Thermal Evolution of Hydrogen Following Water Adsorption on Defective UO$_2$(100)

J. Stultz, M. T. Paffett, and S. A. Joyce*

Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

The evolution of molecular hydrogen from UO$_2$(100) surfaces exposed to water vapor has been studied using temperature programmed desorption. No hydrogen evolution is observed from well-annealed, pristine surfaces. Significant amounts of hydrogen, however, desorb from highly defected, ion-sputtered surfaces at ∼400 K. Annealing studies show that the most of the defects are healed after heating to 750 K. Successive water exposures also heal these defects. These results indicate that the defect is likely an oxygen vacancy (reduced uranium site). On annealing, oxygen diffuses from the near-surface region to fill the surface vacancy. The dissociative adsorption of water also fills the oxygen vacancy. As the damage resulting from ion sputtering is similar to that caused by the recoil atom formed during radioactive decay, the thermal chemistry at defects may be an indirect, but significant, factor in the radiation chemistry of adsorbed species on alpha-emitting materials.

Introduction

Gas generation during the storage of surplus actinide materials represents a significant safety concern because of increased flammability and pressure hazards. The presence of some amount of water adsorbed on these materials is unavoidable, even with the most careful of packaging conditions. Once sealed, both thermal and nonthermal interactions of water with the actinide material can lead to hydrogen generation and container pressurization. The radioactivity of the actinide material leads to radiolysis of adsorbed water, potentially producing water vapor, H$_2$, O$_2$, and H$_2$O$_2$. Generally, the actinide bearing materials are stored as oxides to preclude further reactions evolving gas and/or involving the very reactive native metal. Recent evidence suggests that defect sites present on these actinide oxide surfaces could contribute to thermal reaction pathways to hydrogen generation and pressurization.

Although there is a fairly extensive literature on the interactions of liquid water with oxidized uranium, motivated either by nuclear fuel concerns or environmental fate and transport, there have been considerably fewer studies of vapor phase water interactions with well-characterized single crystal or thin film UO$_2$. To our knowledge, there is only one study of water vapor interactions with a single-crystal surface of UO$_2$. Room-temperature studies of water vapor interactions with a stoichiometric UO$_2$(100) single crystal surface have been previously conducted using X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS), and electron stimulated desorption (ESD).[1] Using labeled D$_2$^{18}O, Hedhili et al.[1] have shown that ^{18}O is incorporated into the surface, yet no evidence for hydroxyl formation was observed. Although water dissociation must occur for the oxygen exchange to take place, the fate of the hydrogen was not determined in these experiments. There are a number of related studies on the oxidation of uranium metal with water vapor. Early photoemission studies identified the presence of adsorbed hydroxyls.[2] More recently, two groups have studied the evolution of hydrogen from water-oxidized uranium surfaces, using a variety of techniques, including temperature programmed desorption (TPD).[3,4] Both studies saw two desorption peaks at

∼350 and ∼500 K which were assigned to hydroxyl recombination and uranium hydride decomposition. Ultraviolet photoelectron spectra (UPS) after successively higher annealing temperatures showed that the lower temperature peak in the TPD was associated with the hydroxyl recombination.[4]

Ion bombardment of surfaces produces numerous defects at the surface and the near-surface region. In addition to the sputtered surface species, which yield surface vacancies, the collisional cascade creates lattice defects such as vacancy/interstitial (i.e., Frenkel) pairs. In compounds, preferential sputtering of one element is often observed. In general, lower mass and lower binding energy species are more likely to be sputtered. For metal oxides, the preferential sputtering of oxygen becomes more pronounced as the metal becomes heavier.[5] For UO$_2$, oxygen depletion of the near-surface region has been observed using XPS after ion bombardment.[6] Based on TRIM code[7] calculations the initial sputtering rate of O is four times greater than U for UO$_2$ bombarded by 5 keV Ar ions.

There have been many studies of the radiation-induced generation of hydrogen from adsorbed water, particularly on oxides. The radiolytic hydrogen yields for interfacial water are often considerably higher than for pure water.[8] Two recent studies on UO$_2$ samples, using high energy He^{2+} and low energy electrons, showed significant H$_2$(g) production.[9,10] In both experiments, much of the hydrogen production is initiated by the electronic excitations induced by the radiation as both electrons and high energy ions produce little lattice damage in the near surface region. For alpha emitting materials such as U or Pu, significant lattice damage does, however, result from the recoil atom. For example, in ^{239}Pu metal, the 5 MeV alpha creates ∼200 displacements over the 10 micron track, whereas the 80 keV ^{235}U recoil creates ∼2000 displacements over a 10 nm track.[11] The displacement damage from the recoil occurs through collisional cascades similar to those produced in ion sputtering.[12] A recoil atom created within ∼10 nm of the surface could, therefore, produce significant damage at the surface. These defects may alter the surface chemistry, leading to additional mechanistic participation in gas generation.

The goal of the present study is to expand on these earlier results by studying water adsorption at lower temperatures (100 K). Furthermore, the role surface defects, especially those which

* To whom correspondence should be addressed. E-mail: sjoyce@lanl.gov.

simulate recoil damage, may have in thermal reactions leading to hydrogen evolution following water adsorption on actinide oxides is explored by conducting thermal programmed desorption experiments on both well annealed UO$_2$(100) single-crystal surfaces and UO$_2$(100) surfaces with higher defect concentrations.

Experimental Section

All experiments were performed in an ultrahigh vacuum (UHV) system, with a base pressure of 8 × 10^{-10} Torr. The UO$_2$(100) single crystal was mounted using a Ta support sled with a thin gold foil insert (melted) to provide good thermal and electrical contact. Ta wires were spot-welded to the support sled to provide connections to the sample probe feedthroughs. This sample mount allows resistive heating and liquid nitrogen cooling of the UO$_2$(100) single crystal. Temperatures were measured using a chromel/alumel (Type K) thermocouple spot-welded to the support sled.

TPD measurements were performed with selected mass monitoring using an SRS model RGA200 quadrupole mass spectrometer. Temperature ramps of 2 K/s were provided by using a digital direct current power supply controlled with a PID controller providing a linear heating ramp from 90 to 1000 K.

Sample cleaning was performed by first Ar ion sputtering the sample for 30 min typically at 5 keV and 6 μA/cm^2, followed by annealing the sample to 1000 K for a period of 1 min three times. Auger electron spectroscopy (AES) was used to determine sample cleanliness. X-ray photoelectron spectroscopy (XPS), using a similar procedure in a separate system, showed that these sputter/annealing cycles produce stoichiometric UO$_2$, free of any reduced uranium species. As the overwhelming background gas was H$_2$, with smaller amounts of methane, water, and carbon monoxide, water exposures were performed by backfilling the chamber via a leak valve using D$_2$O, rather than H$_2$O, which had been purified with several freeze−pump−thaw cycles. Unless otherwise noted, all water exposures were done with the sample at 90 K. Control experiments, where both annealed and sputtered samples were cooled to 90 K but not exposed to D$_2$O, showed no hydrogen evolution upon heating.

For the intentional damage studies, samples were typically sputtered with 5 keV argon ions at a current density of 6 μA/cm^2 for 20 min. A series of experiments were also performed where the sputter time was varied. Most of the effects reported below were also observed for sputter times as low as 2 min.

Results and Discussion

Figure 1 compares TPD spectra for deuterium (mass 4) desorption from annealed and sputtered UO$_2$(100) surfaces following approximately 1 L (1 Langmuir = 1 × 10^{-6} Torr s) exposures to D$_2$O. The main peak in the defective surface spectrum around 400 K is not observed in the spectrum for the annealed surface. It is proposed that D$_2$O adsorbs dissociatively at surface defects to form hydroxyls. Previous studies[2−4] have shown that surface hydroxyls on oxidized uranium metal are stable at least to room temperature. Other mechanisms for hydrogen production such as the desorption of adsorbed molecular hydrogen or the decomposition of a metal−hydride species are inconsistent with the high desorption temperatures and/or the amounts observed in these studies. The well-annealed surface has a negligible defect concentration resulting in only adsorption of water at low temperatures. This physisorption is observed in the lower temperature feature (∼180 K) which is an ionizer cracking product from water desorption. Measurements following room-temperature exposure to D$_2$O for the same
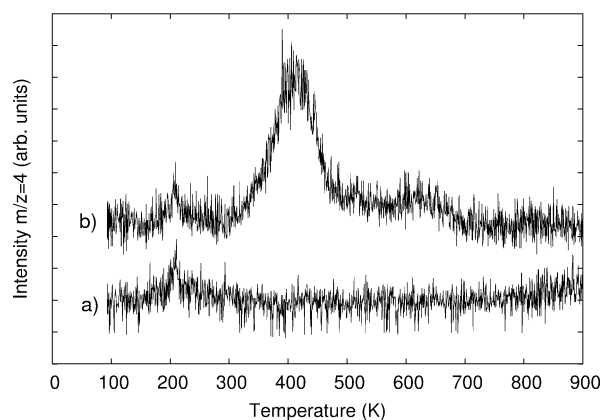

Figure 1. TPD spectra for hydrogen desorption (*m/z* 4) from an annealed (a) and sputtered (b) UO$_2$(100) surface, after a 1 L exposure to D$_2$O. Sputtering conditions were: 5 keV Ar$^+$ at 6 μA/cm^2 for 20 min.
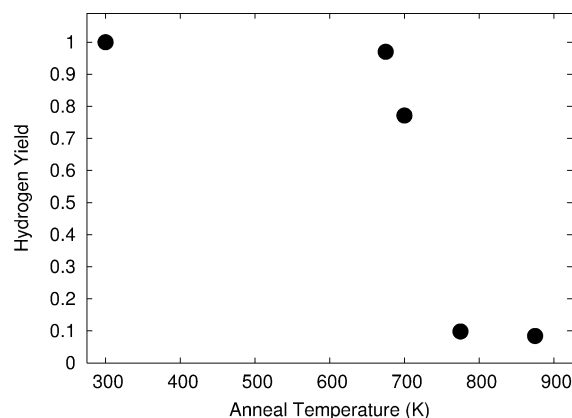

Figure 2. Hydrogen yield as a function of post-sputter anneal temperature. Intensities have been normalized to the hydrogen yield for the unannealed surface.

surfaces showed analogous results with a smaller intensity of the 400 K peak.

To confirm that the hydrogen evolution from the sputtered surface is due to water dissociation at surface defects, hydrogen desorption spectra were collected as a function of post-sputtering annealing temperature. Sputtering creates oxygen vacancies at the UO$_2$(100) surface, which are healed by heating the sample causing oxygen to diffuse from the sample bulk to reoxidize the surface. Figure 2 displays the results of TPD collected by first sputtering the sample and then annealing to different temperatures for a period on 1 min prior to water exposure. As the annealing temperature increases, the amount of hydrogen desorption slowly decreases until the sample is annealed above 700 K. The results from annealing at 775 and 875 K indicate that nearly all of the surface defect sites responsible for the hydrogen desorption have been healed. Annealing the sample to 1000 K, eliminates any detectable D$_2$(g) production. An estimate of the diffusion coefficient, *D*, can be made using the relationship

$$D = x^2/2t$$

Assuming a time of ∼50 s, and a distance of 1 nm, *D* equals 10^{-16} cm^2/s. There is a considerable literature on diffusion of both oxygen and uranium in UO$_2$,[13] although much of this earlier work is at higher temperatures (>1300 K). Recent studies, using ^{18}O as a tracer and SIMS to measure diffusion lengths, have been conducted at slightly lower temperatures (between 900 and 1050 K)[14] At these temperatures, oxygen is the
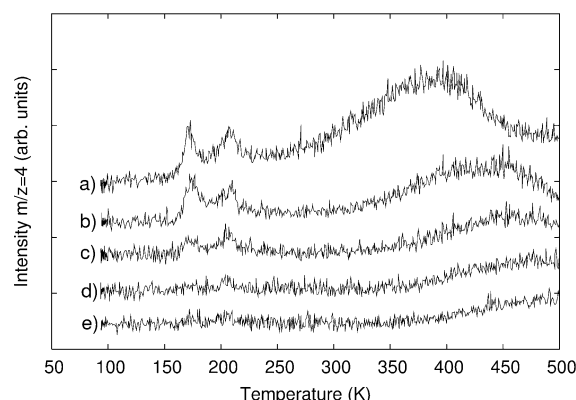
Figure 3. TPD spectra for successive D_2O exposures to a sputtered $UO_2(100)$ surface. The maximum temperature in these experiments was 500 K, lower than necessary to thermally anneal the defects (see text and Figure 2). Part (a) is the trace after the first 1 L exposure to D_2O. Parts (b–e) are successive 1 L exposures.

predominant diffusing species. An Arrhenius extrapolation of these results to 750 K yields a *D* of 7×10^{-16} cm²/s.

The hydrogen evolution from the defective $UO_2(100)$ surface results from the dissociative adsorption of D_2O at defect sites to form adsorbed hydroxyls. The D_2 has been shown above to desorb from the sample surface at around 400 K. There are no high-temperature desorption peaks observed at *m/z* 20 or 32 to suggest that there is high-temperature reaction which leads to gas-phase evolution of a product containing the oxygen from the water. This oxygen could, therefore, remain at the surface and heal the defects that lead to $D_2(g)$ generation. To provide experimental evidence of the reoxidation of the sample by water, TPD experiments were performed for successive D_2O exposures to the sputtered sample surface. To minimize thermally healing the defects, the TPD heating ramps for this series of experiments was terminated at 500 K, at which point the majority of $D_2(g)$ has desorbed but still ∼200 K lower than where the defects are observed to be thermally annealed. Figure 3 shows the results of these experiments for a sample sputtered for 20 min with 5 keV Ar ions. After the first D_2O dose, there is a significant decrease in the amount of hydrogen desorption for the second and subsequent exposures. The hydrogen desorption peak also exhibits a shift to higher temperatures for each successive D_2O exposure. Because hydrogen is observed after an initial saturation water dose, it is proposed that both surface and subsurface oxygen vacancies are formed during the 20 min sputtering. After each water exposure, the surface is now oxygen-rich compared to the near subsurface region. Oxygen from the surface, formed after dehydrogenation, will heal the surface defect or diffuse into the sample surface during the temperature ramp of the TPD, leaving progressively fewer defects at the surface. Shorter sputtering times were used to create surface defects but limit the extent of subsurface vacancies. For a 2 min sputter time, it was found that the same initial hydrogen desorption was observed, but no hydrogen was seen for subsequent D_2O doses. This indicates that for a sputter time of 2 min, the surface defect concentration is saturated without significant formation of subsurface defects.

Although TPD traces are generally difficult to quantify, the low temperature (∼180 K) feature in the D_2 TPD, associated with molecular water desorption, allows for at least a semi-quantitative measure of the amount of D_2 produced at the defects. Assuming a water coverage of 2 monolayers and the measured fragmentation ratio of ∼60 for D_2O^+/D_2^+ in our system, we estimate the coverage of hydroxyls to be approximately 20% for the highly damaged surfaces. This coverage is presumably

lower than that observed in previous experiments on the water oxidation of uranium metal. Given that the hydrogen production is likely a second-order process, where the peak desorption temperature, T_p, would shift to higher temperatures with decreasing coverage, the coverage differences may account for the ∼50 K difference in T_p observed between these two experiments. Other factors, such as simple differences in temperature calibration or a competition between hydroxyl recombination/ D_2 desorption and hydride formation, may also be important. The shift of T_p to higher temperatures with successive water exposures and the associated decrease of the amount of hydrogen produced can be explained by a second-order process as well.

Conclusion

Experimental evidence indicates that sputter-induced defects on $UO_2(100)$ can contribute to hydrogen evolution from the dissociative adsorption of water. Well-annealed, stoichiometric $UO_2(100)$ surface do not evolve measurable quantities of hydrogen. This observation suggests that defects present even on well-annealed samples, such as steps, do not contribute to hydrogen production. Both the annealing studies of surfaces with no adsorbed water and the successive exposures to water suggest that the defect responsible for water dissociation is some form of oxygen vacancy. The collisional cascades associated with sputtering and recoil are not subtle events and produce a wide variety of structural defects, some or all of which may contribute to hydrogen production, thus precluding a more specific identification of the defect type. Oxygen diffusion out of the bulk, which becomes important around 700 K for the time scales in these experiments, can heal the defects at or near the surface. A single water exposure can heal a saturation concentration of surface defects by incorporating the oxygen into the surface. However, near-surface defects are not readily healed by water exposures, so oxygen diffusion from the freshly healed surface, can lead to further hydrogen evolution on successive water exposures. The defects created during ion sputtering are suggested to be similar to those produced by recoils in radioactive decay. These defects may therefore represent an indirect, but important, channel in radiation chemistry.

References and Notes

(1) Hedhili, M. N.; Yakshinskiy, B. V.; Madey, T. E. *Surf. Sci.* **2000**, *445*, 512.
(2) Winer, K.; Colmenares, C. A.; Smith, R. L.; Wooten, F. *Surf. Sci.* **1987**, *183,* 67.
(3) Balooch, M.; Hamza, A. V. *J. Nucl. Mater.* **1996**, *230*, 259.
(4) Manner, W. L.; Lloyd, J. A.; Paffett, M. T. *J. Nucl. Mater.* **1999**, *275*, 37.
(5) Hofmann, S. *Rep. Prog. Phys.* **1998**, *61*, 827.
(6) Chong, S. V.; Barteau, M. A.; Idriss, H. *Surf. Sci. Spectra* **2001**, *8*, 297.
(7) The TRIM/SRIM codes are available at www.srim.org
(8) Petrik, N. G.; Alexandrov, A. B.; Vall, A. L. *J. Phys. Chem. B* **2001**, *105*, 5935.
(9) LaVerne, J. A.; Tandon, L. *J. Phys. Chem. B* **2003**, *107*, 13623.
(10) Joyce, S. A.; Stultz, J.; Paffett, M. T. Unpublished results.
(11) Wirth, B. D.; Schwarz, A. J.; Fluss, M. J.; Caturla, M. J.; Wall, M. A.; Wolfer, W. G. *MRS Bull.* **2001**, *26*, 679.
(12) Robinson, M. T. *J. Nucl. Mater.* **1994**, *216*, 1.
(13) Meachen, J. A. *Nucl. Energy* **1989**, *28*, 221.
(14) Sabnioni, A. C. S; Ferraz, W. B.; Millot, F. *J. Nucl. Mater.* **2000**, *278*, 364.