Measurements of the refractive index of yttrium in the 50–1300-eV energy region

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The first experimental results to our knowledge on the refractive index $n = 1 - \delta + ij\beta$ of yttrium in the extreme-ultraviolet and soft x-ray energy ranges are discussed. To determine the absorptive part $\delta$, transmittance measurements were performed on pure yttrium films in the 50–1300-eV energy region at beamline 6.3.2 of the Advanced Light Source. The dispersive part $\beta$ was then calculated from the absorption results by means of the Kramers–Kronig transformation. Compared with prior tabulated values, the new set of data for the refractive index of yttrium is in better agreement with the sum rules and contains previously unresolved fine structure information in the regions of the $M_{4,3}$ and $M_{4,5}$ absorption edges, where yttrium-based multilayer mirrors operate. © 2002 Optical Society of America

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1. Introduction

There has been interest in the development of extreme-ultraviolet (EUV) instrumentation with multilayer coatings for a number of applications such as microscopy, spectroscopy, EUV lithography, and astronomy. The 8–11-nm wavelength region in particular has become important for astronomy because of the observation of intense emission lines from various cosmic sources, such as the Fe XVIII spectral line observed at 9.392 nm from rotating stars and white dwarf systems during the Extreme Ultraviolet Explorer mission. High-reflectance multilayers would enable recording and high-resolution imaging of weak EUV spectra, hence revealing detailed information about temperature, plasma confinement, and magnetic field of such cosmic objects.

Mo/Y has proven to be one of the most promising material pairs for multilayers operating in the 8–11-nm (155 eV down to 113 eV) region because of its high and relatively stable reflectance. Normal-incidence reflectance of 38.4% at 9.482 nm has been achieved with Mo/Y magnetron-sputtered multilayers (see Table 1). Recently, Mo/Y has been used successfully to coat a diffraction grating, thus enabling normal-incidence multilayer grating spectrometry in the 9-nm wavelength region. A key parameter needed to model and design a reflective multilayer structure is the refractive index of its constituent materials. One of the most comprehensive and up-to-date sources for the refractive index of materials in the EUV and soft x-ray regions is the angle-independent forward atomic scattering factors by the Center for X-ray Optics (CXRO), Lawrence Berkeley National Laboratory (LBNL). These factors have been compiled by use of available experimental and theoretical photoabsorption data for 92 elements in the energy region 10–30,000 eV. Fairly accurate values for the refractive index can be obtained from the forward atomic scattering factors by the independent atom approximation, where each atom within the material is assumed to interact with light in the same way as if the atom were free. However, it has been determined experimentally that the atomiclike approximation for condensed matter is invalid at the energies below approximately 50 eV where absorption is due to valence electrons and in the vicinity of absorption edges where the refractive index is sensitive to the chemical environment and the geometry of atoms within solids. In the case of yttrium, other than an experimental data set for the refractive index of yttrium in the 5–24-nm (248 eV down to 50 eV) region incorporated in the IMD pro-
gram by Windt,8 to our knowledge no experimental results have ever been published in the region above 30 eV. Therefore the values of the atomic scattering factors in Ref. 6 have relied exclusively on theoretical calculations. Moreover, the operating region of Mo/Y multilayers is in the vicinity of the yttrium M4,5 (155.8-eV) absorption edge, where fine features would be expected in the absorption spectrum. Thus it would be useful to experimentally determine the yttrium refractive index in these energy regions to obtain more accurate values that can be applied in the modeling of the performance of yttrium-based x-ray optics.

There are several techniques such as reflectance, transmittance, interferometry, and ellipsometry for determination of the refractive index of materials. Transmittance is one of the most robust and accurate methods if there is a capability to fabricate good quality ultrathin samples to overcome strong absorption in the EUV region. Transmittance has been used successfully in the past to determine the optical constants of several materials in the EUV and soft x-ray ranges9–11 and it was chosen as the preferred method for this study.

In this paper we report on the first experimental results to our knowledge on the absorption of yttrium in the 50–1300-eV energy region. A brief summary on the theory of the refractive index of materials in the EUV and soft x-ray regions is given in Section 2. Sample preparation and transmittance measurements are described in Section 3. The results are discussed in Section 4, followed by the conclusions in Section 5.

## 2. Index of Refraction

In the EUV and soft x-ray regions, where photon energies are in the same order of magnitude as the binding energies of inner atomic electrons of low-Z and intermediate-Z elements (Z is an atomic number), absorption becomes the dominant process when light interacts with matter. Both dispersive and absorptive properties of materials are commonly expressed in terms of the energy-dependent optical constants δ and β of the complex refractive index $\tilde{n} = 1 - \delta + i\beta$. When light passes through matter, its intensity is exponentially attenuated in the following manner:

$$I = I_0 \exp \left( -\frac{4\pi\beta x}{\lambda} \right),$$

where $\lambda$ is the wavelength of radiation; $x$ is the thickness of the material; and $I_0$ and $I$ are the incident and transmitted intensities, respectively. The transmittance $T$ of a material can be expressed as

$$T = \frac{I}{I_0} = \exp \left( -\frac{4\pi\beta x}{\lambda} \right).$$

This relation implies that β can be obtained experimentally from transmittance measurements if the film thickness of the material under study can be accurately determined. The dispersive part δ of the refractive index can be calculated from the Kramers–Kronig relation

$$\delta(E) = \frac{2}{\pi} \int_{0}^{\infty} \frac{E'\beta(E')}{E^2 - E'^2} \, dE',$n where $E = hc/\lambda$ is the photon energy. The integral nature of Eq. (3) requires complete knowledge of β over a semi-infinite energy range to determine δ at a single photon energy $E$. Once the optical constants δ and β versus energy are determined, a set of integral constraints can be applied to evaluate their accuracy. These constraints, known as rules, arise because the causality and dynamic laws of motion governing the temporal response of matter to an applied electromagnetic field12,13 are transferred to frequency space. Partial sum rules can be written in terms of the effective number of electrons $N_{\text{eff},A_k}$ in the atom contributing to the absorption and dispersion up to energy $E$ as

$$N_{\text{eff},A_k}(E) = Z^a - \frac{2m\varepsilon_0}{\pi^2 n_a^2 \varepsilon_{\text{eff}}^2 \hbar^2} \int_{E}^{\infty} E' A_k(E') \, dE',$n where $k = 1, 2, 3$, and optical data $A_k$ are represented in one of the following forms: $A_1 = \varepsilon_2, A_2 = 2\beta$, and $A_3 = \text{Im}(e^{-\gamma})$. $n_a$ is the atomic density of material, $\varepsilon(E) = \hbar^2 = \varepsilon_{\text{eff}}(E) + i\varepsilon\gamma(E)$ is the complex dielectric function of the material, and $Z^a = Z - (Z/82.5)^3.37$ is the atomic number reduced by a relativistic correction.6 In this theoretical framework the model of Lorentzian oscillators is used to describe the electrons bound to the atom, where each electron has a characteristic resonant energy and acts as a dipole radiator at all energies. The term oscillator strength is thus used to describe the quantity inside the integral of Eq. (4). The partial sum rules of Eq. (4) are valid only in the case of nonoverlapping energy bands, i.e., when the absorptive and dispersive processes occurring up to energy $E$ are sufficiently isolated from processes taking place in all other spectral regions. If an accurate and self-

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### Table 1. Measured Reflectance of Multilayers Operating at Normal Incidence in the 8–11-nm Wavelength Region

<table>
<thead>
<tr>
<th>Multilayer</th>
<th>Reflectance (%)</th>
<th>Wavelength (nm)</th>
<th>Incidence Angle (degrees from normal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Sr&lt;sup&gt;6&lt;/sup&gt;</td>
<td>48.3 (unstable)</td>
<td>10.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Mo/Y&lt;sup&gt;6&lt;/sup&gt;</td>
<td>35.4</td>
<td>9.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Pd/C</td>
<td>27.0</td>
<td>10.6</td>
<td>5.0</td>
</tr>
<tr>
<td>Ru/C</td>
<td>19.0</td>
<td>10.6</td>
<td>5.0</td>
</tr>
<tr>
<td>Co/C</td>
<td>12.5</td>
<td>10.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Pd/BaC</td>
<td>12.0</td>
<td>8.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

<sup>6</sup>Ref. 2.
<sup>7</sup>Although Mo/Sr exhibits the highest reflectance, it degrades completely within a day of exposure in air.3
<sup>8</sup>Mo/Y is the next best candidate, exhibiting high reflectance and excellent time stability.4
consistent set of optical data $A_k$ is used to compute the oscillator strength, all three versions of Eq. (4) result in $N_{\text{eff},A_k}(E = 0) = 0$. A nonzero result for $N_{\text{eff},A_k}(E = 0)$, i.e., missing or excess oscillator strength, would indicate that there are flaws in the optical data set in some region of the spectrum. By plotting $N_{\text{eff},A_k}$ versus energy and noting the energy levels where characteristic absorptions occur, it may be possible for one to identify the specific spectral regions where deficiencies exist in the optical values. Thus, for any given material, the sum rules are useful as guidelines for the evaluation of data subsets and the construction of composite data sets covering the entire spectrum. In Subsection 4.B, the sum rules of Eq. (4) are used to test a new set of optical data for yttrium.

3. Experiment

A. Sample Preparation

We fabricated yttrium films using an ultrahigh vacuum dc magnetron-sputtering deposition system. A detailed description of this system has been given in a previous paper. The base pressure in the deposition chamber was $2 \times 10^{-9}$ Torr after three days of bakeout at 130 °C to minimize contamination. We maintained process pressure at 2.0 mTorr using a steady argon flow at 40 SCCM (SCCM denotes cubic centimeter per minute at STP) during deposition. The yttrium sputter target was operated at a dc power of 50 W, and the yttrium film deposition rate was 0.086 nm/s. Details of the method used to determine the yttrium deposition rate are given in subsection 3.B. The purity of the yttrium target was quoted as 99.5% by its manufacturer (ACI Alloys, San Jose, Calif.). Additional tests were performed to verify the yttrium target and the deposited film purity, as is discussed in Subsection 3.C.

Each yttrium film was deposited on a 5 mm × 5 mm silicon nitride membrane, fabricated by means of low-pressure chemical vapor deposition. The membrane fabrication involved 111 SCCM of a Si$_2$Cl$_2$H$_2$ (dichlorosilane) flow and 30 SCCM of NH$_3$ (ammonia) flow at a temperature of 800 °C and a pressure of 300 mTorr. The deposition rate was 5 nm/min. The stoichiometry of the resulting membranes was Si$_{10}$N$_{11}$ with a density of 3.4 g/cm$^3$ and a thickness of 100 ± 10 nm. As we explain in Subsection 3.D, the contribution of the silicon nitride to the overall transmittance of the Y/Si$_{10}$N$_{11}$ samples is normalized out in the measurements. Therefore the 20% uncertainty in knowledge of the silicon nitride thickness does not ultimately affect the accuracy of the measured refractive index of yttrium.

B. Yttrium Thickness and Density

The reliability of the transmittance method depends strongly on accurate knowledge of the film thickness and density of the material under investigation. In this study, we determined the yttrium film thickness and density using two independent methods. All yttrium films used in the thickness and density tests were deposited under exactly the same conditions as the yttrium samples made for refractive-index measurements, discussed in Section 4. First, yttrium films of various thicknesses were deposited on silicon wafer substrates, and their specular reflectance was measured as a function of angle by use of an x-ray diffractometer (Cu $K_\alpha$ line source emitting at 8048 eV). Examples of reflectance versus diffraction angle of three yttrium films are plotted in Fig. 1(a). We determined the film thickness by fitting the diffraction data to the Fresnel equations. The fitting parameters include the yttrium film thickness and the roughness of both the silicon substrate and the yttrium surface expressed in the form of a Debye–Waller factor. A value of $\delta = 1.25 \times 10^{-5}$ and $\beta = 6.86 \times 10^{-7}$ from Ref. 6 was used for the refractive index $\bar{n} = 1 - \delta + i\beta$ of yttrium at the Cu $K_\alpha$ energy. Yttrium was assumed to have a bulk density of 4.46 g/cm$^3$ in these calculations, given that the refractive index is relatively insensitive to small density variations at this short wavelength. The slope of the fitted thicknesses versus deposition time yields the deposition rate of yttrium $r = 0.086$ nm/s, as is illus-
trated in Fig. 1(b). On the basis of this rate, any yttrium film thickness can be calculated from its known deposition time. Yttrium thickness determined in this manner is accurate to within ±2 nm. Although the minimum thickness that can be reliably determined with this method is limited by the non-linearity of the deposition rate at short deposition times, all yttrium films used in this study were well above the minimum thickness threshold.

Rutherford backscattering spectrometry (RBS) was used for determination of the yttrium density in this study. Briefly, a 50-nm-thick yttrium film was bombarded with 2.3-MeV He\(^{++}\) ions, and the backward-scattered ions and their energies were measured at two different angles. The number of the backscattered ions is proportional to the atomic concentration of the material under investigation. The energy of the He\(^{++}\) backscattered ions is directly related to the depth and the mass of the material atoms. An yttrium density of 4.43 ± 0.18 g/cm\(^3\), relatively close to the bulk density of 4.46 g/cm\(^3\), was inferred from this method.

C. Yttrium Purity
The RBS technique was also used to verify the yttrium sputtering target and deposited film purity. RBS tests proved to be critical for this study because of the difficulties that we encountered in obtaining a high-purity yttrium target. Prior to obtaining the yttrium target used for this study, we tested two other targets (each quoted for a high purity of 99.9%) from two different companies. The quoted purity usually refers to metallic composition only, and gaseous impurities are not taken into account by the target manufacturers. RBS tests on two dc magnetron-sputtered 50-nm-thick yttrium films from the two targets revealed 25% and 39% atomic oxygen content, respectively. Thus both targets were dismissed as unacceptable for fabrication of pure yttrium samples. On the other hand, the RBS-analyzed 50-nm-thick yttrium film from the third target that was eventually selected for this study contained no detectable amount of oxygen, even though it was left in air for several days before characterization. All three yttrium films used in this comparison were deposited under exactly the same conditions. Therefore it was concluded that the amount of oxygen present in the first two yttrium films was incorporated in the targets and was not a result of film oxidation during or after deposition.

The powder hot pressing method applied in the fabrication of the first two targets may explain the high amount of oxygen assimilated in them. In fact, the recommended method for high-purity metal targets is vacuum-arc melting and casting,\(^{15}\) which was applied for the yttrium target used in this study. Regarding contaminants other than oxygen, RBS analysis on yttrium films from the target used in this study showed atomic concentrations of 0.5% argon and 0.1% tungsten. The presence of argon in the film is due to the argon process gas used during deposition (see Subsection 3.A). The negligible amount of tungsten is attributed to the tungsten filament used in the arc-melting process during the yttrium target fabrication.

The above-mentioned results show that yttrium films made from a pure target with the deposition technique described in Subsection 3.A are stable against oxidation. This conclusion contradicts previous reports that yttrium films oxidize readily,\(^{5,16}\) which could be a result of different deposition conditions or impurities included in the source material.

D. Transmittance Measurement Setup
Three yttrium films of 30-, 52-, and 90-nm thickness were deposited on silicon nitride membranes as discussed in Subsection 3.A. After deposition, the samples were kept in a dessicator and were transported to beamline 6.3.2 of the Advanced Light Source at LBNL. A detailed description of this beamline can be found elsewhere.\(^{17,18}\) In brief, a variable-space grating monochromator utilizing 200-, 600-, and 1200-lines/mm gratings provides a spectral range extending from 50 to 1300 eV (from 25 nm down to 1 nm). The monochromator exit slit was set to a width of 50 μm for all measurements. Depending on the photon energy and grating used, the spectral resolving power \(E/\Delta E\) varied from 300 to 3500 across the 50–1300-eV region. Energy was calibrated with a relative accuracy of 0.011% rms and could be determined with 0.007% repeatability. Second-harmonic and stray-light suppression at various energies were achieved with a selection of filters installed at the beamline. At low energies where higher harmonics are present, an order suppressor consisting of three grazing-incidence mirrors was used in addition to filters. Any residual broadband scattered light from the beamline is suppressed with use of trimming slits located just upstream of the reflectometer. In this way, a spectral purity of 99% or better is achieved throughout the beamline spectral range.\(^{18}\) The current measured from the vertically refoocusing mirror at the beamline was collected to normalize the signal against the storage ring current decay. The base pressure in the measurement chamber was below 1.2 × 10\(^{-6}\) Torr. A GaAsP photodiode with a 5 mm × 5 mm active area was used as a detector. Transmittance measurements on the yttrium samples were performed in 1.0-eV steps except for the energy regions around absorption edges where steps as small as 0.2 eV were used to better resolve fine structures.

4. Results and Discussion

A. Transmittance Measurements
Transmittance versus energy measurements were performed on each of the three silicon nitride membranes that were used as substrates for the 30-nm-, 52-nm-, and 90-nm-thick yttrium films, respectively. Transmittance was also measured after yttrium film deposition on each of the three samples. Figure 2 illustrates the procedure applied to obtain the transmittance \(T_y\) of the pure yttrium films. To a first-
order approximation, where scattering from the film is negligible, \( T_Y = \frac{T_{Si_3N_4} + Y}{T_{Si_3N_4}} \). \( T_{Si_3N_4} \) and \( T_{Si_3N_4} + Y \) are the experimental transmittances of the bare silicon nitride membrane [Fig. 2(a)] and after the deposition of the 90-nm-thick yttrium coating on the membrane [Fig. 2(b)], respectively. The advantage of this method is that the contribution of the membrane is normalized out in the final results. The same technique was used to obtain the transmittance of all three yttrium films. Thus any uncertainty in thickness, density, and composition of the membrane substrates did not ultimately affect the absorption results for yttrium. Transmittance results for the three yttrium films are plotted in Fig. 3. The fine structure that is due to the yttrium \( M_{4,5} \) (155.8-eV) and yttrium \( M_{2,3} \) (298.8-eV) edges is clearly resolved for the first time to our knowledge in the literature on this material. There is no evidence of any contaminants such as oxygen, nitrogen, or carbon in the spectra of the three yttrium films, which is in good agreement with the RBS results presented in Subsection 3.C.

B. Absorption and Dispersion Results

On the basis of the transmittance results from the 30-nm-, 52-nm-, and 90-nm-thick yttrium films, the absorption \( \beta \) was determined by a linear fit of \( \ln(T) \) versus \( x \). As shown in Fig. 4, a straight line was formed, and the slope of \( \ln(T) \) was used to obtain \( \beta \) at each energy according to Eq. (2). In Fig. 5 the \( \beta \) values extracted from the measured transmittances in the 50–1300-eV region are plotted in comparison with the tabulated values derived from the atomic scattering factors assuming bulk density of 4.46 g/cm\(^3\). Significant differences between the measured and the tabulated results can be observed in the expanded plot from 50 to 250 eV, which includes...
the region of particular interest (100–155 eV) where Mo/Y multilayers operate. Fine structure is present in the measured data, which was not resolved in the previously tabulated values.

To construct a set of absorption data covering the entire spectrum as needed for calculation of the dispersion according to Eq. (3), the present set of experimental β values was combined with data from other researchers. In the 0.1–30-eV energy region, optical data were available from Weaver et al. in terms of the polarized complex dielectric constants. In the energy region above 1300 eV, values were obtained from the yttrium atomic scattering factors in the CXRO tables, assuming bulk density. To verify the accuracy of the entire set of data for β, the sum rule \( N_{\text{eff,}\beta}(E) \) of Eq. (4) was applied. The β sum results are plotted in Fig. 6 in comparison with the β sum results derived from the tabulated atomic scattering factors. At \( E = 0 \) eV, the new β values yield \( N_{\text{eff,}\beta}(E) = 0 \), whereas the tabulated values yield \( N_{\text{eff,}\beta}(E) = 1.3 \). As discussed in Section 2, the non-zero result of \( N_{\text{eff,}\beta}(E) \) at \( E = 0 \) indicates that there is a systematic error in the tabulated yttrium absorption results in some spectral region. The sum rules plotted in Fig. 6 indicate that integrated oscillator strength equivalent to 1.3 electrons is missing from the tabulated absorption values. The new measurements in the 50–1300-eV region appear to recover the 1.3-electron deficiency. After the consistency of the new absorption data set was confirmed, \( \delta \) was calculated with the Kramers–Kronig integration of Eq. (3). Only slight differences between the new \( \delta \) and the tabulated \( \delta \) appear in the regions around yttrium absorption edges as can be seen in Fig. 7. The results of the \( \varepsilon_2 \) and \( \text{Im} (\varepsilon^{-1}) \) sum rules with the new set of yttrium data are also consistent, as is shown in Fig. 8. The plots in Fig. 8 indicate that the new absorption measurements and dispersion calculations are

\[
\frac{N_{\text{eff,}\beta}(E)}{N_{\text{eff,}\mu}(E)} \quad \text{and} \quad \frac{N_{\text{eff,}\varepsilon}(E)}{N_{\text{eff,}\mu}(E)}
\]

gradually rising plateaus at the onset of the lowest core-level absorption (\( M_{4,5} \) edge at 155.8 eV). The three sums show identical results from there on until they reach the value \( Z^* = 38.83 \) at \( E \to \infty \).
consistent and result in an improved set of yttrium optical constants.

The values for the refractive index $n = 1 - \delta + i\beta$ of yttrium determined in this study were used to calculate the ideal normal-incidence reflectance of Mo/Y multilayers in the 95–155-eV region (13 nm down to 8 nm). The following parameters were applied: the number of bilayers $N = 120$ and the thickness ratio of the absorber layer (molybdenum) to the bilayer thickness $\Gamma = 0.425$. Yttrium was the first layer whereas molybdenum was the last layer within the multilayer stack. Perfectly smooth silicon substrate surface and multilayer interfaces were assumed in these calculations. It should be noted that the structure parameters $\Gamma$ and $N$ can be further adjusted to obtain the highest possible reflectance for a Mo/Y multilayer at a particular wavelength. In Fig. 9 the reflectance results are plotted in comparison with those predicted with the previously available data. At an 11.5-nm wavelength, for example, the difference between the reflectances calculated with the new and previous optical data is 4% and becomes even higher at longer wavelengths. Several parameters are often involved in the fitting of experimental reflectance data from multilayer optics operating in the EUV region. Use of an accurate set of optical constants to model these experimental results is therefore critical to obtain meaningful values for fitted multilayer parameters such as surface oxide, interface roughness, and diffuson.

5. Conclusion

The refractive index $n = 1 - \delta + i\beta$ of yttrium was determined experimentally in the 30–1500-eV energy range for the first time to our knowledge in the literature. The absorption $\beta$ was obtained through transmission measurements on dc magnetron-sputtered yttrium films of verified purity and thick-

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References and Note

1. Information about the Extreme Ultraviolet Explorer mission and the observed spectral lines can be obtained at http://ssl.berkeley.edu/euwe.


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