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The reactions of water vapour on the surfaces of stoichiometric and reduced uranium dioxide: A high resolution XPS study

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Abstract

The reaction of water with stoichiometric and O-defective UO_2 thin film surfaces is studied by high-resolution photoelectron spectroscopy using synchrotron X-rays radiation. The decomposition of D_2O molecules and the oxidative healing of defects on the reduced surfaces was observed and quantified. D_2O adsorption on the stoichiometric UO_2 surface at 300 K showed small amounts of OD species (ca. 532 eV) probably formed on trace amounts of surface defects, while at 95 K D_2O ice (533.5 eV) was the main surface species. On the contrary, a large signal of OD species was seen on the 300 K-Ar^+-sputtered (reduced) surface, UO_{2-x}. This was concomitant with a rapid healing of surface defects as monitored by their U4f signal. Quantitative analysis of the OD signal with increasing temperature showed their disappearance by 550 K. The disappearance of these species while hydrogen molecules are still desorbing from the surface as monitored by TPD [S.D. Senanayake, H. Idriss, Surf. Sci. 563 (1–3) (2004) 135; S.D. Senanayake, R. Rousseau, D. Colegrave, H. Idriss, J. Nucl. Mater. 342 (2005) 179] is shedding light on the re-combinative desorption mechanism from dissociatively adsorbed water molecules on the surfaces of this defective metal oxide.

Keywords: Uranium oxides; Synchrotron radiation; XPS; TPXPS; UO_{2-x}; UO_2; U4f; O1s; Argon-ions sputtering; D_2O; Surface hydroxyls

1. Introduction

Uranium oxides are of great interest due to the large demand and consumption of nuclear energy in the world. As one of the primary starting materials and waste products of nuclear power, there have been questions raised about the outcome of large quantities of depleted uranium and oxide materials [1]. The need to dispose of this spent fuel safely in an environmentally conscious and effective manner has become crucial and is currently being addressed aggressively [2]. An alternative solution to long-term permanent storage has been to use this material in engineering applications and in chemical processes such as tank amour, artillery shell coating [3] and catalysis [4]. Previous studies have shown that uranium oxides have been successfully used as promoters and supports for reactions such as desulphurization [5], decomposition of volatile organic compounds (VOCs) [6] and in stabilizing reaction pathways towards production of novel chemical compounds such as furan from acetaldehyde [7] and acetylene from hydrogenation of CO [8]. At present studies are extending the use of uranium oxides as nanoparticles in mesoporous (MCM) catalysts for several application including catalysis [9]. However, ultimately any process using uranium oxides will still generate the solid waste.

Water as one of the most fundamental components of life on earth is interesting for many reasons. Its interaction with a multitude of surfaces has been studied in the past and is continued at present [10] across all fields of materials science. The possibility to provide clean H_2 fuel from H_2O dissociation promises a source of new age alternative fuel cells in the future [11]. With respect to uranium oxides the interaction of water vapor with nuclear materials leads to the formation of H_2 and O_2 through radiolytic processes. This combination can lead to a potentially dangerous and hazardous scenario when applied to storage environments.

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UO_2 is one of the most stable oxides in the complex uranium-oxide system (UO, U_4O_9, U_3O_7, $U_{16}O_{37}$, U_8O_{19}, U_2O_5, U_3O_8, $U_{12}O_{35}$, and UO_3) and is considered a model metal oxide substrate. At room temperature, it is a Mott–Hubbard insulator ($4 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$) with an increase in conductivity at higher temperatures (>400 K). The UO_2 unit cell is a simple cubic fluorite structure (5.47 Å) with the low index (1 1 1) face the most energetically favorable (1.069×10^{-7} J/cm^2) followed by the (1 0 0) (1.52×10^{-7} J/cm^2) and the (1 1 0) (1.539×10^{-7} J/cm^2) surfaces. A stable hyper-stoichiometric surface (UO_{2+x}) is known to form when UO_2 incorporates two extra O atoms into the lattice occupying interstial positions, shifting two existing lattice oxygen atoms and leaving behind two vacancies, thus forming the so called "2:2:2" cluster. The reduced surface of UO_2 (termed UO_{2-x}) has been reported using XPS in several studies [8,12–14]. The sputtering of the UO_2 surface facilitates the removal of O atoms from the surface leaving an amorphous surface layer with uranium cations in less than +4 oxidation states.

Several previous works have paid close attention to the uranium dioxide surfaces with respect to H_2O and D_2O. Balooch and Hamza [16], Manner et al. [17] and Winer et al. [18] have undertaken work on oxidized uranium and uranium metal surfaces, while other works by Senanayake and Idriss [13] (1 1 1), Stultz et al. [19] and Hedhili et al. [20] have studied the same reaction on the surfaces of oxidized and reduced UO_2 single crystals. All the above groups mentioned have reported the dissociation of H_2O/D_2O over the reduced surfaces (U/UO_{2-x}) and molecular adsorption over the stoichiometric surface of UO_2. A TPD study following dissociative adsorption of H_2O on UO_2 (1 1 1) single crystal surface showed a proportionality with the quantity of O-defects present [13]. As a comparison to single crystal UO_2, a recent study by Senanayake et al. [21] of D_2O on polycrystalline UO_2 (prepared by H_2 reduction of α-U_3O_8) at 1 atm yields a small desorption of D_2. This is explained as due to healing of trace surface O-defects as well as the capacity of UO_2 to accommodate extra oxygen atoms (UO_{2+x}). The aim of this work is to study the oxidation mechanism induced upon contact of D_2O vapor with the stoichiometric and reduced surfaces of UO_2 using high resolution XPS.

2. Experimental

Experiments were performed using synchrotron radiation at the National Synchrotron Light Source (NSLS) in Upton, NY on beam line U12a. The UHV system used is a custom-made (Oak Ridge National Labs) stainless steel chamber that is maintained at 1×10^{-10} Torr with a CTI Cryotorr 8 cryopump and a Balzers TPU 170 turbo pump mounted on the chamber. The pressure inside the UHV system is measured by a Granville Phillips—GP-307 ion gauge and a UTI mass spectrometer is used to analyze the residual gases. A Physical Electronics—PHI (20-115) sputter gun is in place to clean and reduce the sample. The beam of light enters the chamber by way of a 2.75 in. flange and a pneumatic gate valve. The VSW EA125 (EAC 2000 controller) electron analyzer is a multi-channel hemispherical analyzer mounted at 65° from the beam entrance. The sample mount used is composed of a copper heating/cooling block that is connected to a 360° free-rotatable *xyz* manipulator at the top of the chamber. The sample is spot-welded onto tantalum wire (0.25 mm diameter) and is screwed to the heating/cooling block. Heating occurs resistively by current applied to the top of the copper unit at a power feedthrough using a Hewlett-Packard power supply interfaced to a RHK 310 temperature controller which allows for linear ramping of the applied current. Sample cooling is achieved by manually filling a liquid N_2 reservoir inside the mount through the top of the feedthrough and manipulator. A K-type thermocouple is drawn from the top of the chamber to the copper unit and spot welded onto the sample by way of a small-drilled hole in the back of the mount.

The surface investigated is a thin film of UO_2 (1000 Å) deposited onto a molybdenum back plate of 1 cm in diameter and 1 mm in total thickness. The thin film is formed by sputtering UO_2 onto the Mo substrate and mentioned in previous works [5,14]. The sample was cleaned prior to experimentation by several cycles of light Argon sputter (1–2 kV, 15 mA, 10 μA drain current) and annealing under O_2 (1×10^{-5} Torr, 600 K). The stoichiometry and purity of the surface was confirmed with XPS of U4f and survey regions of the sample. The defective surface was obtained by heavy sputtering using Argon (3–4 kV, 15 mA, 20 μA dc) for extended periods of time while the sample was maintained at 300 K. D_2O was placed into a stainless steel container attached to a dosing line and introduced into the UHV chamber using the precision dozer attached to the system. Prior to use D_2O was cleaned with several freeze pump thaw cycles using liquid N_2. Temperature programmed X-ray photoelectron spectroscopy (TPXPS) study was undertaken by linearly annealing (1 K/s) the adsorbate-covered sample to incremental temperatures and cooling the surface (~0.25 K/s) for scanning to either 95 or 300 K. The photon energy of the synchrotron beam was maintained at 625 eV for scans of all regions, with different pass energy (U4f 10 eV, O1s 5 eV and valence regions 20 eV) and different total number of coadded counts/scans (U4f 5000 c/s, O1s 10,000 c/s and valence regions 500 c/s) for respective regions.

3. Results

Fig. 1 shows the XPS spectra for the stoichiometric surface (A) before Ar^+-sputtering, after Ar^+-sputtering at 300 K, (B) and at 95 K (C). The details of the oxidation–reduction of the surface is reported and discussed elsewhere [15]. The stoichiometric surface, spectrum A, has the $U4f_{7/2}$ and $U4f_{5/2}$ peaks at 380.0 and 390.8 eV in addition to two satellite-peaks (S^1 and S^2) at 386.7 and 397.3 eV, respectively. The position of these peaks is in good agreement with a large number of XPS results of "stoichiometric" UO_2 surfaces where all U cations are in a +4 oxidation state [12–15,17,21]. Upon sputtering with argon ions at 300 K (spectrum B), a shoulder on the lower binding energy side of the 4f peaks is seen. In that regard, two points are worth indicating.

1. This region (the low binding energy side of the 4f U^{4+}) is relatively complex and contains contribution from U cations

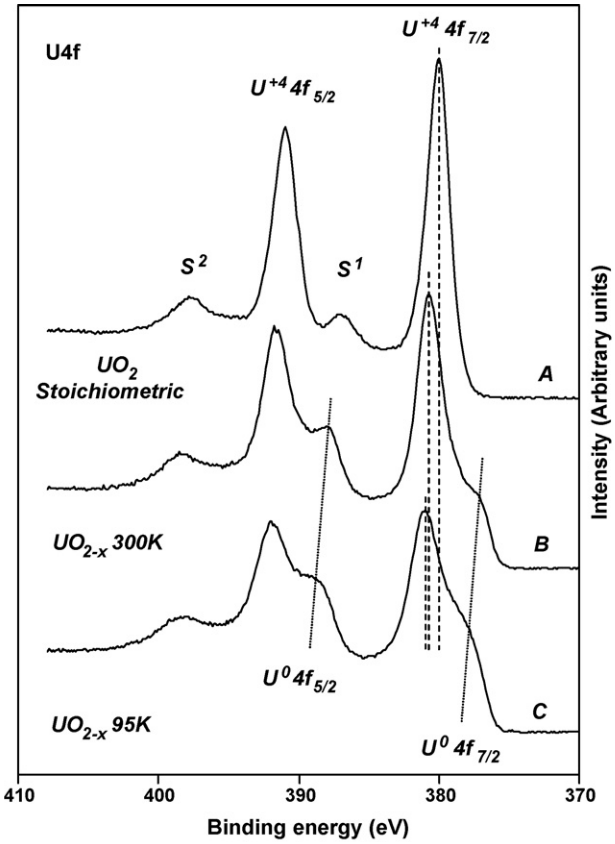

Fig. 1. HRXPS U4f of UO_2 thin film: (A) UHV annealed ‘‘stoichiometric’’; (B) Ar^+-ions sputtered at 300 K; (C) Ar^+-ions sputtered at 95 K.

in different oxidation states including U metal [8,13–15]. The maximum of the shoulder is found at 377.2 eV in the $U4f_{7/2}$ region. There are no reported solid state pure binary compounds of U oxides, where U cations have a formal oxidation state less than +4; thus, there are no reference lines between U^{+4} and U^0 from pure compounds. UO is a known compound in the gas phase [22] but no reported XPS U4f lines are known and while U carbides have been studied [23] detailed analyses of the U4f region is not available.

2. The formation of the reduced species is accompanied by a shift of the spectrum to higher binding energy (ca. +0.6 eV); positioning the $4f_{7/2}$ and $4f_{5/2}$ peaks at 380.6 and 391.3 eV, respectively. This is consistent with the formation of an n-type semiconductor [13]. The S^1 satellite contribution is masked by the emergence of the $U^0 4f_{5/2}$ peak leaving only the S^2 visible at 398.1 eV.

Sputtering at lower temperatures showed a more pronounced effect. Spectrum C shows the effect of sputtering at 95 K (all other conditions were kept constant). The shoulder at the low binding energy side of the $U4f_{7/2}$ at 378.3 eV has become considerably broader. The S^2 peak sits at 398.3 eV with the masked S^1 peak continued to be indistinguishable from the $4f_{5/2}$ of the U^{+x} contribution. The shift to higher binding energy of the spectrum is also consistent with increasing the doping concentration of the n-type semiconductor. The corresponding O1s spectra, not shown, are addressed elsewhere [15]. Assuming that the O/U of the nominally stoichiometric surface is 2.00, the heavily reduced surface would correspond to $UO_{1.44}$. while that of the reduced surface at 300 K (spectrum A) is $UO_{1.7}$.

3.1. D_2O on the stoichiometric UO_2 surface at 300 K

Fig. 2 (a and b) shows the effect of adsorbing 10 L of D_2O at 300 K on the O1s lines of stoichiometric UO_2. The initial stoichiometric surface has the O1s at 530.5 eV with a FWHM at 1.5 eV. With D_2O adsorption the O1s peak broadens

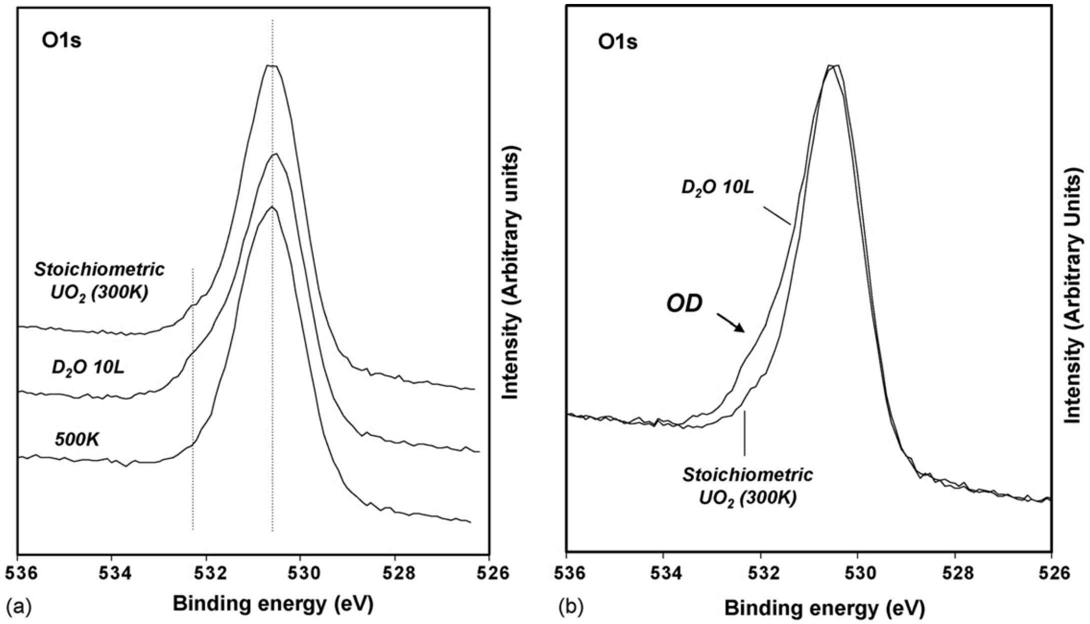

Fig. 2. HRXPS O1s of UO_2 thin film: (a) O1s before and after adsorption of 10 L of D_2O at 300 K; (b) the same 300 K-O1s spectra as in part a, superimposed to point the presence of surface hydroxyls.

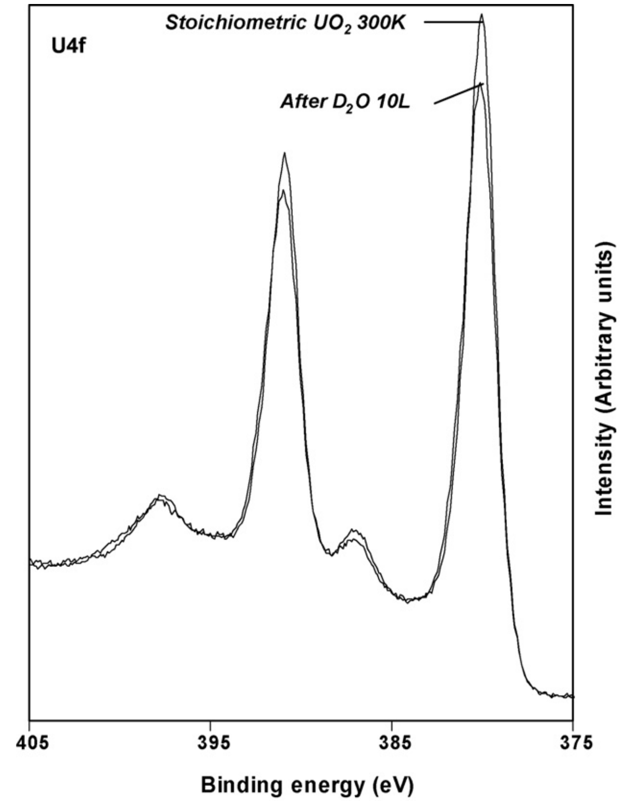

Fig. 3. HRXPS U4f of stoichiometric UO_2 thin film before and after 10 L of D_2O at 300 K.

(FWHM = 1.7 eV) with a shoulder visible on the higher binding energy side. When the two spectra are overlapped as shown in Fig. 2b, the difference is clear at ~532.3 eV (or about 1.7 eV above the lattice O1s position). This shoulder is attributed to OD species as seen in previous works over numerous surfaces [10] it is not attributed to D_2O as the O1s of the D_2O is at about 3 eV above the lattice O1s (see Fig. 4 for mere details). When the surface is annealed to 500 K most of the OD signal has been removed and the FWHM of the lattice O1s at 530.5 eV has returned to 1.5 eV.

The effect of water adsorption on the U4f region is shown in Fig. 3. The initial stoichiometric surface has peaks corresponding to $Uf4_{7/2}$ (380.0 eV), $U4f_{5/2}$ (390.9 eV) and two satellites (386.8 and 397.4 eV). Upon D_2O adsorption the $U4f_{7/2}$ line is attenuated by 11% while that of the O1s is attenuated by 8%. Since the kinetic energy of the photoelectron is larger in the case of U4f in our experiment (95 eV for O1s versus 245 eV for $U4f_{7/2}$) the adjusted screening of U ions would higher when compared to that of the O1s. Water adsorption is expected to occur via the interaction of one oxygen lone pair of the water molecule with the empty surface states, mainly from U cations [25], as a typical Lewis acid–base type interaction. In other words the adsorption occurs on the uranium cations and they are thus far more sensitive to surface coverage than the lattice O1s.

3.2. D_2O on the stoichiometric UO_2 surface at 95 K

In order to distinguish between non-dissociatively adsorbed water from surface hydroxyls the adsorption of D_2O on the stoichiometric surface at 95 K was conducted and the O1s is shown in Fig. 4. The lattice O1s at 530.3 eV, is slightly broader than the corresponding one at 300 K. At 95 K, it is possible that there is contribution of small amounts of OH species from moisture adsorbed onto the cooled surface from inside the UHV system during the cooling process. With introduction of D_2O (5 L) a secondary peak forms at 533.5 eV (ca. 3 eV above the lattice O1s) attributed to D_2O ice forming on the UO_2 surface. The D_2O peak slowly disappears with increasing temperature and has totally desorbed by 300–350 K as shown in Fig. 4. The lattice O1s sharpens and increases in intensity with heating to 400 K.

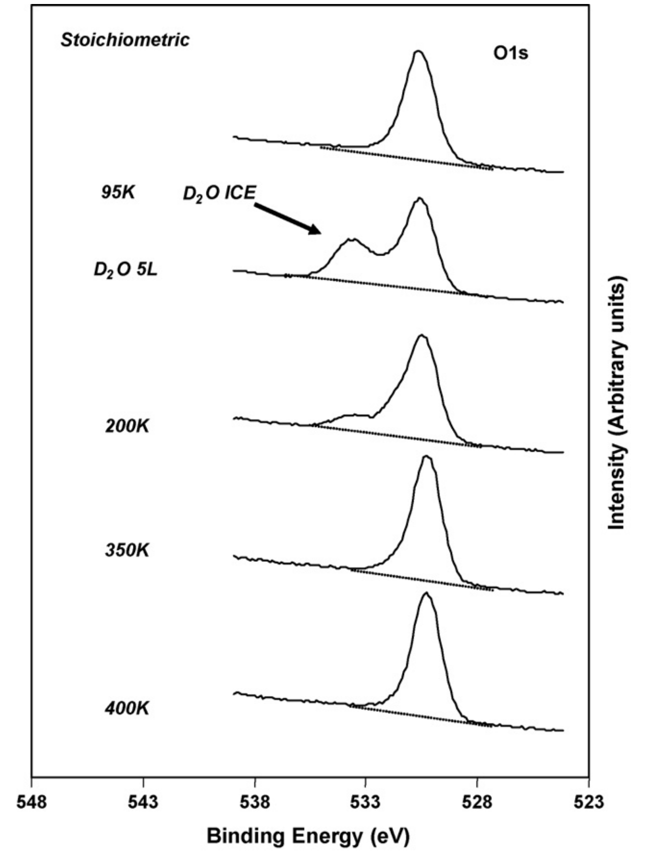

Fig. 4. HRXPS O1s of stoichiometric UO_2 thin film. Adsorption of D_2O at 95 K followed by annealing at the indicated temperatures.

3.3. D_2O on the reduced UO_{2-x} surface at 300 K

The reaction of D_2O on the 300 K-Ar ions-sputtered UO_2 surface ($UO_{1.7}$) is shown in Figs. 5 and 6. The U4f region scans are shown in Fig. 5 with the initially reduced surface being oxidized upon exposure to D_2O (8 L). The first spectrum (a), before adsorption, shows the presence of the U4f peaks attributed to U cations in lower oxidation states, formed upon Ar^+-sputtering, at the lower binding energy side of the U^{4+}4f peaks (very similar to the one presented in Fig. 1 B). The second spectrum (b) shows the effect of 8 L exposure of D_2O. The U4f lines attributed to reduced states have decreased considerably and the S^1 peak of the satellite has become clearly separated form the U^{4+} ($U4f_{5/2}$) peak. Annealing to higher

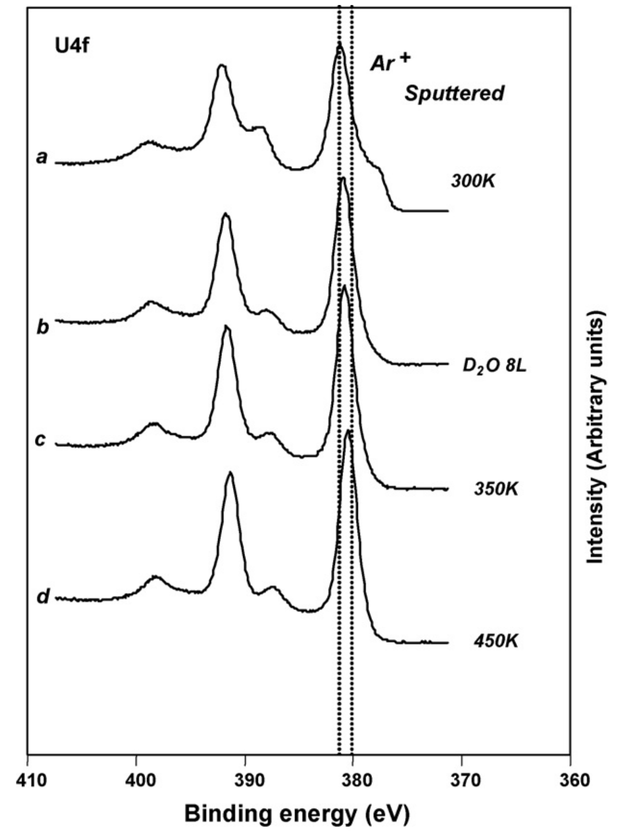

Fig. 5. HRXPS U4f of defected-UO_2 thin film. Dissociative-adsorption of D_2O at 300 K followed by annealing at the indicated temperatures.

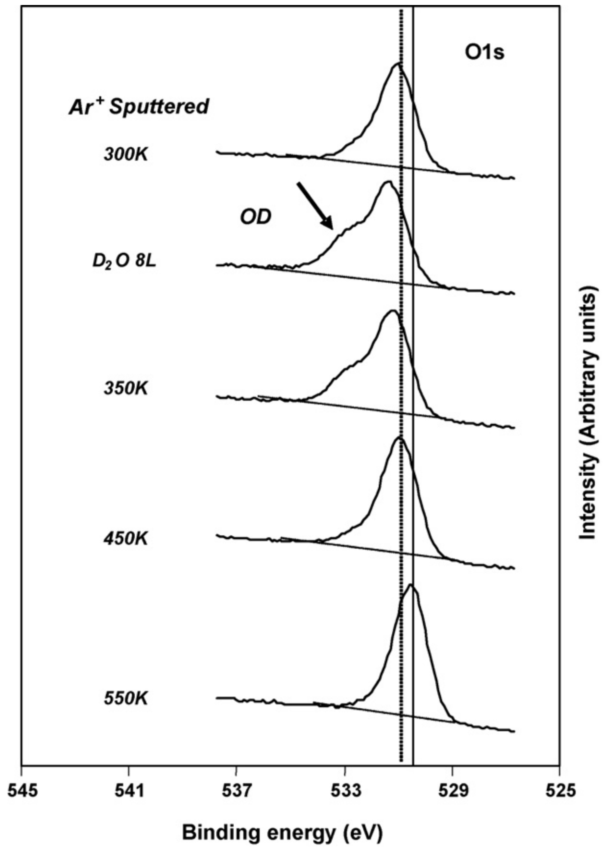

Fig. 6. HRXPS O1s of defected-UO_2 thin film. Dissociative-adsorption of D_2O at 300 K followed by annealing at the indicated temperatures.

temperatures further oxidized the surface with the U4f peaks sharpened and shifted to lower binding energies. By 450 K the $U4f_{7/2}$, $U4f_{5/2}$, S^1 and S^2 peaks are at 380.0, 390.8, 386.6 and 397.2 eV, respectively (very close to those of stoichiometric UO_2). The surface oxidation (spectrum b) is a clear indication that water is completely dissociated to regenerate surface defects. Complete surface oxidation occurs by farther annealing to higher temperature. In previous works, we have shown that this is due to oxygen diffusion from the bulk to the surface [13,15]. In other words, there are two unrelated phenomena presented in Fig. 4: (i) surface oxidation due to D_2O dissociative adsorption (a highly exothermic process [26]) and (ii) surface oxidation due to oxygen migration from the bulk (a process requiring an activation barrier (E_a) in the order of 100 kJ/mol in bulk UO_2 [27]; $D = D_o \exp(-E_a/RT)$, $D_o = 10^9$ nm^2/s).

Fig. 6 shows the O1s region, in which the first spectrum is of the initial sputtered surface with lattice O1s peak at 530.9 eV. Upon exposures of 8 L D_2O, the O1s peak of the lattice shifts to higher binding energy, 531.2 eV. A shoulder attributed to OD appears on the high side at ~532.7 eV. The 1.5 eV difference between the two O1s peaks is considerably smaller than that observed upon water adsorption on the stoichiometric surface (in Fig. 4, the difference between D_2O and O1s is found equal to 3.0 eV). The shoulder attributed to OD is removed by 450 K while the lattice O1s sharpens and shifts to 530.6 eV by 550 K. The O1s behavior mirrors that of the U4f (Fig. 5).

4. Discussion

The main results of this work are the following.

1. Water does not dissociate on the surface of a stoichiometric UO_2 thin film surface, the trace amounts of hydroxyls observed are most likely due to trace defects not healed by prolonged annealing.
2. The creation of surface defects results in water partial and total dissociation. At 300 K a large fraction of U cations in lower oxidation states created upon sputtering are healed. In addition, a large O1s signal due to surface hydroxyl groups is seen.
3. Healing of the surface can be monitored by both the core level U4f band width (multiple oxidation states of the U4f) and band position (shift from n-type semiconductor (O-defected) to intrinsic semiconductor or farther to a p-type semiconductor (excess O atoms)).

Previous TPD work on defective UO_2 single crystal [13] and polycrystalline materials [21] has shown that irreversible adsorption of water molecules dissociatively adsorbed gave two hydrogen desorption peaks at ca. 400 and 500–550 K. The 400 K peak populates first (at low coverage as well as at low defects concentrations) indicating that the second peak (the 500 K) is originating from further water dissociation.

There are at least two interpretations for these two peaks and they are given as follows (for simplicity we will make no distinction between D_2O and H_2O).

4.1.1. Interpretation I

The first peak originates from the recombination of two already made U–H species. This is intuitive since at low surface coverage there are many surface defects and they favor total dissociation of H_2O to H(a) and O(a) [24]. The position of the first peak is in line with H_2-TPD of U polycrystalline where recombinative desorption occurred at the same temperature [16]. The second desorption of hydrogen, the one occurring at high temperature and at high surface coverage is due to U–OH and U–H recombinative desorption. The reason being that at high surface coverage there are less sites for total dissociation and thus more surface hydroxyls are present. Since, it takes more energy to dissociate UO–H species than U–H species then the second desorption can naturally be explained by thermodynamics.

4.1.2. Interpretation II

The first peak observed during TPD is due to U–H + UO–H recombination as well as due to U–H + U–H recombination while the second peak is due to U–H + U–H recombination from deeper layers. This is in line with a previous interpretation by Paffett and co-workers [17] and is also in agreement with the increasing of the population of the second peak with increasing defects concentration [13]. The argument is also thermodynamic since migration from deeper layer will require higher energy.

It is worth mentioning that unlike what is often indicated in literature two adsorbed OH species cannot directly give H_2 since OH dissociation yield H^+ (because the electron affinity of oxygen does not allow in a thermal reaction for homolytic dissociation). In other words each H^+ ion needs to take an electron from the surface and this can only be given from reduced U centers). That is why we have neglected the recombination of two U–OH species directly to H_2 as a distinct route.

Thus, the study of the stability of surface hydroxyls becomes crucial to further understand the reaction of water. The presence of OD species is clear in this work. Fig. 7 compares H_2 desorption from a defective UO_2(1 1 1) single crystal surface (from ref. [13]) and the hydroxyl signal from this work. As seen in the figure the hydroxyl signal decreases while the first H_2 peak desorbs. There are no hydroxyl left on the surface during the second H_2 desorption. Thus, according to our spectroscopic data the second peak is not reasonably linked to OD (OH) species since there is none left. The most plausible interpretation is that this second peak originates from the dissociation of U–H species but in deeper layers; that explains their higher desorption temperature since they need to diffuse through an already oxidized surface barrier.

It is unclear why the surface is oxidized upon water dissociative adsorption at 300 K (Fig. 5). It is difficult to assume that H_2 molecules desorb upon formation since TPD shows desorption above 300 K. Moreover, we have performed a similar study at 95 K and the surface was also oxidized upon exposures to D_2O molecules. One possible explanation is that part of water is totally dissociated and that H atoms diffuse away from the adsorption sites taking one electron per one H atom with them.

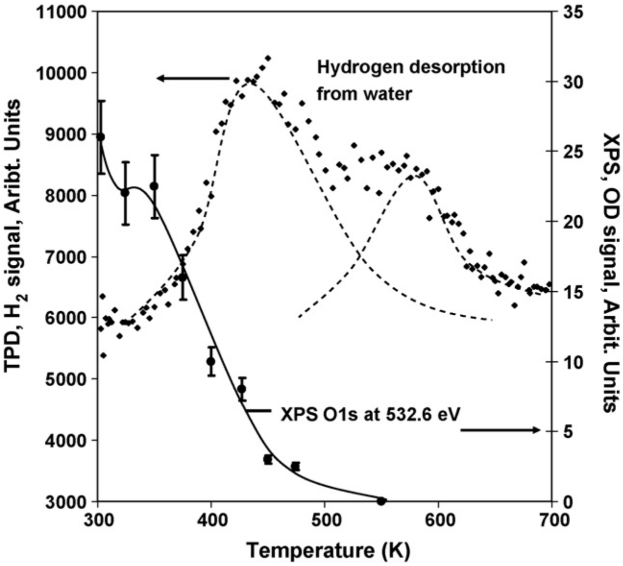

Fig. 7. Computed intensity of the OD signal, such as those presented in Fig. 6, as a function of temperature together with hydrogen desorption during H_2O-TPD on oxygen-defected UO_2(1 1 1) single crystal surfaces (from ref. [13]).

5. Conclusions

The reaction of water molecules on the stoichiometric and O-defected UO_2 thin film surfaces has been studied by high resolution XPS provided from X-ray synchrotron light.

The annealed "stoichiometric" surface does not dissociate water molecules and shows a weak adsorption at room temperature. The O-defected surface dissociatively adsorbs water molecules in order to restore their structure. Monitoring of the surface hydroxyl signals as a function of surface temperature revealed that hydrogen evolution (as a consequence of water dissociation) is only partly due to U–H and UO–H recombination.

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References

[1] DOE-Owned Spent Nuclear Fuel Strategic Plan, US Department of Energy, September, 1996.
[2] M.E. Long, Natl. Geographic 202 (1) (2002) 2.
[3] C. Giannardia, D. Dominicic, J. Environ. Radioact. 64 (2–3) (2003) 227.
[4] S. Dai, M.C. Burleigh, M.J. Haire, M.V. Konduru, E. Myers, S.H. Overbury, Z. Zhang, Advances in depleted uranium technology, in: Waste Management 2001 Symposium, 2001.
[5] Q. Wu, B.V. Yakshinskiy, T. Gouder, T.E. Madey, Catal. Today 85 (2003) 291.
[6] C.S. Heneghan, G.J. Hutchings, S.R. O'Leary, V.J. Boyd, S.H. Taylor, I.D. Hudson, Catal. Today 54 (1999) 3.
[7] H. Madhavaram, H. Idriss, J. Catal. 206 (2002) 155.
[8] S.D. Senanayake, A. Soon, A. Kohlmeyer, T. Sohnel, H. Idriss, J. Vac. Sci. Technol. A 23 (2005) 1078.
[9] D. Kumar, S. Varma, V.S. Kamble, N.M. Gupta, J. Mol. Catal. A 223 (1–2) (2004) 251.
[10] M.A. Henderson, Surf. Sci. Rep. 46 (2002) 1 (and references therein).
[11] J. Alper, Science 299 (2003) 1686.
[12] S.D. Senanayake, H. Idriss, Surf. Sci. Spectra, in press.
[13] S.D. Senanayake, H. Idriss, Surf. Sci. 563 (1–3) (2004) 135.
[14] M.N. Hedhili, B.V. Yakshinskiy, T.W. Schlereth, T. Gouder, T.E. Madey, Surf. Sci. 574 (2005) 17.
[15] S.D. Senanayake, G.I.N. Waterhouse, T.E. Madey, H. Idriss, Langmuir 21 (2005) 11141.
[16] M. Balooch, A.V. Hamza, J. Nucl. Mater. 230 (1996) 259.
[17] W.L. Manner, J.A. Lloyd, M.T. Paffett, J. Nucl. Mater. 275 (1999) 37.
[18] K. Winer, C.A. Colmenares, R.L. Smith, F. Wooten, Surf. Sci. 183 (1987) 67.
[19] J. Stultz, M.T. Paffett, S.A. Joyce, J. Phys. Chem. B 108 (7) (2004) 2362.
[20] M.N. Hedhili, B.V. Yakshinskiy, T.E. Madey, Surf. Sci. 445 (2000) 512.
[21] S.D. Senanayake, R. Rousseau, D. Colegrave, H. Idriss, J. Nucl. Mater. 342 (2005) 179.
[22] M.C. Heaven, J.-P. Nicolai, S.J. Riley, E.K. Parks, Chem. Phys. Lett. 119 (1985) 229.
[23] M. Eckle, R. Eloirdi, T. Gouder, M.C. Tosti, F. Wastin, J. Rebizant, J. Nucl. Mater. 334 (2004) 1.
[24] N. Shamir, E. Tiferet, S. Zalkind, M.H. Mintz, Surf. Sci. 600 (2006) 657.
[25] K.N. Kudin, G.E. Scuseria, R.L. Martin, Phys. Rev. Lett. 89 (2002) 266402–266411.
[26] ΔH of the oxidation of one molecule of UO to one molecule of UO_2, in the gas phase, by H_2O is −245 kJ/mol
[27] H. Madahavaram, H. Idriss, J. Catal. 224 (2004) 358.