

**Determining Chemical Composition
Of Sputtered Uranium Oxide Thin Films
through X-Ray Photoelectron Spectroscopy**

Kristi Adamson

Department of Physics & Astronomy

Brigham Young University

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Advisor: Dr. David Allred

Thesis Coordinator: Dr. Justin Peatross

Signature:_____

Signature:_____

Department Chair: Dr. Scott Sommerfeldt

Signature:_____

Abstract

This study involves the chemical composition of thin films (100-200?) of uranium oxide, created through DC magnetron sputtering, as deposited as well after aging in the lab for a time lapse of over one year. The oxidation state of the uranium oxide films is investigated through x-ray photoelectron spectroscopy (XPS). The sample is placed under high vacuum and bombarded with x rays of known energies, producing photoelectrons. The energy of the ejected electrons is determined by an electron detector, and the number of electrons collected at each energy is counted. By this method, the bonding energy of the electrons at and near the surface is determined. The data shows that the surface oxidizes gradually over a period of months. By comparing our work with that of Teterin [1] ("A Study of Synthetic and Natural Uranium Oxides by X-Ray Photoelectron Spectroscopy." J. Phys. Chem. Minerals. 1981) it is concluded that the valence electrons of the uranium samples are intermediate between UO_2 and UO_3 , with UO_3 becoming more prominent as the sample has more time to oxidize. The composition below the surface is studied by using a beam of energetic argon ions to sputter off layers of the film, while periodically examining the sample with XPS. Nitrogen is also detected in the film, making up approximately 15% of the composition. It may have been incorporated into the samples during reactive sputtering. The amount of oxygen appears constant with depth and appears consistent with UO_2 . After over one year of exposure to atmosphere, the surface layer of the uranium trioxide is approximately 1nm thick.

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I. Introduction

The study of thin films (100-200?) as multilayer or single surface mirrors in the extreme ultraviolet (EUV) radiation range has been growing in the scientific community over the past years [1], [2]. Producing reliable mirrors at in this range will prove beneficial in many areas of technology, specifically lithography, medical equipment and space observation [3].

The physics department at Brigham Young University produced thin films containing uranium that were used in the IMAGE satellite project in 2000 for this purpose. It had been suggested that, theoretically, uranium should have very high reflectance in the desired range, and thus uranium/silicon multilayer reflectors were the initial product. But as the films sat open to atmosphere, the uppermost uranium layer bonded with the oxygen, chemically altering the surface of the mirrors. However, these altered films actually served better in their intended optical purpose than had been anticipated [4]. This has fostered more study of uranium oxide films as EUV mirrors.

One particular difficulty with uranium dioxide is that it is chemically unstable, especially when in the form of a powder or thin film [5]. Thus the samples require continuous compositional studies to determine the rate of oxidation as the films are left open to atmosphere.

II. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive method that uses the photoelectric effect to determine the composition of thin films. Aluminum is bombarded with high-energy electrons (10keV) to create a stream of x rays. As these low energy x rays are quickly absorbed by air, the measurements must be conducted at extremely low pressures. In the system employed for this study, the base pressure was 10^{-6} torr. These x rays then impinge on our films. If the x ray has sufficient energy, an atom is ionized, and an electron is ejected from the sample. A position sensitive electron detector determines the kinetic energy of the electron. The hemispherical shape of the detector disperses the electrons across a resistive plate according to their energy. By analyzing the position of the electron after traversing the hemisphere, its energy can be determined.

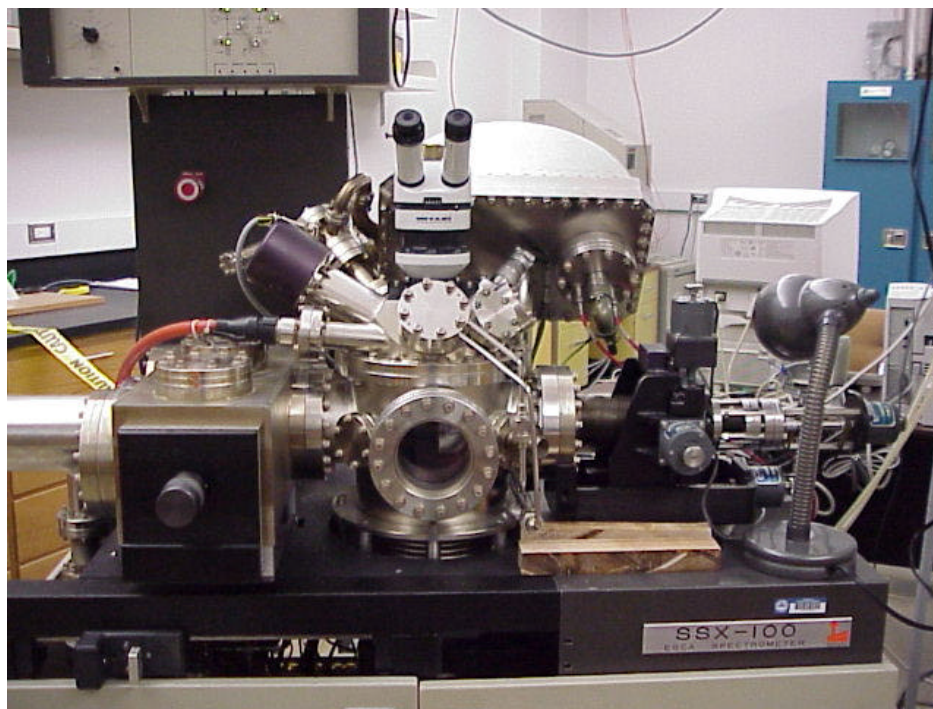


Figure 1. The X-Ray spectroscopy system used in this study. An ESCA SSX-100, located in the Brigham Young University Department of Chemistry and Biochemistry

By knowing the energy of the original x ray and the kinetic energy of the emitted electron (provided it experiences no energy loss from collisions), the energy with which the electron was bound to the atom, E_b , can easily be determined by the following equation:

$$E_b = h\nu - E_k$$

where $h\nu$ is the energy of the incident x ray and E_k is the kinetic energy of the ejected electron. Each atom or molecule has characteristic energies with which their electrons are bound. Thus from this binding energy, information can be obtained about the relative abundance of different elements in a sample and its approximate chemical composition.

The sampling depth from which the electrons escape without energy loss depends on two factors: the kinetic energy of the electron and the electron escape angle. Beyond 100eV, an electron with greater kinetic energy can travel through more material before undergoing inelastic scattering and thus losing its energy. Hence, weakly bound electrons come from deeper in the sample.

As can be seen qualitatively from figure 2, the sampling depth is proportional to the cosine of the electron escape angle.

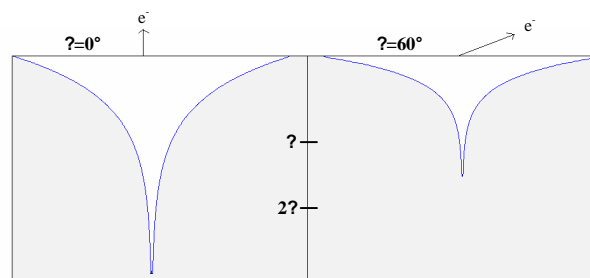


Figure 2. The dependence of sampling depth on escape angle of electrons. [6]

Electrons escaping at an angle near normal can travel further within the sample before scattering and thus the sampling depth will be greater. [7] Electrons escaping at a near-grazing angle will give more information about the surface.

While XPS reveals information only about the near-surface region of our sample, we can incorporate this technique with ion sputtering, which allows the composition to be determined at different depths within the film. The sample is bombarded with argon ions, which effectively sputter off layers of the film. As the sample is sputtered away, it is periodically scanned by XPS to ascertain the chemical composition. However, the depth at which we scan can only be determined qualitatively, as there are no determined sputtering rates for uranium oxides. A rough model, in which we assume constant density throughout the sample, is used to determine relative depth composition.

III. Background

Several XPS studies have been done of bulk uranium oxides in an attempt to understand oxidation rates and bonding parameters of oxygen and uranium [8], [9], [10]. An effort of special interest is determining which electrons in uranium are involved in the bonding process and the effects these bonds have on the energies of various uranium electron bands. As the uranium becomes more oxidized, the molecular orbitals shift in binding energy. These shifts are used to qualitatively understand the behavior of uranium sample oxidation.

Teterin [8] extensively studied various uranium oxides using XPS. The studied samples were in the form of both finely dispersed powders and compact pressed powders on indium and titanium substrates. Spectra were taken three times for each sample. The data obtained from each type of sample was the varied only within experimental limits. The positions of the uranium $4f_{5/2}$ and $4f_{7/2}$ energy peaks are especially helpful in determining composition as it changes with the different amounts of oxygen. Figure 3 from Teterin shows how the peaks shift to higher binding energies with increased oxidation.

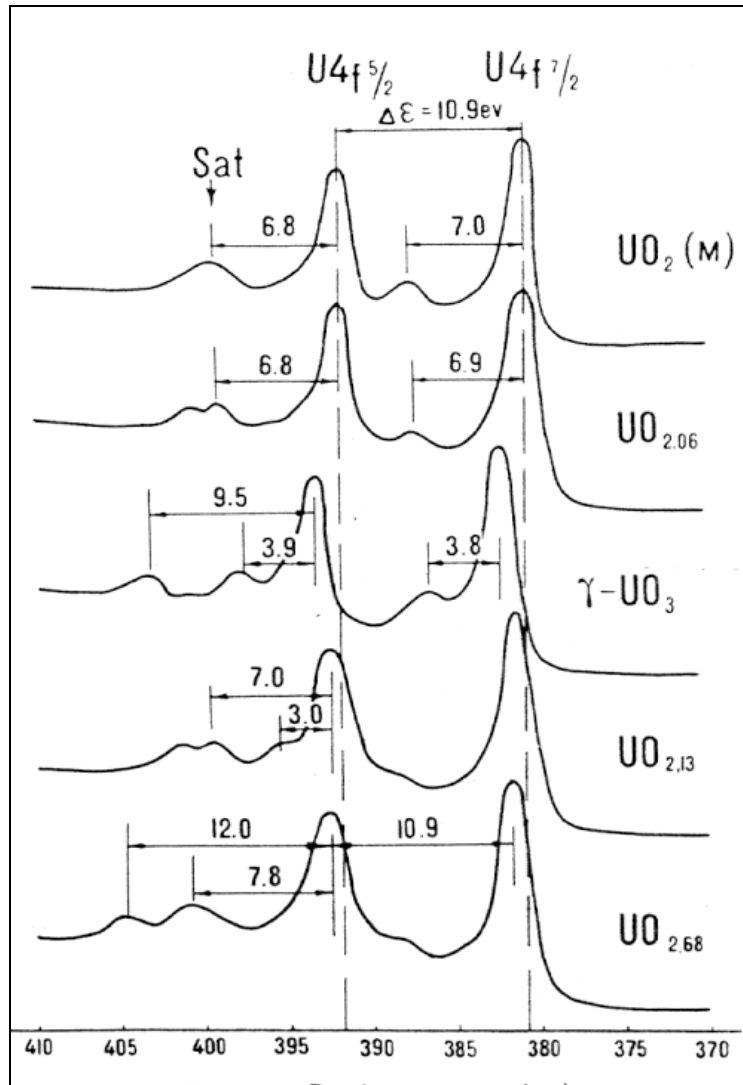


Figure 3. Relative intensity versus binding energy for electrons in the $U4f_{5/2}$ and $4f_{7/2}$ orbitals [8]

The O1s energy peak also shows great variance for different oxidation states. As can be seen from figure 4, it is actually composed of two closely positioned peaks that vary in intensity as oxidation changes. The higher energy peak becomes more prominent as O/U ratio changes from 2 to 3.

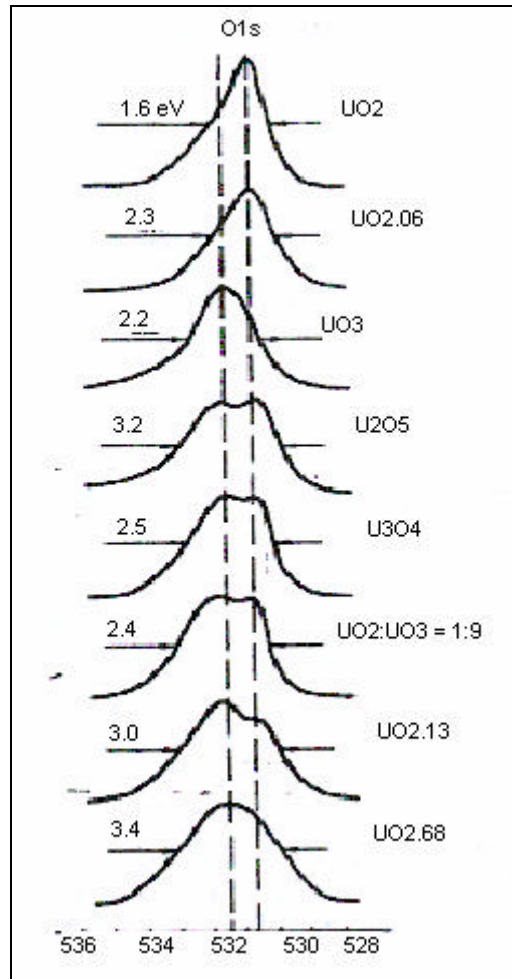


Figure 4. Relative intensity versus binding energy for electrons in the O1s orbital. [8]

Comparison to published data can provide qualitative information as to the behavior of the films, but cannot necessarily give quantitative indications. Thus a more exact determination of the composition can be established from a relative comparison of electron energy peak areas.

The number of photoelectrons per second (N) in a specific spectra peak can be determined the equation:

$$N = n \cdot f \cdot s \cdot q \cdot g \cdot I \cdot A \cdot T$$

where n represents the number of atoms of the element per cm^3 in the sample, f is the x-ray flux in photons/ cm^2/sec , s is the photoelectric cross-section for the atomic orbital of

interest in cm^2 , θ is a factor of angular efficiency of the instrumental arrangement in radians, based on the angle between the photon path and the detected electron, η represents the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, λ is the mean free path of the photoelectrons in the sample in cm, A is the area of the sample in cm^2 , and T is the detection efficiency for electrons emitted from sample[11].

The above equation can be solved for n and a ratio of atoms per element can be determined by the equation:

$$\frac{n_1}{n_2} = \frac{N_1 \cdot S_2}{N_2 \cdot S_1}$$

where S is defined as the atomic sensitivity factor. Values of S can be determined experimentally and are known for most elements [12].

In the ion sputtering process, it is valuable to know the depth at which each scan is being taken. Without a definitive knowledge of the sample's composition, it is not possible to determine an exact sputtering rate. However, it is known that the sputtering rate will be proportional to the density of the sample as well as the sputtering time. As our results show fairly constant composition, we will assume uniform density and determine a relative scanning depth based solely on the sputtering time.

IV. Experimental Procedure

The samples of uranium oxide are produced through DC magnetron sputtering. The uranium is deposited on silicon wafers in the presence of oxygen (partial pressure of 3×10^{-4} torr) creating a uranium oxide film. The base vacuum pressure is maintained below 4×10^{-6} torr, while the partial pressure of argon is 4×10^{-3} torr. The uranium is allowed to deposit to a thickness of approximately 30nm [15].

The thicknesses are determined with atomic force microscopy, low-angle x-ray diffraction and ellipsometry. The reflectance of the samples is measured by the monochromator at Brigham Young University as well as by the synchrotron at the University of California Berkeley.

An SSX-100 ESCA (Electron Spectroscopy for Chemical Analysis) Spectrometer is used to gather electron binding energies. It is calibrated monthly by the Au4f line, which is located at a binding energy of 83.98eV, as well as the Cu2p and 3p lines at 75.13eV and 932.66eV, respectively, to ensure consistently precise results. The pressure within the chamber is maintained at $2-6 \times 10^{-9}$ torr for high resolution scans. All scans shown in this paper are done with a detector angle of 35° , unless otherwise noted. Compositions are determined through comparison to other works [8] as well as computed using the analysis program, ESCAVB [13], which employs the peak area comparison method.

In sputtering the sample, a SPECS ion gun system (PU-IQE 12/38) was used. A spot of 1.5 mm^2 was rastered for 20-120 seconds between each XPS scan.

Between tests and scans, samples are stored in plastic containers which are left open to atmosphere.

V. Data

Surface Composition

The surface of a sample of uranium oxide was measured through XPS over the course of one year. Figures 5 and 6 below show the survey scans of the sample (for more graphs, see appendix).

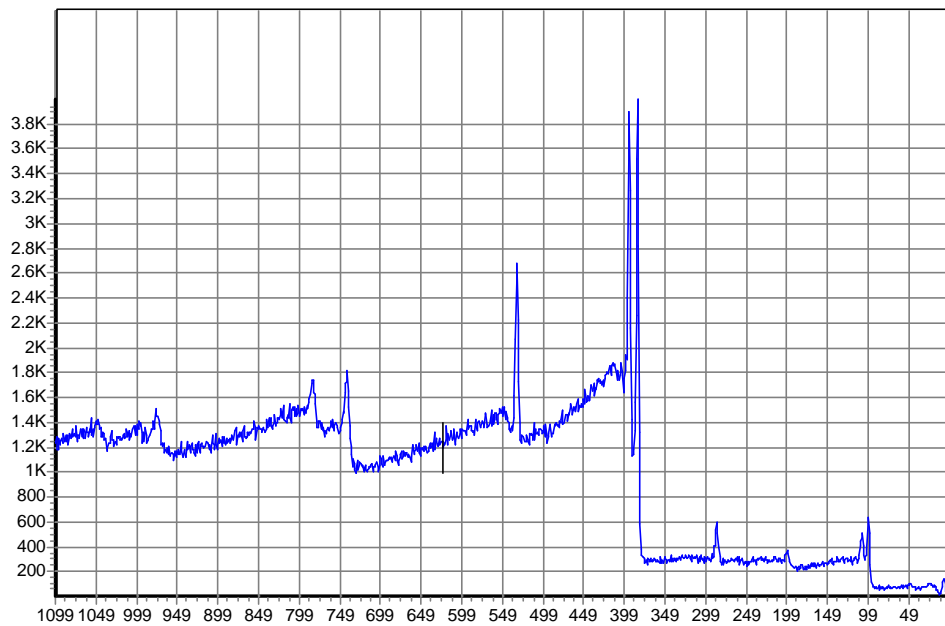


Figure 5. Survey scan of initial uranium oxide sample

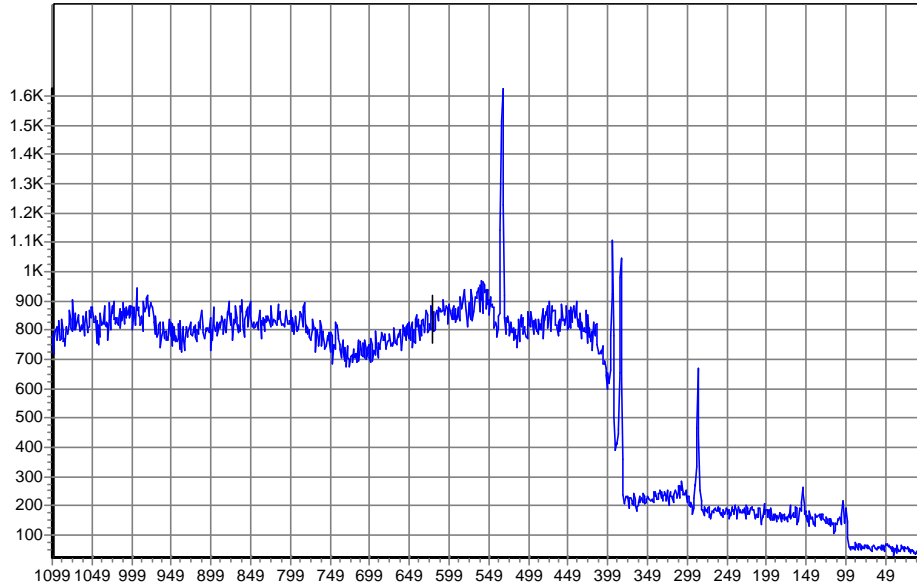


Figure 6. Survey scan of uranium oxide 52 weeks after deposition

Identifying Peaks: 99eV – U5d _{5/2}	393eV – U4f _{5/2}
107eV – U5d _{3/2}	531eV – O1s
153eV – Si2s	740eV – U4d _{5/2}
198eV – U5p _{3/2}	783eV – U4d _{3/2}
285eV – C1s	975eV – O Auger
382eV – U4f _{7/2}	

By comparing areas underneath the major peaks of uranium, oxygen and carbon, the relative composition of the surface was determined and is displayed in figure 7.

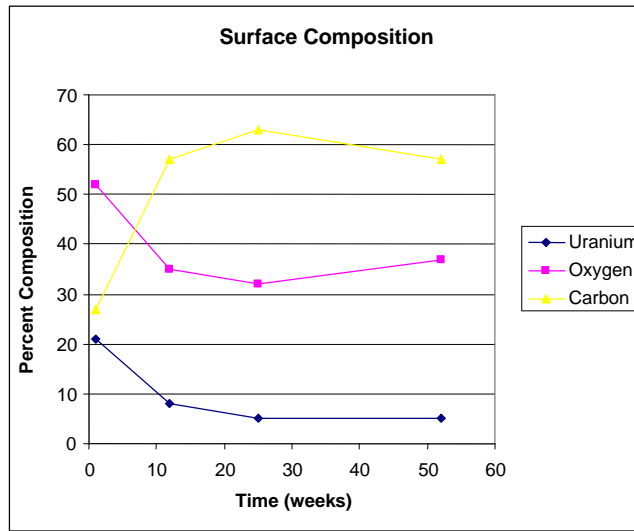


Figure 7. Percentage composition with time determined by peak area comparison.

To see more clearly the behavior of the O1s and U4f peaks, high resolution scans were performed over small energy ranges. Figures 8-10 show the $U4f_{7/2}$ and $U4f_{5/2}$ peaks, and figures 11 and 12 show the O1s peak. (For more graphs, see appendix.)

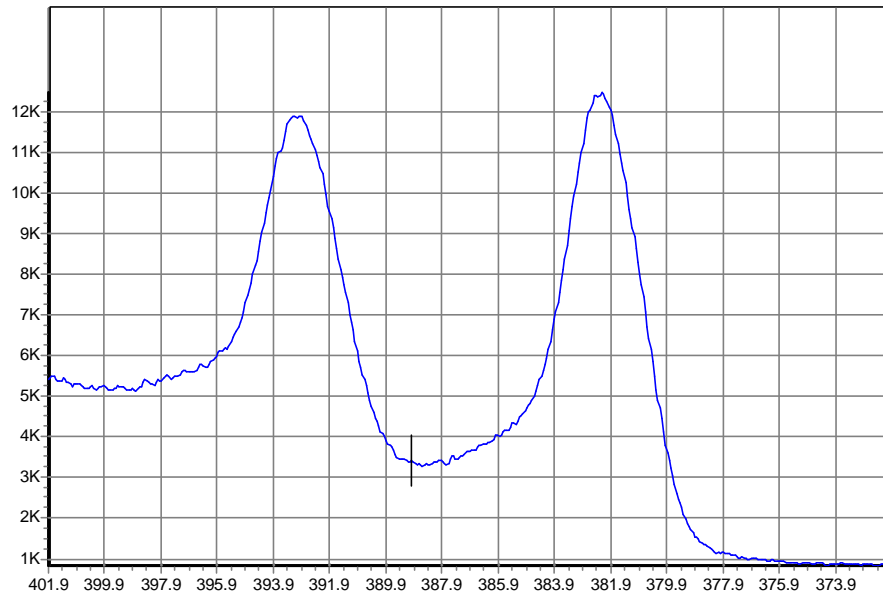


Figure 8. $U4f_{5/2}$ and $U4f_{7/2}$ peaks of initial sample.

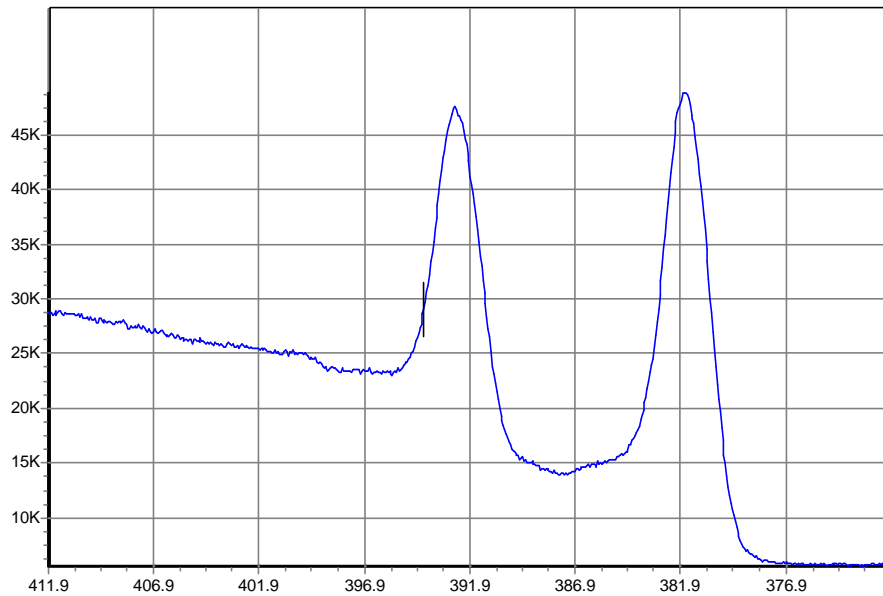


Figure 9. $U4f_{5/2}$ and $U4f_{7/2}$ peaks of sample 12 weeks after deposition.

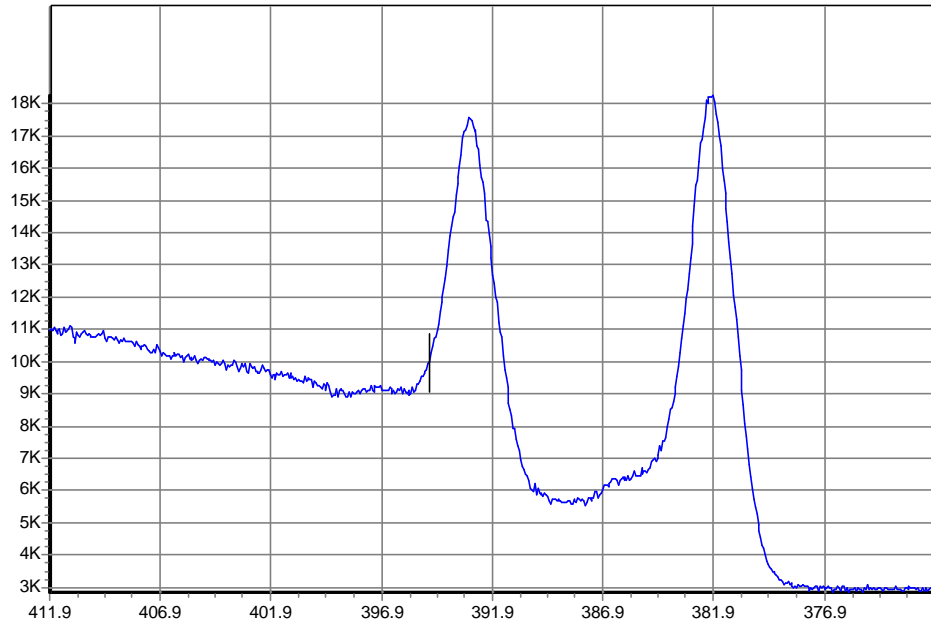


Figure 10. $U4f_{5/2}$ and $U4f_{7/2}$ peaks of sample 52 weeks after deposition.

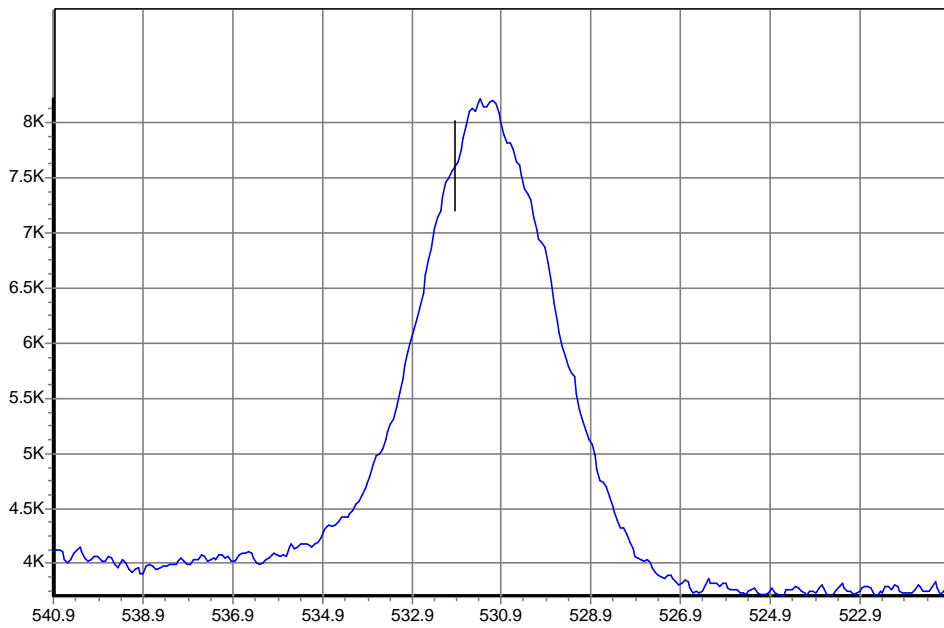


Figure 11. $O1s$ peak of initial sample.

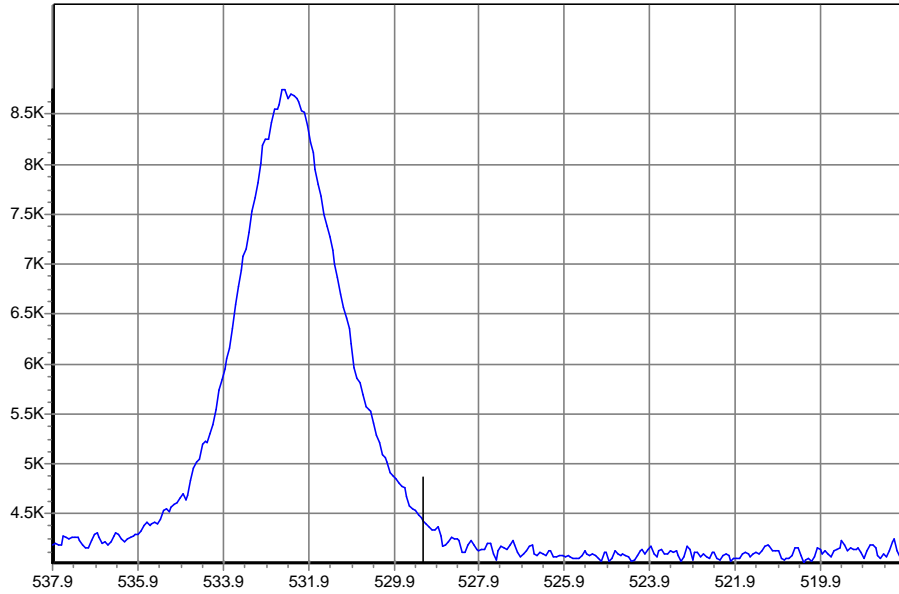


Figure 12. O1s peak scanned 52 weeks after deposition.

After allowing time (over a year) for the sample to come to a fairly stable state, the surface was sputtered with an argon ion gun and the composition was determined with depth. Figure 13 below shows the composition calculated through relative peak areas.

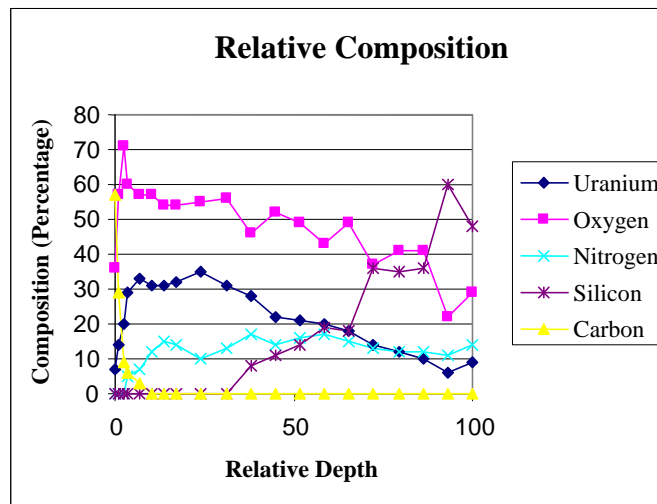


Figure 13. Relative composition with relative depth determined through peak area comparison.

The $U4f_{5/2}$, $U4f_{7/2}$ and $O1s$ peaks were also looked at with higher resolution and the peak energies are charted below.

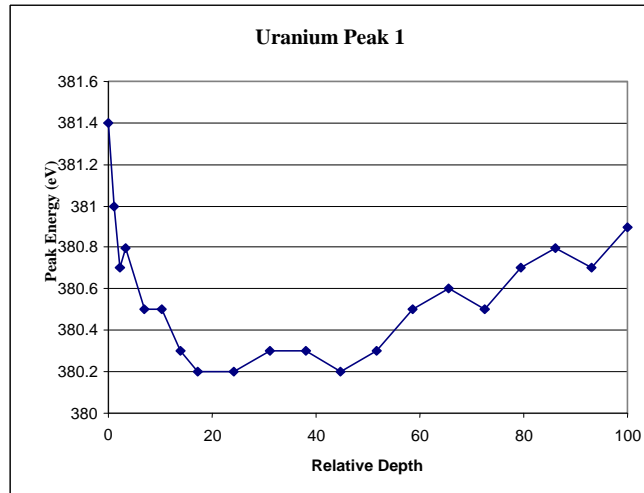


Figure 14. Position of $U4f_{7/2}$ peak with depth.

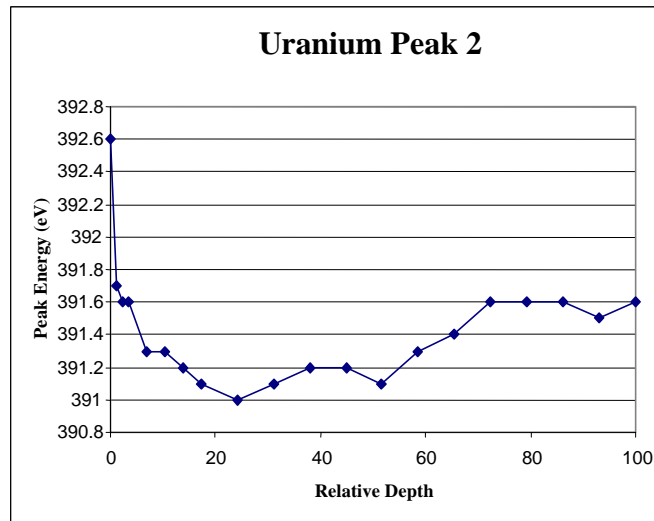


Figure 15. Position of $U4f_{5/2}$ peak with depth

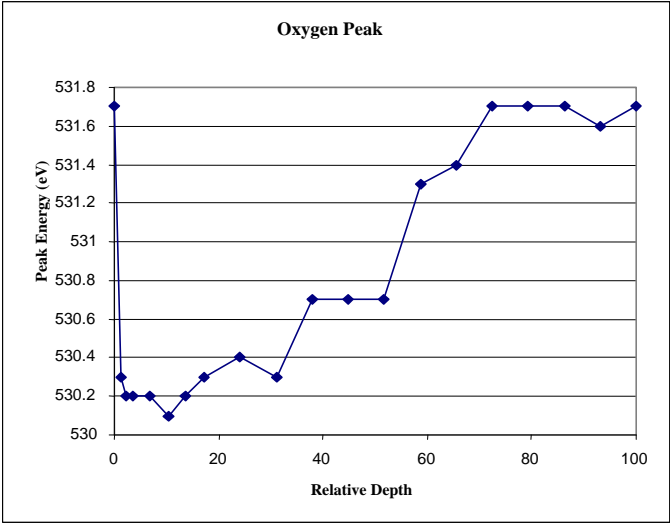


Figure 16. Position of O1s peak with depth.

VI. Discussion

From the two observed peaks, we see two different trends. On the surface the O1s peak indicates that the sample is moving to a higher oxidation state. Figure 17 shows how the composition changes with time, with composition ascertained by comparison to Teterin[8]. It appears as though the surface of the sample will completely oxidize to UO_3 with time.

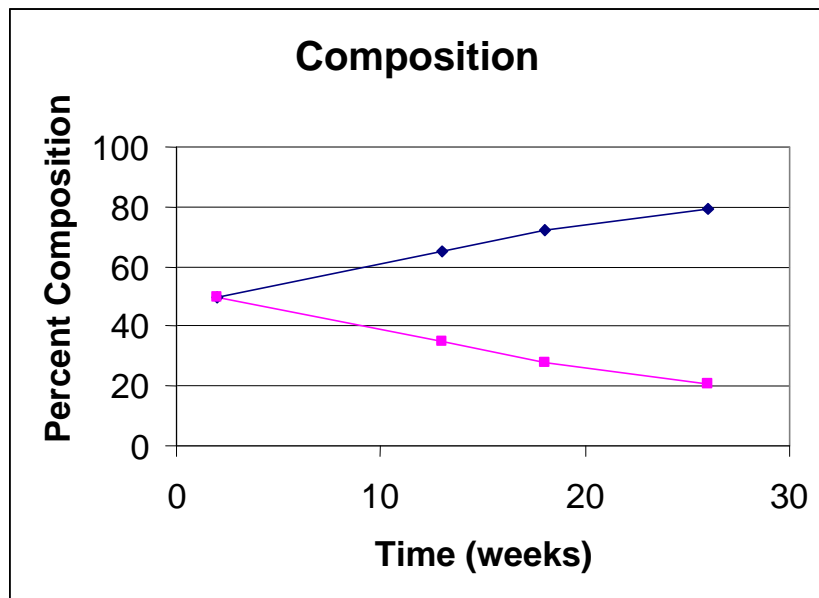


Figure 17. Oxidation states of uranium oxide over time. The top line represents the percentage of UO_3 while the bottom represents that of UO_2 .

The U4f peaks, however, show a different trend. If the sample is shifting to a higher oxidation state, the uranium peaks should move to a higher energy. Yet, we can see from the charts that the peaks moved to a lower energy, indicating that the sample is moving to a lower oxidation state. This trend occurred for the first 18 weeks, after which the peaks began to shift to higher energies. This is due to the fact that, as noted previously, the sampling depth of XPS is a function of the electron's kinetic energy. The kinetic energy for the ejected O1s electrons is approximately 950eV while that of the U4f

electrons is 1110eV. From studying figure 18 [14], the difference in sampling distance can be determined. (The y-axis is measured in nanometers, while the x-axis is in electron volts.)

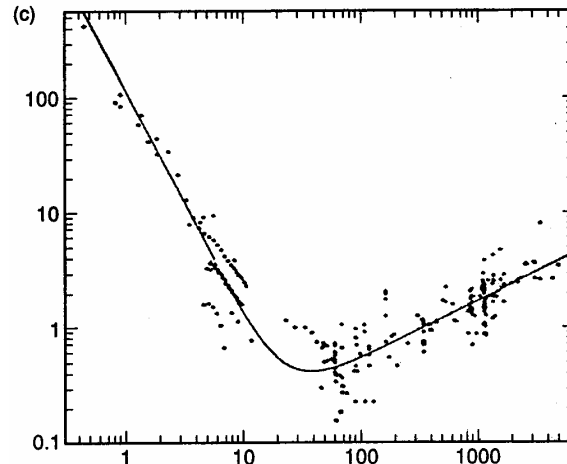


Figure 18. The sampling distance of an electron as a function of energy [14]

Thus, the difference in kinetic energy equates to a difference in sampling depth. Hence, the O1s peak is somewhat more sensitive to oxidation near the surface, while the U4f peaks probe the oxidation condition to a somewhat greater depth. It is obvious that the two trends are not identical.

The scans run at larger angles are in agreement with what was determined for the U4f and O1s peaks at 30°. The scan done at 55° (which samples a greater depth than 75°) shows a slightly lower oxidation state than the scan done at 75°, but a higher oxidation state than that at 30°.

The depth profiling data indicates non-uniform composition throughout the sample. The uranium at the surface is in a higher oxidation state than the rest of the sample. As we penetrate deeper into the sample, the uranium to oxygen ratio is fairly consistent with UO₂. As the silicon wafer is approached, the amount of oxygen goes up.

This may be due to bonding of oxygen with silicon; however, the shift in the uranium peaks indicates that the uranium is also bonding with more oxygen. Thus the top and bottom of the sample both have higher oxidation states than the bulk of the sample.

Nitrogen is detected below the surface of the sample, increasing to and leveling off at approximately 15% of the composition. The position of the nitrogen peak is at 398eV, while the $U4f_{7/2}$ peak is at 391eV. The proximity to the uranium peak creates difficulty in detecting the presence of nitrogen, as the uranium peak will overlap the nitrogen peak. Thus it is more likely that the amount of nitrogen is consistently 15% throughout the sample, it is simply not detected until the uranium peaks begin to decrease.

VII. Conclusion

Based on the data collected through x-ray photoelectron spectroscopy, it appears that the uranium oxide samples continue to oxidize after deposition, approaching a stable composition after a period of several weeks. In comparing to Teterin [8], it appears that the surface is initially UO_2 and slowly oxidizes to UO_3 . However, the depth profiling of the film indicates that bulk of the sample remains at the initial composition of UO_2 . Near the silicon wafer, the oxidation state may be higher.

The surface easily collects high amounts of carbon which may cause problems in the reflectance of the mirrors. This problem has been under investigation by members of the BYU thin films research group. It has been found that UV cleaning effectively removes all carbon from the surface of silicon oxide films with a relatively short amount of exposure time (approximately 5 minutes). However it is possible that this may cause further oxidation or other damage to the surface. More studies are needed to determine the effect of this cleaning on other surfaces, such as uranium oxide.

Although the uranium was believed to be sputtered only in the presence of oxygen, nitrogen may also have been present as it is found consistently throughout the films. It is unknown how this nitrogen may be bonded to the uranium oxide. Further investigation is needed to determine what role the nitrogen plays in our compound. Pressures of nitrogen in the DC sputtering chambers were not recorded. Additional investigation of the initial depth profile is required to determine if this is indeed the source.

Appendix

A. Survey scans of uranium oxide sample

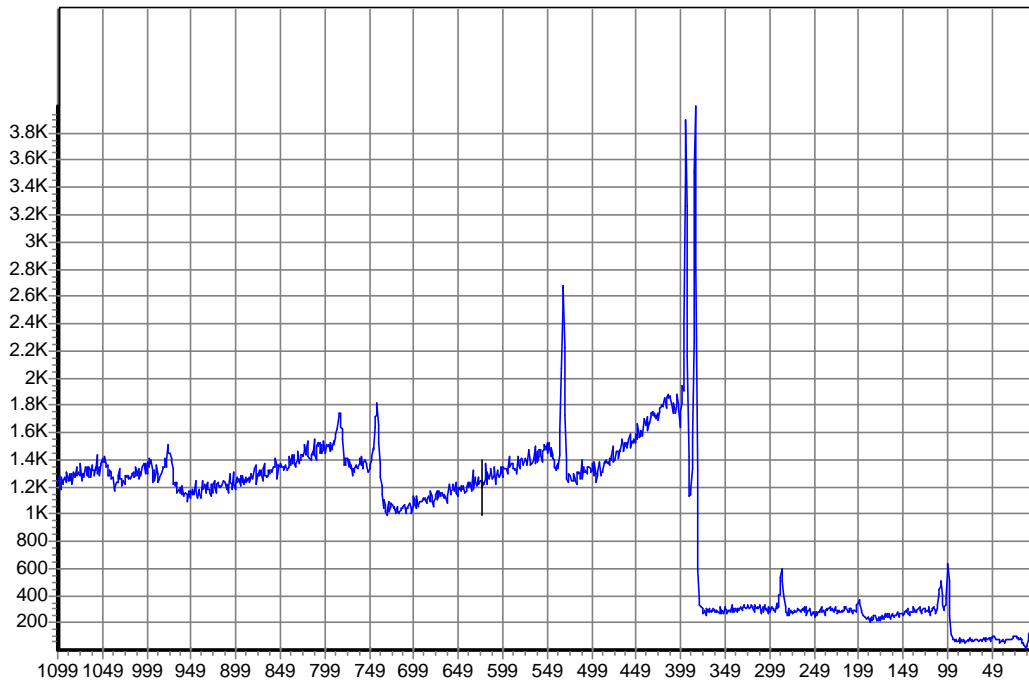


Figure 19. Survey scan of initial uranium oxide sample.

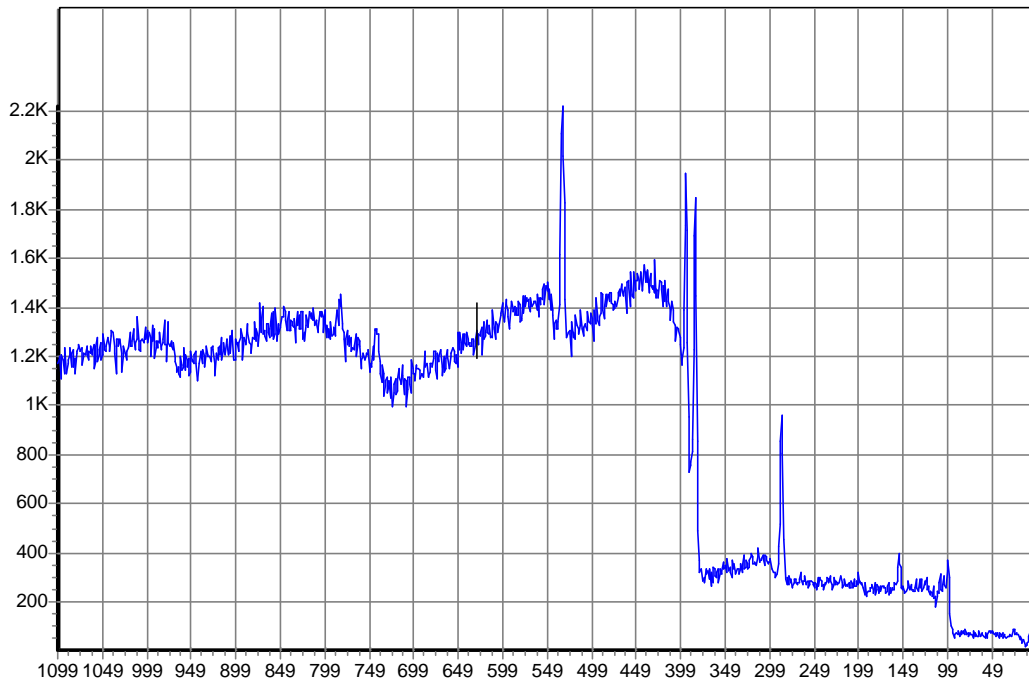


Figure 20. Survey scan of uranium oxide sample 12 weeks after deposition.

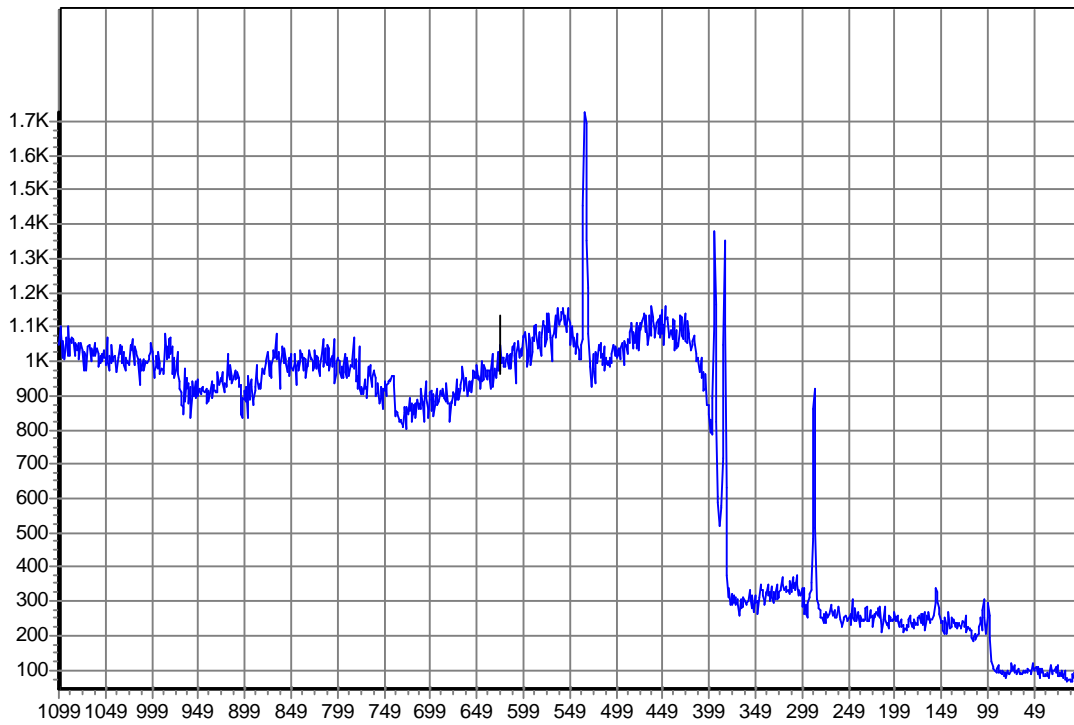


Figure 21. Survey scan of uranium oxide sample 25 weeks after deposition.

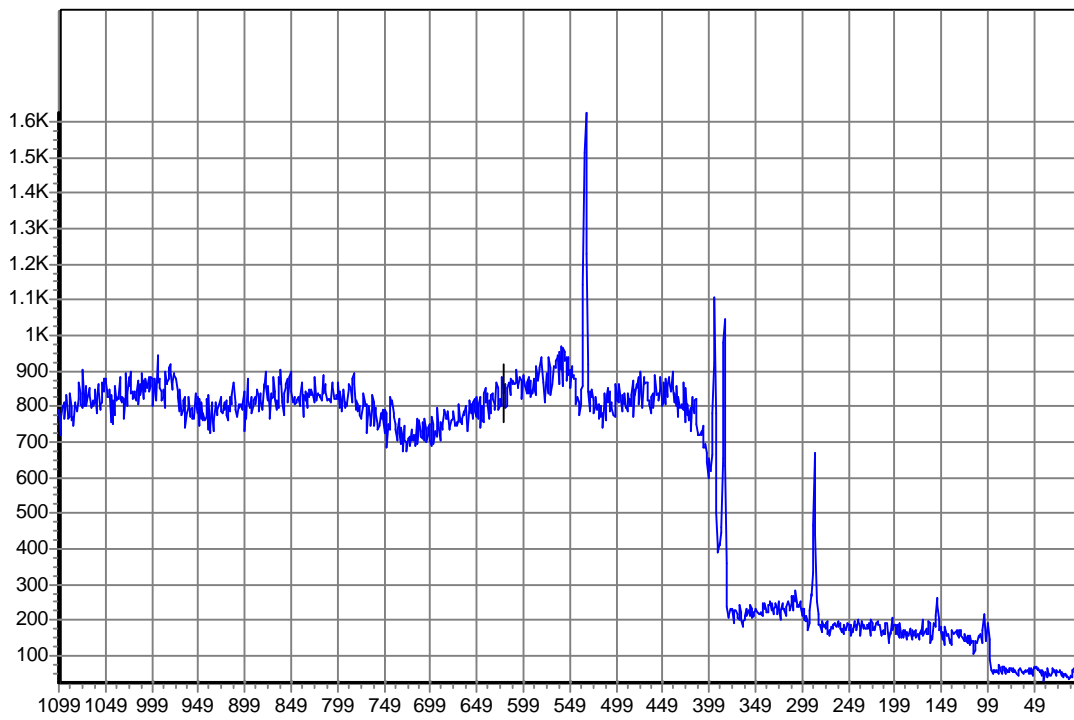


Figure 22. Survey scan of uranium oxide sample 52 weeks after deposition.

B. High-resolution scans of $U4f_{7/2}$ and $U4f_{5/2}$ peaks

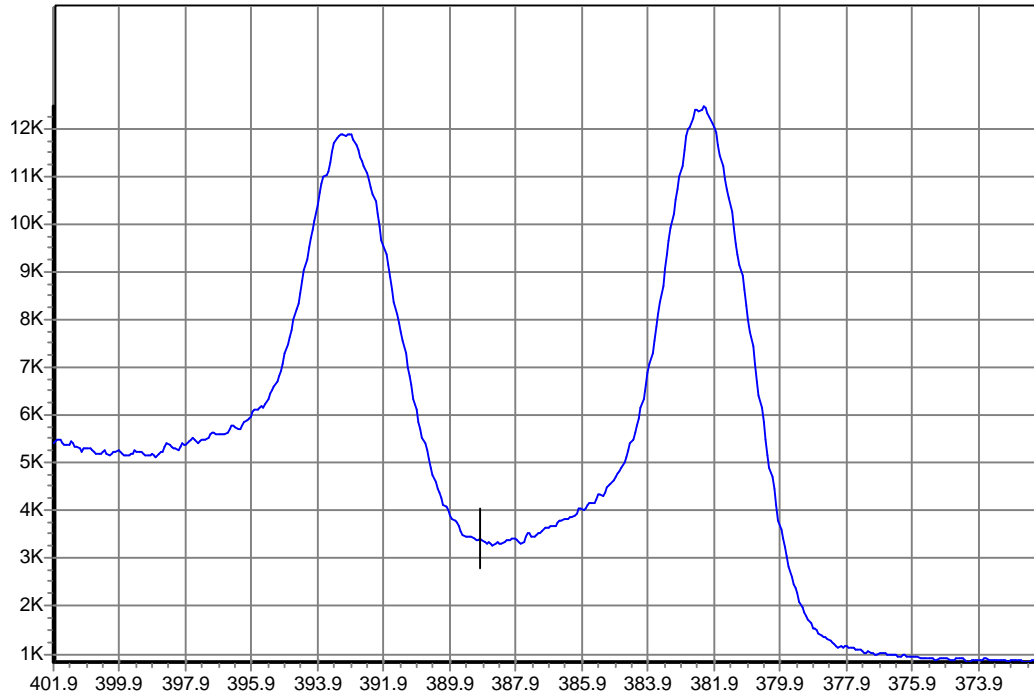


Figure 23. $U4f_{7/2}$ and $U4f_{5/2}$ peaks of initial uranium oxide sample.

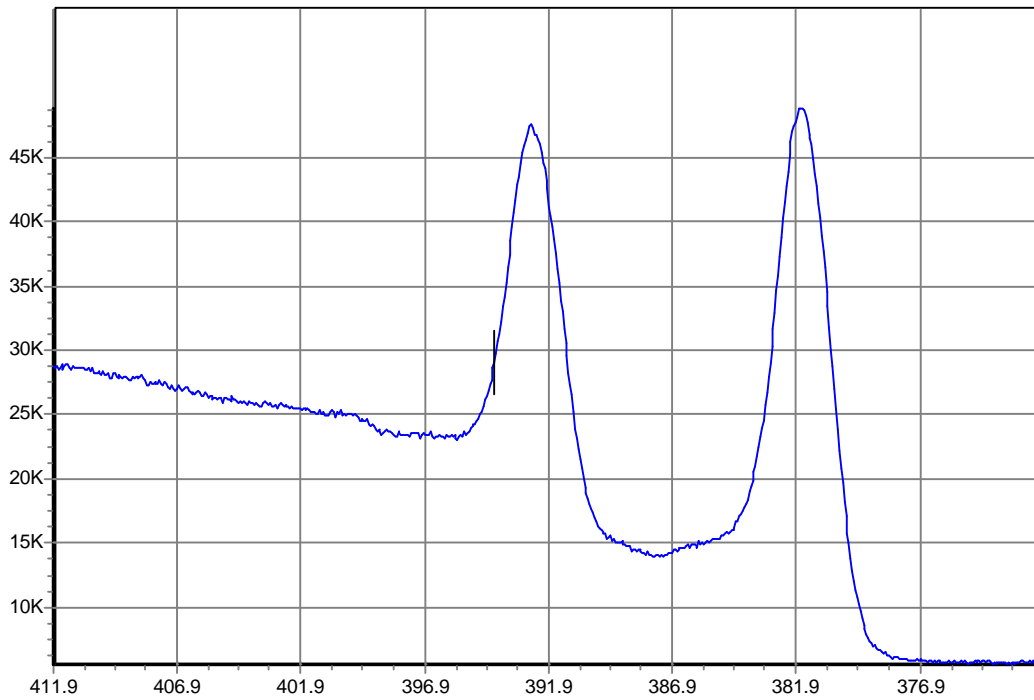


Figure 24. $U4f_{7/2}$ and $U4f_{5/2}$ peaks of uranium oxide sample 12 weeks after deposition.

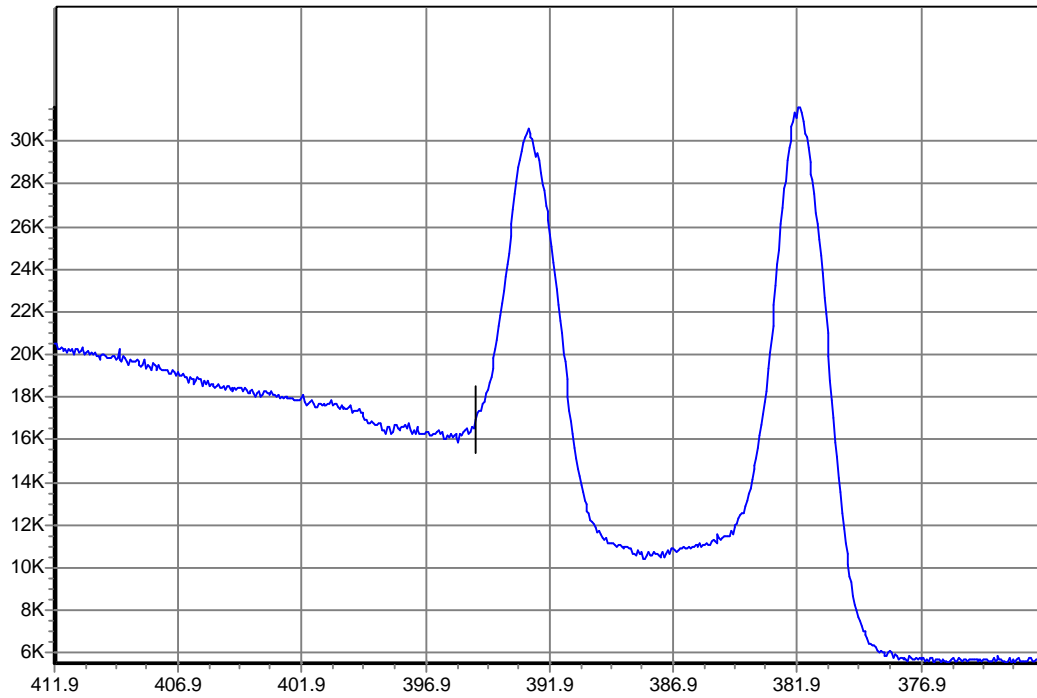


Figure 25. $U4f_{7/2}$ and $U4f_{5/2}$ peaks of uranium oxide sample 25 weeks after deposition.

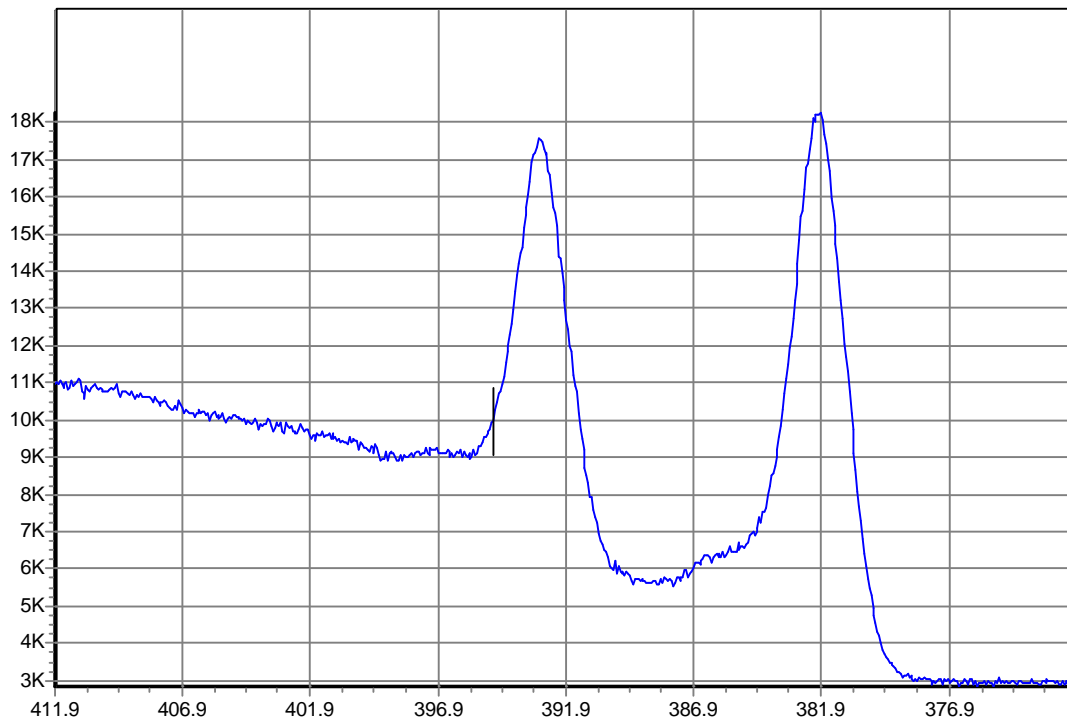


Figure 26. $U4f_{7/2}$ and $U4f_{5/2}$ peaks of uranium oxide sample 52 weeks after deposition.

C. High-resolution scans of O1s peak of uranium oxide sample

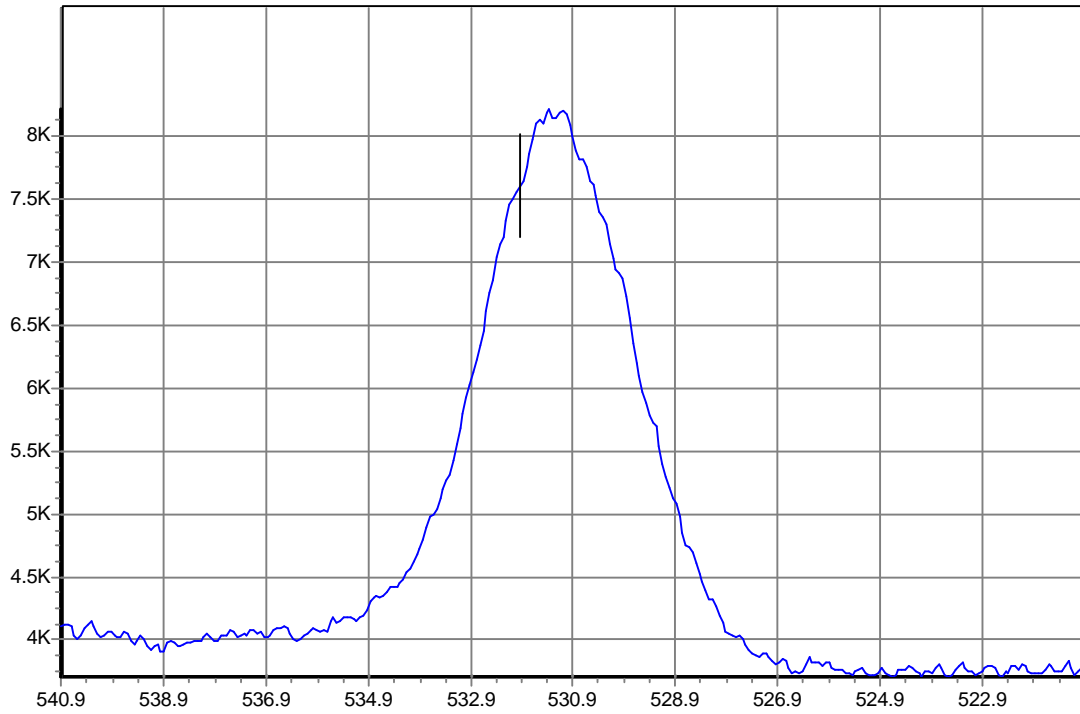


Figure 27. O1s peak of initial uranium oxide sample.

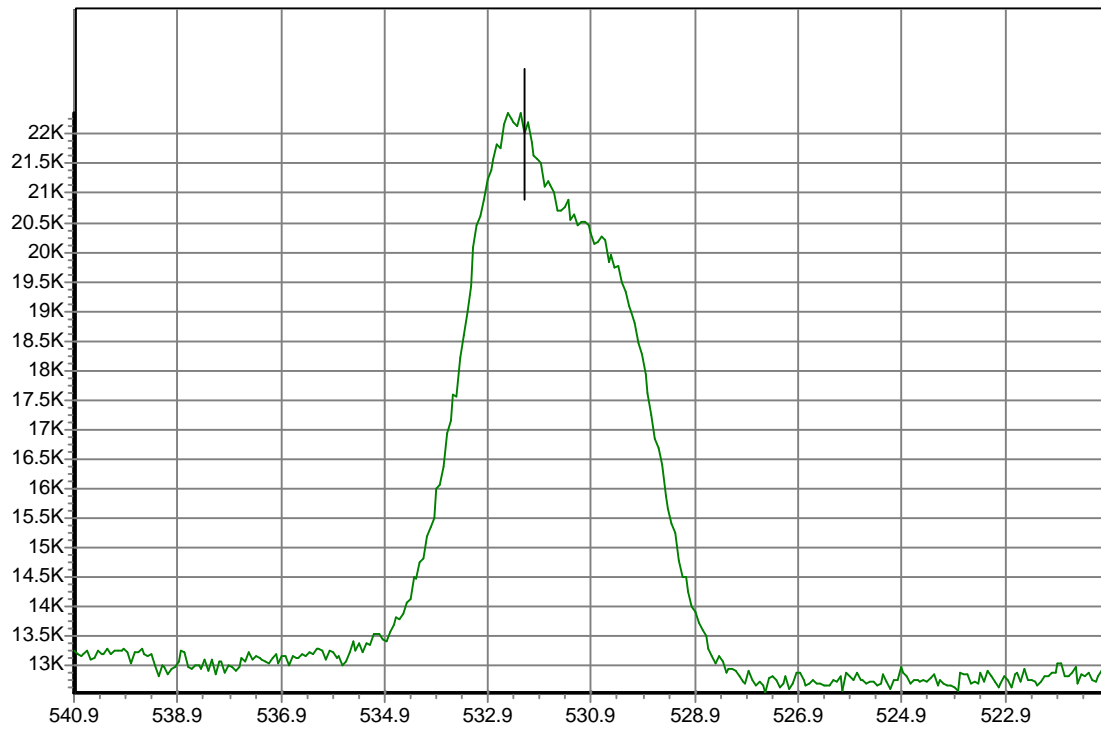


Figure 28. O1s peak of uranium oxide sample 12 weeks after deposition.

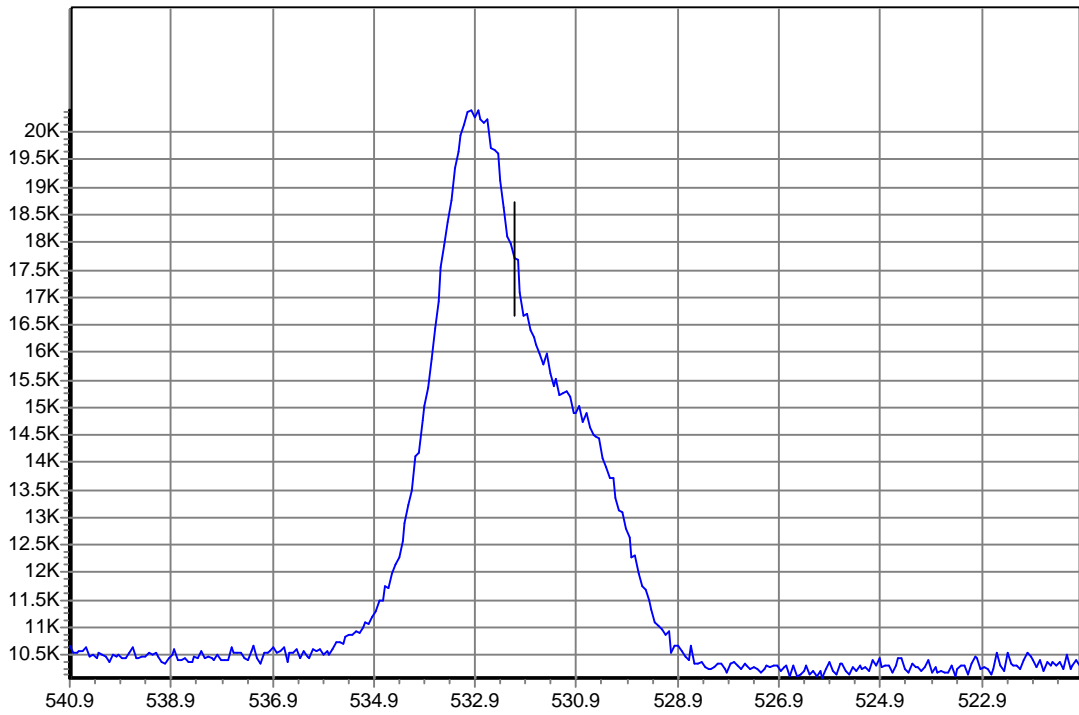


Figure 29. O1s peak of uranium oxide sample 25 weeks after deposition.

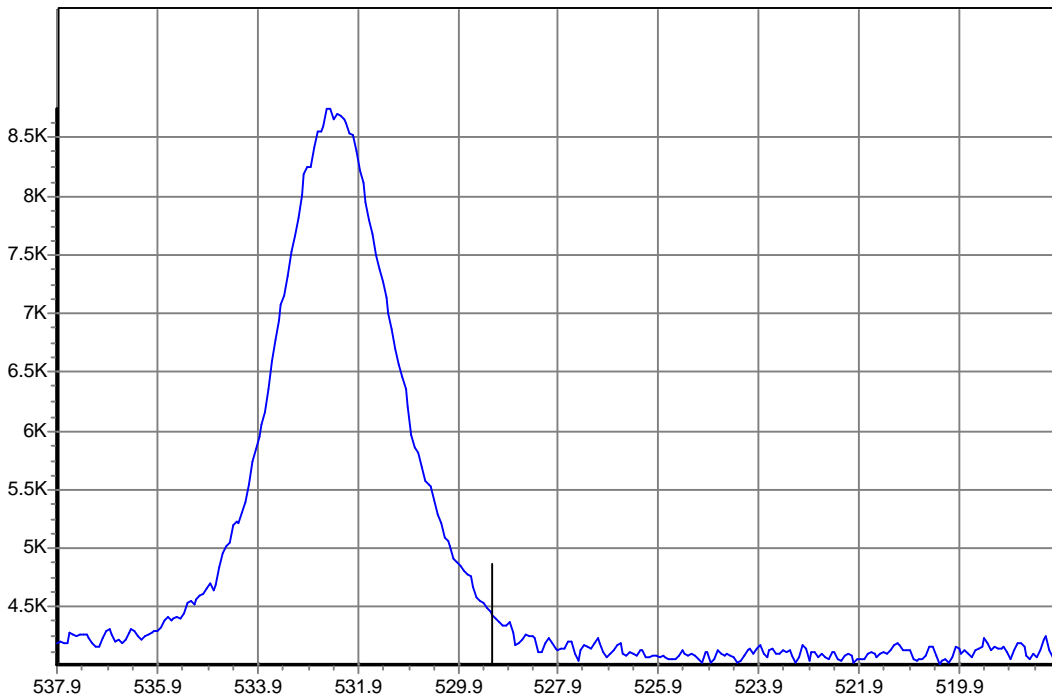


Figure 30. O1s peak of uranium oxide sample 52 weeks after deposition.

Bibliography

- [1] R. A. M. Keski-Kuha, "Layered synthetic microstructure technology considerations for the extreme ultraviolet." *Appl. Opt.* **23**, 3534-3537 (1984).
- [2] D. Attwood, *Soft X Rays and Ultraviolet Radiation*. (Cambridge University Press, Cambridge, 1999), pp. 59-61, 371.
- [3] D. Attwood, "Soft X Ray Microscopy and EUV Lithography: Imaging in the 20-50nm Region" colloquium given Jan. 9, 2002 at Brigham Young University, Dept. Physics & Astronomy.
- [4] M. B. Squires, "On Determining the Optical Constants of Sputtered U and a-Si at 304 and 584 ? ." Honors Thesis, Brigham Young University, 1999.
- [5] E. H. P. Cordfunke, *The Chemistry of Uranium*. (Elsevier Publishing Company, Amsterdam, 1969), pp.64-97.
- [6] R. Painter, <http://goliath.inrs-ener.quebec.ca/surfsci/arxps/sampling.html>, March 16, 2002.
- [7] J. R. Baird and C. S. Fadley, "X-Ray Photoelectron Angular Distributions with Dispersion-Compensating X-Ray and Electron Optics." *J. Elec. Spec. Relat. Phenom.* **11**, 39-65 (1977).
- [8] Y. A. Teterin, V. M. Kulakov, A. S. Baev, N.B. Nevzorov, I.V. Melnikov, V. A. Streltsov, L. G. Mashirov, D. N. Suglabov, A. G. Zelenkov. "A Study of Synthetic and Natural Uranium Oxides by X-Ray Photoelectron Spectroscopy." *J. Phys. Chem. Minerals.* **7**, 151-158 (1981).
- [9] G. C. Allen and N. R. Holmes. "Characterization of Binary Uranium Oxides by Infrared Spectroscopy." *Appl. Spec.* **48**, 525-530 (1994).
- [10] Y. A. Teterin, "Structure of X-Ray Photoelectron, Emission and Conversion Spectra and Molecular Orbitals of Uranium Compounds." *J. Struc. Chem.* **39**, 850-857 (1998).
- [11] J. F. Moulder, , W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*. (Physical Electronics, Inc., Eden Prairie, MN, 1992).
- [12] C. D. Wahner et al, *Surf. Interface Anal.* **3**, 211 (1981).
- [13] *ESCA NT Software for Surface Science Instruments*. Version 3.0, (Service Physics Inc, Bend OR, 2000).

- [14] M. P. Seah, W. A. Dench. "Compilation of Experimental Data Determined with Various Electron Energies for a Large Variety of Materials." *Surf. Interface. Anal.* I (1979).
- [15] S. Lunt, "Determining the Indices of Refraction of Reactively Sputtered Uranium Dioxide Thin Films From 46 to 584 Angstroms." M. S. Thesis, Brigham Young University, 2002.