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Full Length Article

Thorium effect on the oxidation of uranium: Photoelectron spectroscopy (XPS/UPS) and cyclic voltammetry (CV) investigation on $(U_{1-x}Th_x)O_2$ (x = 0 to 1) thin films

P. Cakir[a,b,*], R. Eloirdi[a], F. Huber[a], R.J.M. Konings[a,b], T. Gouder[a]

[a] European Commission, Joint Research Centre, P.O. Box 2340, D-76125, Karlsruhe, Germany
[b] Department of Radiation Science and Technology, Delft University of Technology, Mekelweg 15, 2629, JB Delft, The Netherlands

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ABSTRACT

Thin films of $U_{1-x}Th_xO_2$ (x = 0 to 1) have been deposited via reactive DC sputter technique and characterized by X-ray/Ultra-violet Photoelectron Spectroscopy (XPS/UPS), X-ray Powder Diffractometer (XRD) and Cyclic Voltammetry (CV) in order to understand the effect of Thorium on the oxidation mechanism. During the deposition, the competition between uranium and thorium for oxidation showed that thorium has a much higher affinity for oxygen. Deposition conditions, time and temperature were also the subject of this study, to look at the homogeneity and the stability of the films. While core level and valence band spectra were not altered by the time of deposition, temperature was affecting the oxidation state of uranium and the valence band due to the mobility increase of oxygen through the film. X-ray diffraction patterns, core level spectra obtained for $U_{1-x}Th_xO_2$ versus the composition showed that lattice parameters follow the Vegard's law and together with the binding energies of U-*4f* and Th-*4f* are in good agreement with literature data obtained on bulk compounds. To study the effect of thorium on the oxidation of $U_{1-x}Th_xO_2$ films, we used CV experiments at neutral pH of a NaCl solution in contact with air. The results indicated that thorium has an effect on the uranium oxidation as demonstrated by the decrease of the current of the oxidation peak of uranium. XPS measurements made before and after the CV, showed a relative enrichment of thorium at the extent of uranium at the surface supporting the formation at a longer term of a thorium protective layer at the surface of uranium-thorium mixed oxide.

1. Introduction

Thorium-Uranium mixed oxides are interesting nuclear fuel materials. Compared to uranium- plutonium mixed oxide, the higher thermal stability and melting temperature results in a larger margin to melting [1]. The use of Thorium-Uranium mixed oxide results in the production of smaller quantities of Transuranium elements [2].

During the geological storage of used nuclear fuel, the radionuclides embedded in the uranium fuel matrix, which are produced during the reactor irradiation, can be released via the dissolution of the fuel matrix. Uranium has two stable oxidation states, (IV) and (VI), and several mixed valence phases (i.e. U_3O_7, U_4O_9, U_3O_8). The solubility of uranium increases several magnitudes as the oxidation state increases from U (IV) to U (VI) in the matrix [3]. On the other hand, ThO_2 is chemically stable, having one oxidation state (IV), and its dissolution is reported to be extremely difficult [4].

Since the first contact of the material with the environment happens on the surface, our interest is to observe changes and the evolution of the oxide layer forming at the interface. In this work, thin films of (U, Th) mixed oxides formed by sputter deposition technique [5] are used instead of using bulk material [6–9]. The use of thin films to simulate the surface of bulk compounds results in a high flexibility for compositional changes (O/(U + Th) or U/Th ratios). Moreover, it allows deposition of layers of different thickness onto variable substrates, with different microstructure when changing the temperature and gas pressure during the deposition.

Materials such as uranium – thorium oxides, are difficult to study by photoelectron spectroscopy [10], which is due to their semiconductor properties as a result of which the flow of current cannot be achieved properly along the bulk sample thickness. This aspect can be limited or avoided by the use of thin films because the low thickness results in a low resistance and the voltage drop can be neglected [11,12].

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[*] Corresponding author at: European Commission, Joint Research Centre, P.O. Box 2340, D-76125, Karlsruhe, Germany.

E-mail address: Pelin.cakir@ec.europa.eu (P. Cakir).

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The main goal of this study is to understand the effect of the stable tetravalent actinide Th(IV) onto uranium dioxide and to follow the electronic structure, oxidation state and redox reactions on the surface.

The paper is divided into three sections. The first part investigates the relative oxygen affinity between uranium and thorium, by bringing them into competition. The second part examines the effect of high temperature and low temperature deposition on the surface properties such as oxygen diffusion and atomic segregation. Also in this part, we compare $U_{1-x}Th_xO_2$ (x = 0 to 1) thin films to bulk materials to confirm their use as model, by analysing their electronic structure and lattice parameters versus their composition. The third part consists of electrochemical studies on $U_{1-x}Th_xO_2$ films (X = 0 to 1). Electrochemistry, especially cyclic voltammetry (CV) of UO_2 samples has been intensively employed [13–18] however to the best of our knowledge, there has been no CV record on uranium-thorium mixed oxides, probably due to the semiconductor properties. The objective of the current CV studies is to examine the oxidation of $U_{1-x}Th_xO_2$ before and after the CV using XPS, looking at the composition and the oxidation state.

2. Experimental

The thin films of $U_{1-x}Th_xO_2$ (x = 0 to 1) were prepared in-situ by direct current reactive co-sputtering from thorium and uranium metal targets in a gas mixture of Ar (6N) and O_2 (6N). The oxygen concentration in the films was adjusted by changing the O_2 partial pressure (10^{-8} mbar–6×10^{-6} mbar), while the Ar partial pressure was maintained at 5×10^{-7} mbar. The composition of the films is controlled by changing the respective target voltages for U and Th target. The thin films were deposited onto silicon wafer (111) substrates, which were cleaned by Ar ion sputtering (4 keV) for 1 min. The plasma in the diode source was maintained by injection of electrons of 50–100 eV energy (triode setup), allowing working at low Ar pressure in absence of stabilizing magnetic fields. After deposition, the thin films were transferred to the XPS-UPS analysis chamber without exposing them to air.

Photoelectron spectroscopy data were recorded using a hemispherical analyser from Omicron (EA 125 U5). The spectra were taken using Mg Kα (1253.6 eV) radiation with an approximate energy resolution of 1 eV. UPS measurements were made using He*II* (40.81 eV) excitation radiation produced by a high intensity windowless UV rare gas discharge source (SPECS UVS 300). The total resolution in UPS was 0.1–0.05 eV for the high resolution scans. The background pressure in the analysis chamber was 2×10^{-10} mbar. The spectrometer was calibrated by using Au-$4f_{7/2}$ line of metal to give a value at 83.9 eV BE and Cu-$2p_{3/2}$ line of metal at 932.7 eV BE for XPS, and on He*I* and He*II* Fermi-edges for UPS. Photoemission spectra were taken at room temperature. Quantification of the spectra was done using CasaXPS software (version 2.3.13Dev50). As Relative Sensitivity Factors, Scofield cross-sections for Mg-Kα radiation [19] were taken. An example of peaks deconvolution with the CasaXPS software is reported in Fig. 1.

For the electrochemical study, a standard 3-electrode setup was used with a working electrode composed of $U_{1-x}Th_xO_2$ (x = 0.00, 0.10, 0.44, 0.84, 1.00) thin films deposited onto gold foil surface; the reference electrode was an Ag/AgCl (3 M KCl) electrode and a Pt wire as counter electrode. Gold foils were first cleaned with Ethanol/1N H_2SO_4/H_2O then heated till 300 °C under ultra-high vacuum (UHV). As adhesion layer, an interface composed of a (U,Th) metal layer was deposited at 300 °C between the gold foil and the $U_{1-x}Th_xO_2$ film. All potential values in this paper are versus Ag/AgCl. The measurements were carried out with a stationary electrode in an unstirred solution. The electrolyte was a 0.01 M NaCl solution at neutral pH in contact with air. Experiments were carried out at room temperature (22 ± 3 °C) in a closed Teflon electrochemical cell with an electrolyte volume of 3 ml. Applied potentials were not corrected for voltage drop because of the negligible electrode resistance of the film electrodes [11]. Before the scans, the electrodes were preconditioned at the most cathodic potential for 5 min to reduce any higher oxides formed during the transportation. The cyclovoltammetry (CV) measurements were recorded in potential sweep cycles in a first series (15 cycles) from $-1.000\,V_{Ag/AgCl}$ up to $+0.600\,V_{Ag/AgCl}$, and back to $-1.000\,V_{Ag/AgCl}$ and then in a second series (15 cycles) from $-1\,V_{Ag/AgCl}$ to $0.8\,V_{Ag/AgCl}$ at a scan rate of $0.010\,V\,s^{-1}$. Ultrapure water from a MilliQ-system (>18 MΩ) was used. Chemicals were all p.a. grade (Merck, Darmstadt).

Table 1
Binding energy of $4f_{5/2}$ core level peak for Th metal, U metal, ThO_2 and UO_2.

Substance	$4f_{5/2}$ (eV)	satellite
Th metal	342.3 [20,43]	–
U metal	388.40 [44]	–
ThO_2	346.8 [20,45]	7.3
UO_2	390.95 [11,46]	6.7

The X-ray diffraction analyses were made on a conventional Phillips PW3830 powder diffractometer with a Cu X-ray tube (40 kV, 30 mA, Kα1 = 0.1540560 nm). Films of about 360 nm (1 Å/s) thicknesses were deposited at 100 °C on a Si (111) wafer. The patterns were recorded at room temperature in a step scan mode over a 2Θ range of [10–100]°, with a step size of 0.01° and a count time of 5 s per step.

3. Results and discussion

3.1. Relative oxygen affinity

To measure the relative oxygen affinity of thorium and uranium, a series of thin films were deposited successively by increasing the oxygen partial pressure with a low increment and analysing them in-situ by XPS. The U-*4f* and Th-*4f* core level spectra enable to investigate the oxidation of uranium and thorium through their binding energy (BE) peak, their shape and their satellites. As reference values, Table 1 reports the $4f_{5/2}$ BE of thorium and uranium present in the metal and in the dioxide, as well as the corresponding satellite.

Fig. 2 reports U-$4f_{5/2}$ and Th-$4f_{5/2}$ core level spectra of $(U,Th)O_x$ (x < 2) thin films obtained successively by co-deposition under slight increase of oxygen partial pressure and (U,Th) metal film spectra are used as reference (red plots). It should be noted that the oxygen partial pressures used in this experiment are not universal values, but vary according to the experimental set-up. The BE and the peak shapes obtained for (U,Th) metal are in agreement with those reported in literature for single and bulk element of uranium and thorium [20,21].

The initial adding of oxygen during deposition affects first the thorium as shown by the relative increase of the *d*-screened peak whereas the uranium peak keeps constant in shape and in binding energy. The quicker oxidation of thorium relative to uranium is confirmed by the further and nearly complete oxidation of thorium (green curves) while for uranium the *f*-screened peak is still the main peak. This simple experiment demonstrates an obvious and much stronger affinity of oxygen for thorium than for uranium, as shown by the oxidation of uranium starting only once thorium is nearly completely oxidised. This is in agreement with the higher stability (lower Gibbs energy of formation) of Th^{4+} relatively to U^{4+}. The shift to lower binding energy of Th-*4f* and U-*4f* peaks is taking place due to the decrease of Fermi-energy linked to charge carrier depletion [22,23] in the sample, as reported in a previous study on ThO_2 [20]. It is a coherent shift, occurring for all photoemission lines (including O-*1s*). The thickness of the oxide layer is small enough to allow electrons to tunnel through. This avoids the charging upon photoemission and still permits a well-defined Fermi-level [24].