

Journal of Visualized Experiments

U2O5 film preparation via UO2 deposition by direct current sputtering and successive oxidation and reduction with atomic oxygen and atomic hydrogen. --Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE59017R2
Full Title:	U2O5 film preparation via UO2 deposition by direct current sputtering and successive oxidation and reduction with atomic oxygen and atomic hydrogen.
Keywords:	U2O5 / UO3 / UO2 / film / DC sputtering / X-ray photoemission spectroscopy / oxidation / reduction
Corresponding Author:	Rachel Eloirdi European Commission Joint Research Centre Karlsruhe, BW GERMANY
Corresponding Author's Institution:	European Commission Joint Research Centre
Corresponding Author E-Mail:	rachel.ELOIRDI@ec.europa.eu
Order of Authors:	Rachel Eloirdi Thomas Gouder Frank Huber Roberto Caciuffo
Additional Information:	
Question	Response
Please indicate whether this article will be Standard Access or Open Access.	Open Access (US\$4,200)
Please indicate the city, state/province, and country where this article will be filmed . Please do not use abbreviations.	Karlsruhe, Germany

Rachel Eloirdi

European Commission
Joint Research Centre
Postfach 2340, 76125 Karlsruhe/Germany

+49 7247 951 803
rachel.eloirdi@ec.europa.eu

Subject: Revision JoVE submission JoVE59017R1

**"U₂O₅ film preparation via UO₂ deposition by direct current sputtering and successive
oxidation and reduction with atomic oxygen and atomic hydrogen"**

"

Authors: Thomas Gouder, Frank Huber, Rachel Eloirdi, Roberto Caciuffo

Dear Editor,

As requested we revised our paper based on the editorial comments. We would like to thank you again and we hope that changes made to the manuscript answered to your expectation.

We are looking forwards to hearing from you soon and we thank you in advance for the interest and the consideration that you give to our paper.

Best Regards

Rachel Eloirdi

TITLE:

U₂O₅ Film Preparation via UO₂ Deposition by Direct Current Sputtering and Successive Oxidation and Reduction with Atomic Oxygen and Atomic Hydrogen

AUTHORS AND AFFILIATIONS:

Thomas Gouder¹, Frank Huber¹, Rachel Eloirdi¹, Roberto Caciuffo¹

¹European Commission, Joint Research Centre, Directorate for Nuclear Safety and Security, Postfach, Karlsruhe, Germany

Corresponding Author:

Rachel Eloirdi

rachel.eloirdi@ec.europa.eu

Tel: +49 7247 951 803

Email Addresses of Co-authors:

Thomas Gouder (thomas.gouder@ec.europa.eu)

Frank Huber (frank.huber@ec.europa.eu)

Roberto Caciuffo (roberto.caciuffo@ec.europa.eu)

KEYWORDS:

U₂O₅, UO₃, UO₂, film, DC sputtering, X-ray photoemission spectroscopy, oxidation, reduction

SUMMARY:

This protocol presents the preparation of U₂O₅ thin films obtained *in situ* under ultra-high vacuum. The process involves oxidation and reduction of UO₂ films with atomic oxygen and atomic hydrogen, respectively.

ABSTRACT:

We describe a method to produce U₂O₅ films *in situ* using the Labstation, a modular machine developed at JRC Karlsruhe. The Labstation, an essential part of the Properties of Actinides under Extreme Conditions laboratory (PAMEC), allows the preparation of films and studies of sample surfaces using surface analytical techniques such as X-ray and ultra-violet photoemission spectroscopy (XPS and UPS, respectively). All studies are made *in situ*, and the films, transferred under ultra-high vacuum from their preparation to an analyses chamber, are never in contact with the atmosphere. Initially, a film of UO₂ is prepared by direct current (DC) sputter deposition on a gold (Au) foil then oxidized by atomic oxygen to produce a UO₃ film. This latter is then reduced with atomic hydrogen to U₂O₅. Analyses are performed after each step involving oxidation and reduction, using high-resolution photoelectron spectroscopy to examine the oxidation state of uranium. Indeed, the oxidation and reduction times and corresponding temperature of the substrate during this process have severe effects on the resulting oxidation state of the uranium. Stopping the reduction of UO₃ to U₂O₅ with single U(V) is quite challenging; first, uranium-oxygen systems exist in numerous intermediate phases. Second, differentiation of the oxidation states of uranium is mainly based on satellite peaks, whose intensity peaks are

weak. Also, experimenters should be aware that X-ray spectroscopy (XPS) is a technique with an atomic sensitivity of 1% to 5%. Thus, it is important to obtain a complete picture of the uranium oxidation state with the entire spectra obtained on $U4f$, $O1s$, and the valence band (VB). Programs used in the Labstation include a linear transfer program developed by an outside company (see **Table of Materials**) as well as data acquisition and sputter source programs, both developed in-house.

INTRODUCTION:

Uranium oxide is the main component of nuclear waste, and its solubility in water is linked to uranium oxidation state, increasing from U(IV) to U(VI). Thus, UO_{2+x} oxidation during geological storage is an important and crucial safety issue^{1,2}. This motivates studies of reaction mechanisms governing the surface interactions between uranium oxides and the environment³⁻⁶. This knowledge is essential to all aspects of treating waste from nuclear fuel cycles.

While tetravalent and hexavalent uranium are well-established and common as solid-state systems, this is not the case for pentavalent uranium, despite its stability in uranyl complexes and occurrence in aqueous solution. In uranium oxides, U(V) is considered a metastable intermediate, and it is not reported as single-state but rather as coexisting with U(IV) and U(VI) species. For this reason, nothing has been reported about the chemical and physical properties of U_2O_5 . This is also due to a common feature of corrosion experiments, in which samples are exposed to a corrosive environment. This creates a steep gradient in oxidation states between the surface (exposed to the oxidants) and bulk of the sample. The change takes place within the analysis depth. Thus, different oxidation states are observed simultaneously, not because of mixed valence, but as an artefact of an incomplete reaction resulting in a heterogeneous layer. These two problems can be resolved by using thin films instead of bulk samples. Large numbers of diverse systems can be prepared with little starting material, and the surface-bulk gradient is avoided because there is no bulk.

The method reported here allows *in situ* preparation of a very thin layer (some tens of atomic layers deposited on an inert substrate) and analysis of its surface without contact with the atmosphere. This is one of the advantages of the Labstation (**Figure 1**), which is a modular machine composed of different chambers kept under dynamic ultra-high vacuum (UHV), reaching pressures of 10^{-9} – 10^{-11} mbar. Chambers are dedicated to preparation of the thin films, surface treatment (gas adsorptions), and characterisation by surface spectroscopies techniques [e.g., x-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), low energy electron diffraction spectroscopy (LEED)]. Samples are mounted on specific sample holders and transferred between different chambers through a linear transfer chamber using a transport wagon. All chambers are connected to this central chamber through a valve so they can be isolated at any moment (e.g., for gas filling or servicing). Recuperation of the sample holder/sample from the linear transfer chamber is accomplished by a transfer rod mounted on each chamber. The Labstation base system has been manufactured by an external company (see **Table of Materials**). Extensions and modifications have been added afterwards depending on experimental requirements, resulting in a unique equipment at JRC Karlsruhe. Extensions include the sputter source (a core element for thin film preparation), which has been developed in-house

along with the sputter and data acquisition programs. The loading of the sample holder/sample from an ambient atmosphere to ultra-high vacuum is done *via* a load lock chamber specially designed to perform multiple sample handling and minimize the time to reaching the final pressure of about 10^{-8} – 10^{-9} mbar, thus limiting air contamination of the system. The Labstation is the result of years of experience and expertise in the surface science field at JRC Karlsruhe.

To pass from one chamber to another, the sample is mounted on a transport wagon driven by an external magnet, controlled by a computer program (**Figure 2**) and moving along the linear transfer chamber of about 7 m to predefined stop positions in front of the chambers.

Without a similar or close installation, the experiment might be difficult to reproduce. However, this installation contributes to the PAMEC laboratory that contributes to the open access program at JRC, in which external users are invited to submit proposals reviewed by a panel of international scientific experts. Their evaluation then allows users to access the infrastructure operated by the JRC. After requests and in the frame of collaborations, thin films can be prepared for external users for analyses and experiments performed outside JRC Karlsruhe.

In this report, we provide a detailed protocol of the growth of single-valence U_2O_5 thin films, obtained by successive steps involving oxidation and reduction of UO_2 with atomic oxygen and atomic hydrogen, respectively. Unlike UO_2 and UO_{2+x} , direct deposition of U_2O_5 and UO_3 films by DC sputtering cannot be done. Therefore, we first proceed to the deposition of a UO_2 film, oxidize it into UO_3 using atomic oxygen, then reduce it back to U_2O_5 with atomic hydrogen. The oxidation and reduction times and sample temperature during the process have effects on the result and are important to master. Correct composition was verified with high-resolution X-ray photoelectron spectroscopy, which provides direct and quantitative evidence for uranium $5f^1$ electronic configuration, as expected for the U(V).

PROTOCOL:

1. Sample Holder Preparation

NOTE: Handling of the sample holder outside of the Labstation under an ambient atmosphere should be performed with gloves and clean tweezers.

1.1. Sample holder preparation and *ex situ* cleaning

1.1.1. Clean a gold (Au) foil (0.025 mm thickness, 99.99%, see **Table of Materials**) of size 8 x 8 mm with acetone. Place the foil on a stainless steel or molybdenum holder specifically designed for the Labstation and fix the foil on the holder by spot welding tantalum wires.

1.1.2. Clean the sample holder and foil again with acetone and let it dry under ambient atmosphere before introduction to the Labstation.

NOTE: A photo of the sample holder with a gold foil is displayed in the inset of **Figure 1**.

1.2. Introduction of the sample holder to the Labstation

1.2.1. Close the UHV valve between the load lock chamber and garage chamber (C1/C2). Untighten the screw, fixing the door of C1, and open the nitrogen valve to bring the pressure to atmospheric pressure, enabling opening of the door.

1.2.2. Introduce the sample holder to C1. Close the door of C1 and open the valve for the primary vacuum.

1.2.3. Close the valve to the primary pump once the primary vacuum reaches a pressure of about 1 mbar. Open the valve linked to the UHV turbomolecular pump immediately afterwards. Wait until the pressure reaches 10^{-7} mbar.

NOTE: This last step can take a minimum of 1 to 3 h, depending on sample outgassing.

1.3. Transfer to the preparation chamber (B1)

1.3.1. Move the transport wagon from the transfer chamber to the intermediate chamber and close the valve between C2 and C3. Open the valve located between C1 and C2. Use the transfer rod of C1 to transfer the sample holder to C2.

NOTE: C2 is an intermediate chamber between C1 and the linear transfer chamber common to all chambers of the Labstation. It separates the load lock chamber, which has a poor vacuum (10^{-7} mbar) from the rest of the system (around 10^{-9} mbar). Sample transfers can be rapidly performed at a relatively poor vacuum in the load lock while keeping the Labstation clean.

1.3.2. After the sample holder sits on the wagon in C2, bring back the transfer rod to C1 and close the valve between C1 and C2. Open the valve between C2 and the linear transfer chamber C3.

1.3.3. Position the wagon in the linear transfer chamber and connect it to the driving magnet before closing the valve between C2 and C3.

1.3.4. Use the program Linear Transfer Control (LTC, **Figure 2**) to transfer the wagon to the position of the preparation chamber B1.

1.3.5. Open the valve between the linear transfer chamber and the preparation chamber B1. Use the transfer rod to position the sample in the preparation chamber B1. Once the transfer rod is back to its initial position, close the valve between the linear transfer chamber and preparation chamber B1.

1.4. *In situ* cleaning of the sample holder

1.4.1. Open the argon valve to reach a pressure of 5×10^{-5} mbar.

1.4.2. Position the sample holder surface in the vertical to face the ion gun (IG10/35, see **Table of Materials**).

1.4.3. Switch on the ion gun to start Ar ion sputtering (2 keV, 10 mA emission current) and keep cleaning for 10 min. Switch off the ion gun.

1.4.4. Bring the thermocouple in contact with the sample holder, then switch on the e-beam heater to anneal the sample at 773 K for 5 min. After an initial rise (into the 10^{-7} mbar range), the pressure falls back to about 10^{-8} mbar, indicating outgassing completion. Switch off the e-beam heater and let the sample cool down to room temperature (RT).

1.4.5. Open the valve between the preparation chamber B1 and linear transfer chamber, then position the sample holder on the wagon using the transfer rod. Close the valve of the B1 chamber.

1.5. Sample holder characterization

NOTE: High-resolution X-ray photoelectron spectroscopy (XPS) measurements were performed using a hemispherical analyser (see **Table of Materials**). A micro-focus source (see **Table of Materials**) equipped with a monochromator and operating at 120 W was used to produce a radiation of Al K α ($E = 1486.6$ eV). Calibration of the spectrometer was done using the $4f_{7/2}$ line of an Au metal, producing a value of 83.9(1) eV binding energy (BE), and the $2p_{3/2}$ line of a Cu metal at 932.7(1) eV BE.

1.5.1. Transfer the wagon by remote control using the LTC program to the position of the analysis chamber A4.

NOTE: The background pressure in the analysis chamber is 2×10^{-10} mbar.

1.5.2. Open the valve of the analyses chamber A4 and use the transfer rod to take the sample from the linear transfer chamber to analyses chamber A4. Close the valve of the analysis chamber A4.

1.5.3. Transfer the sample to the analysis position using the acquisition program (**Figure 3**).

1.5.4. Switch on the cooling water and X-ray source of the spectrophotometer (anode voltage = 15 keV, emission current = 120 mA).

1.5.5. Start the data acquisition using the acquisition program (**Figure 3**).

NOTE: Optimization of the sample position can be performed with the acquisition program to obtain maximal signal intensity.

NOTE: Photoemission spectra were taken from the sample surface kept at RT.

1.5.6. Start the measurement of an overview spectrum using the following parameters: $KE_{ini} = 100$ eV, $KE_{fin} = 1500$ eV, scan time = 300 s, N° of points = 1401, pass energy = 50 eV, slit = 7×20 mm diameter, mode = 1.5 keV/medium area mode.

NOTE: The absence of a C1s peak at about 284.5 eV BE indicates that the surface is clean.

1.5.7. Start the acquisition of Au4f core level spectrum with the following parameters: $KE_{ini} = 1396.6$ eV, $KE_{fin} = 1406.6$ eV, scan time = 60 s, number of points = 201, pass energy = 30 eV, slit = 6 mm diameter, mode = 1.5 keV/medium area mode.

NOTE: This latter measurement will be compared to the spectrum after deposition of the UO_2 film on the gold foil to evaluate corresponding thickness of the film.

1.5.8. Once the surface of the sample holder (Au foil) has been analyzed, open the valve of the analysis chamber A4 to position the sample holder on the wagon in the linear transfer chamber using the transfer rod.

2. Thin Film Preparation

NOTE: Uranium oxide thin films are prepared *in situ* by direct current (DC) sputtering using a uranium metal target and gas mixture of Ar (6 N) and O_2 (4.5 N) partial pressure.

2.1. Deposition of UO_2 film

2.1.1. Transfer the wagon carrying the sample holder to the position of the preparation chamber B2 by remote control using the LTC program.

2.1.2. Open the valve of the preparation chamber B2, and with the transfer rod, position the sample holder under the sputter source, located in the middle of B2.

NOTE: Before the sputtering process, ensure that the shutter of the sputter source is closed.

2.1.3. Close the valve to isolate the B2 chamber from the linear transfer chamber. Then, open the O_2 valve and adjust the oxygen partial pressure to 2.5×10^{-5} mbar. Open the argon valve gas to reach a partial pressure of 5×10^{-3} mbar.

2.1.4. Use the sputtering program (**Figure 4**) to enter the following parameters: deposition time = 300 s, uranium target voltage = -700 V, uranium target current = 2 mA, filament heating = 3.3 V/3.9 A, filament working voltage = 40 V.

NOTE: Wait for about 120 s of sputtering with the closed shutter of the sputter source.

2.1.5. Start the timer immediately after opening the shutter of the sputter source to allow deposition of UO_2 on the Au foil.

NOTE: To work at low Ar pressure without stabilizing magnetic fields, injections of 25–50 eV energy (triode setup) were enabled to maintain the plasma in the diode.

2.1.6. Stop the sputtering after 300 s, using the corresponding program, and close the Ar and O_2 gas valves.

NOTE: The blue light of the plasma will disappear and all sputtering parameters will fall to zero.

NOTE: Wait until the pressure of the preparation chamber B2 reaches 10^{-8} mbar.

2.1.7. Bring the sample in preparation chamber B1, and for a smooth annealing of the sample, switch on the e-beam heater and set the temperature to 573 K.

NOTE: Wait for 3 to 5 min before stopping the heating.

2.2. UO_2 sample characterisation

NOTE: For characterisation of the sample by XPS, the same procedure described for the sample holder characterisation should be followed.

2.2.1. Open the valve between the preparation chamber B1 and linear transfer chamber to transfer the sample to the wagon using the transfer rod. Set the transfer rod back to the preparation chamber B1, then close the valve to isolate it from the linear transfer chamber.

2.2.2. Follow the same procedure described in steps 1.5.1 to 1.5.6.

NOTE: The overview spectrum enables control of the quality of the UO_2 film by excluding additional impurity peaks ($\text{C}1s$, cross-contamination from the sputter source housing) and controlling (roughly) the U:O ratio of the film.

2.2.3. Start acquisition of the $\text{Au}4f$ core level (similar parameters as in step 1.5.7).

2.2.4. Proceed to the acquisition of $\text{U}4f$, $\text{O}1s$, and valence band (VB) using the following parameters: pass energy = 30 eV, slit = 7 x 20 mm diameter, mode = 1.5 keV, medium area.

$\text{U}4f$: $\text{KE}_{\text{ini}} = 1066.6$ eV	$\text{KE}_{\text{fin}} = 1126.6$ eV	Scan time = 300 s	N° of points = 601
$\text{O}1s$: $\text{KE}_{\text{ini}} = 946.6$ eV	$\text{KE}_{\text{fin}} = 966.6$ eV	Scan time = 300 s	N° of points = 201
Vb : $\text{KE}_{\text{ini}} = 1473.6$ eV	$\text{KE}_{\text{fin}} = 1488.6$ eV	Scan time = 1800 s	N° of points = 601

NOTE: The obtained spectra for the UO_2 film are reported in **Figure 5**.

2.3. Oxidation of UO_2 with atomic oxygen

NOTE: The atom flux (see **Table of Materials**) is specified to $>10^{16}$ atoms/cm²/s, corresponding to an exposure up to 20 s of roughly 10 Langmuirs (i.e., 1.33×10^{-3} Pa•s).

2.3.1. Transfer the wagon carrying the sample to the preparation chamber B3. Open the valve of the preparation chamber B3, and with the transfer rod, position the sample inside B3 in front of the atom source. Close the valve to isolate the chamber from the linear transfer chamber.

2.3.2. Set the sample temperature to 573 K. Wait 5 min to allow the sample to reach the holder's temperature.

2.3.3. Open the oxygen valve and set the partial pressure to 1.2×10^{-5} mbar O_2 . Switch on the cooling water for the atom source.

2.3.4. Switch on the atomic source and set the current to 20 mA. Pay attention to the exact time to oxidize the sample with the atomic source. If oxidation time is too short, the oxidation to UO_3 can be incomplete as reported in **Figure 6**.

2.3.5. Wait 20 min to achieve complete oxidation of UO_2 into UO_3 and switch off the atomic source before closing the oxygen valve. Once the pressure of the preparation chamber B3 is 10^{-7} mbar, open the valve to transfer the sample to the wagon present in the linear transfer chamber. Then, close the valve of the preparation chamber B3.

2.4. Analysis of UO_3 obtained after oxidation of UO_2 with atomic oxygen

2.4.1. Transfer the sample to the analyses chamber following steps 1.5.1 to 1.5.6; then, for the analyses, follow the same procedure as described in step 2.2.4.

NOTE: The corresponding spectra of UO_3 are reported in **Figure 7**.

2.5. Reduction of UO_3 by atomic hydrogen

2.5.1. To transfer the sample to the preparation chamber B3, follow steps 2.3.1 and 2.3.2.

2.5.2. Open the hydrogen valve and set the partial pressure to 3×10^{-5} mbar. Switch on the cooling water for the atom source. Switch on the atomic source and set the current to 30 mA.

2.5.3. Wait for 60 s of reduction time before switching off the atomic source. Pay attention to the exact time taken to reduce the sample with the atomic source. If reduction time is too long, then UO_{2+x} is further reduced to UO_2 as reported in **Figure 8**. If this occurs, the sample must be oxidized again with atomic oxygen (as we did to get UO_3), whose corresponding spectra are reported in **Figure 9**.

2.6. Analysis of U₂O₅ obtained after reduction of UO₃ with atomic hydrogen

2.6.1. Transfer the sample to the analysis chamber following steps 1.5.1 to 1.5.6; then, for the analyses, follow the same procedure as described in step 2.2.4.

NOTE: The obtained spectra of U4f, O1s, and the VB are reported in **Figure 10**. As an example of incomplete reduction to U₂O₅, similar spectra as shown in **Figure 6** are obtained.

REPRESENTATIVE RESULTS:

The identification of U(V) can be easily done by a characteristic energy of the shake-up satellite accompanying the characteristic U4f doublet. The binding energy at which appears the satellite, associated with intrinsic energy loss processes, depends on the uranium oxidation state.

Uranium 4f core level X-ray photoemission spectra are recorded for U(IV) in UO₂ (red curve), U(V) in U₂O₅ (green curve), and U(VI) in UO₃ (pink curve), then compared to U(0) in uranium metal (black curve) in the left part of **Figure 11**. The corresponding O1s core level spectra are superposed and reported in the right part of **Figure 11**.

In the center part of **Figure 11**, the U4f_{7/2} core level peaks have been shifted to superpose the main lines (upper half), allowing visualization of the energy separation (ΔE) between the satellite and main line (lower half). With increasing oxidation state, the energy separation increases, while satellite intensity decreases. Spectra were obtained on thin films of about 20 monolayers in thickness. The satellite energy peak and the 4f_{5/2} (4f_{7/2}) emission line were used as a fingerprint for the oxidation state of the uranium atoms. The valence band spectra of UO₂, U₂O₅, and UO₃ obtained on the same films are reported in **Figure 12**.

The spectra described in the protocol are corresponding to UO₂ films (**Figure 5**) obtained after deposition in the preparation chamber B2. This film is then oxidized with atomic oxygen. Depending on the oxidation time, the result can be UO_{2+x} (as reported in **Figure 6**) or UO₃ (as reported in **Figure 7**). Also, if atomic reduction with hydrogen on UO₃ is too long, it will return to UO₂ as reported in **Figure 8**. In this case, reoxidation to UO₃ as reported in **Figure 9** should take place before reducing it again with an appropriate time to get U₂O₅, as displayed in **Figure 10**. The results show that the oxidation and reduction processes are completely reversible.

FIGURE AND TABLE LEGENDS:

Figure 1: Photograph and schematic of the Labstation machine developed at JRC Karlsruhe to enable *in situ* surface science studies.

Figure 2: Screenshot of the linear transfer control program. The program enables transfer of the wagon carrying the samples (I to V) along the linear transfer chamber at different chamber positions.

Figure 3: Screenshot of the acquisition program. Once the measurement conditions are

introduced, a series of measurements can be performed automatically after switching on the X-ray generator. The sample position window enables positioning of the sample in the analyses chamber. The adjustment along x, y, and z can be done to optimize the intensity of the signal.

Figure 4: Screenshot of the sputter control program. The sputtering conditions can be selected with this program developed in-house. Among the variables to be defined are the heating and working voltages of the filament and the voltages of up to two targets.

Figure 5: $U4f$, $O1s$, and valence band spectra after deposition of a UO_2 film, measured by high-resolution X-ray photoemission spectroscopy. The peak and satellite positions are characteristic of a UO_2 sample.

Figure 6: $U4f$, $O1s$, and valence band spectra after oxidation of UO_2 with atomic oxygen, measured by high-resolution X-ray photoemission spectroscopy. The oxidation time is too short, thus the oxidation to UO_3 is incomplete. The satellite and peak positions are characteristic of UO_{2+x} and not of the UO_3 reported in Figure 7.

Figure 7: $U4f$, $O1s$, and valence band spectra measured after oxidation of UO_2 film with atomic oxygen using high-resolution X-ray photoemission spectroscopy. The peak and satellite positions are characteristic of a UO_3 sample.

Figure 8: $U4f$, $O1s$, and valence band spectra measured after reduction of UO_3 with atomic hydrogen. The reduction time is too long, thus the U_2O_5 is further reduced to UO_2 . The satellite and peak positions are characteristic of a UO_2 and not the U_2O_5 sample reported in Figure 10.

Figure 9: $U4f$, $O1s$, and valence band of the sample obtained in Figure 8 and re-oxidized with atomic oxygen to UO_3 . The satellite and peak positions are characteristic of a UO_3 sample. The processes of reduction and oxidation are thus reversible.

Figure 10: $U4f$, $O1s$, and valence band spectra after reduction of UO_3 film with atomic hydrogen, measured by high-resolution X-ray photoemission spectroscopy. The peak and satellite positions are characteristic of a U_2O_5 sample.

Figure 11: $U4f$ and $O1s$ core level X-ray photoemission spectra of U(IV) in UO_2 (red curve), U(V) in U_2O_5 (green curve), and U(VI) in UO_3 (pink curve), then compared to U(0) in uranium metal (black curve).

Figure 12: Valence band spectra of U(IV) in UO_2 (red curve), U(V) in U_2O_5 (black curve), and U(VI) in UO_3 (pink curve).

DISCUSSION:

The initial results obtained on the thin films of U_2O_5 of about 30 monolayers (ML) in thickness, together with the corresponding core level spectroscopy obtained with high-resolution X-ray photoemission spectroscopy, have been reported in a previous publication⁷. The evolution of the

uranium state during the oxidation process of UO_2 into UO_3 was reported through X-ray photoelectron spectra obtained on thin films of two to 50 layers in thickness in a wide range of the O:U ratio (**Figure 11, Figure 12**). Film oxidation and film reduction were obtained by exposing the films to atomic oxygen and atomic hydrogen, respectively. The homogeneity of the films with uranium oxidation states from IV to VI could be confirmed due to their small thickness and the reaction temperatures. Thin films of uranium oxides are deposited on a substrate using direct current sputtering with a sputter source developed at JRC Karlsruhe. The sputter source is installed in a chamber kept under ultra-high vacuum, like all the chambers of the Labstation. While UO_2 can be obtained directly, UO_3 and U_2O_5 films are only obtained after further treatment with atomic oxygen and atomic hydrogen. The binding energy of the main peaks and their satellites positions allow differentiation between the oxidation states of uranium in uranium oxide films produced *in situ*. High-resolution spectroscopy is necessary to differentiate the different oxidation states, as the satellite binding energies are close and have low intensities.

In 1948, pure pentavalent uranium, U_2O_5 , was identified for the first time⁸. Later, its synthesis was described based on high temperature (673–1073 K) and high pressure (30–60 kbar) of a mixture of UO_2 and U_3O_8 ⁹. However, the existence and stability of U_2O_5 at ambient temperature and pressure conditions have been questioned, suggesting a lower limit of $x = 0.56$ – 0.6 for the single-phase region below U_3O_8 ¹⁰. So far, preparation of U_2O_5 at high pressure and temperature or during a thermo-reduction process was not reproducible; often, it was not possible to assign a single oxidation state to obtained samples. Some of a U_2O_5 bulk sample preparation appeared as mixtures of UO_2 or UO_3 with coexistence of U(V) with U(IV) or U(VI), as for U_4O_9 and U_3O_8 . For instance, Teterin et al.¹¹ reported the leaching process of U_3O_8 in sulphuric acid followed by thermal treatment in a helium atmosphere, claiming that the results were related to U_2O_5 . This conclusion could be easily excluded due to a resulting two-peak structure in their XPS spectra. A mixture of U(V) and U(VI) species could explain the result, excluding the formation of a single U(V) oxidation state expected for U_2O_5 .

Our method of preparation allows preparation of thin films of uranium oxide with single oxidation states of U(IV), U(VI), and U(V). The entire process of sample preparation takes place *in situ* within an instrument maintained at ultra-high vacuum. It was found that reduction of UO_3 by atomic hydrogen does not proceed to UO_2 but can be stopped at U(V). The time factor is very important as well as the temperature of the sample during the reduction process. With the high-resolution photoemission spectrometer, it was shown that a pure sample of U_2O_5 can be prepared *in situ*. Preparing thicker films should be a next step in looking at the crystallographic structure and bulk properties with *ex situ* techniques.

ACKNOWLEDGEMENTS:

The authors have no acknowledgements.

DISCLOSURES:

The authors have nothing to disclose.

REFERENCES:

- 485 1. Shoesmith, D. W., Sunder, S., Hocking, W. H. Electrochemistry of UO₂ nuclear fuel.
486 *Electrochemistry of Novel Materials*. eds. Lipkowski, J, Ross, P. N. (New York, N.Y.), (1994).
- 487 2. Shoesmith, D. W. Fuel corrosion processes under waste disposal conditions. *Journal of Nuclear*
488 *Matter*. **282**, 1–31 (2000).
- 489 3. Gouder, T., Shick, A. B., Huber, F. Surface interaction of PuO₂, UO_{2+x} and UO₃ with water ice.
490 *Topics in Catalysis*. **56**, 1112–1120 (2013).
- 491 4. Cohen, C. *et al.* Water chemisorption on a sputter deposited uranium dioxide film — Effect of
492 defects. *Solid State Ionics*. **263**, 39–45 (2014).
- 493 5. Seibert, A. *et al.* The use of the electrochemical quartz crystal microbalance (EQCM) in
494 corrosion studies of UO₂ thin film models. *Journal of Nuclear Matter*. **419**, 112–121 (2011).
- 495 6. Majumder, I. *et al.* Syntheses of U₃O₈ nanoparticles from four different uranyl complexes:
496 Their catalytic performance for various alcohol oxidations. *Inorganic Chimica Acta*. **462**, 112–122
497 (2017).
- 498 7. Gouder T. *et al.* Direct observation of pure pentavalent uranium in U₂O₅ thin films by high-
499 resolution photoemission spectroscopy. *Scientific Reports*. **8**, 8306/1-7 (2018)
- 500 8. Rundle, R. E., Baeziger, N. C., Wilson, A. S., MacDonald, R. A. The structures of the carbides,
501 nitrides and oxides of uranium. *Journal of the American Chemical Society*. **70**, 99 (1948).
- 502 9. Hoekstra, H. R., Siegel, S., Gallagher, F. X. The uranium-oxygen system at high pressure. *Journal*
503 *of Inorganic and Nuclear Chemistry*. **32**, 3237 (1970).
- 504 10. Kovba, L. M., Komarevtseva, N. I., Kuz'mitcheva, E. U. On the crystal structures of U₁₃O₃₄
505 and delta-U₂O₅. *Radiokhimiya*. **21**, 754 (1979).
- 506 11. Teterin, Y. A. *et al.* A study of synthetic and natural uranium oxides by X-ray photoelectron
507 spectroscopy. *Physics and Chemistry of Minerals*. **7**, 151–158 (1981).

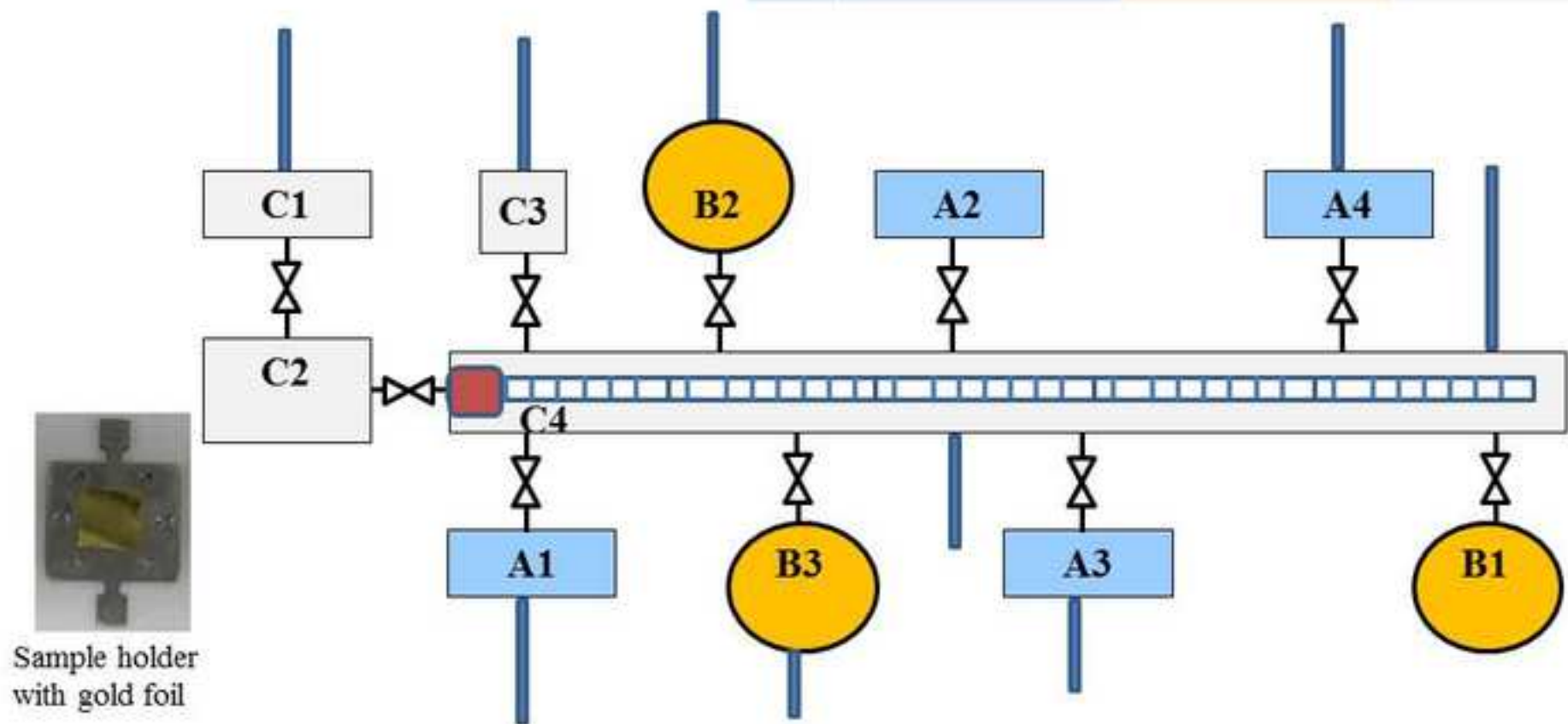
Figure1

[Click here to access/download;Figure;Figure_1_Labstation_scheame_v7.jpg](#)



 Transfer rod
 Wagon carrying sample

	A	B	C
	Analyse	Preparation	Transient
1	HREELS	Conditioning & Film deposition by evaporation	Load
2	AFM	Film deposition by DC Sputtering	Intermediate
3	TPD	Atomic source	Storage
4	XPS, UPS, BIS, ...		Linear transfer



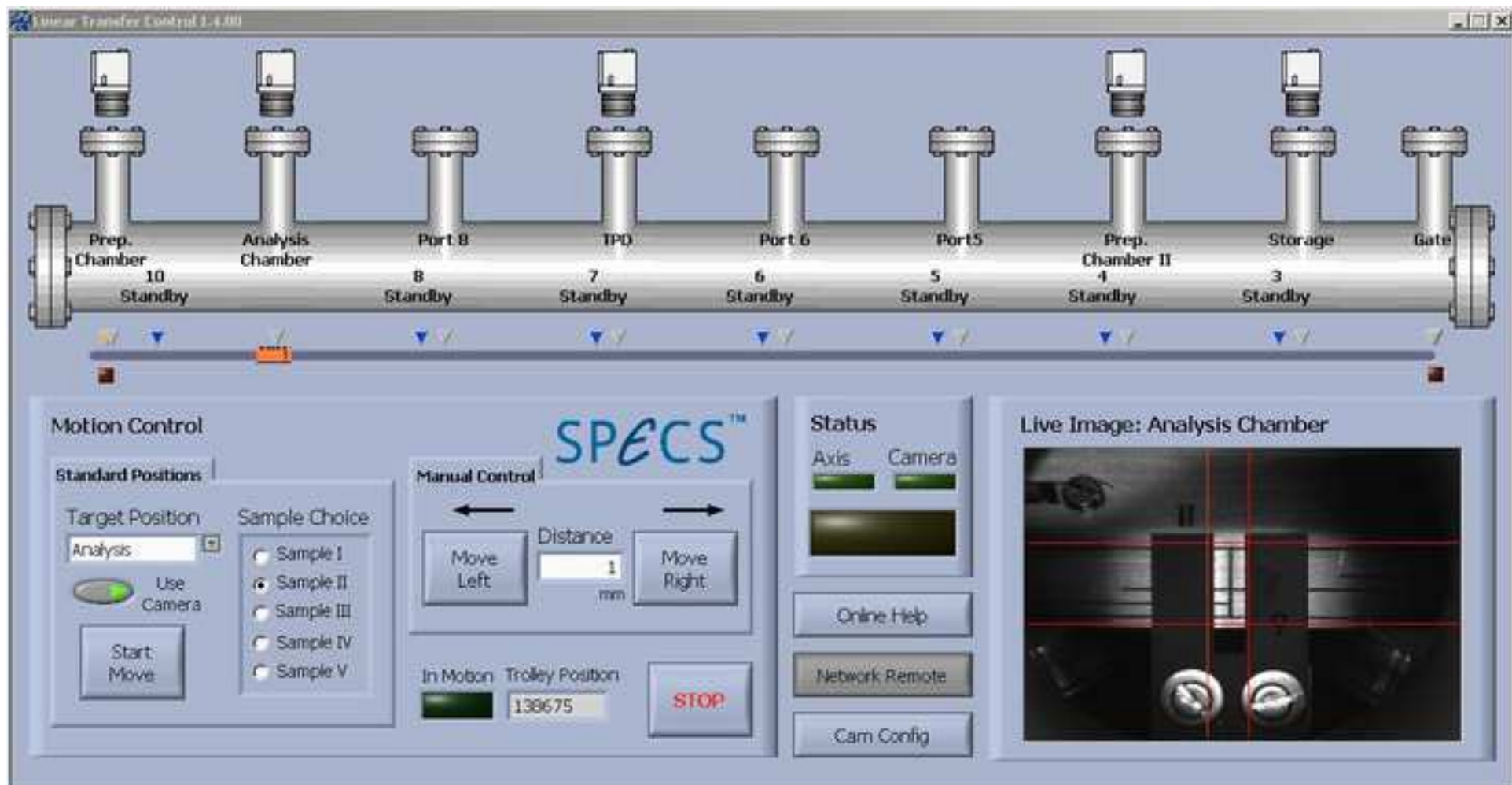


Figure3

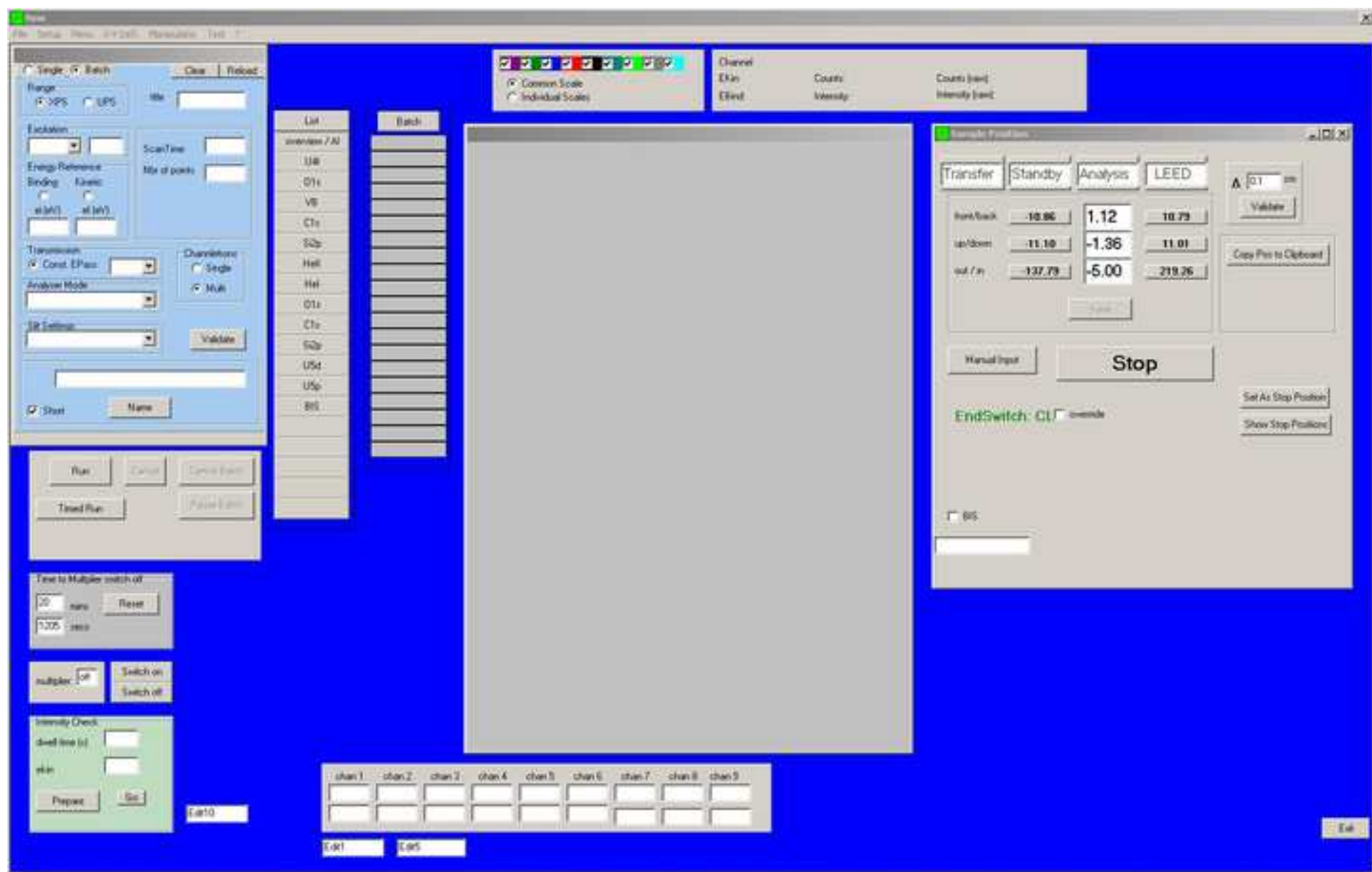
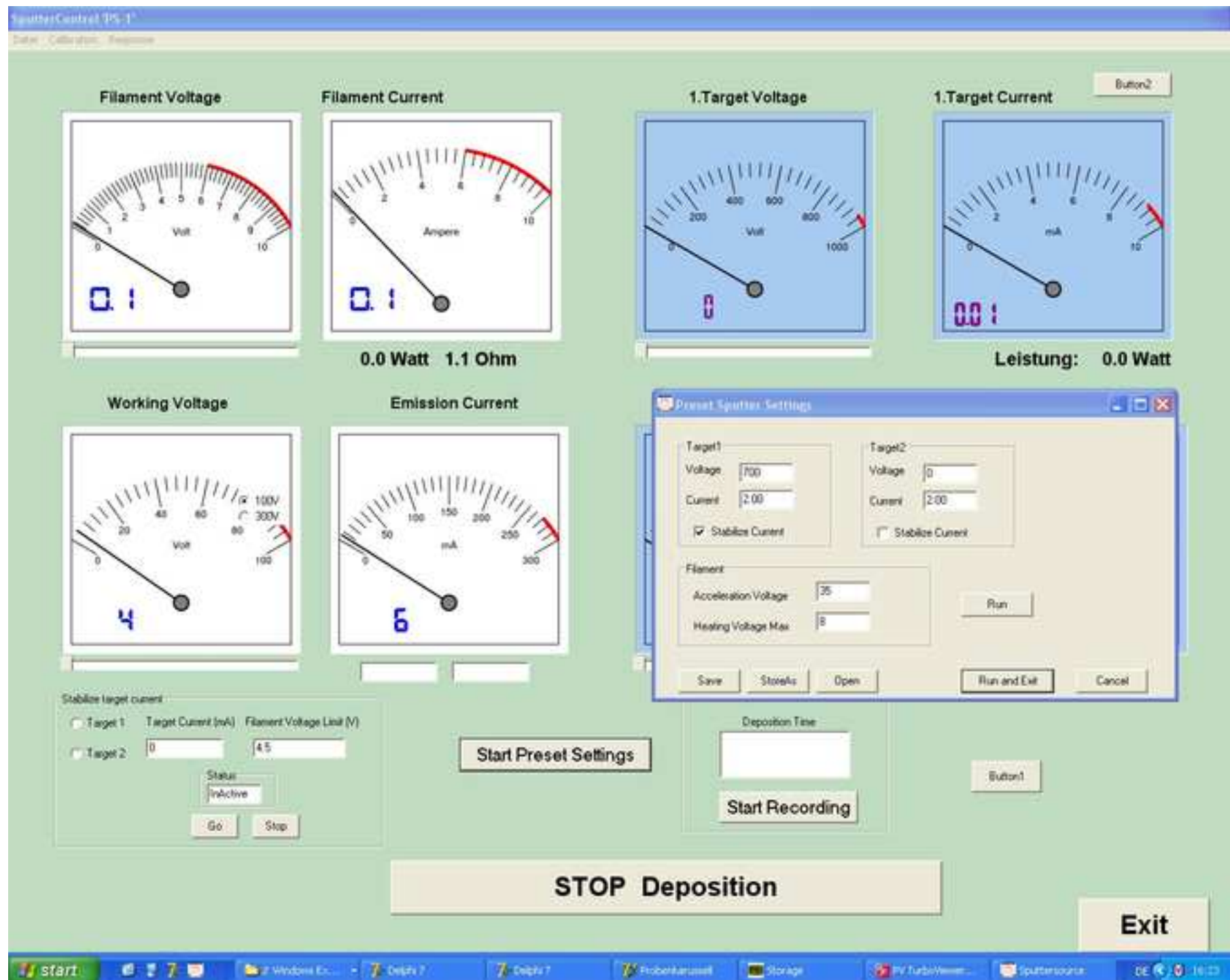
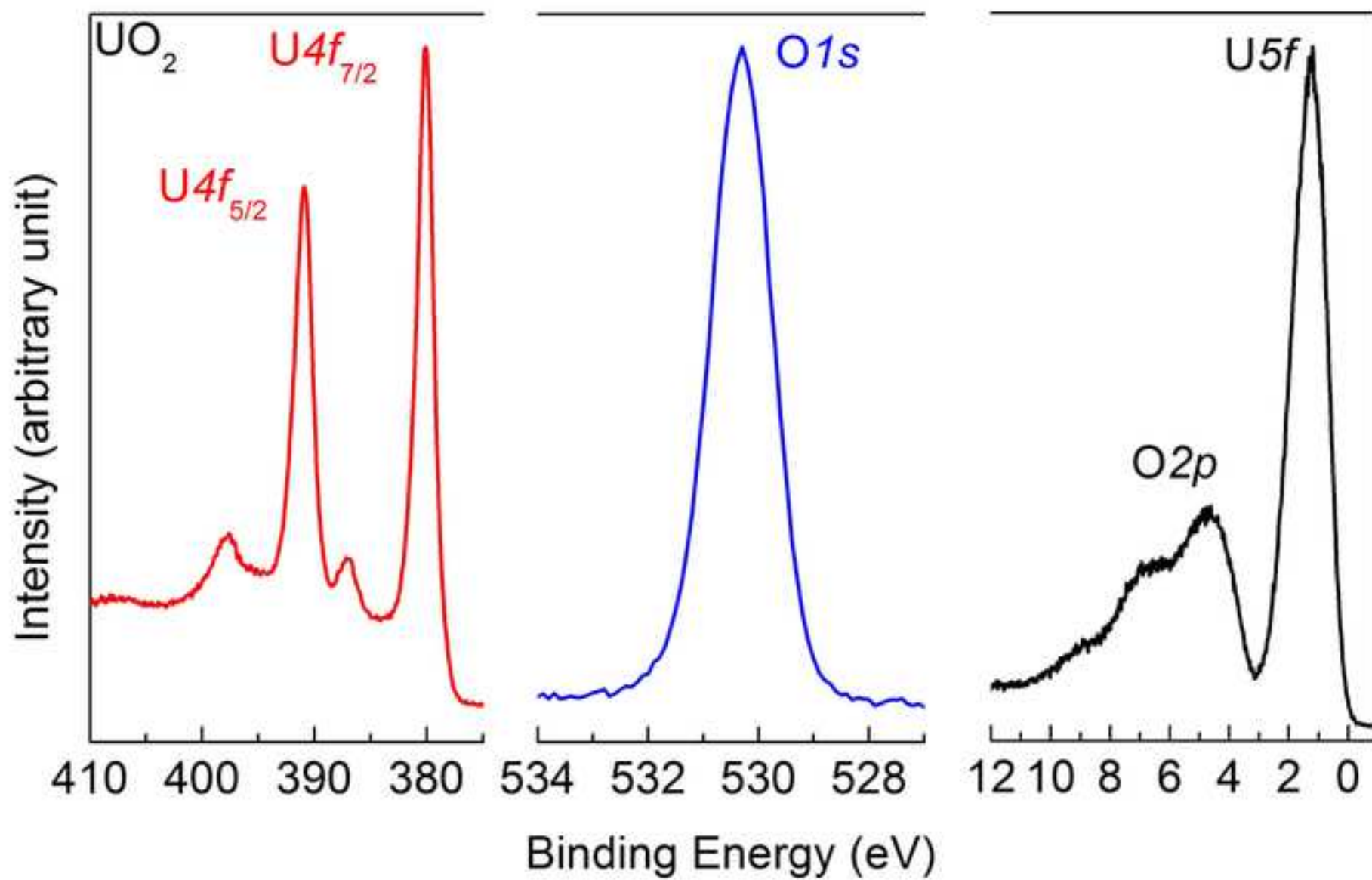
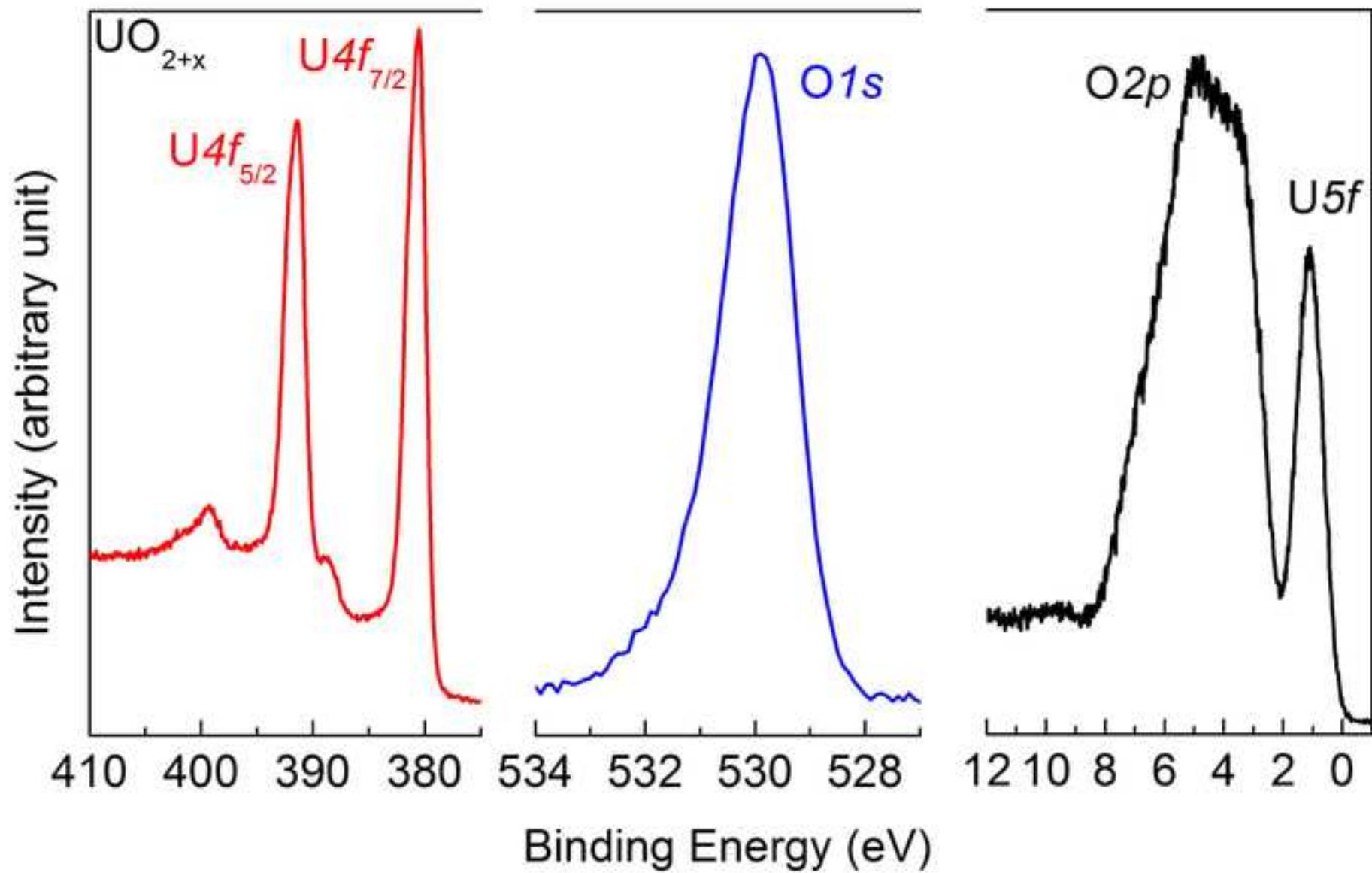
[Click here to access/download;Figure;Figure_3_Acquisition.jpg](#)

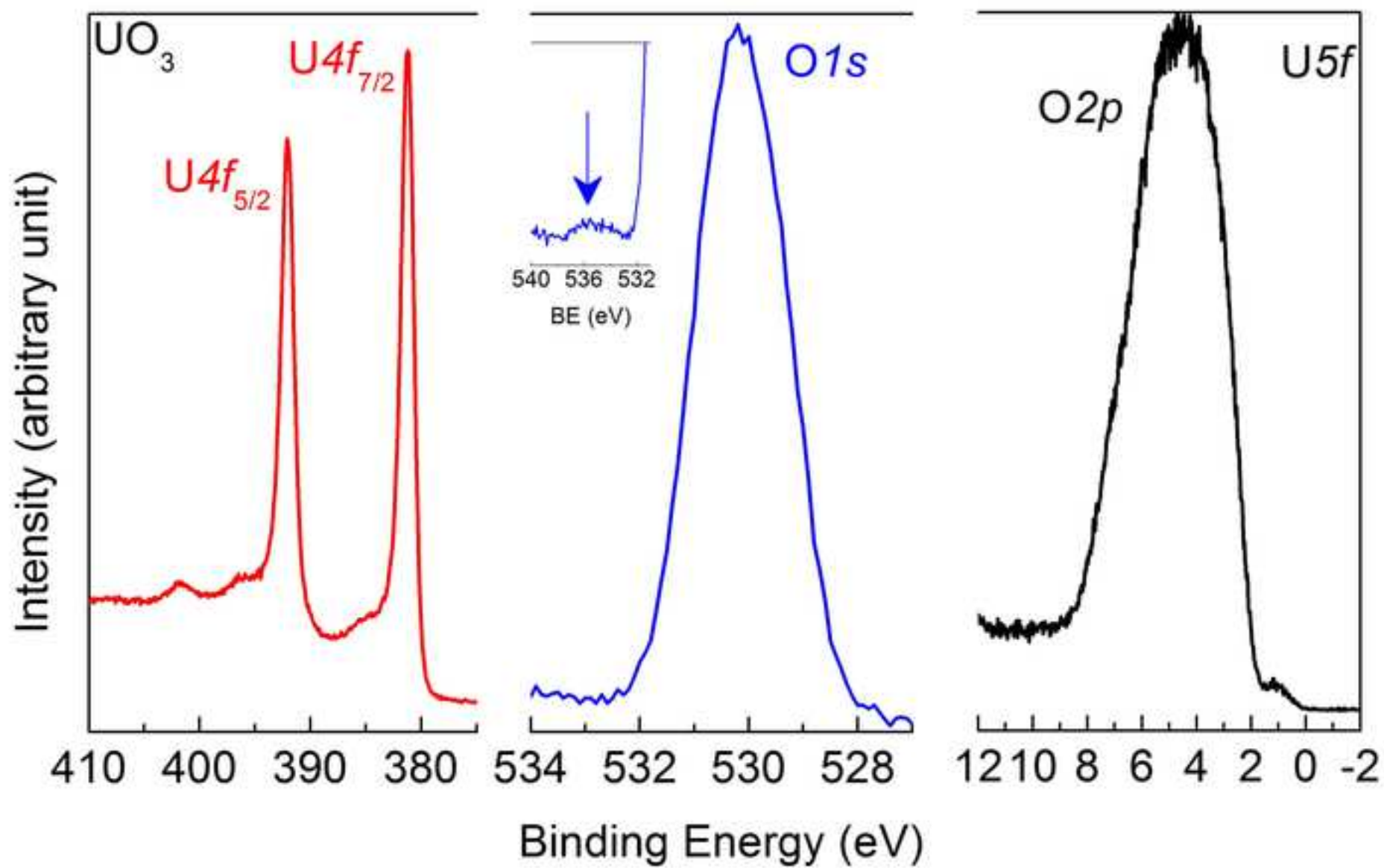
Figure4

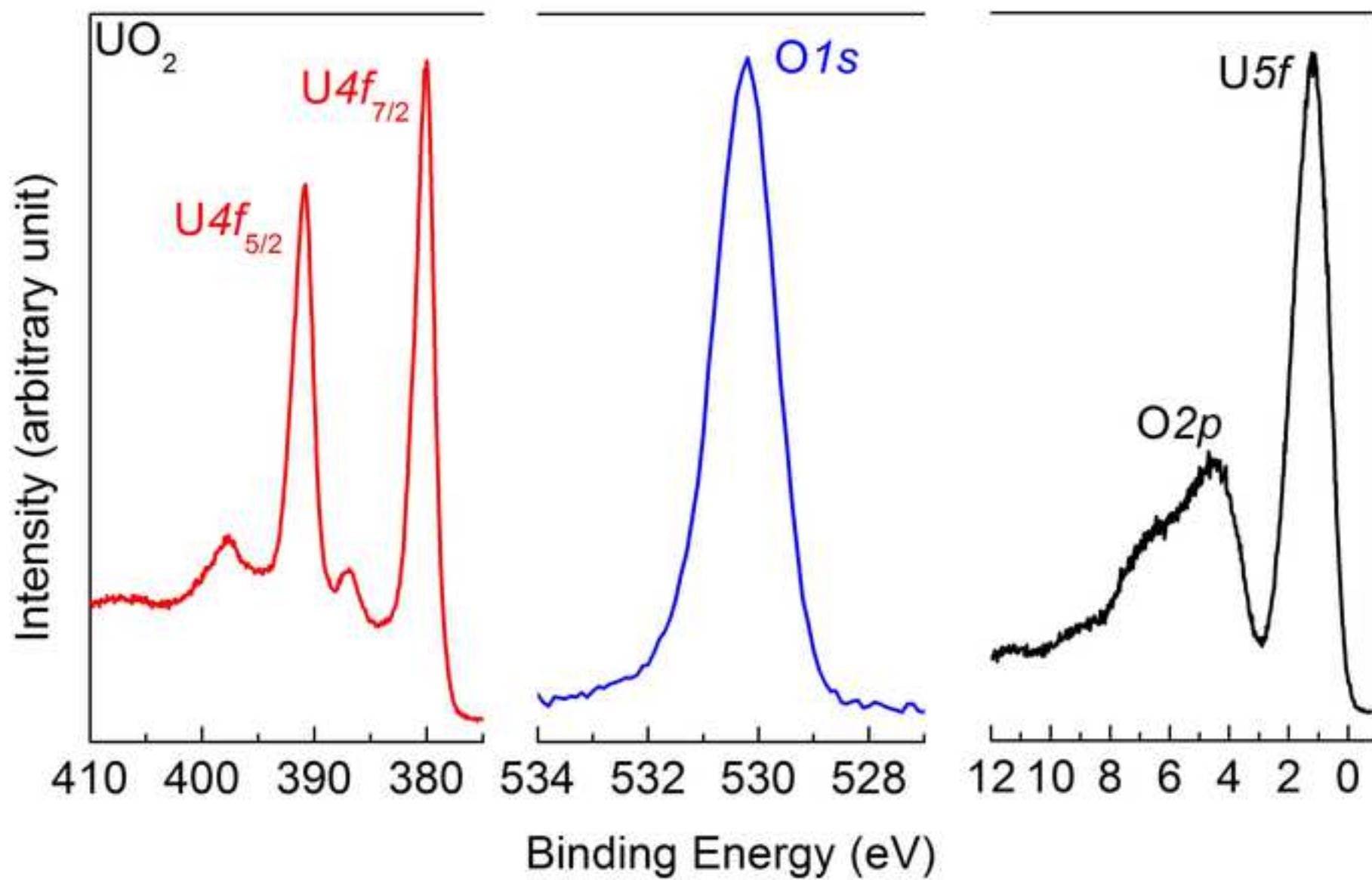
[Click here to access/download;Figure;Figure_4_sputter_source.jpg](#)











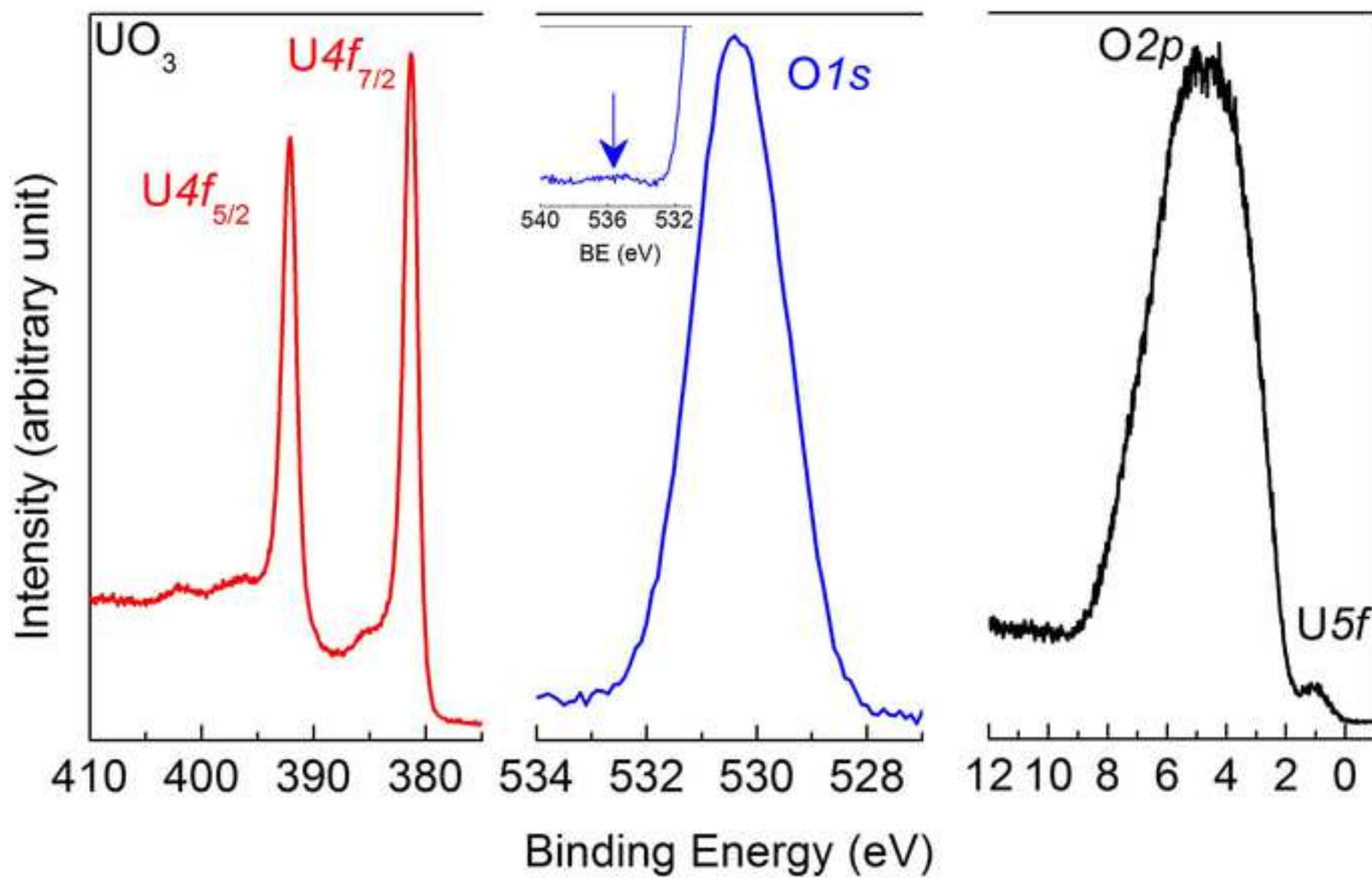
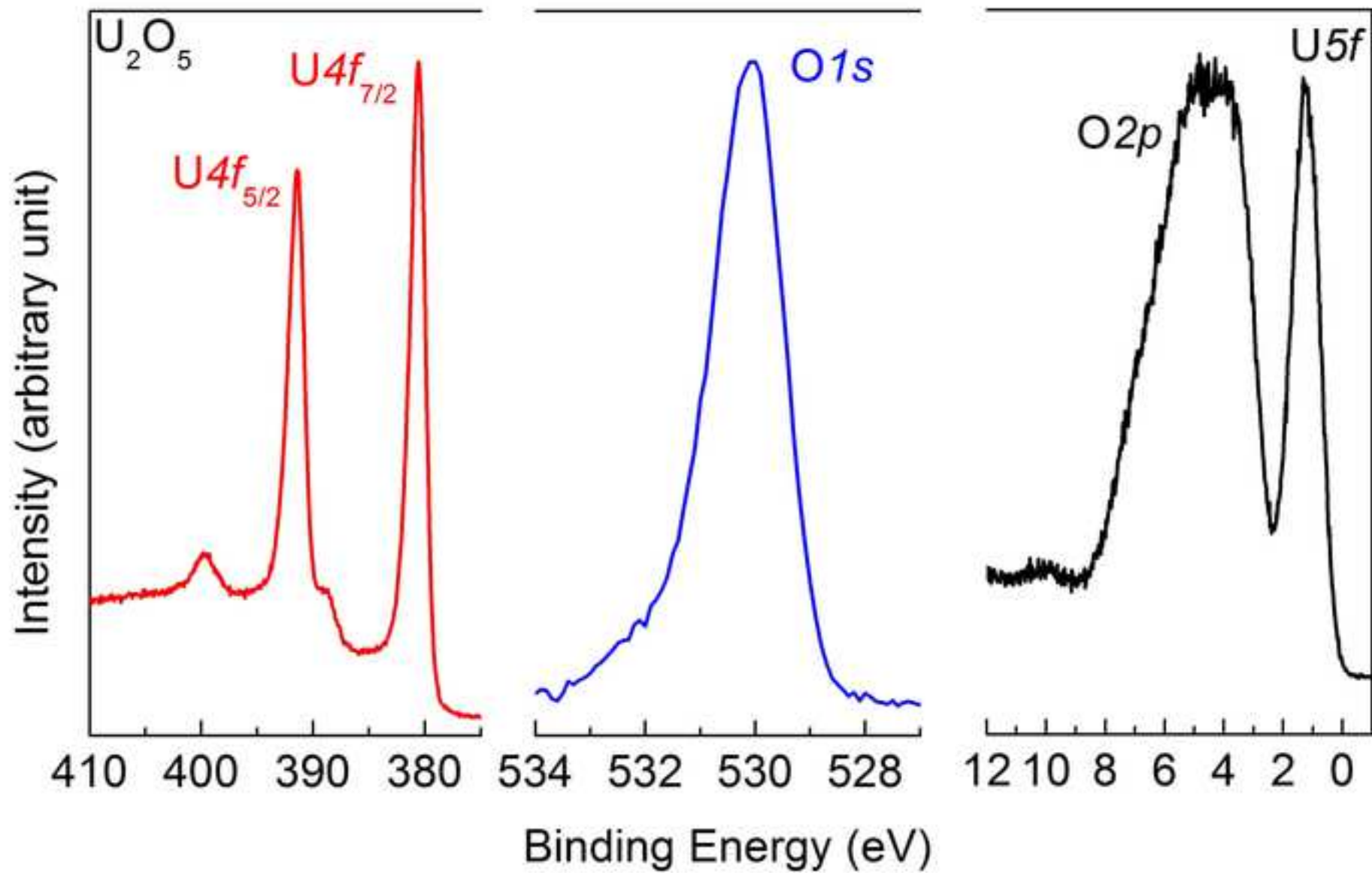
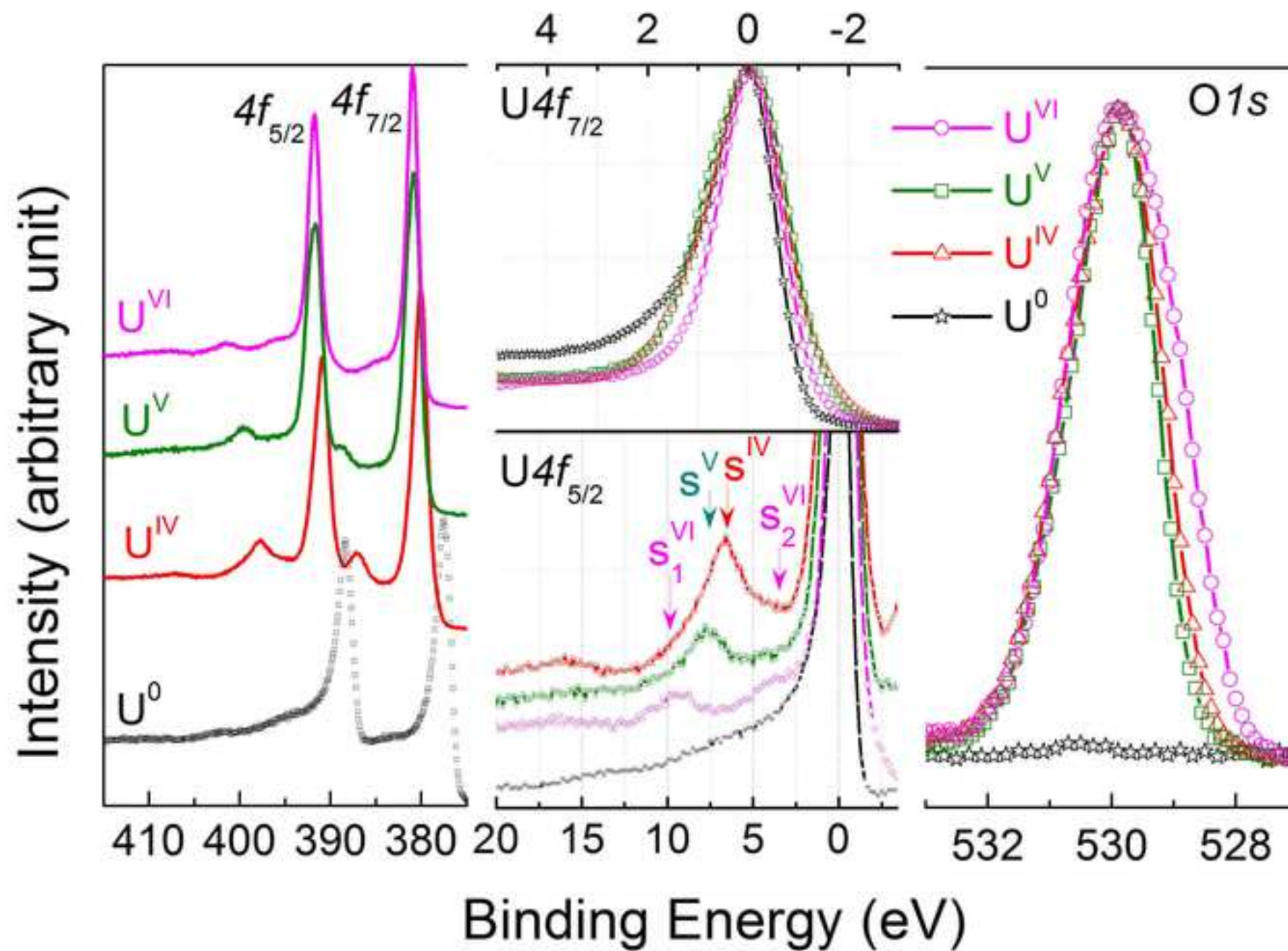
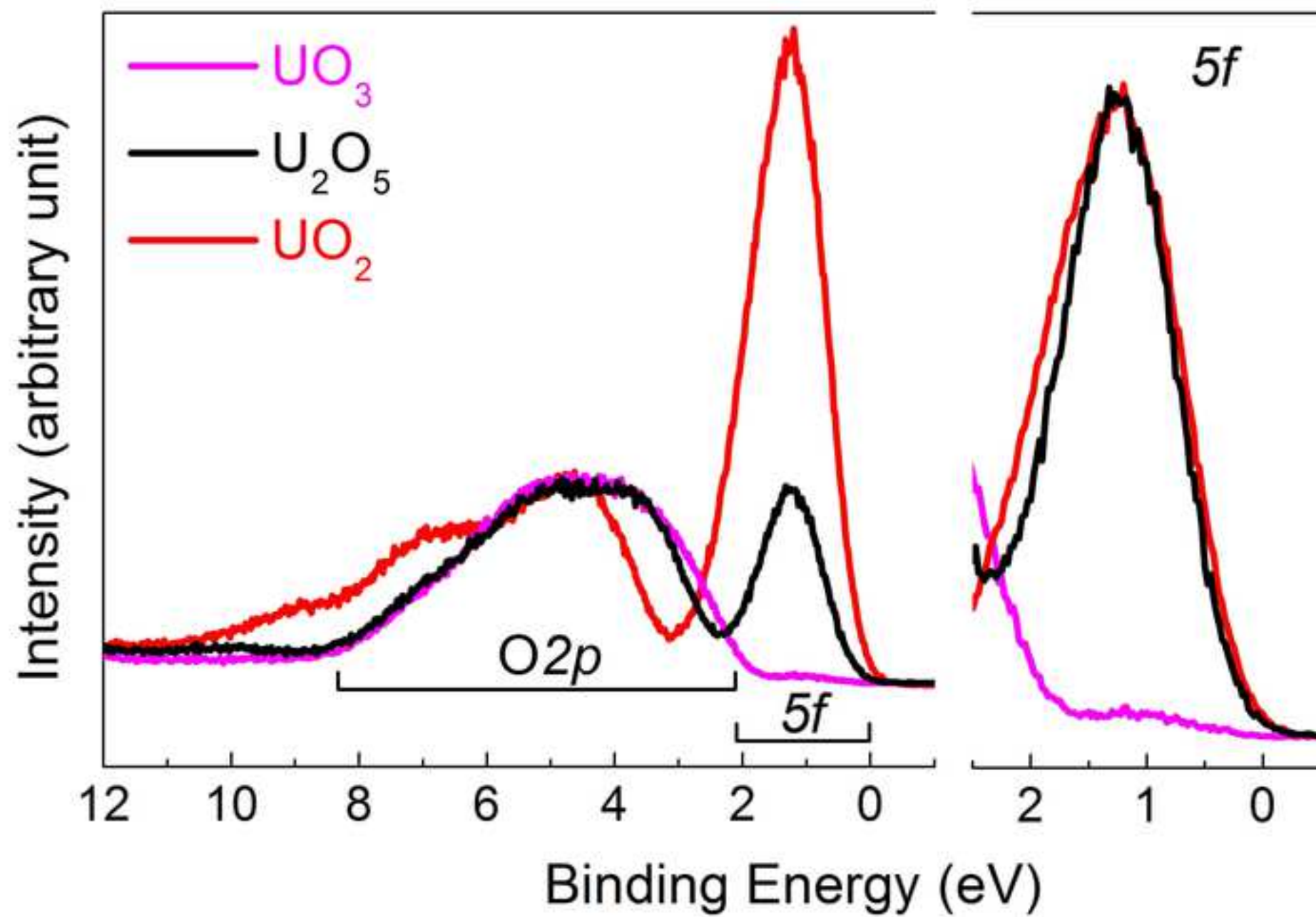


Figure10







Name of Material/ Equipment	Company	Catalog Number	Comments/Description
1ary dry scroll vacuum pump	Agilent	SH-100	All chambers except B1
1ary pump	EDWARDS	nXDS10i 100/240V	B1 chamber
Acetone			
Acquisition programme	Developed in-house		
Analyser	Specs	Phoibos 150 hemis	A4 chamber
Argon	BASI		6N
Atomic source	GenII plasma source	Tectra	B3 chamber
Au foil	Goodfellow		
CasaXPS programme	CasaXPS		
Gauge 1ary vacuum	PFEIFFER	TPR 280 (2011/10)	All chambers
Gauge 2ary vacuum	VACOM	ATMION ATS40C	All chambers
Hydrogen gas	BASI		6N
Ion gun source	Specs	IG10/35	B1 chamber
Linear transfer programme	Specs		Program delivered with the station
Origin programme	Origin	OriginPro 8.1SRO	
Oxygen gas			6N
Sampler e-beam heater power supply	Specs	SH100	B1 chamber
Sampler resistance heater	Made in-house	power supply + Eurotherm	B3 chamber
Sputtering programme	Developed in-house		
Stainless steal or Molybdenum substrate	in house		
Ta wire	Goodfellow		

turbo pump	PFEIFFER	TC 400	All chambers
Uranium target	in house	in house	Natural uranium target
Vacuum gauge controller	VACOM	MVC-3	All chambers
X-ray source	Specs	XRC-1000 MF	Equipped with a monochromator

ARTICLE AND VIDEO LICENSE AGREEMENT

Title of Article:	U2O5 film preparation via UO2 deposition by direct current sputtering and successive oxidation and reduction with atomic oxygen and atomic hydrogen.
Author(s):	Thomas Gouder, Frank Huber, Rachel Eloirdi, Roberto Caciuffo

Item 1: The Author elects to have the Materials be made available (as described at <http://www.jove.com/publish>) via:

☐

Standard Access

☒

Open Access

Item 2: Please select one of the following items:

☒

The Author is **NOT** a United States government employee.

☐

The Author is a United States government employee and the Materials were prepared in the course of his or her duties as a United States government employee.

☐

The Author is a United States government employee but the Materials were NOT prepared in the course of his or her duties as a United States government employee.

ARTICLE AND VIDEO LICENSE AGREEMENT

1. **Defined Terms.** As used in this Article and Video License Agreement, the following terms shall have the following meanings: **"Agreement"** means this Article and Video License Agreement; **"Article"** means the article specified on the last page of this Agreement, including any associated materials such as texts, figures, tables, artwork, abstracts, or summaries contained therein; **"Author"** means the author who is a signatory to this Agreement; **"Collective Work"** means a work, such as a periodical issue, anthology or encyclopedia, in which the Materials in their entirety in unmodified form, along with a number of other contributions, constituting separate and independent works in themselves, are assembled into a collective whole; **"CRC License"** means the Creative Commons Attribution-Non Commercial-No Derivs 3.0 Unported Agreement, the terms and conditions of which can be found at: <http://creativecommons.org/licenses/by-nc-nd/3.0/legalcode>; **"Derivative Work"** means a work based upon the Materials or upon the Materials and other pre-existing works, such as a translation, musical arrangement, dramatization, fictionalization, motion picture version, sound recording, art reproduction, abridgment, condensation, or any other form in which the Materials may be recast, transformed, or adapted; **"Institution"** means the institution, listed on the last page of this Agreement, by which the Author was employed at the time of the creation of the Materials; **"JoVE"** means MyJoVE Corporation, a Massachusetts corporation and the publisher of The Journal of Visualized Experiments; **"Materials"** means the Article and / or the Video; **"Parties"** means the Author and JoVE; **"Video"** means any video(s) made by the Author, alone or in conjunction with any other parties, or by JoVE or its affiliates or agents, individually or in collaboration with the Author or any other parties, incorporating all or any portion

of the Article, and in which the Author may or may not appear.

2. **Background.** The Author, who is the author of the Article, in order to ensure the dissemination and protection of the Article, desires to have the JoVE publish the Article and create and transmit videos based on the Article. In furtherance of such goals, the Parties desire to memorialize in this Agreement the respective rights of each Party in and to the Article and the Video.

3. **Grant of Rights in Article.** In consideration of JoVE agreeing to publish the Article, the Author hereby grants to JoVE, subject to **Sections 4** and **7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Article in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Article into other languages, create adaptations, summaries or extracts of the Article or other Derivative Works (including, without limitation, the Video) or Collective Works based on all or any portion of the Article and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. If the "Open Access" box has been checked in **Item 1** above, JoVE and the Author hereby grant to the public all such rights in the Article as provided in, but subject to all limitations and requirements set forth in, the CRC License.

ARTICLE AND VIDEO LICENSE AGREEMENT

4. **Retention of Rights in Article.** Notwithstanding the exclusive license granted to JoVE in **Section 3** above, the Author shall, with respect to the Article, retain the non-exclusive right to use all or part of the Article for the non-commercial purpose of giving lectures, presentations or teaching classes, and to post a copy of the Article on the Institution's website or the Author's personal website, in each case provided that a link to the Article on the JoVE website is provided and notice of JoVE's copyright in the Article is included. All non-copyright intellectual property rights in and to the Article, such as patent rights, shall remain with the Author.

5. **Grant of Rights in Video – Standard Access.** This **Section 5** applies if the "Standard Access" box has been checked in **Item 1** above or if no box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby acknowledges and agrees that, Subject to **Section 7** below, JoVE is and shall be the sole and exclusive owner of all rights of any nature, including, without limitation, all copyrights, in and to the Video. To the extent that, by law, the Author is deemed, now or at any time in the future, to have any rights of any nature in or to the Video, the Author hereby disclaims all such rights and transfers all such rights to JoVE.

6. **Grant of Rights in Video – Open Access.** This **Section 6** applies only if the "Open Access" box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby grants to JoVE, subject to **Section 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Video in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Video into other languages, create adaptations, summaries or extracts of the Video or other Derivative Works or Collective Works based on all or any portion of the Video and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. For any Video to which this **Section 6** is applicable, JoVE and the Author hereby grant to the public all such rights in the Video as provided in, but subject to all limitations and requirements set forth in, the CRC License.

7. **Government Employees.** If the Author is a United States government employee and the Article was prepared in the course of his or her duties as a United States government employee, as indicated in **Item 2** above, and any of the licenses or grants granted by the Author hereunder exceed the scope of the 17 U.S.C. 403, then the rights granted hereunder shall be limited to the maximum

rights permitted under such statute. In such case, all provisions contained herein that are not in conflict with such statute shall remain in full force and effect, and all provisions contained herein that do so conflict shall be deemed to be amended so as to provide to JoVE the maximum rights permissible within such statute.

8. **Protection of the Work.** The Author(s) authorize JoVE to take steps in the Author(s) name and on their behalf if JoVE believes some third party could be infringing or might infringe the copyright of either the Author's Article and/or Video.

9. **Likeness, Privacy, Personality.** The Author hereby grants JoVE the right to use the Author's name, voice, likeness, picture, photograph, image, biography and performance in any way, commercial or otherwise, in connection with the Materials and the sale, promotion and distribution thereof. The Author hereby waives any and all rights he or she may have, relating to his or her appearance in the Video or otherwise relating to the Materials, under all applicable privacy, likeness, personality or similar laws.

10. **Author Warranties.** The Author represents and warrants that the Article is original, that it has not been published, that the copyright interest is owned by the Author (or, if more than one author is listed at the beginning of this Agreement, by such authors collectively) and has not been assigned, licensed, or otherwise transferred to any other party. The Author represents and warrants that the author(s) listed at the top of this Agreement are the only authors of the Materials. If more than one author is listed at the top of this Agreement and if any such author has not entered into a separate Article and Video License Agreement with JoVE relating to the Materials, the Author represents and warrants that the Author has been authorized by each of the other such authors to execute this Agreement on his or her behalf and to bind him or her with respect to the terms of this Agreement as if each of them had been a party hereto as an Author. The Author warrants that the use, reproduction, distribution, public or private performance or display, and/or modification of all or any portion of the Materials does not and will not violate, infringe and/or misappropriate the patent, trademark, intellectual property or other rights of any third party. The Author represents and warrants that it has and will continue to comply with all government, institutional and other regulations, including, without limitation all institutional, laboratory, hospital, ethical, human and animal treatment, privacy, and all other rules, regulations, laws, procedures or guidelines, applicable to the Materials, and that all research involving human and animal subjects has been approved by the Author's relevant institutional review board.

11. **JoVE Discretion.** If the Author requests the assistance of JoVE in producing the Video in the Author's facility, the Author shall ensure that the presence of JoVE employees, agents or independent contractors is in accordance with the relevant regulations of the Author's institution. If more than one author is listed at the beginning of this Agreement, JoVE may, in its sole

ARTICLE AND VIDEO LICENSE AGREEMENT

discretion, elect not take any action with respect to the Article until such time as it has received complete, executed Article and Video License Agreements from each such author. JoVE reserves the right, in its absolute and sole discretion and without giving any reason therefore, to accept or decline any work submitted to JoVE. JoVE and its employees, agents and independent contractors shall have full, unfettered access to the facilities of the Author or of the Author's institution as necessary to make the Video, whether actually published or not. JoVE has sole discretion as to the method of making and publishing the Materials, including, without limitation, to all decisions regarding editing, lighting, filming, timing of publication, if any, length, quality, content and the like.

12. **Indemnification.** The Author agrees to indemnify JoVE and/or its successors and assigns from and against any and all claims, costs, and expenses, including attorney's fees, arising out of any breach of any warranty or other representations contained herein. The Author further agrees to indemnify and hold harmless JoVE from and against any and all claims, costs, and expenses, including attorney's fees, resulting from the breach by the Author of any representation or warranty contained herein or from allegations or instances of violation of intellectual property rights, damage to the Author's or the Author's institution's facilities, fraud, libel, defamation, research, equipment, experiments, property damage, personal injury, violations of institutional, laboratory, hospital, ethical, human and animal treatment, privacy or other rules, regulations, laws, procedures or guidelines, liabilities and other losses or damages related in any way to the submission of work to JoVE, making of videos by JoVE, or publication in JoVE or elsewhere by JoVE. The Author shall be responsible for, and shall hold JoVE harmless from, damages caused by lack of sterilization, lack of cleanliness or by contamination due to

the making of a video by JoVE its employees, agents or independent contractors. All sterilization, cleanliness or decontamination procedures shall be solely the responsibility of the Author and shall be undertaken at the Author's expense. All indemnifications provided herein shall include JoVE's attorney's fees and costs related to said losses or damages. Such indemnification and holding harmless shall include such losses or damages incurred by, or in connection with, acts or omissions of JoVE, its employees, agents or independent contractors.

13. **Fees.** To cover the cost incurred for publication, JoVE must receive payment before production and publication the Materials. Payment is due in 21 days of invoice. Should the Materials not be published due to an editorial or production decision, these funds will be returned to the Author. Withdrawal by the Author of any submitted Materials after final peer review approval will result in a US\$1,200 fee to cover pre-production expenses incurred by JoVE. If payment is not received by the completion of filming, production and publication of the Materials will be suspended until payment is received.

14. **Transfer, Governing Law.** This Agreement may be assigned by JoVE and shall inure to the benefits of any of JoVE's successors and assignees. This Agreement shall be governed and construed by the internal laws of the Commonwealth of Massachusetts without giving effect to any conflict of law provision thereunder. This Agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall be deemed to be one and the same agreement. A signed copy of this Agreement delivered by facsimile, e-mail or other means of electronic transmission shall be deemed to have the same legal effect as delivery of an original signed copy of this Agreement.

A signed copy of this document must be sent with all new submissions. Only one Agreement is required per submission.

CORRESPONDING AUTHOR

Name:

Rachel Eloirdi

Department:

Directorate G, Nuclear Safety and Security

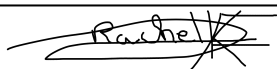
Institution:

European Commission, Joint Research Centre

Title:

Dr.

Signature:



Date:

30.08.2018

Please submit a **signed** and **dated** copy of this license by one of the following three methods:

1. Upload an electronic version on the JoVE submission site
2. Fax the document to +1.866.381.2236
3. Mail the document to JoVE / Attn: JoVE Editorial / 1 Alewife Center #200 / Cambridge, MA 02140

Please find below the answers to the editor comments written in red, thanks for your review.

Editorial comments:

Note that some changes have been made to better fit JoVE formatting guidelines (see attached).

1. Formatted according to JoVE guidelines (see attached), the length of the highlighted portion of the protocol is currently ~4 pages; our limit is 2.75. Please reduce the length of the protocol that is highlighted.

We decreased the length of the highlighted portion of the protocol and after checking it is according to us less than 3 pages, about 2.75 pages.

2. Please number Figures in order (e.g., Figure 5 is only mentioned after Figure 12).

We updated the figures number and checked that it is mentioned in the order.

Previous version	Present version
Fig. 1	Fig. 1
Fig. 2	Fig. 2
Fig. 3	Fig. 3
Fig. 4	Fig. 4
Fig. 5	Fig. 11
Fig. 6	Fig. 12
Fig. 7	Fig. 5
Fig. 8	Fig. 6
Fig. 9	Fig. 7
Fig. 10	Fig. 8
Fig. 11	Fig. 9
Fig. 12	Fig. 10

3. Figure 1: Should this be ‘Wagon carrying sample’?

Correction done

4. The legend to Figure 6 is not correct.

Correction done

5. Please move references to the main text (i.e., not an endnote).

Correction done