chemisorption on defective and annealed UO_2 films, obtained by reactive sputter deposition, were studied over a temperature range of 300–500 K,

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http://dx.doi.org/10.1016/j.ssi.2014.05.003
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using combined measurements of direct recoil spectrometry (DRS) and XPS. The results suggest a modified chemisorption model of H_2O on these surfaces.

2. Experimental

2.1. Sample preparation

Stoichiometric polycrystalline thin films (100 nm) of UO_2 were prepared at the Institute for Transuranium Elements (ITU) by direct-current sputter deposition from native U metal with Ar/O_2 mixtures, as sputter and reaction gas. The films were deposited onto a Mo foil substrate (~1 cm^2 area, 1 mm thickness) cleaned in situ with Ar^+ ions while heated to 570 K for at least 25 min before deposition. The plasma in the diode source is maintained by injection of electrons of 50–100 eV energy. This allows a low sputter gas pressure of down to 10^{-2} Torr. The uranium metal target was held at -800 V while no sample bias was applied. The background pressures in the preparation and analysis chambers were below 2.7×10^{-8} Torr and 4×10^{-10} Torr, respectively. After deposition, the samples were characterized by X-ray diffraction (XRD), utilizing a Bragg–Brentano θ/2θ diffractometer with Cu K_α radiation. Signals of the UO_2 film and the underlying Mo substrate were observed. Crystallinity of the films is to be expected for sputter deposition, in which the high energy of the impinging particles allows surface atoms to rearrange and move into the most stable positions. The relatively broad FWHM of the UO_2 peaks indicates that the crystallite size is small, about 100 nm, as estimated also by SEM and AFM measurements. The diffraction lines of the UO_2 surface layer show a (200) preferred orientation and are shifted to slightly higher 2θ values. This means that the lattice parameter is slightly smaller than the one of the stoichiometric UO_2 powder sample and is therefore in accordance with slightly hyperstoichiometric UO_{2+x} [8], ultraviolet photoelectron spectroscopy (UPS), and XPS characterizations of the sample after preparation showed clean surface with calculated O/U ratio of 2.02. This exact ratio is less relevant after sputtering and annealing (see Section 2.3). The samples were packed and sent under argon atmosphere to the Nuclear Research Centre-Negev (NRCN), where the adsorption experiments have been performed.

2.2. The experimental system

An ultra-high-vacuum (UHV) chamber, pumped by turbo-molecular and titanium sublimation pumps (to a base pressure of ~2×10^{-10} Torr) was employed, incorporated with Auger electron spectroscopy (AES), XPS and direct recoil spectrometry (DRS), as described in Ref. [9]. The DRS technique is relatively unfamiliar, thus a brief description is presented here.

DRS [10] is based on irradiation at grazing angle (15° ± 1°, beam to surface and surface to detector, in this study) of the surface atoms with a pulsed beam of 3 keV Ar^+ ions. The incoming Ar^+ ions recoil surface atoms and ions in a forward direction, and both are detected by an electron multiplier. Time of flight measurements of the recoiled ions and neutrals from the surface generate distinct peaks of the different atomic masses composing the surface. It is a nondestructive technique — ~10^{11} impinging ions/cm^2 per spectrum, so practically, there is no effect of the ion beam on either the substrate composition or the adsorbates. The main advantages of the DRS are detection of light atomic masses (including hydrogen), probing the most top atomic layers, and being non-destructive. The DRS technique is favorable for quantitative composition analysis compared to other low energy ion scattering techniques (LEIS/SIMS), since both ions and neutral atoms are measured. Hence, neutralization effects do not form significant complication. The DRS can also probe different geometrical arrangements of the adsorbed species due to the so-called "shadowing" model. This shadowing effect will be further addressed in the Discussion section.

2.3. The experimental procedure

The stoichiometric UO_2 sample was mounted onto the sample manipulator and spot welded to two Ta wires and a chromel–alumel thermocouple to provide resistive heating and temperature monitoring.

Distilled water was purified with several freeze-pump-thaw cycles, and sample dosing was performed by backfilling the chamber with water vapor via a leakage valve.

Prior to each experiment, the sample was moderately sputtered-cleaned, and then annealed for 5 min under oxygen atmosphere (2×10^{-5} Torr) at 600 K. Surface sample defects were obtained by 30 min 5 keV Ar^+ sputtering with a current density of ~1 μA/cm^2 at room temperature (RT). The sputtering process continued while the sample temperature was elevated to the desired one, in order to minimize (as possible) the annealing effect. Both sputtered and annealed samples were monitored by the DRS technique, during water vapor exposures under pressures of 2×10^{-8}–2×10^{-7} Torr at the temperature range of 300–500 K (at 50 K steps). The hydrogen intensities, H(DR), were normalized to the Argon single scattered, Ar(SS_0), intensity prior to water exposure, to reduce experimental differences due to system instabilities. Al Kα source ($h\upsilon = 1486.6$ eV) was used for XPS experiments and the spectra were taken before each experiment (clean, reduced or oxidized sample), and after 100 L water vapor exposure.

3. Results

The DRS normalized intensities of the H(DR) peaks vs. water vapor exposure on the annealed surface, are presented in Fig. 1 over the temperature range of 300–500 K. The saturation values for the hydrogen accumulation curves decrease with increasing temperature without any noticeable pressure dependence (regions (a) and (b) in Fig. 1). The annealed sample exhibits a Langmuir adsorption curve behavior up to 400 K.

The hydrogen accumulation curves for the sputtered surface (Fig. 2) show rapid adsorption up to ~5 L, having a significantly higher H(DR) intensity, compared to the annealed sample. Saturation is achieved below 10 L. Due to sputtering, the initial oxygen concentrations on the defected surface are relatively low but increase with rising temperatures (see Discussion).

While for the annealed surface there is no significant dependence of O(DR) on H_2O exposure dose or temperature (not presented), for the sputtered surface (Fig. 3) the O(DR) intensities increase at RT with water exposure and the initial oxygen top surface concentration increases with rising temperature.

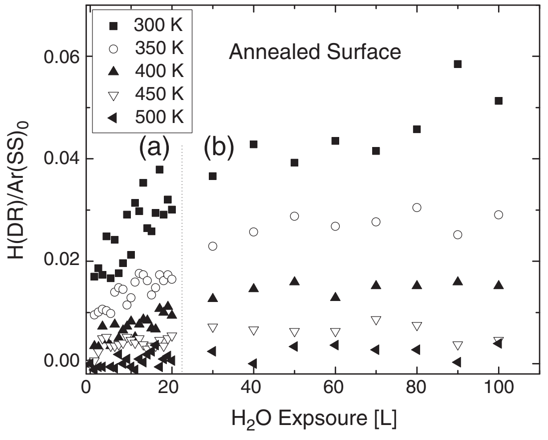

Fig. 1. H(DR)/Ar$(SS)_0$ normalized intensity vs. water exposure for the annealed, stoichiometric sample, at the range of 300–500 K and different pressures: (a) 2×10^{-8} Torr, (b) 2×10^{-7} Torr.

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