Measurements of the Optical Constants of Scandium in the 50-1300eV Range

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ABSTRACT

Scandium containing multilayers have been produced with very high reflectivity in the soft x-ray spectrum. Accurate optical constants are required in order to model the multilayer reflectivity. Since there are relatively few measurements of the optical constants of Scandium in the soft x-ray region we have performed measurements over the energy range of 50-1,300 eV. Thin films of Scandium were deposited by ion-assisted magnetron sputtering at Linköping University and DC Magnetron sputtering at CXRO. Transmission measurements were performed at the Advanced Light Source beamline 6.3.2. The absorption coefficient was deduced from the measurements and the dispersive part of the index of refraction was obtained using the Kramers-Kronig relation. The measured optical constants are used to model the near-normal incidence reflectivity of Cr/Sc multilayers near the Sc $L_{2,3}$ edge.

Keywords: Index of refraction, EUV, soft x-ray, Sc

1. INTRODUCTION

Scandium is an important optical material in the extreme ultraviolet (EUV) and soft x-ray bands of the spectrum. In the EUV range of 25-35 eV, Sc/Si multilayers have been fabricated with a near-normal incidence reflectivity above 50%. In the soft x-ray region near 400 eV, the highest near-normal incidence reflectivity has been achieved¹ with Cr/Sc multilayer mirrors just below the Sc $L_{2,3}$ edges (403.6 eV, 398.7 eV). This energy is in the important “water window” between the Carbon K edge (248.2 eV) and the Oxygen K edge (543.1 eV) where proteins are absorbent and the watery cytoplasm is transparent.

Modeling the properties of multilayer mirrors requires an accurate knowledge of the material optical constants. In the case of Scandium there have been very few measurements in the soft x-ray region. The available tabulated data² for Scandium published by Henke *et al.* in 1993 are based on theoretical calculations and interpolation from measurements on neighboring elements. These tables also do not include the fine structure near absorption edges. A comprehensive study of Scandium in the EUV and soft x-ray region would allow for better modeling of scandium multilayers.

This research tabulates the optical constants δ and β for Scandium using freestanding thin film Scandium samples sandwiched between Silicon capping layers. Sample deposition and preparation is described in experiment subsection of this paper. The optical constant β is determined from the absorption measurements of freestanding Scandium films. The measurements were carried out in a photon energy range of 50 eV to 1,300 eV using the Advanced Light Sources beamline 6.3.2 as described in the experimental section of this paper. From β the Kramers-Kronig analysis was performed to determine the real part of the index of refraction, $1-\delta$. Finally the determined optical constants are used to model the measured reflectance from a Cr/Sc multilayer at energies which span the Sc L edge.

2. EXPERIMENT

1. Sample Preparation

The samples used in this experiment were Scandium films with thickness ranging from 50 nm to 500 nm. The first samples were deposited at Linköping University on silicon nitride membranes. From the results of those measurements it was decided to fabricate freestanding films because of the close proximity of the N K edge (409.9 eV) to the Scandium Sc L_{2,3} edge (403.6 eV, 398.7 eV). The freestanding films were fabricated by depositing a trilayer of Si/Sc/Si on photoresist-coated wafers. After gluing a frame to the film the photoresist was dissolved by soaking in acetone. The freestanding films were made in Berkeley by DC Magnetron sputtering in a system with a base pressure of 10⁻⁷ Torr. The first samples fabricated in this way disintegrated in the acetone due to the high stress of the films. In order to minimize the stress, the Argon pressure was varied in the range of 2.3 to 4.5 mTorr depending on the thickness. An oxidation barrier of 5nm of Silicon was deposited immediately before and after the Sc with out breaking vacuum. Pieces of the silicon wafers that were not used for filters were used in Rutherford Back Scattering (RBS) measurements and in soft x-ray reflectance measurements to determine the thickness of the Sc layer, and contaminants in the film. The film thickness was determined to be: 49 nm, 100 nm, and 192 nm to an accuracy of 5% using soft x-ray reflectivity versus angle. However the 486 nm sample was too thick for this method and RBS measurements were used to determine its thickness. The results of the RBS measurement showed that scandium samples were 99.9% pure Scandium which was consistent with the target manufacturers purity specification. There were no detectable amounts of Argon or Oxygen in the samples within the limits of <1.5% and < 1.0% respectively.

2. Instrumentation

The transmission measurements were performed using the Calibrations and Standards beamline³ at the Advanced Light Source, beamline 6.3.2. This is one of the synchrotron's bending magnet beamlines, which operates in the range of 50 eV to 1,300 eV with a resolving power up to 7000. The high spectral purity of this beamline was essential to making the accurate transmission measurements required in this work. Second order and stray light is suppressed using various filters and at low energies (<600 eV) higher order light (third and fourth orders) is suppressed using a grazing incident triple reflection order suppressor. The end result is a beam with a spectral purity greater than 99%. The photon energy near the Sc L edge was calibrated using the absorption spectrum of nitrogen gas¹ and in this range is accurate to 0.02 eV.

3. RESULTS

Transmission measurements of the four Si/Sc/Si films were performed from 50 eV to 1,300 eV with a variable spacing of points depending on absorption features of the samples. For example around 400 eV near the Scandium edge a spacing of .2 eV was used while at 1,200 eV a spacing of 5 eV was used. Extra care for absolute accuracy and high resolution was given to measurements near the Scandium edge to resolve the fine structure. Measurement reproducibility was .1% for measurements greater than 2% transmission. The transmission measurements were obtained by the expression:

$$T = ((I - D)/R) / ((I_0 - D_0)/R_0)$$

Where I is the photodiode current (proportional to the transmission through the film), D is the average value of the dark current (the current noise when no light is in the chamber), and R is the ring current. We double normalize using ring current because of its proportional decay with the number of photons. The I₀, D₀, R₀ are the same as the incident (transmission) data except that the transmission measurement is taken when an empty filter holder. D and D₀ may be different values depending on the amplification gain needed for I and I₀.

Once the transmission measurements were obtained the absorption coefficient μ in units of [cm²/g] was obtained through the equation:

$$T = T_0 \exp(-\mu \rho x)$$

Figure 1. The transmission versus energy of four Si/Sc/Si films with Sc thickness of 49, 100, 193, and 486 nm. The structure is due to the L-absorption edges of Silicon (100 eV) and Sc (400 eV) and the K edge of carbon at 284 eV.

Figure 2. The transmission near the Scandium $L_{2,3}$ edge. The two dips in reflectivity represent the two edges. Also note that on the thick 486nm sample the two edges are washed out due to the background of scattered light.

Figure 3. Fitting of μ versus thickness at photon energies of 150, 600, and 900 eV. The dashed lines are fits where the slope is $-\mu\rho$.

Where x is the thickness [cm] and ρ is the density of Sc. We assumed the films had the bulk density of 2.99g/cm^3 . This was checked by comparing the thickness obtained by x-ray reflectivity and RBS for the 100 nm film. Plotting $\ln(T)$ versus sample thickness for each photon energy gives a linear relationship where the slope is $-\mu\rho$ and the intercept is T_0 . Examples of determining μ at three different energies are shown in figure 3. The linear fits of the data were very good and yielded standard deviations around 0.005. When the transmission fell below 1% the measurement was not used in the linear fit analysis due to the significant influence of scattered and higher order light.

T_0 is the extrapolation to zero film thickness and ideally this would be unity. However T_0 is less than one because of the silicon capping layer and oxide and the residual photoresist. Plotting T_0 versus photon energy thus provides an indication of the contamination of the samples (figure 4). It also assumes that the thickness of the capping layer and photoresist are the same for all samples. Because of the method of deposition of the thin foil this assumption is justified. The fit of the contamination of the samples yields 20nm of residual photoresist and the 10nm of Si/SiO₂ capping layer. There is some distortion around the Scandium L edge caused by slight errors in sample thickness. Small discontinuities occurred when the transmission of a sample dropped below 1% and the data was no longer used. These discontinuities were more apparent in the T_0 than in μ .

Figure 4. The transmission extrapolated to zero Sc thickness, T_0 as a function of photon energy. Please note the Silicon $L_{2,3}$ edge (100 eV), the carbon K edge (284eV) and the oxygen K edge (543eV). The lack of an Argon $L_{2,3}$ edge (250eV, 248eV) is consistent with RBS measurements. The fit to the calculated data is composed of 20nm photoresist, 7nm Si, and 3nm SiO₂.

Looking at μ as a function of photon energy (figure 5) there are some striking differences from the previous tabulated measurements. There is a large absorption peak near the edge that is a factor of 4 larger than the tabulated data from the CXRO webpage⁵. The strong absorption near edge structure is explained by the fact that Scandium has an almost empty 3d band and thus a large density of empty d states for L edge transitions from the 2p shell.

Figure 5. This measured absorption coefficient (points) compared with the tabulated values of scandium absorption from reference 2. Notice the strong near edge effect at the Scandium L edge that was not incorporated in the tabulated values.

From μ it is straightforward to calculate the complex part of the index of refraction, β where $n = 1 - \delta + i\beta$ by the formula:

$$\beta = \lambda\mu/4\pi$$

The real part was calculated using Kramers-Kronig analysis:

$$\delta = (2/\pi) \int_0^{\infty} \frac{E' \beta(E')}{E^2 - E'^2} dE'$$

To perform the above integral, the absorption spectrum, β , of Scandium was needed over a wide range of energy. The values calculated in this work were combined with the tables from the CXRO web page at energies above 1,300 eV and the measurements of Uspenski *et. al*⁶ below 50 eV and the values given by Weaver⁷ for energies from 0.1 eV to 5 eV. As a self-consistency check of the data the sum rule was calculated by integrating μ as described in previous works⁸. The integral gave a value of 20.35 which is only 3% lower than the atomic number of Sc, $Z=21$.

The derived optical constants are compared the tabulated values in Fig. 6. The values of both β and δ are in good agreement with recent measurements by Uspenski *et. al*. The optical constants in the region near the Sc L edge are

shown in Fig. 7. The strong absorption peak in β causes δ to go more negative for energies just below the edge. This would tend to increase the theoretical reflectance of Sc containing multilayer mirrors in this region.

Figure 6. This graph shows the optical constants for δ and β over the entire EUV and soft X-ray range. Notice the good agreement with the results of Uspenskii *et. al.* for lower photon energies.

Figure 7. The optical constants near the Scandium $L_{2,3}$ edge. Notice the drop in δ is lower than in the tabulated values which increases the theoretical reflectivity of Sc containing multilayer mirrors in this region.

Figure 8. The reflectivity modeled with the old and new optical constants for a Cr/Sc mirror are compared with measurements. The mirror parameters were $d=1.6205$ nm, $\Gamma = .66$ and $N = 300$ bilayers. Note the improved agreement with the new optical constants especially near the edge. The highest reflectivity occurs at 398 eV just below the Sc L_3 edge.

Figure 9. Reflectivity of the Cr/Sc multilayer at 72 degrees where the Bragg peak occurs above the Sc L edge. The model using the new optical constants better fits the side peak near 400 eV.

Using the new index of refraction for Scandium a comparison to a Cr/Sc multilayer was performed. The d spacing of the multilayer was calculated using Cu K α reflectometry. Gamma and the number of periods were obtained during the deposition of the mirror allowing us to model reflectivity using roughness as the only parameter. The multilayer was then scanned from 390 to 410 eV (across the scandium edge) where its reflectivity would be the highest. Wavelength scans were performed at .1 degrees of sample angle rotation. Thus the peak reflectivity should follow the Bragg law of $\lambda=2d \sin(\theta)$, where θ is the grazing angle of incidence. The highest reflectivity was observed at 398 eV, just below the Sc L₃ edge. The old optical constants as well as the new optical constants were used to model the measured reflectivity curves. Both models used the same parameters (d and Γ) while the roughness was fitted for each using the 78° data. Then the reflectivity was calculated at other angles up to and beyond the scandium edge (see graphs figures 8 and 9). Notice how well the model using the new optical constants tracks the data compared to previous constants. Even above the scandium edge the new model predicts the large tail of the data that is not predicted using the tabulated optical constants.

4. CONCLUSION

Precise measurements of the index of refraction of Scandium in the range of 50 eV to 1,300 eV are presented in this research. The experiment measured the absorption of Scandium and from these measurements allowed for the calculation of the optical constants. The results revealed a strong absorption structure around the Scandium L_{2,3} edge, that was not included in previous tabulations of Scandium absorption. The reflectivity modeled with the new optical constants was in good agreement with measurements on a Cr/Sc multilayer mirror. The new optical constants will be available on the CXRO website at: http://www.cxro.lbl.gov/optical_constants/

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