Direct index of refraction measurements at extreme-ultraviolet and soft-x-ray wavelengths

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Coherent radiation from undulator beamlines has been used to directly measure the real and imaginary parts of the index of refraction of several materials at both extreme-ultraviolet and soft-x-ray wavelengths. Using the XOR interferometer, we measure the refractive indices of silicon and ruthenium, essential materials for extreme-ultraviolet lithography. Both materials are tested at wavelength (13.4 nm) and across silicon’s $L_2$ (99.8 eV) and $L_3$ (99.2 eV) absorption edges. We further extend this direct phase measurement method into the soft-x-ray region, where measurements of chromium and vanadium are performed around their $L_3$ absorption edges at 574.1 and 512.1 eV, respectively. These are the first direct measurements, to our knowledge, of the real part of the index of refraction made in the soft-x-ray region. © 2006 Optical Society of America

1. Introduction

Index of refraction is a fundamental optical property of materials. Accurate knowledge of this property is critical at extreme-ultraviolet (EUV) and soft-x-ray (SXR) wavelengths for a wide variety of applications. Exact values of the refractive index, at wavelength, are needed in the design of multilayer mirrors for EUV lithography. The SXR spectral region encompasses the absorption edges of many magnetic materials. Correct knowledge of the index of refraction of these materials at SXR wavelengths, especially around their absorption edges, is crucial for magnetic material studies at these wavelengths.

At EUV and SXR wavelengths, the index of refraction is complex, strongly wavelength dependent, and highly absorptive. The index of refraction at these wavelengths can be written as

$$n(\omega) = 1 - \delta(\omega) + i\beta(\omega),$$

where $\delta$ and $\beta$ are both real numbers and strongly wavelength dependent. The high absorption and wavelength dependence make it difficult to perform direct experimental measurements of $\delta$ at wavelength. In the past, absorption measurements have been used to experimentally determine the imaginary part of the index of refraction. The real part of the refractive index is then determined by performing the Kramers–Kronig transformation on the absorption data. The $\delta$ values, i.e., the dispersive properties of the material, determined by this indirect method are inevitably subject to errors in the absorption measurements. This source of error is particularly significant near the absorption edges where refractive indices change abruptly. In addition, the data taken to establish $\beta$ do not include bound–bound electron transitions, near-edge x-ray-absorption structure, or extended x-ray-absorption fine structure. Another indirect method previously used to determine the index of refraction at EUV wavelengths is x-ray reflectance from material surfaces. In this case, index of refraction is extracted by the least-squares fitting of Fresnel coefficients to the measured reflectance curves. As this is a reflec-
tance measurement, its accuracy is sensitive to surface roughness, chemistry, and contamination. Additional errors occur in the least-squares fitting process when the condition $\beta/\delta \ll 1$ is not met. Surface effects that are significant with reflection measurements are negligible for a thick sample used in transmission, as is done with the technique used in this paper. Index of refraction measurements have also been performed in the SXR region using Bragg scattering from specially prepared multilayered samples. Although these measurements are able to directly measure the real and imaginary parts of the atomic scattering factor (and thus the refractive index), a knowledge of $\beta$ is required to formulate a correction factor to attain accurate values of $\delta$.9,11

Here we employ an experimental technique that uses coherent radiation to directly measure, at wavelength, both the real and the imaginary parts of the refractive indices of silicon, ruthenium, chromium, and vanadium. Silicon, chromium, and vanadium are measured about their $L_3$ absorption edges of 99.2, 574.1, and 512.1 eV, respectively. The interferometric method employed here directly measures the phase change induced by the material and is therefore more accurate than other indirect techniques that lead to uncertainty in the dispersive values about their edges. In addition, ruthenium and silicon are also measured at a 13.4 nm wavelength (92.5 eV), where EUV lithography operates. Ruthenium and silicon are used to fabricate multilayer mirrors that serve as image-forming optical elements in EUV lithography. Accurate knowledge of the phase-shifting portion of the refractive index of these two materials at 13.4 nm is desired but, to our knowledge, has never been directly measured before.

The interferometric measurement technique utilized allows the real and imaginary parts of the index of refraction to be directly and independently determined at wavelength. The vanadium and chromium measurements demonstrate the capability of the XOR interferometer to directly measure the index of refraction up to 580 eV; this is the first direct measurements of $\delta$ made in the SXR region.

2. Experimental Setup

Figure 1 displays the schematic setup used to measure index of refraction at beamline 12 of the Advanced Light Source (ALS).12 Two different experiments are performed using this setup: one at EUV and the other at SXR wavelengths. Although the optical descriptions of these two experiments are identical, two different sets of experimental parameters are employed depending on the wavelength region. The optical setup as shown in Fig. 1 will be explained using the EUV experiment as an example, and the details of the SXR experiment will follow.

For the measurement at EUV wavelengths, a free-standing 5 µm diameter pinhole is placed at the exit plane of the beamline as a spatial filter to provide coherent illumination into the interferometer. The size of the pinhole is therefore chosen such that it is slightly smaller than the lateral coherence length of the incident undulator radiation. An XOR pattern, i.e., bitwise eXclusive-OR (XOR) of a zone plate and a grating, is placed downstream of the pinhole. This element creates two equal-intensity off-axis foci at its back focal plane. The distance $z$ between the pinhole and the XOR pattern is chosen such that the radius of the first Airy null produced by the pinhole is twice as large as that of the XOR diameter, i.e.,

$$z \approx \frac{Dd}{1.22\lambda},$$

where $D$ is the diameter of the XOR, $d$ is the diameter of the pinhole, and $\lambda$ is the wavelength employed. This twice-filled criterion ensures a relatively uniform illumination onto the XOR pattern. The XOR used in the EUV experiments has a diameter $D$ of 400 µm, an outer zone width $\Delta r$ of 200 nm, and a grating period $g$ of 16 µm. It is patterned in a layer of nickel placed on top of a silicon nitride window. The thickness of the nickel absorber layer is 200 nm and that of the silicon nitride window is 100 nm.

The sample mask is placed at the back focal plane...
of the XOR where the two equal-intensity foci illuminate the window pairs. The focal length $f$ of the XOR is the same as that of the underlying zone plate used to obtain the XOR pattern, and is given by

$$f = \frac{D\Delta r}{\lambda}. \quad (3)$$

At a 13.4 nm wavelength (92.5 eV photon energy), the focal length of the XOR pattern is 5.97 mm. The sample mask contains seven window pairs as shown in Fig. 1. Four of these pairs (sample pairs) consist of one empty window and one sample window, whereas the remaining three pairs (reference pairs) consist of two empty windows. The sample pairs create the sample material data by introducing an additional phase shift and absorption in one of the windows, and the reference pairs generate the reference fringes by permitting the wavefronts to pass unaltered. The material under test is deposited on the sample mask by sputtering. The nonwindow absorber portion of the sample mask contains 300 nm nickel. After passing the sample mask, the two wavefronts propagate a distance $z$ to the CCD camera where they form the interference pattern. The water-cooled, back-thinned CCD camera directly records the resulting fringe pattern on its active area, which extends 1 in. $\times$ 1 in. (2.54 cm $\times$ 2.54 cm) with $1024 \times 1024$ pixels. As the distance between the CCD and the pinhole is fixed at 405 mm by the experimental chamber, the distance from the sample mask to the CCD is a function of wavelength.

For SXR wavelengths the experimental layout is the same as for EUV wavelengths; however, the dimensions of several of the elements are modified to adjust for the decreased illumination angle and absorption level associated with this energy region. The pinhole has a 2.5 $\mu$m diameter to accommodate the source characteristics and create the required level of spatial coherence at energies greater than 500 eV.\textsuperscript{16} The absorber used for the pinhole is 2.1 $\mu$m of gold. This is a significantly thicker pinhole absorber than what was used at EUV wavelengths. As will be discussed below, this thick layer of gold is required to eliminate the unwanted higher-order harmonics from the undulator. The XOR used at SXR wavelengths has a diameter of 280 $\mu$m, an outer zone width of 140 nm, and a grating period of 7.84 $\mu$m. For a wavelength of 2.5 nm ($\sim$500 eV in photon energy), the focal length $f$ is again given by Eq. (3) as 15.7 mm. A layer of gold 200 nm thick is used as an absorber material as it has a low transmission, $8.0 \times 10^{-3}$, at 500 eV.\textsuperscript{17} The XOR is placed $p = 248$ mm downstream of the pinhole for it to achieve the same twice-overfill requirement at a photon energy of 500 eV. The sample mask is laid out with the same pattern of window pairs as for EUV experiments. The absorber material of the sample mask is comprised of 1 $\mu$m of gold. In the SXR setup, the distance from the pinhole to the CCD is 1.44 m. This is $\approx$3.6 times the length of the EUV setup. This increased length is to accommodate the decreased angle leaving the XOR pattern due to the shorter wavelength employed.

The SXR radiation used for this experiment is obtained by utilizing the third harmonic from an 8 cm period undulator. However, radiation in higher-order harmonics will also be transported by the beamline to the entrance of the XOR interferometer, i.e., the pinhole plane, and an extraordinarily thick pinhole absorber is therefore needed to filter out the higher-order harmonics. Here we examine the effect of the various beamline elements and the transportation of

<table>
<thead>
<tr>
<th>Photon Energy (eV)</th>
<th>Transmission of 2.1 $\mu$m Gold</th>
</tr>
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<tbody>
<tr>
<td>3 500.0</td>
<td>$9.71 \times 10^{-23}$</td>
</tr>
<tr>
<td>5 833.3</td>
<td>$1.39 \times 10^{-13}$</td>
</tr>
<tr>
<td>7 1266.7</td>
<td>$2.27 \times 10^{-6}$</td>
</tr>
</tbody>
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\textsuperscript{17} Ref. 17.

Fig. 2. (a) $\delta$ and (b) $\beta$ measurements taken in the vicinity of 92.5 eV (13.4 nm) for ruthenium. The experimental data are shown with error bars and referenced against data taken using absorption measurements.\textsuperscript{23} The error bars on the data are a result of changing upstream alignment of the system due to the time of data acquisition. This changing alignment effects the pinhole illumination, specifically in the vertical direction as discussed in the text.
higher-order harmonics by the beamline. For a given energy in the first harmonic, $E_1$, the photon energy of the higher-order harmonics is given by

$$E = nE_1,$$

where $n$ is the harmonic number. For the 500 eV third-harmonic radiation that this beamline is optimized for, fifth- and seventh-order harmonics of $E_5 = 833.3$ eV and $E_7 = 1166.7$ eV are also generated, although at significantly reduced flux levels. The specific beamline used in this experiment contains an angular aperture, demagnifying glancing-incidence mirrors, and a monochromator. As the harmonics become greater constrained in angle as the harmonic number increases, the angular aperture designed to select the third harmonic would also allow the fifth and seventh harmonics to pass. The demagnifying mirrors used in this beamline are 2 deg glancing-incidence mirrors coated in either gold, iridium, or tungsten. The reflectivity of these materials at glancing incidence does not vary greatly from 500 to 1200 eV; thus no significant suppressing of higher-order harmonics can be achieved with these mirrors. The beamline monochromator is comprised of a varied-line-space grating and a vertical exit slit. The grating disperses the radiation for a specific wavelength and then the exit slits select the wavelength to be used. The grating equation describing the monochromatization effect can be expressed as

$$q = \frac{n}{\Lambda},$$

where $q$ is the diffraction order of the grating, $\lambda_0/n$ is the wavelength of the $n$th-order harmonics, $\theta_i$ is the incident angle, $\theta_f$ is the reflected angle, and $\Lambda$ is the grating period. The wavelength is expressed to include order number, following the convention of Eq. (4). From Eq. (5), we see that for an increased harmonic number $n$, there is a matching $q$ such that the reflected angle of the grating remains a constant. This enables the fifth and seventh orders to pass through the exit slit of the monochromator when the monochromator is set for the third order.

Although the power from the fifth and seventh harmonics is low compared with that of the third harmonic, these harmonics are still evident on the downstream CCD as the number of electrons per photon produced at the CCD camera increases with increasing energy. Without a thick absorber, the fifth and seventh harmonics are projecting through the gold absorber and thus the entire higher-order beam is recorded on the CCD. This is in comparison with the small percentage of the third harmonic that is propagated to the CCD camera after being filtered by the pinhole. It is therefore of crucial importance to have the absorber material of the pinhole mask to be heavily absorbing at these higher energies so as to prevent the higher-order harmonics from transmit-
ting through and being recorded on the CCD camera. The transmission of 2.1 \( \mu \text{m} \) of gold, utilized for SXR spatial filtering, for the third, fifth, and seventh harmonics is summarized in Table 1. Since the fringe patterns generated by the higher-order harmonics have significantly different fringe periods, the effects of higher-order harmonics are eliminated by employing a Fourier-transform method\(^{21,22} \) together with a Gaussian filter in the Fourier domain.

3. Results

A. Extreme-Ultraviolet Experiments

The indices of refraction of ruthenium and silicon are measured in the vicinity of 92.5 eV, the photon energy of great interest for EUV lithography multilayer coatings. A Fourier-transform method\(^{21,22} \) was used to extract both the phase shift and the visibility from the interferograms. The Fourier-transform method used here to determine the phase shift \( \Delta \phi \) has the advantage that the phase information contained in the spatial-frequency-modulated fringes is isolated into the first-order peaks in the Fourier (i.e., spatial-frequency) domain. Filtering of the first-order peak in the Fourier domain removes the effect of all stray light that does not have an identical spatial frequency as that of the fringes. In addition, the extracted values are averaged over the full area of the interference pattern.

Figure 2 displays the results of the ruthenium measurements. The experimental data are shown with error bars and are plotted against values derived from Ref. 23. At 13.4 nm, the experimentally measured values of \( \delta \) and \( \beta \) are 0.104 and 0.0139, respectively. For \( \delta \) this is approximately a 5\% difference from the reference values,\(^{23} \) and for \( \beta \) this is a 13\% difference. A large difference was not expected between the values of the refractive index found using direct measurement and the referenced values as there are no absorption edges in the vicinity of the wavelength region from which we acquired the data. The deviation of our results from the highly accurate measurements of Ref. 23 raised the issue of the

Fig. 5. (a) \( \delta \) and (b) \( \beta \) measurements taken about 512.1 eV (2.42 nm) for vanadium. The experimental data are shown with error bars and referenced against data taken using absorption measurements.\(^{23} \) The sample used had a thickness of 350 nm and a RBS-determined density of 5.89 g/cm\(^3 \). Note the increase in the magnitude of the error bars at energies higher than the absorption edge.

Fig. 6. (a) \( \delta \) and (b) \( \beta \) measurements taken about 574.1 eV (2.16 nm) for chromium. The experimental data are shown with error bars and referenced against data taken using absorption measurements.\(^{23} \) The sample used had a thickness of 310 nm and a RBS-determined density of 7.12 g/cm\(^3 \). Note the increase in the magnitude of the error bars at energies higher than the absorption edge.
accuracy of the density–thickness product for the ruthenium sample. This issue is addressed below with Rutherford backscattering (RBS) measurements.

The error bars on the δ and β measurements are a result of the variation within each of the four sample interferograms and each of the three reference interferograms. This variation can be attributed to electron-beam drift. The beam drift over the duration of the exposure causes a fluctuation in pinhole illumination. This variation in pinhole illumination, particularly in the vertical direction, greatly affects the visibility of an interferogram. As a result, the value of β, as it is determined by the visibility alone, has a larger error bar as compared with that of δ.

Figure 3 displays the experimental results taken from the silicon sample across its L₂ (99.8 eV) and L₃ (99.2 eV) absorption edges. These data are shown with error bars and are referenced against two sets of data. First, the data are referenced against absorption measurements, the same as was done with ruthenium. The sample is analyzed using RBS. In RBS measurements, high-energy ions incident on a sample are scattered by the atoms of that sample. The energy and number of scattered ions provides information on the composition of the sample, the distribution of those components, and the thickness of the sample. The results of this RBS analysis are shown in Fig. 4. This analysis concluded that the sputtered sample was 93.96% silicon, 5.98% argon, and 0.06% indium. The large percentage of argon can be attributed to the argon-rich environment of the sputtering chamber. Reference data for Si₀.₉₃Ar₀.₉₉In₀.₀₆ are shown in Fig. 3 with a dashed curve. For our Si₀.₉₃Ar₀.₉₉In₀.₀₆ sample, δ = 0.0015 and β = 0.0022 at 13.4 nm.

As expected, the experimental results match closely with the literature at photon energies below the absorption edge. Around the absorption edge, observable differences occur in both δ and β values. Since the δ values here are obtained experimentally by a direct phase measurement, they provide a valuable independent check for other indirect methods in the literature. It is especially important for the δ values about the material's absorption edge where traditional absorption methods have difficulty obtaining accurate results for δ.

B. Soft-X-Ray Experiments

Figures 5 and 6 show the results of the index of refraction measurements on vanadium and chromium, respectively. These measurements were taken across their respective L₃ absorption edges at 512.1 and 574.1 eV. The data are plotted with error bars and are referenced against values found using absorption measurements. Measurements at SXR wavelengths were made possible through use of a new tunable coherent SXR branchline at the ALS. The monochromator of the coherent SXR beamline was set during data acquisition to create a relative spectral bandwidth of 0.1%. This corresponds to an energy bandwidth of ~0.5 eV for the measurements made here. The beamline was spectrally characterized for these measurements based on the absorption edge of each sample material.

As in the EUV measurements, the error bars on the β values are greater than that seen on the δ values. This is again due to an interferometric method being used to determine the index of refraction. Also, for the SXR beamline the size of the focal spot at the pinhole is 44 µm by 2.7 µm FWHM. The measurements are thus once again sensitive to changes in upstream illumination, particularly in the vertical direction as discussed previously in this text. Discrepancies between measured and referenced values are once again expected due to the differing strengths of the two techniques.

4. Conclusions

This paper demonstrated the ability of the XOR interferometer to perform direct index of refraction measurements at SXR energies up to 580 eV. This is a greater energy than the 281.8 eV of the first SXR interferometer and a lower energy than the 8.05 keV of the first x-ray interferometer. As the separation of the two beams of the XOR interferometer is wavelength independent, this technique can be readily extended to the ~1 keV range where limited techniques exist for direct phase measurement.

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