The EUV and soft x-ray reflectance of reactively sputtered uranium oxides

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ABSTRACT

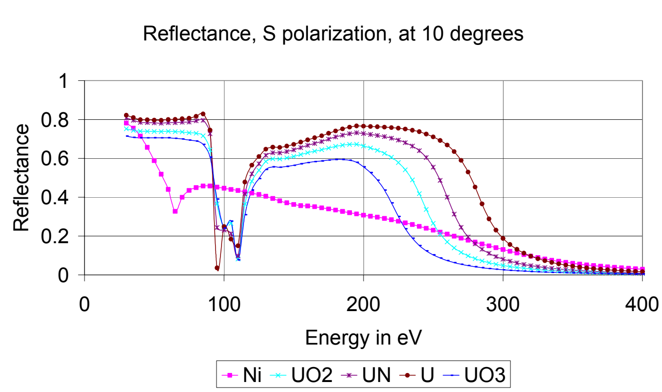
We have measured as a function of angle the reflectivity of a set of five reactively sputtered uranium oxide (here presumed to be, UO_2) thin films on beam line 6.3.2. This has allowed us to determine refractive indices for UO_2 for the first time below 30 nm.[1] We modeled the films as bilayers, as a 5-nm thick overlayer of UO_x, with x>2 ~3, on the UO_2 layer. The identity of the two layers and their presumed thickness was based on information members of our group had obtained via XPS, XRD and ellipsometry by mid 2002. Tables 1 and 2, respectively, show the optical constants over the range 4.6 nm to 17.5 nm (about 70 to 270 eV) for UO_2 and the top layer using this model. These were derived using a least-squares model. The columns labeled "calculated" are the optical constants based on the atomic scattering factor approach using bulk densities of the oxides. Our measured indices of UO_2 differ from those calculated by ASF by about 2. Using these results we can calculate that UO_x reflects not as well as the ASF model predicts for UO_2. It still can be expected to reflect better at about 5-10° than standard materials over much of the range between 150 and 300 eV.

Table 1: Optical Constants for UO_2

	Measured		**Calcuated (*f*1 & *f*2) [17]**		$\frac{\delta_M}{\delta_C}$	$\frac{\beta_M}{\beta_C}$
λ in Å	δ	β	δ	β		
46	0.0065 ± 0	8.0861e-4 ± 0	0.0116	0.0011	0.56	0.74
56	.0103 ± 0	.0012 ± .0001	0.0187	0.0025	0.55	0.48
68	.0173 ± .0001	.0040 ± .0001	0.0302	0.0065	0.57	0.62
85	.0298 ± .0005	.0151 ± .0007	0.0491	0.0271	0.61	0.56
100	.0344 ± .0011	.0458 ± .0011	0.0674	0.0693	0.51	0.66
125	- .0038 ± .0002	.0129 ± .0001	0.0057	0.0399	-	0.32
140	.0229 ± .0002	.0103 ± .0003	0.0509	0.017	0.45	0.61
155	.0362 ± .0002	.0158 ± .0002	0.0782	0.0281	0.46	0.56
175	.0547 ± .0003	.0246 ± .0005	0.1058	0.0464	0.52	0.53

Table 2: Optical Constants for Top Oxide Layer

	Measured	
λ in Å	δ	β
46	0.0065 ± 0	.0011 ± 0
56	.0103 ± .0001	.0016 ± 0
68	.0161 ± .0001	0031 ± .0001
85	.0295 ± .0002	.0134 ±. 0001
100	.0398 ± .0001	.0269 ±. 0002
125	.0206 ± .0001	.0091 ±. 0002
140	.0360 ± .0001	.0151 ±. 0001
155	.0495 ± .0001	.0151 ±. 0001
175	.0639 ± .0002	.0038 ± .0002



BACKGROUND

Uranium metal has noteworthy optical properties throughout the much of the EUV and soft x-ray region. Our group has been depositing uranium-based multilayer mirrors for almost a decade. We have proposed the development of broadband, low-angle-of-incidence, single-surface mirrors for the soft x-ray band from about 0.1 to 0.3 keV[2]. These could have special application in soft x-ray astronomy and soft x-ray optics. Calculations indicated that mirrors with a single layer of reasonably thick UO_2 would have approximately double the reflectance of conventional Ni mirrors at 10 degrees at 0.2 keV. (See the figure). The effect for x-ray astronomy would be to quadruple the signal for spectrographs since these require two bounces, reflectance going as the square of the intensity. This would similarly benefit the performance of the low-angle of incidence optics used in many synchrotron beamline light sources.

We studied the deposition and subsequent tarnishing of uranium thin films and multilayers while preparing mirrors for the EUV instrument in the IMAGE spacecraft[3]. Uranium is subject to extensive oxidation in laboratory air, more than 10 nm in a week. We have also determined that sputter deposited uranium oxide changes much less slowly. Three years ago, in collaboration with a University of Colorado group, we measured the low angle reflectance of a bare “uranium” (uranium oxide) film at the C K line, about 275 eV, using a Manson source. We learned that it reflected significantly better than Ni films at some angles and wavelengths. Calculations showed that both UO_2 and, to some extend, UO_3, could also be suitable materials for high reflectance at short wavelengths. Please see the figure.

Prior to ALS measurements we deposited uranium oxide films on Si wafer pieces (100 orientation) by reactively sputtering (DC magnetron) uranium in argon/oxygen. We measured the films at the ALS 2-9 days after their being deposited. All films were stored in air. We also characterized the films in other ways.

1. To obtain thicknesses. For this we used spectroscopic ellipsometry, x-ray diffraction (XRD) and atomic force microscope, AFM, measurements across an abrupt edge in the film.
2. To understand and limit roughness. AFM was used. Smooth films are important both for obtaining optical constants and for high performance mirrors. It is to obtain smooth films we chose reactive sputtering, rather than depositing uranium and letting it oxidize. Based on bulk density we calculate that UO_2 possesses approximately twice the volume of the uranium film from which it oxidizes. Such expansion could lead to surface roughening. It is better for it to be deposited in an already oxidized state so that post-deposition changes are minimal. The rms roughness we measured was about 0.3 nm across a 1000-nm line.
3. XPS to determine the oxidation state of the deposited film and the speed at which it transforms. Ellipsometry has also been helpful for this purpose. It was discovered that while UO_2 forms on pure uranium metal at room temperature in ambient pressure air and seems to stabilize over time, the surface of the film will continue to oxidize slowly towards UO_3, that is towards U^{+6}. U has 6 electrons beyond the closed shell at Z = 86. Oxidation stops at +6.
4. VUV/ EUV reflectance. We measured the reflectance as a function of angle of UO_x films at 10.25, 21.6, 23 and 41 eV using a McPherson monochromator. From this we compute optical constants of UO_x.

FINAL COMMENTS

Subsequent XPS performed about 8 months after the ALS reflectances indicated that $x \geq 3$ only at the very top of the film and showed that it falls by about one unit by ~0.3 nm below the surface. This does not match the optical model, which would have x>~2 in the top 5-nm overlayer. Therefore, we presume that x <2, that is, the reactively sputtered film is not precisely

UO_2. In fact, it deviates from 2 in other ways. Up to 15 at. % nitrogen is also present and the N+O stoichiometry may dip below x=2. This is currently the subject of active research.[4]

As was mentioned, the optical constants obtained in this study for reactively sputtered thin film $U0_2$ differ from theoretical constants calculated by CXRO [17]. No experimental values for the optical constants of $U0_2$ in the full range from 46 Å to 175 Å have been previously reported so the measured data can only be compared to ASF model calculations in this region. These results indicate that the principles for computing the optical constants of compounds in the EUV are still not fully understood.

Differences in the measured optical constants of $U0_x$ and those obtained from atomic scattering factors could be due to several factors. However, none is completely satisfactory. First, we examined differences in density between the films studied and the reported density of the bulk compounds, 10.96 g/cm^3 for UO_2 and about 14 for UN[5]. This could account for the low δ and β in the measured data if they were off by the same ratios at all energies. In addition, the thin film compounds would have to be very low density, by about a factor of 2 for UO_2 and more than a factor of 2 for U(O, N). We studied this effect using ellipsometry and XRD. The XRD data proved to be fairly independent of density. The ellipsometric data seemed to show that the density of our films were at least similar to the density of the films used by Schoenes.[6] Thus, it appears that the differences in constants are not entirely due to density affects. The differences could also be due to the atomic scattering factor theory not being completely accurate in the EUV where electrons are still bound and especially near resonances. The optical constants of uranium oxide will not be the sum of U plus O at the appropriate densities for the compound as calculated from atomic scattering factors at every wavelength, but over a large enough range the model should hold. The role of post deposition annealing and substrate heating will be investigated. We plan to study the matter further, making additional measurements at the ALS.

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[1] This abstract is drawn primarily from the Master of Science thesis of Shannon Lunt, Department of Physics and Astronomy, Brigham Young University, August 2002, *Determining the Indices of Refraction of Reactively Sputtered Uranium Dioxide Thin Films from 46 to 584 Angstroms*, BYU, Provo, UT 2002. Contact the BYU library at http://www.lib.byu.edu/hbll/. The thesis can be viewed in pdf format at volta.byu.edu .

[2] David D. Allred, Matthew B. Squires, R. Steven Turley, Webster Cash, and Ann Shipley, “Highly Reflective Uranium Mirrors for Astrophysics Applications,” in *X-ray Mirrors, Crystals and Multilayers*, Andreas K. Freund, Albert T. Macrander, Tetsuya Ishikawa, and James. T. Wood, Editors, Proc. SPIE 4782 , pp 212-223 , SPIE, Bellingham, WA, 2002.

[3] D. D. Allred, R. S. Turley, M. B. Squires, “Dual-function EUV multilayer mirrors for the IMAGE mission,” in EUV, X-Ray and Neutron Optics and Courses, Carolyn A. Macdonald, Kenneth A. Goldberg, Juan R. Maldonado, H. Heather Chen-Mayer, Stephen P. Vernon, Editors, Proceedings of SPIE Vol. **3767**, 280-287 (1999).

[4] TEM work shows the presence of fcc nanocrystallites with a lattice size of 0.5 nm. (Hollilyne Drury and Megan Rowberry unpublished.) This is too small for UO_2 but correct for x~1. N_2 is a background gas in the sputter system.

[5] The density of U(O,N) is not known, but should approach that of UN. Uranium is capable, as are a large number of transition elements, of forming fcc compounds the rock-salt (B1) structure with a number of nonmetals. These can be thought of as the nonmetals sitting in the octahedral site in the metal-defined fcc lattice. These compounds are capable of considerable mixed stoichiometry and nonstoichiometry. By which it is meant, first, that one nonmetal can substitute for another and, second, there can be a number of vacant sites in the nonmetal positions. In the case of uranium the oxide structure is stabilized by nitrogen, which has been to be present.

[6] J. Schoenes, “Optical Properties and Electronic Structure of UO_2,” J. Appl. Phys., 49, 1463-5 (1978).