

Characterization of Optical Constants for Uranium from 10 nm to 47 nm

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Abstract

We use a laser-high-harmonics-based extreme ultraviolet polarimeter to determine the optical constants of elemental uranium in the wavelength range 10-47 nm. The constants are extracted from the measured ratio of p-polarized to s-polarized reflectance from a thin uranium film deposited in situ. The film thickness is inferred from a spectroscopic-ellipsometry measurement of the sample after complete oxidation in room air. Uranium has been used as a high-reflectance material in the EUV. However, difficulties with oxidation have prevented its careful characterization previous to this work. We find that measured optical constants for uranium vary significantly from previous estimates.

I. INTRODUCTION

Multilayer mirrors in the extreme ultraviolet (EUV) wavelength range (10-100 nm) are essential optical elements for applications such as lithography, astronomy, and high-resolution microscopy[1–3]. To design mirrors with optimal performance, the optical constants need to be measured for materials in the EUV. Unfortunately, the optical properties of relatively few materials are well-characterized in this wavelength range[4–6]. For instance, we recently found that accepted optical constants for copper metal in the EUV were incorrect due to inadvertent sample oxidation[7]. A lack of experimental characterization is especially common for materials in the actinide series where reactivity, toxicity, and (sometimes) radioactivity adds challenges to performing optical measurements.

Uranium (U) has demonstrated good performance as a multilayer component in the extreme ultraviolet, but the literature contains little measured data for its optical properties in the EUV. Faldt and Nisson [8] measured optical constants of uranium evaporated in-situ in the wavelength range from 50 nm to 2000 nm, which overlaps only the long-wavelength portion of the EUV. They used ellipsometry and normal-incidence reflectometry. On the other hand, Cukier and co-workers[9] measured the photoabsorption of uranium films at the much shorter wavelengths of 2.7 nm to 9.5 nm, where oxidation was prevented using aluminum capping layers. For a large range of wavelengths in the EUV, no data are available for elemental uranium.

Members of our group produced multilayer uranium/silicon mirrors for use on the IMAGE satellite launched in 2000,[1] which required high reflectance at 30.4 nm but low reflectance at 58.4 nm. These multilayers were designed using theoretical values for the optical constants of uranium at the design wavelengths[10–13]. However, the fabricated mirrors reflected differently than predicted, which raises questions about the accuracy of these theoretical values.

In this paper we present the measured optical constants of uranium in the range from 10 nm to 47 nm characterized using the high-harmonics-based polarimeter described in Ref. [14] and the polarization-ratio reflectance measurement technique described in Ref. [15]. To our knowledge, this is the first time the optical constants of elemental uranium have been measured in this wavelength range. We find that the measured constants differ significantly from theoretical values[10–13] referenced on the Center for X-ray Optics (CXRO)

website[16]. The revised constants would have significantly aided in the design of the IMAGE mirror[1] and resolve discrepancies in the previous work between multilayer designs and the measured reflectance data [17].

II. DEPOSITION OF URANIUM AND MEASUREMENTS

We made our measurements using an EUV polarimeter instrument based on laser-generated high harmonics. This instrument, which is described in Ref. [14], uses 800 nm, 10 mJ, 35 fs, 10 Hz laser pulses focused into a noble gas to produce polarized and directional high-harmonic light in the EUV wavelength range. Many harmonic frequencies (with wavelengths distributed throughout the EUV) simultaneously emerge from the focus in a collimated beam embedded in the residual laser beam.

We adapted the polarimeter instrument to accommodate evaporation equipment for in situ deposition of thin films on a substrate, as shown in Fig. 1. We used silicon substrates that were naturally oxidized, with SiO₂ layers between 1 nm and 3 nm (measured with spectroscopic ellipsometry). At the beginning of a measurement, we placed a substrate in the sample holder and cleaned it with a xenon excimer lamp (Resonance LTD) to minimize hydrocarbon contamination. The system was then pumped to a pressure of 10⁻⁴ torr with the reflectance chamber and deposition area open to each other. The substrate was then rotated until it pressed against an o-ring attached to a flexible bellows, creating a seal that temporarily isolated the deposition chamber from the reflectance chamber. The deposition chamber was evacuated further to a pressure of 10⁻⁵ torr.

We prepared the sample by evaporating depleted uranium of purity >99.7% horizontally onto the substrates at a distance of 35 cm using a tungsten basket (R.D. Mathis, B12B-3X.025W16). A shutter covered the substrate during the early phase of evaporation. After about 30 s of evaporation, pressure in the deposition chamber dropped rapidly as the uranium removed molecules in the deposition region, effectively becoming a pump. After the pressure dropped below 10⁻⁶ torr the shutter was opened for 10 seconds. This time frame allowed a deposition of about 2-3 nm of uranium metal (approximately 0.2 nm/s). The sample was deliberately made thin to allow a more accurate determination of optical constants (see [15]).

The sample was rotated back into the measurement chamber within minutes of deposition and without breaking vacuum, and then polarization-ratio reflectance measurements were

performed on samples (at room temperature) using the technique described in [15]. After the measurements, the uranium samples were exposed to atmosphere and the thickness of the oxidized sample was measured with spectroscopic ellipsometry.

We found that our thin films of uranium oxidized completely in less than the time required to vent the chamber and make an ellipsometry measurement (~ 5 minutes). This result was unexpected because oxidation rates previously reported on bulk samples suggest a slower room-temperature oxidation rate, about 0.37 nm/hour[18, 19]. This rate suggests that we should have been able to see the oxide thickness growing, something we recently observed for copper[7]. Atomic force microscope (AFM) measurements showed our uranium films to have less than 1 nm RMS roughness on a $1\ \mu\text{m}\times 1\ \mu\text{m}$ scale. We thus hypothesize that (1) very thin films of uranium may oxidize initially more quickly than bulk or thicker films, or (2) our samples may have microchisms or voids not visible with the AFM that allow it to oxidize more quickly than a bulk sample.

The film thickness for the completely oxidized uranium was characterized with an accuracy of ± 0.3 nm, which was the variation of the thickness across about 2 cm of the sample. The thickness of the unoxidized uranium layer was determined indirectly from the ellipsometric measurement of the oxide layer thickness using the ratio of the densities of the metal and the oxide (densities for bulk uranium and UO_2 were assumed, $19.1\ \text{g}/\text{cm}^3$ and $10.96\ \text{g}/\text{cm}^3$ respectively). We estimate a thickness accuracy of approximately ± 0.7 nm, due to uncertainty in the density and/or composition of the oxide along with variation across the sample.

To measure the optical constants over a wide range of wavelengths, we made measurements using two diffraction gratings in our system. Changing the grating required us to break vacuum, so the data reported in the next section comes from two separate deposition runs. For the short wavelengths, the film thickness was 2.7 nm while for the long wavelengths the thickness was 3.2 nm.

III. RATIO REFLECTANCE DATA AND OPTICAL CONSTANTS FOR URANIUM

Figure 2 shows the ratio reflectance and fit for the uranium film at representative wavelengths of 18.6 nm and 34.8 nm. Each point represents an average of 400 laser shots at

an effective repetition rate of about 3 Hz (because of laser energy discrimination of $\pm 10\%$ described in [14]). The lines show best-fit curves calculated from the model described in [15] with n and κ for the test layer taken as free parameters in a least-squares fitting algorithm (Matlab `nlinfit`). The film thickness was held fixed in the fits, at the value calculated from the measured thickness of the oxidized layer (as described above). The optical constants for the silicon dioxide layer and silicon substrate were also held fixed.

The uncertainties in film thickness affect the uncertainties for the optical constants. As mentioned previously, the uncertainty in the uranium film thickness was ± 0.7 nm. Figure 3 shows how this uncertainty influences the values of optical constants. The solid line in this plot shows the obtained constants of uranium determined using our best estimate for film thickness. The dashed lines show the extent of the change in the optical-constant curve when the thickness was changed by ± 0.7 nm.

To estimate our total measurement error we added in quadrature the statistical error due to the fit (95% confidence intervals for n or κ from the nonlinear regression analysis) and the error due to uncertainty in the film thickness. At an example wavelength of $\lambda = 13.1$ nm (harmonic order $q = 61$) our uncertainty of ± 1 nm in film thickness yielded an uncertainty in n of ± 0.021 and an uncertainty in κ of ± 0.017 . The optical constants for uranium and these error bars are shown in Fig. 4. The optical constants are also presented in tabular form in Table I. To test for repeatability, the optical constants of uranium were re-measured completely on a second day with film thicknesses of 2.3 nm and 2.9 nm. The data sets agree well within our error bars.

IV. COMPARISON WITH PREVIOUS MEASUREMENTS AND ESTIMATES

To our knowledge, this data represents the first measurements of the optical constants of uranium in much of the EUV wavelength range. Figure 5 plots our measured optical constants compared with those reported by other sources. Faldt and Nisson[8] measured the optical constants of evaporated uranium in-situ from 50 to 2000 nm. This data is consistent with the extension of our data to longer wavelengths. Cukier et al.[9] measured the photoabsorption cross section of uranium from 2.7-9.5 nm, preventing oxidation using an aluminum capping layer, and again the data is consistent with our data extended to shorter wavelengths.

Figure 5 also shows the theoretical optical constants for uranium estimated by Henke et al. and cited on the CXRO website[10, 16]. These constants are based on theoretical calculations of the photoabsorption cross section of uranium[11–13]. Previous to our work, these calculations were the only optical constants for uranium available in this region. Henke and coworkers note that these calculations are only applicable far from absorption thresholds and at wavelengths shorter than 24 nm[10]. Much of our data is taken at wavelengths longer than 24 nm, and wavelengths shorter than 24 nm are near an absorption edge (~ 11 nm). Therefore, we do not expect these calculations to match the data very well. However, they do confirm the general trend of our data. Notably, the absorption peaks in our measured data are shifted about 0.5 nm to longer wavelengths (lower energy) compared to those based on theoretical calculations. A similar resonance shift was also recently noticed in the measured constants of thorium and thorium dioxide[20, 21].

V. CONCLUSIONS

We have used our high harmonics-based polarimeter to measure the optical constants of uranium in the range from 10 nm to 47 nm. This is the first time the constants have been measured for elemental uranium in this wavelength region. We find that measured values differ from theoretical estimates in this range. Our measured optical constants for uranium are consistent with the reflectance performance of a multilayer mirror coating created for the IMAGE satellite (see Fig. 6), whereas the previous theoretical estimates are not. This updated knowledge of the optical properties of uranium potentially may allow multilayers involving uranium to be designed with improved performance.

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wavelength	n	κ
53.3	0.830 ± 0.035	0.254 ± 0.025
47.1	0.780 ± 0.032	0.215 ± 0.025
42.1	0.780 ± 0.032	0.187 ± 0.025
38.1	0.788 ± 0.032	0.143 ± 0.027
34.8	0.789 ± 0.033	0.118 ± 0.024
32.0	0.800 ± 0.032	0.092 ± 0.025
29.6	0.828 ± 0.032	0.068 ± 0.024
27.6	0.849 ± 0.032	0.045 ± 0.027
25.8	0.861 ± 0.033	0.053 ± 0.035
24.2	0.868 ± 0.030	0.054 ± 0.030
22.9	0.880 ± 0.036	0.032 ± 0.030
21.6	0.900 ± 0.029	0.040 ± 0.027
21.6	0.891 ± 0.021	0.037 ± 0.028
20.5	0.911 ± 0.043	0.036 ± 0.023
20.5	0.908 ± 0.023	0.034 ± 0.024
19.5	0.912 ± 0.023	0.031 ± 0.021
18.6	0.919 ± 0.021	0.031 ± 0.022
17.8	0.931 ± 0.023	0.027 ± 0.024
17.0	0.934 ± 0.024	0.045 ± 0.019
16.3	0.941 ± 0.025	0.045 ± 0.020
16.3	0.937 ± 0.024	0.039 ± 0.019
15.7	0.950 ± 0.031	0.029 ± 0.021
15.7	0.944 ± 0.030	0.033 ± 0.020
15.1	0.935 ± 0.046	0.053 ± 0.021
14.5	1.008 ± 0.091	0.050 ± 0.039
14.0	1.104 ± 0.081	0.067 ± 0.036
13.6	1.166 ± 0.043	0.168 ± 0.039
13.1	1.171 ± 0.029	0.146 ± 0.016
12.7	1.130 ± 0.036	0.091 ± 0.027
12.3	1.064 ± 0.087	0.051 ± 0.028
11.9	1.216 ± 0.035	0.198 ± 0.027
11.6	1.242 ± 0.029	0.217 ± 0.019
11.3	1.236 ± 0.027	0.232 ± 0.019
11.0	1.196 ± 0.028	0.217 ± 0.015
10.7	1.107 ± 0.032	0.152 ± 0.018
10.4	1.025 ± 0.040	0.098 ± 0.019
10.1	0.961 ± 0.036	0.058 ± 0.019

TABLE I: Optical constants of uranium.

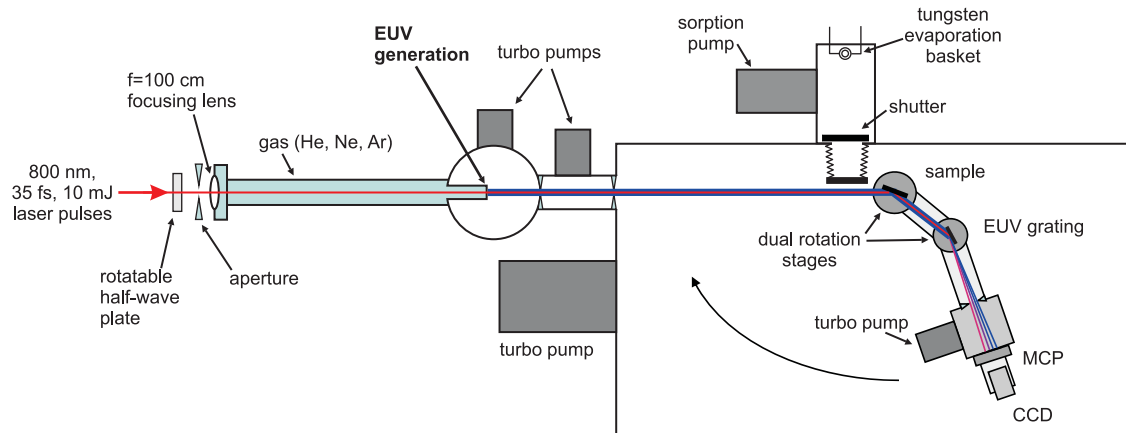


FIG. 1: Polarimeter schematic (top view). 800 nm, 35 fs, and 10 mJ laser pulses are focused into a gas cell to generate harmonics. Thin films are deposited and polarized reflectance measurements are made in-situ.

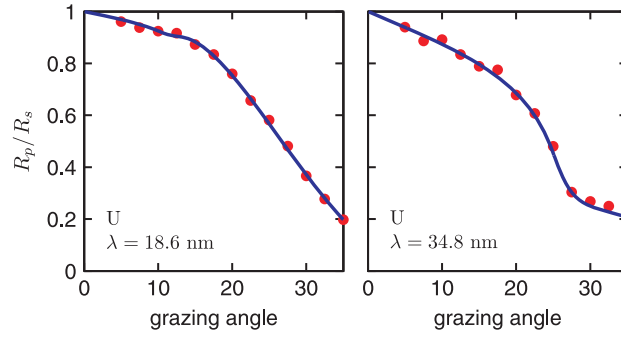


FIG. 2: The measured ratio of p-polarized to s-polarized reflectance and fit of uranium at two representative wavelengths: 18.6 nm and 34.8 nm.

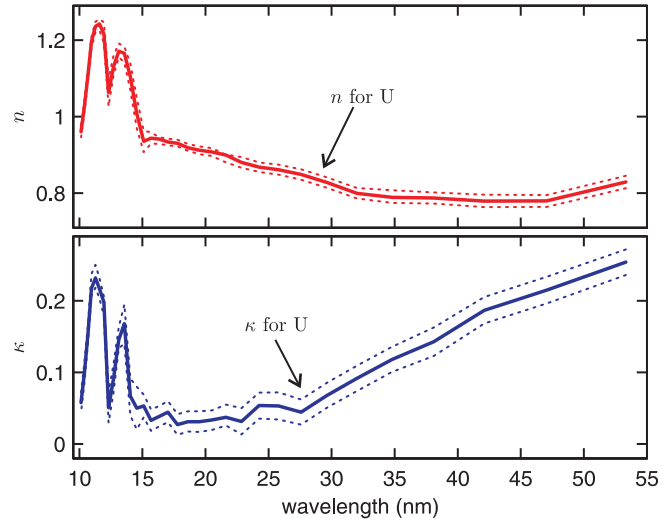


FIG. 3: Solid curves show the measured optical constants of uranium. Dashed curves show the extent of the change when errors due to uncertainty in thickness are included.

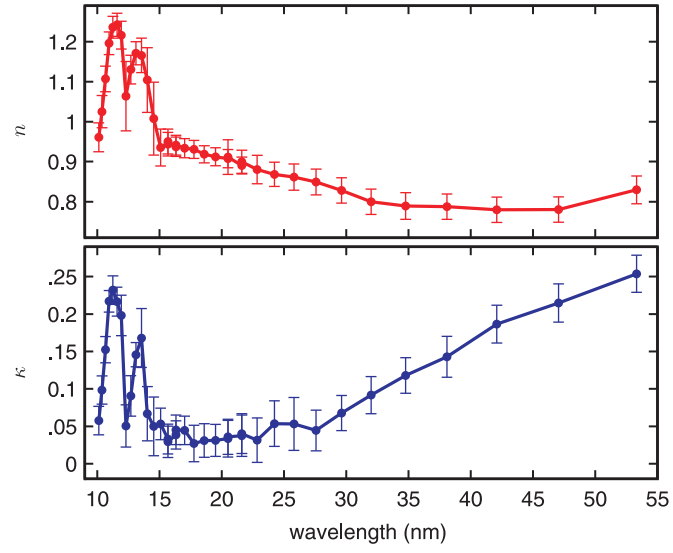


FIG. 4: The optical constants of uranium determined using the ratio reflectance technique. Total error bars are also shown.

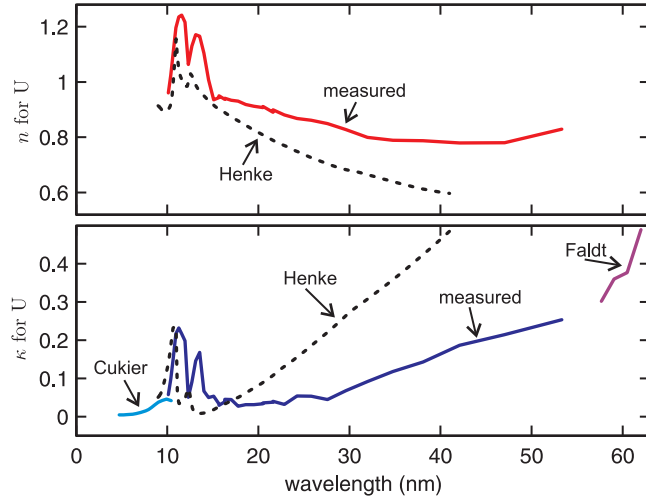


FIG. 5: Measured optical constants of uranium compared with constants for uranium measured by Faldt[8] and Cukier[9]. Also shown are optical constants for uranium determined by Henke[10] which are based on theoretical calculations[11–13].

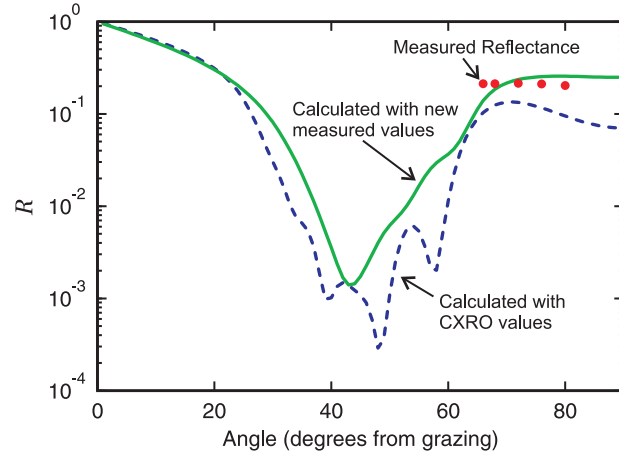


FIG. 6: The measured reflectance (dots) for the IMAGE mirror (described in Ref. [1]) compared with the theoretical reflectance computed with our measured optical constants for U (solid) and computed with the theoretical CXRO constants (dashed) at a wavelength of 30.4 nm. Both computed models use the CXRO data for silicon and assume perfectly sharp boundaries between the layers.