Uranium Oxide as a Highly Reflective Coating from 150-350 eV

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ABSTRACT

We present the measured reflectances (beamline 6.3.2, ALS at LBNL) of naturally oxidized uranium and naturally oxidized nickel thin films from 100-460 eV (2.7 to 11.6 nm) at 5, 10, and 15 degrees grazing incidence. These show that uranium, as UO2, can fulfill its promise as the highest known single surface reflector for this portion of the soft x-ray region, being nearly twice as reflective as nickel in the 124-250 eV (5-10 nm) region. This is due to its large index of refraction coupled with low absorption. Nickel is commonly used in soft x-ray applications in astronomy and synchrotrons. (Its reflectance at 10° exceeds that of Au and Ir for most of this range.) We prepared uranium and nickel thin films via DC-magnetron sputtering of a depleted U target and resistive heating evaporation respectively. Ambient oxidation quickly brought the U sample to UO2 (total thickness about 30 nm). The nickel sample (50 nm) also acquired a thin native oxide coating (<2nm). Though the density of U in UO2 is only half of the metal, its reflectance is high and it is relatively stable against further changes. There are important discrepancies between UO2's actual reflectance with those predicted by the atomic scattering factor model indicative of the need to determine the actual constants of UO2.
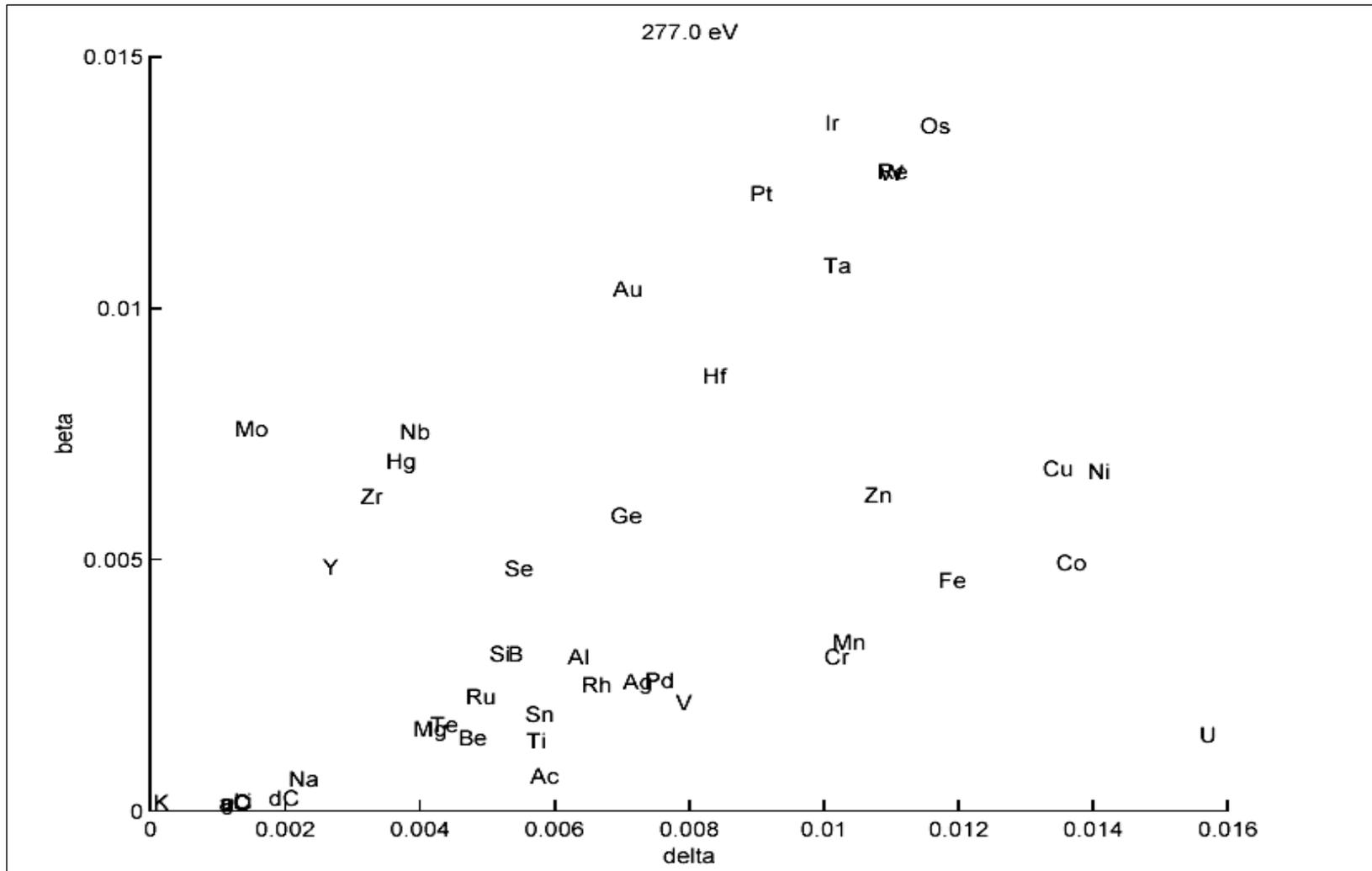
Fig. 1: Delta verses beta plot for several elements at 277 eV (4.48 nm). Nickel and its neighboring 3d elements are the nearest to uranium in this area.
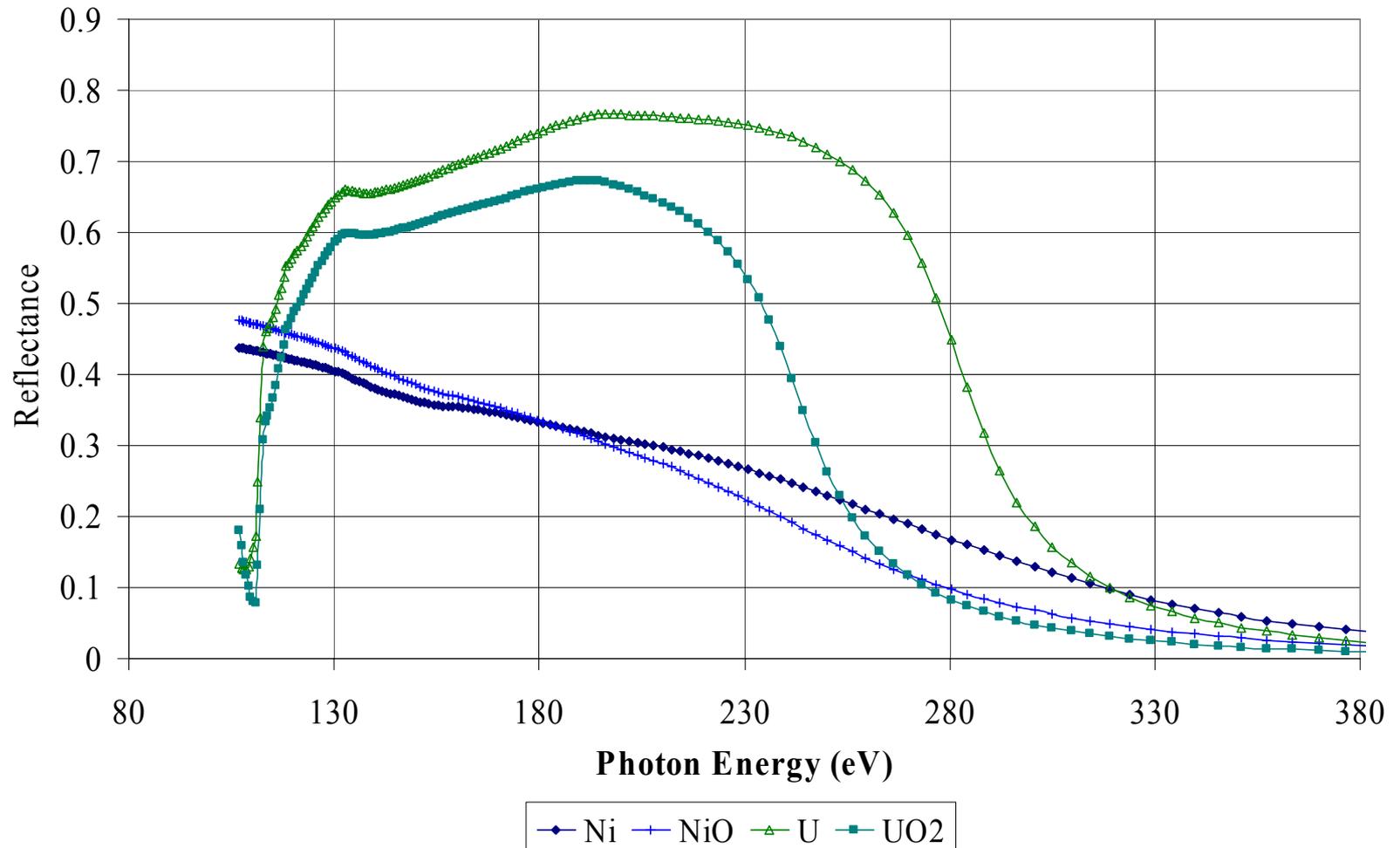
Fig. 2: Here we compare the reflectance for Ni, NiO, U, and UO2 predicted by the atomic scattering factor model from the CXRO website (www-cxro.lbl.gov).
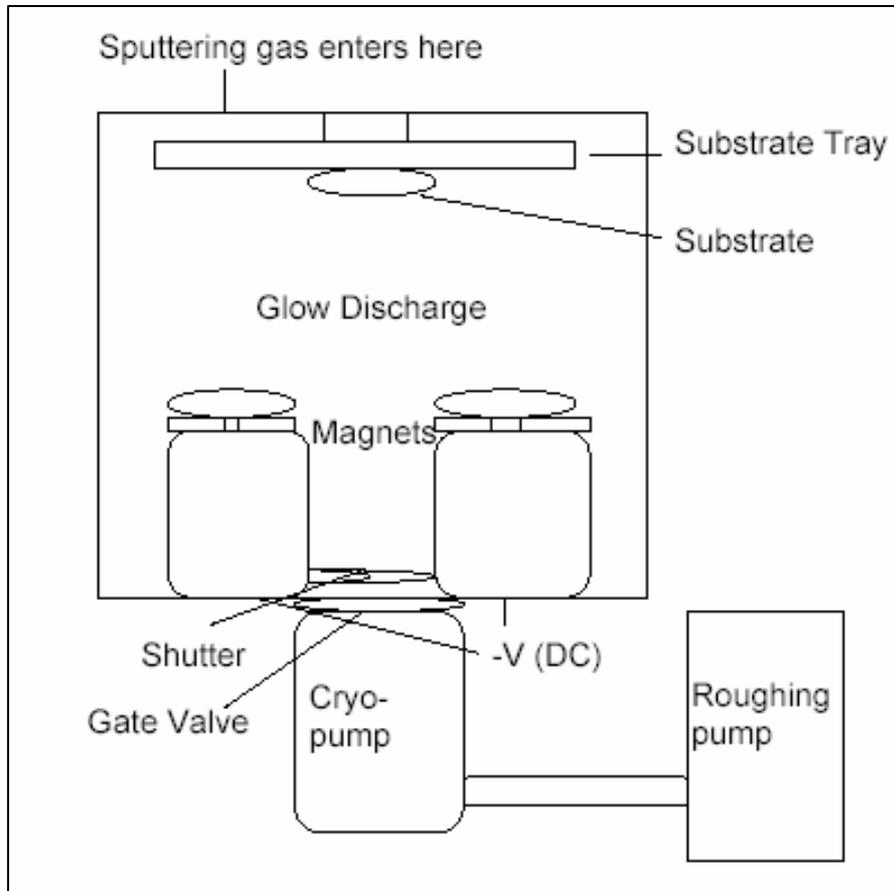
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2. Methodology

Fig. 3: Schematic of DC magnetron sputtering system at BYU.

Sample Creation

2.1 Sample Creation/Experimental Setup
The uranium oxide and nickel samples were deposited on pieces of commercially available, polished silicon test wafers (100 orientation).

•**2.1.1 UO2 DC Magnetron Sputtering**
We used a DC magnetron sputtering system on Brigham Young University campus to deposit the uranium sample. The materials to be sputtered are made into cylindrical targets which are fastened onto the top of the sputter guns. The uranium sputter targets used here were of depleted uranium metal (less than 0.2% U-235). After sputtering, the uranium was allowed to oxidize naturally in laboratory air. Prior to this study, studies of the oxidation rates of uranium thin films have been conducted.

Uranium is subject to extensive oxidation in laboratory air, about 6 nm in 13 min, and more than 13 nm in a day. Oliphant further showed that the uranium oxidizes into films of UO2+x (x~0) which can be a few nanometers thick under typical laboratory conditions (room ambient). It should be noted that many bulk oxides of uranium are known. Even a given composition, such as UO3, many different crystal structures are known. Also UO2 tolerates a large range of nonstoichiometry. The x in UO2+x can reach 0.25 before inducing crystal changes. Members of our group are currently studying these subtleties using XPS and TEM. For the purpose of this paper the oxide will be called UOx; although, it is closest to UO2 whose stoichiometry and handbook density of 10.59 g/cc will be used in calculation in accordance with Oliphant's findings.

- ## 2.1.2 Ni Evaporation
  Our nickel films were prepared by evaporating Ni wire from a resistively heated tungsten boat (RD Mathis Co.) in a large, cryopumped, stainless steel "bell jar" coater. The base pressure of the system was 3.2 x10-4 Pa (2.4 x10-6 torr), high vacuum. A quartz crystal monitor was used to measure the evaporation rate. The source was shuttered as the voltage to the tungsten boat was increased. When the evaporation rate reached about 1-2 nm/s, the shutter was opened and the substrates were coated. Fast deposition rates are known to be preferable in obtaining the highest reflectance for aluminum and many materials. This is probably due to their limiting the extent to which impurities, usually oxygen, are drawn into the film from residual air and water vapor in the vacuum. After the monitor recorded about 91 nm of film the voltage to the source was cut, the box was vented to air and the films removed for further study on June 5, 2003. We found the Ni layer thickness to be 49.7 nm with x-ray diffraction (XRD).

- ## 2.1.3 Thickness determination: Characterization with XRD and IMD Fitting.
  Thin-film interference of x rays was used to determine the thickness of our deposited thin films. Using a Scintag® X-ray diffractometer (XRD), we measured the low-angle reflectance maxima and minima. The Scintag diffractometer produces collimated x ray radiation from a rotating copper target, which was scattered off of the sample. A liquid nitrogen cooled intrinsic germanium detector in photon counting mode was gated to accept Kα radiation (0.154 nm) and reject Kβ and bremstrahlung radiation above and below Cu Kα. Angle scans at low angles (usually from 1-3.5°, 2θ, grazing incidence angles) were taken. These scans showed interference fringes. At first-order approximation, the data can be modeled with an equation which resembles the Bragg diffraction, $m\lambda=2d\sin\theta$, where m is the diffraction order, λ is the wavelength of the diffractometer radiation in the material being measured, d is the layer thickness, and θ is the angle between the incident and refracted beam.[8] The Bragg equation as written above does not take into account the refraction of the x rays in the material. It is adequate for approximating the thickness of the film but to properly obtain the thickness we must match the spectra with a computer model. We used IMD to model our layers. Then by adjusting the thickness of the modeled layer, the diffraction peaks of the model and the measured XRD scan can be compared until the numbers of peaks in the same angle interval are the same and the peak positions match. The computed value for thickness is then approximately the same as the real layer thickness. For nickel, this thickness was 49.7±0.5 nm. For the uranium oxide sample this was 31.8±0.5 nm.

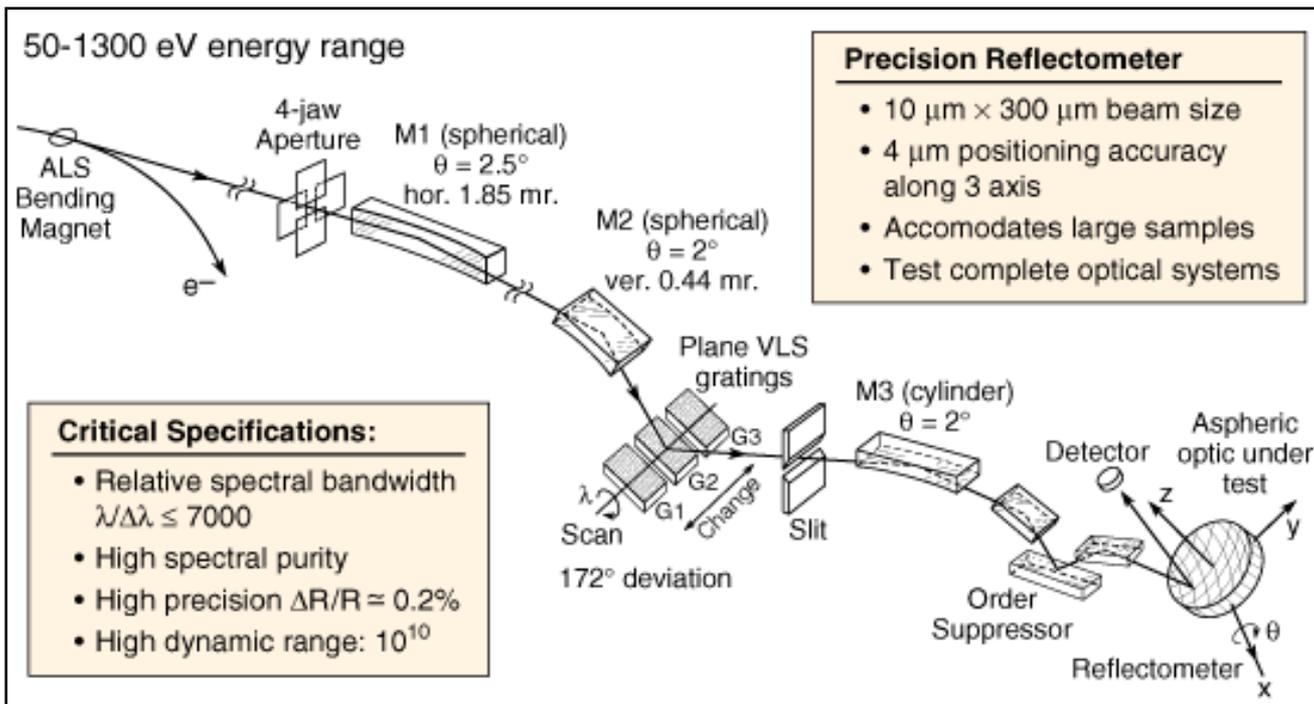**Fig. 4: Schematic of ALS beamline 6.3.2 courtesy of**
http://www-cxro.lbl.gov/ALS6.3.2/.

2.2 ALS Reflectometry

The reflectance measurements where conducted at the Advanced Light Source (ALS) at Lawrence Berkley National Laboratory at the University of California-Berkley on beamline 6.3.2. Fig. 4 shows a schematic of this beamline. This beamline has a reflectometer setup with three gratings (200 lines/mm, 600 lines/mm, and 1200 lines/mm) which allow the user to measure sample reflectance from 50 to 1300 eV (1 to 24.8 nm) at various angles. Different filters corresponding to these gratings select which wavelength ranges are desired. However, the filters do not perfectly suppress other orders than the target order, so the source is not perfectly monochromatic. This non-monochromatic nature can cause reflectances of overlapping wavelength regions to vary slightly as can be seen in Fig. 5-7. Reflectances can also vary from range to range if the beam strikes a differed part of the sample. Some of the measurements were made after the sample had been removed and then returned to the reflectometer. The process of normalization to extract reflectances are described in more detail along with further details on beamline 6.3.2 at the CXRO webpage and can be found in Underwood. 6

3. Measured Data

Note that each chart has three lines (Fig. 5-7). The curves with squares, circles and triangles correspond to the measured reflectance of UOx, NiO on Ni, and Ni on Quartz respectively. This is what these labels mean:

1. UOx stands for uranium with its native oxide which is almost UO_2.
2. NiO on Ni stands for evaporated Ni on a Silicon wafer. We brought a deep UV/ ozone lamp to the ALS for the purpose of cleaning the adventitious carbon-containing layer off our samples. This lamp is known to remove the "organic layer" from the native oxide coating a silicon wafer in about 45 seconds. (This can be seen on silicon surfaces which go from hydrophobic to hydrophilic in about 45 seconds as the carbon containing layer on top dissipates). To insure that the sample had an ample opportunity to lose organic materials we exposed our nickel to three full minutes of UV light. However, the most obvious change was not the elimination of carbon but the darkening of the surface. We take this coloring to be tarnishing (oxidation) of the metal. This oxidation needs to be further investigated to see if the darkening is due to oxidation and what thickness of oxide is produced.
3. Ni on Quartz- This sample wasn't cleaned with UV light. Its surface remained visibly bright. However, the usual surface quality of the quartz is not as high as is typical for the silicon wafers. One of the evidences is in the figure error seen for the nickel on quartz sample. It wasn't flat. At ALS, when we sought to align the sample at low angles we could see the image of the soft x-ray beam smeared out or broken up into several bands depending on the spot on the sample which it illuminated. In contrast, the reflected image off of the nickel-on-silicon-wafer sample focused well. We had previously measured via AFM the surface roughness of silicon wafers and quartz samples with and without coatings. We have always observed the surface smoothness of our quartz sample to be inferior to those of silicon. We had not measured the nanoroughness of the nickel coated quartz sample but speculate that it is rougher than the silicon samples.
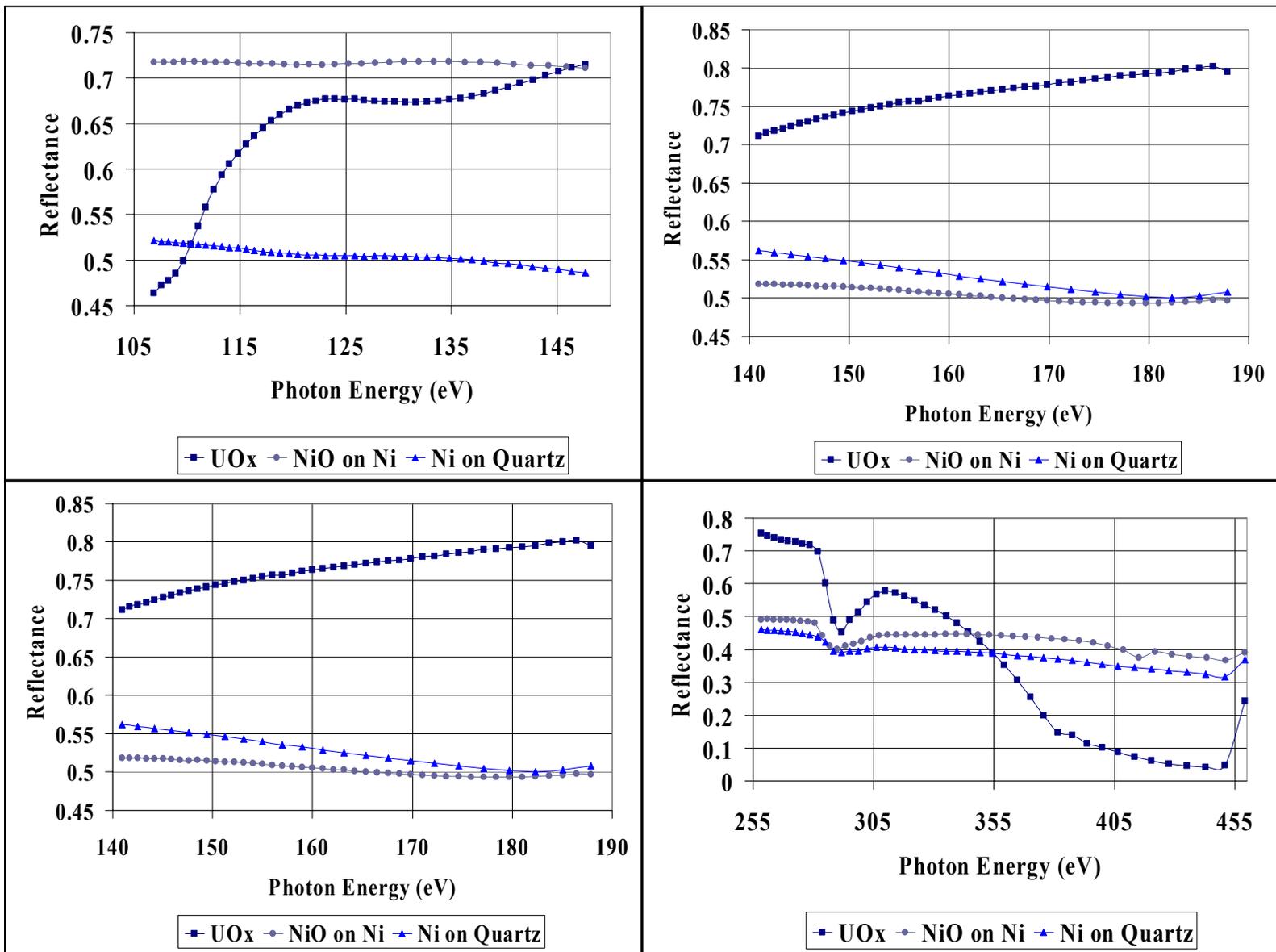
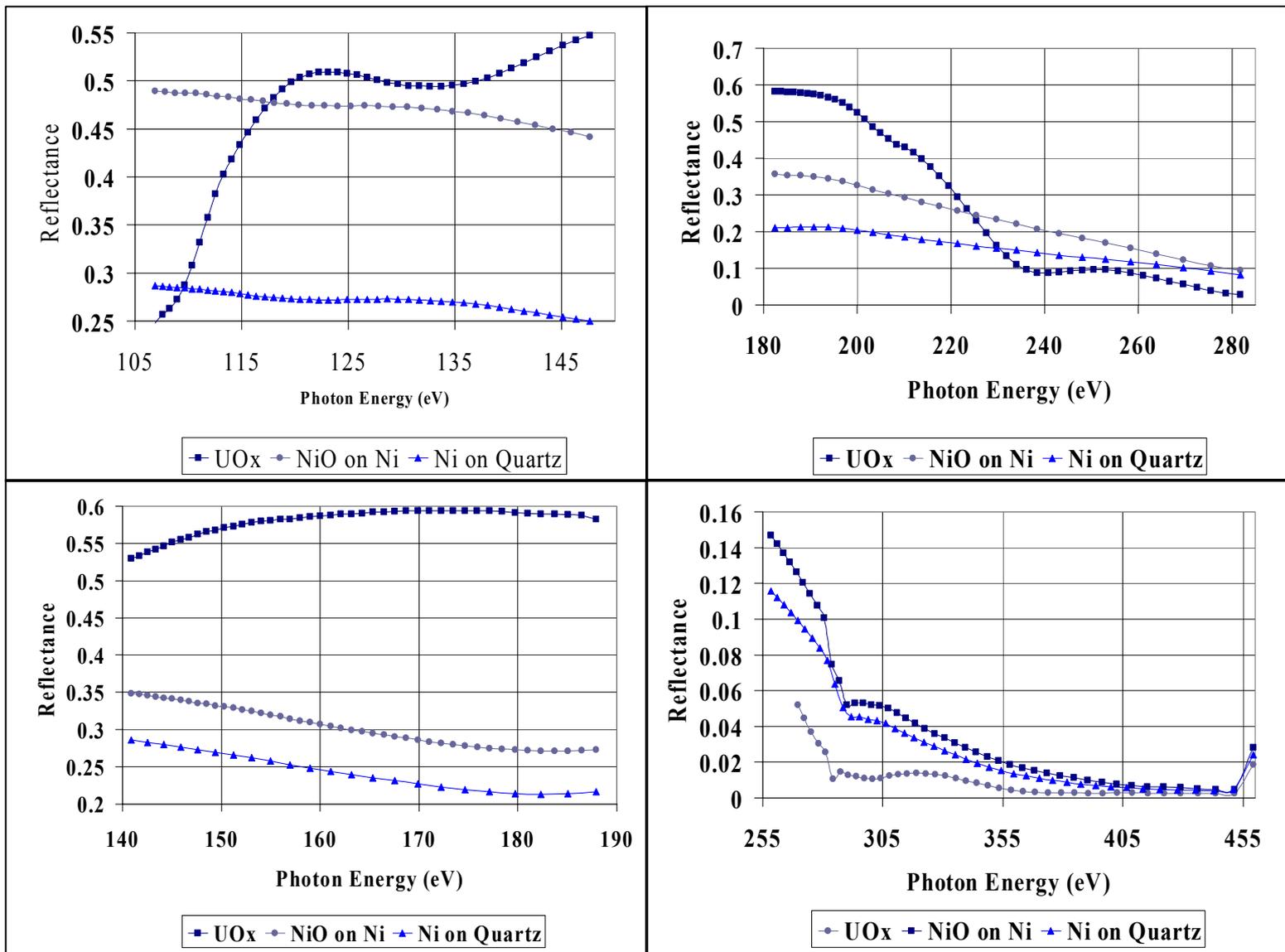**Fig. 5: Measure reflectance of UOx, NiO on Ni, and Ni on quartz at 5 degrees from 106-460 eV.**

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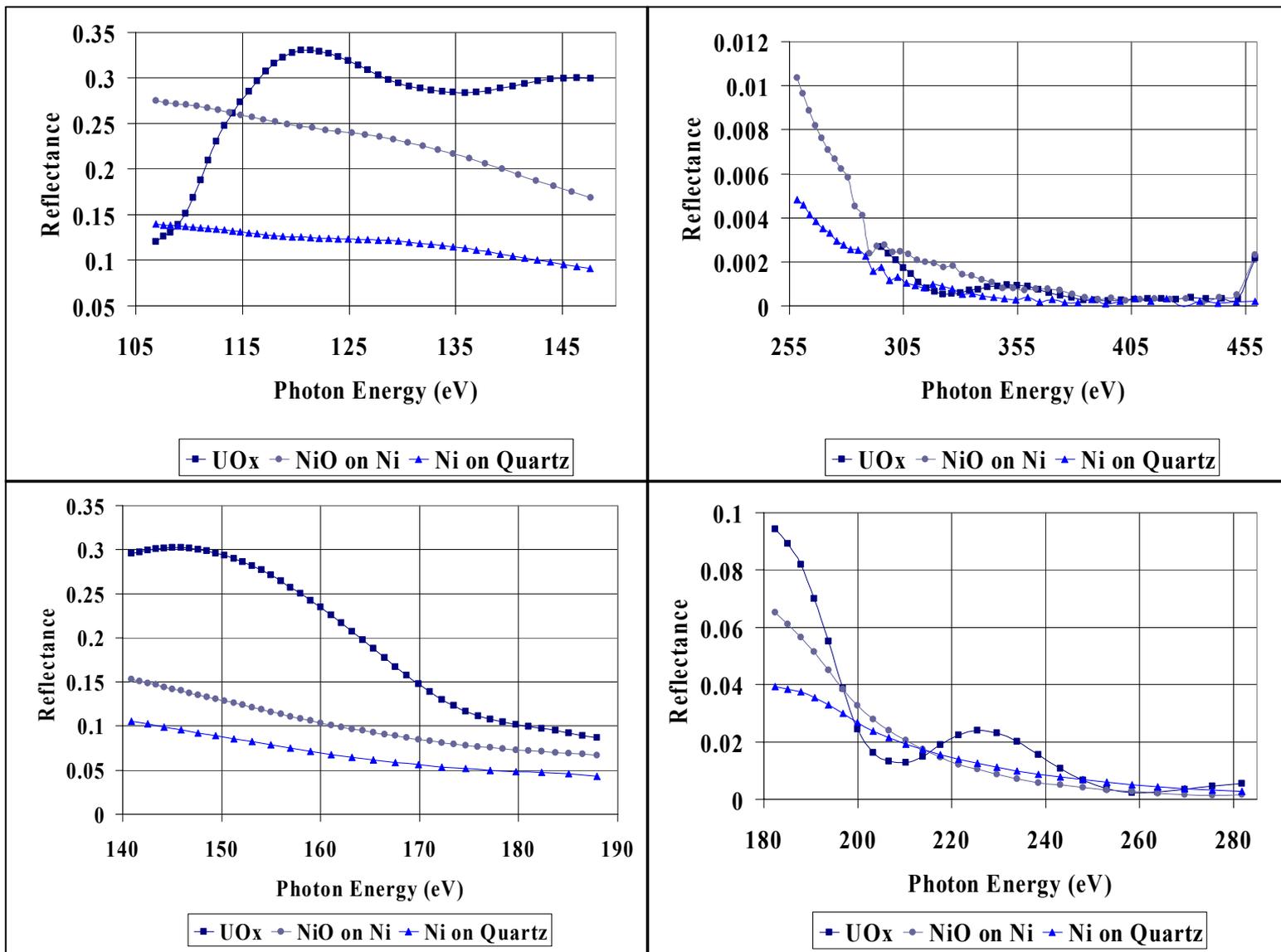**Fig. 6: Reflectance at 10 degrees of UO2, NiO on Ni, Ni on Quartz from 106-460 eV.**

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Fig. 7: Reflectance at 15 degrees of UO2, NiO on Ni, and Ni on Quartz from 106-460 eV.

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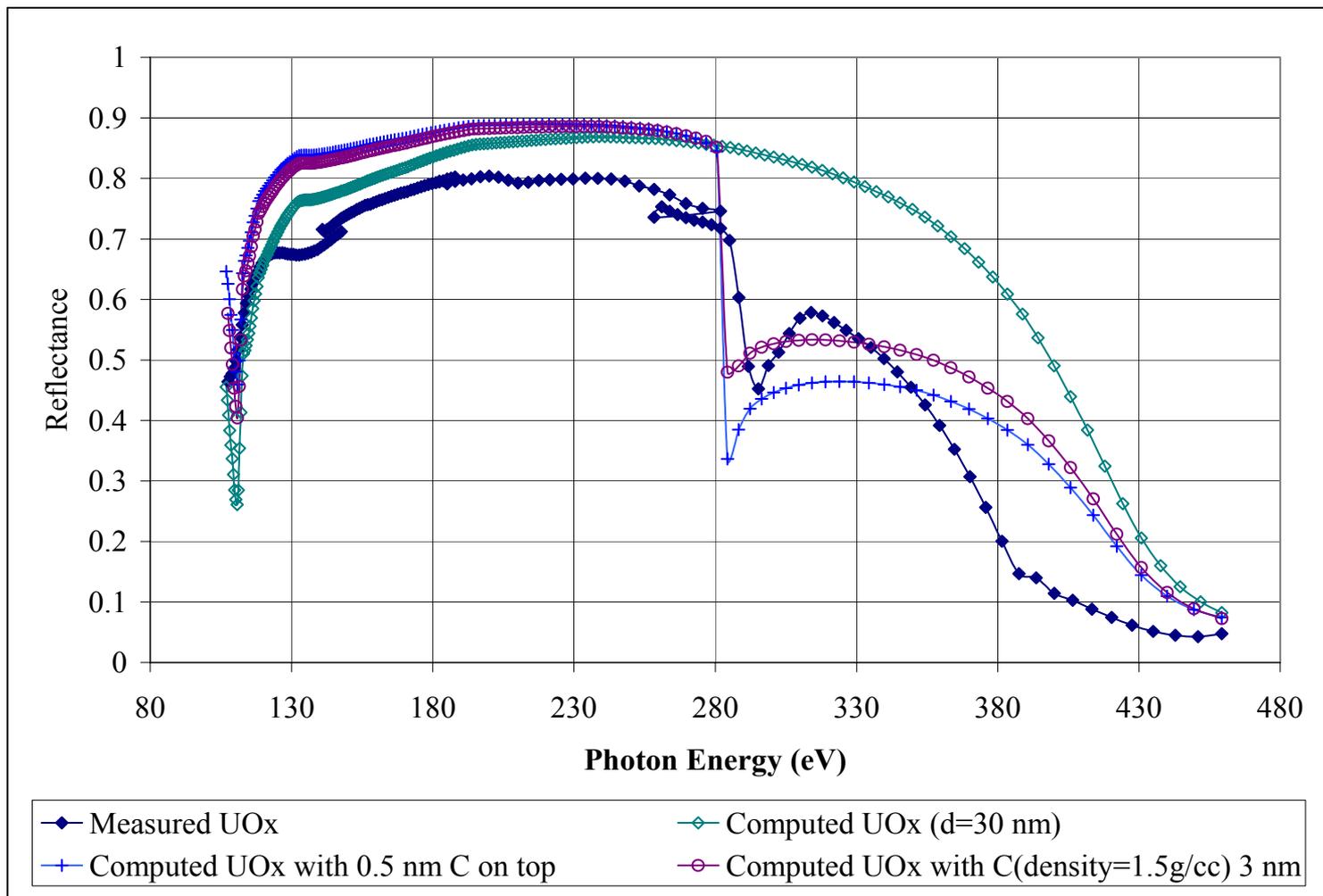# 4. Measured Data Comparison to Atomic Scattering Factor Model

Fig. 8: Reflectances of measured UOx and three structures modeled from the CXRO website. The three structures models are 30 nm of UOx with no carbon contamination on top, 30 nm of UOx with 0. 5 nm of carbon on top, and 30 nm of UOx with 3 nm of carbon contamination on top (density=1.5 g/cc). Notice how the absorption edge predicted by the atomic scattering factor model used in the CXRO models does not appear in the measured data.
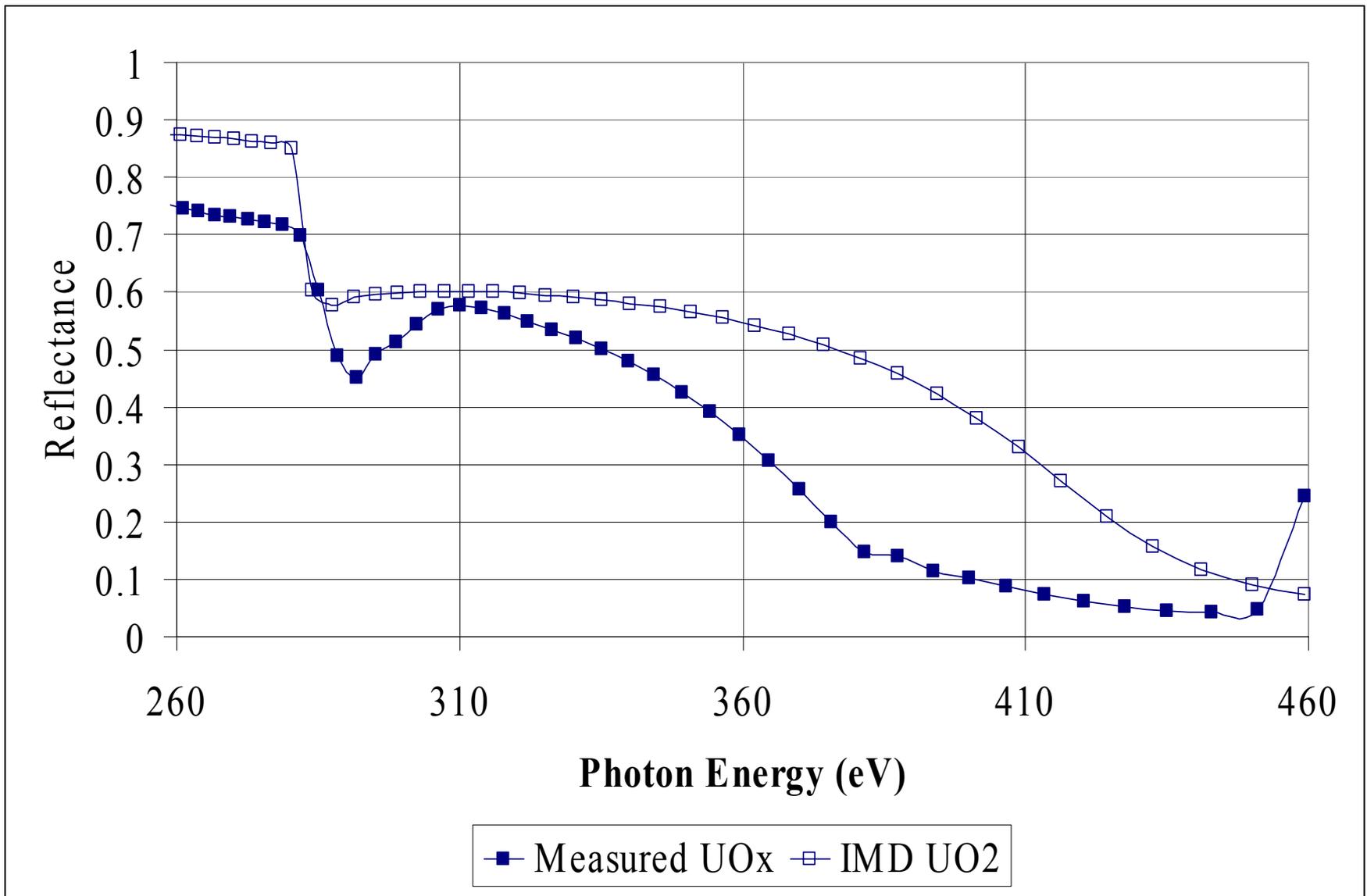
Fig. 9: Measured UOx and IMD computed reflectances (at 5 degrees). The computed structure was modeled as 30.0 nm of UOx on top of silicon with 3.0 nm of carbon contamination on top.
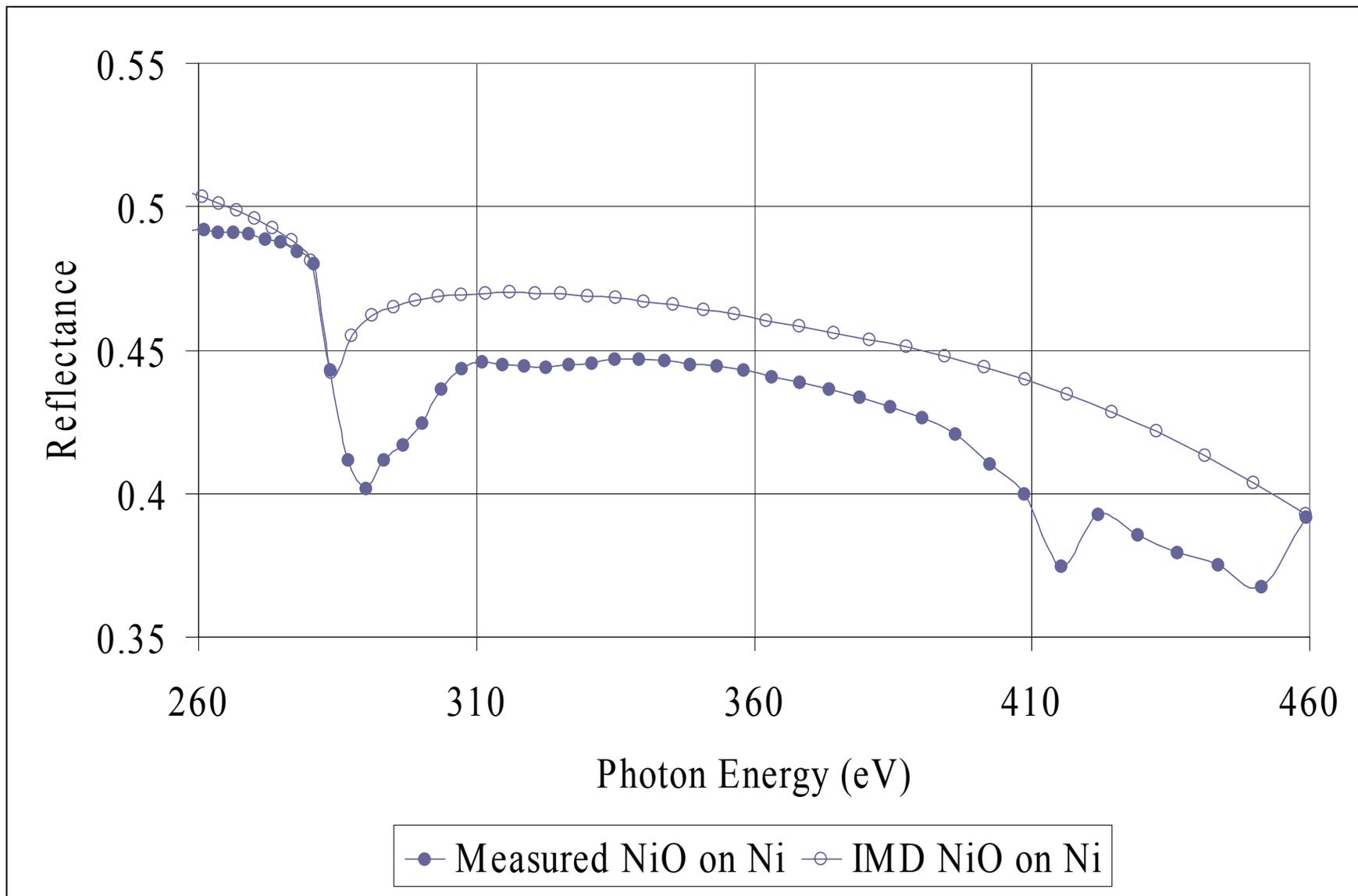
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Fig. 10: Measured NiO on Ni and IMD computed reflectances (at 5 degrees). The computed structure was modeled as 2.0 nm of NiO on top of 47.7 nm of Ni on a silicon substrate with 2.0 nm of surface roughness and 2.0 nm of carbon contamination.
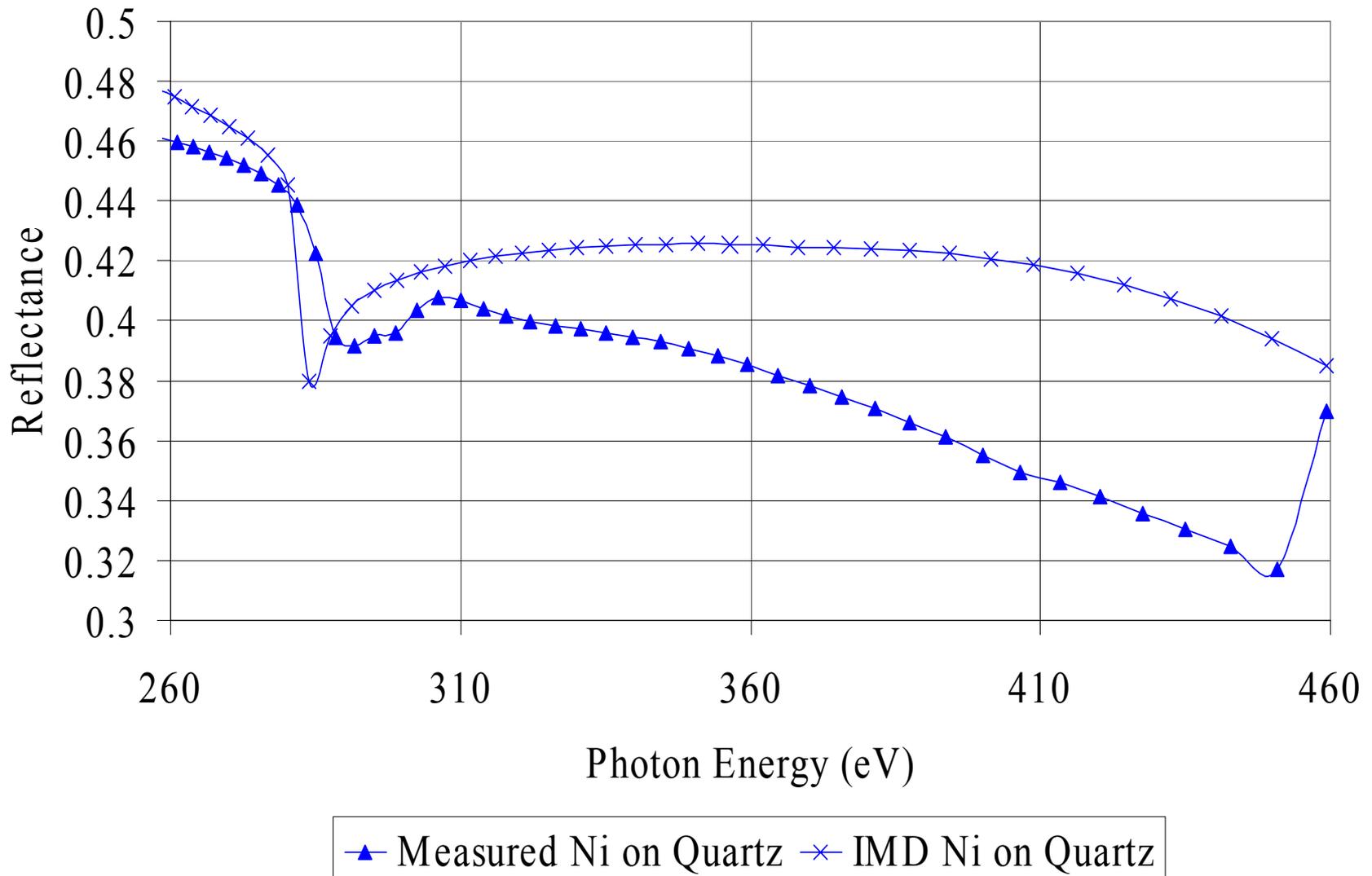
Fig. 11: Measured Ni on quartz and IMD computed reflectance (at 5 degrees). The computed structure was model as 2.0 nm of NiO on top of 47.7 nm of Ni on a quartz substrate with 5.2 nm of surface roughness and 2.0 nm of carbon contamination.

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5. CONCLUSIONS

Naturally oxidized uranium thin film reflectors were found to be more reflective than nickel or nickel oxide on nickel over a large range of angles and wavelengths as predicted by the ASF model. Specifically, uranium reflects more than nickel at 5 degrees grazing incidence from 125-275 eV, at 10 degrees from 118-225 eV, and at 15 degrees from 113-118 eV. We therefore recommend that uranium based mirror coatings should be developed and implemented for future projects where broadband, low angle, soft x-ray mirrors are required. We additionally report that nickel-oxide coatings reflect more than nickel at higher energies (lower wavelengths). (The oxidation rate and oxidation process of nickel are currently being investigated and will be reported in a future article). Another finding of this report is that the complex indices of refraction probably differ noticeably from the reported values from the atomic scattering factor model at the higher wavelengths. We conclude this based upon inability of the ASF model to reproduce the (interference fringe) minimum at about 130 eV in the ASF model and by the fact that the absorption edge is not at 112 eV as reported by the model. We suggest that the absorption or k is less than the ASF model predicts for UO_2. We are in the processes of determining the index of refraction for naturally oxidized uranium over the soft x-ray and EUV range.

ACKNOWLEDGEMENTS

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- b. Matthew B. Squires. The EUV Optical Constants of Sputtered U and a-Si, Honors Thesis, Brigham Young University, Provo, UT, April 1999. http://volta.byu.edu

- The curves for these plots were computed at the CXRO website http://www-cxro.lbl.gov/optical_constants/mirror2.html using the option "thick mirrors", that is, single surface mirrors with zero surface roughness. The refractive indices, which are needed for the calculation, were calculated using the atomic scattering factor model using densities which we supplied the program. We used the CRC Handbook of Chemistry and Physics for densities. That is, there was no effort made to obtain the actual densities of the films.

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- J.H. Underwood *et al*. "Calibration and standards beamline 6.3.2 at the Advanced Light Source." Rev. Sci. Instrum., 67 (9), 1-5 (1996).

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- Program for EUV and X-ray reflectance calculations, courtesy of Prof. David L. Windt: windt@astro.columbia.edu. http://cletus.phys.columbia.edu/windt/idl .