Resonance effects in photoemission from TiO2-capped Mo/Si multilayer mirrors for extreme ultraviolet applications

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In the unbaked vacuum systems of extreme ultraviolet (EUV) lithography steppers, oxide formation and carbon growth on Mo/Si multilayer mirrors (MLMs) are competing processes leading to reflectivity loss. A major contribution to this mirror degradation is a series of surface reactions that are thought to be driven in large part by photoemitted electrons. In this paper, we focus on the resonance effects in photoemission from Mo/Si MLMs protected by thin TiO2 cap layers. In the vicinity of the resonant energy of the mirror, the energy flux of the EUV radiation forming standing wave oscillates throughout the multilayer stack. As a result, light absorption followed by the emission of photoelectrons becomes a complex process that varies rapidly with depth and photon energy. The electron emission is characterized as a function of the EUV photon energy, the angle of incidence, and the position of the standing wave with respect to the solid/vacuum interface. In our experiments, the position of the standing wave was controlled both by deliberately varying the thickness of the Si terminating layer (of the Mo/Si stack) and by depositing C films of various thicknesses on the TiO2. The experimental data are compared with model simulations to examine the changes in photoemission yield due to the presence of carbon and to the changes in the position of the standing wave. We find that carbon deposition can have a dramatic impact on the yield and, therefore, on the rates of electron mediated reactions at the surface. © 2011 American Institute of Physics. [doi:10.1063/1.3575319]

I. INTRODUCTION

Multilayer reflective optics are used widely to focus and direct vacuum ultraviolet, extreme ultraviolet (EUV), and soft x-ray photons. The range of applications includes EUV microscopes, spectrometers, EUV steppers, and EUV solar telescopes.1–4 These mirrors are actually Bragg reflectors. When they are irradiated by resonant light, a standing wave (SW) results with a periodic variation of nodes and antinodes extending from the bulk of the multilayer mirror (MLM) into the vacuum. The scattered waves satisfy the Bragg condition. In extreme ultraviolet lithography (EUVL), a series of chemical reactions, initiated either directly by impinging EUV photons or indirectly by secondary electrons, leads to oxidation or carbon overlayer growth, resulting in degradation of the mirror reflectivity. The reactions involve water and hydrocarbons adsorbed on the surface from an unbaked vacuum environment or from outgassing resists. Photoelectrons generated by incident light striking the mirror are believed to be a major contributor to the dissociation of adsorbed water and hydrocarbons, resulting in oxidation and carbonization, respectively.5

Underwood and Gullikson6 measured simultaneously the total photoelectric current and the reflectivity from a Si-terminated Mo/Si multilayer surface versus the photon energy, thus demonstrating the MLM standing wave phase effect in photoemission. This effect was evidenced by the variation of the detected current as the energy swept through the Bragg peak; the highest yield of photoelectrons occurred when the SW antinode was at the surface of the multilayer. These authors noted that the variation of the total electron yield (TEY) at the Bragg peak is much more rapid than the variation of the reflectivity. Therefore the TEY is a sensitive test for small variations in the d-spacing or angle of incidence on the mirror.

Oestreich et al.7 indicated that mirrors designed so that the field intensity at the surface is minimal may exhibit slower contamination layer growth. Indeed, using a series of uncapped Mo/Si MLMs with different thicknesses of the top Si layer, Malinowski et al.8 observed that minimization of the electric field intensity at the surface led to a reduction of the initial rate of carbon buildup in an EUV + hydrocarbon vapor environment.

Muramatsu et al.9 showed that the simultaneous measurement of the TEY and the Bragg reflection is useful for evaluating the layer/interface structure of multilayer x-ray mirrors. Using this approach, they observed the shrinkage of the Mo/SiC/Si multilayer structure along with disordering at the interface induced by annealing. Later, Tiwari et al.10

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showed that the x-ray SW field can also be used to determine the concentration and location of various trace element contaminants embedded in different layers of the Mo/Si multilayer structure. Miyake et al. measured the wavelength dependencies of the reflectivity and the photoelectron signal. By using a model fit to experimental curves, they concluded that TEY is approximately proportional to the surface electric field intensity.

Ejima presented a method to calculate the TEY of multilayer films and applied it to simulate TEY spectra measured from LiF/Si, Mo/SiC/Si/SiC, and Mo/Si multilayers. In the study of the Mo/Si structure, he showed that the yield changed with the thickness of the top Mo layer, and the reflection phase could be derived from the reflection and TEY measurements.

In this paper, our attention is focused on TiO2-capped Mo/Si MLMs of a type that could potentially be used in commercial EUVL tools. To study how interference effects might affect deposition rates as carbon grows on such optics, we have sputter deposited C on the TiO2 cap in five different thicknesses varying from 0 to 7 nm. To separate the interference effects from those of the varying carbon overlayer, we also studied a series of MLMs for which we deliberately varied the thickness of the terminal Si layer of the Mo/Si stack, also studied a series of MLMs for which we deliberately varied the thickness of the terminal Si layer of the Mo/Si stack, and found that films with thicknesses ≤ 10 nm were amorphous whereas thicker layers (70 nm) exhibited an anatase polycrystalline structure. Based on these results, we believe that our TiO2 caps (formed by the same deposition technique) are amorphous; this was also confirmed by a TEM study (not shown).

The TiO2 cap layer was a thin film (1.2 ± 0.1 nm) produced via dc plasma sputter deposition technique. Filatova et al. characterized the microstructure of such TiO2 layers on Si(100) wafers and found that films with thicknesses ≤ 10 nm were amorphous whereas thicker layers (70 nm) exhibited an anatase polycrystalline structure. Based on these results, we believe that our TiO2 caps (formed by the same deposition technique) are amorphous; this was also confirmed by a TEM study (not shown).

The cap protects the Si layer terminated Mo/Si multilayer structure. X-ray photoelectron spectroscopy (XPS) analysis with a monochromatic Al Kα x-ray source indicates that a fraction of the top Si layer in contact with TiO2 is oxidized, resulting in 1.8 ± 0.2 nm SiO2 (x ≈ 2) at the TiO2/Si interface. This is consistent with an earlier study of TiO2 thin films grown by plasma-enhanced chemical vapor deposition on silicon. The authors found an increase of the apparent dielectric constant with film thickness (up to ten monolayers) and explained it as the formation of an interfacial SiO2 layer.

In samples used for measurements of the photoelectron emission as a function of the contaminating carbon layer thickness, the carbon film was grown on the TiO2 cap via a sputter deposition technique. The resulting layer was an amorphous carbon film with a density of 2.2 ± 0.2 g/cm3 as verified by x-ray diffraction.

The TEYs of the multilayer samples are measured as a function of photon energy and angle of incidence. The experiments are performed under ultrahigh vacuum (UHV) conditions at two different beamlines: U3C (bending magnet) and U5UA (57-pole undulator) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Both beamlines are equipped with grazing monochromators delivering narrow bandpass EUV (~0.1 nm at U3C and ~10⁻⁴ nm at U5UA) on the sample. The light is always with the electric field vector vibrating in the plane of incidence. At U5UA, absolute values of the TEY are based on measurements using a calibrated AXUV-100 silicon photodiode (International Radiation Detectors, Inc.). Precision within a single set of measurements is estimated to be ±10%, with the uncertainty in absolute accuracy being about twice that value. Further details are reported elsewhere. At U3C, the photon flux is measured using a stable SXUV-100 photodiode with 5% absolute accuracy. The TEY as a function of EUV photon energy was measured by recording the sample drain current with an electrometer. The electron energy distribution spectra at a fixed photon energy were measured at the U5UA beamline. The electrons were collected in a narrow solid angle using a hemispherical analyzer operating at a fixed analyzer transmission mode and oriented at 45° with respect to the surface.

The bandpass of the EUV in the experiments done at NSLS was much narrower than the expected bandwidth of the EUV irradiating illumination and projection multilayer optics of a commercial stepper. In the stepper, the spectrum...
of EUV light incident on the wafer is determined by the non-monochromatic spectrum of the plasma source and by the filtering action of the combination of thin film filters and the selective reflection of the MLMs composing the optical system of the tool. We simulated the MLM photoemission expected in such tools by integrating the NSLS narrowband results over the bandwidth of a typical MLM reflectivity curve. To check the validity of this approximation, we did a second set of experiments using the Synchrotron Ultraviolet Radiation Facility (SURF III) at NIST. The experiments were also done under UHV conditions (base pressure: $5 \times 10^{-11}$ Torr). Similar to the EUV in a commercial tool, the EUV in these experiments is produced by a combination of a 300 $\mu$m Be filter and the reflection from a focusing MLM and has a bandwidth of approximately 0.5 nm FWHM. As we describe in Sec. III, good agreement was achieved as expected.

III. RESULTS

A. Electron energy distribution created by 92 eV photons: Comparison of TiO$_2$(001) and TiO$_2$-MLM

Figure 1 shows the electron energy distribution $N(E)$ that we observed under 92 eV EUV irradiation of clean TiO$_2$(011) and air-exposed TiO$_2$-MLM for photoelectrons emitted at 45$^\circ$ to the surface. The inset of Fig. 1 zooms in on the high energy region of the spectra. The tails reveal distinctive features of the top surface layer: core excitations and valence band emission (e.g., strong Ti 3$p$, O 2$s$, and O 2$p$ lines). Photoemission from the thin TiO$_2$ caps is likely influenced by their small thickness and by the underlying substrate beneath the caps, and thus the shape and position of these spectral lines vary slightly from those observed for the bulk crystal. The detailed structure in the valence band is also sensitive to the surface cleanliness and the presence of impurities. The Ti 3$d$ line visible in the TiO$_2$ film spectrum is a signature of Ti$^{3+}$ ions. Overall, the emission from this energy region is very low—almost negligible as compared to the total photoelectron signal.

The dominant feature of the photoelectron spectra plotted in Fig. 1 is the intense peak at low kinetic energies (0–15 eV). Table I presents several characteristics of the spectra for samples of clean TiO$_2$(011) and for air-exposed TiO$_2$(011) and a TiO$_2$ cap layer. The low energy secondary emission peak contains approximately 90% of the photoelectrons as indicated by parameter $\delta_{15}$, the fraction of electrons with an energy below 15 eV. The secondary electron structure shown in Fig. 2 is produced by photoelectrons that have lost their energies in inelastic scattering events involving both inner-shell and valence electrons.

Table I presents a summary of the amount of secondary photoemission occurring in the range from 0 to 15 eV and the total amount of photoemission integrated overall energies for three different samples: clean TiO$_2$(011), air-exposed TiO$_2$, and air-exposed TiO$_2$-MLM. We also list results for

![FIG. 1](Color online) Electron energy distributions detected for TiO$_2$(011) (dashed curve) and TiO$_2$-MLM (solid curve) under 92 eV photon irradiation. Intense peaks at low kinetic energies (<15 eV) are due to secondary electrons. The inset zooms in on the high energy region of the spectra to show the observed core and valence band features: Ti 3$s$ and Ti 3$p$ excitations, Ti 3$d$ originating from Ti$^{3+}$ defects, and oxygen O 2$s$ and O 2$p$ lines. The spectra in the inset are shifted vertically for clarity. The data are measured at beamline US5U, at NSLS at BNL.

![FIG. 2](Color online) Schematic energy band diagram of amorphous TiO$_2$ film. The bottom of the conduction band and the top of the valence band are marked as $E_{CB}$ and $E_{VB}$, respectively; $E_F$ and $E_L$ are the Fermi and core levels. The initial energy distribution $N_f(E)$ of electrons produced as a result of the absorption of an EUV photon $h\nu$ is redistributed as $N_d(E)$ by inelastic scattering events while electrons pass through the solid. It is modified further to $N_f(E)$ during the transport of electrons across the vacuum/solid interface to the distant location of the detector.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta_{15}$</th>
<th>FWHM, eV</th>
<th>$Y$, e/ph + 0.003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean TiO$_2$(011)</td>
<td>94</td>
<td>3.0</td>
<td>0.031</td>
</tr>
<tr>
<td>Air-exposed TiO$_2$(011)</td>
<td>97</td>
<td>2.6</td>
<td>0.028</td>
</tr>
<tr>
<td>Air-exposed TiO$_2$-MLM</td>
<td>86</td>
<td>2.3</td>
<td>0.035</td>
</tr>
<tr>
<td>Clean Ru(0001)</td>
<td>86</td>
<td>2.7</td>
<td>0.021</td>
</tr>
<tr>
<td>&gt;2 nm C on Ru</td>
<td>86</td>
<td>2.7</td>
<td>0.013</td>
</tr>
</tbody>
</table>
clean Ru(0001) taken from Ref. 21 to provide a comparison between the two leading capping layer candidates for EUVL MLMs for those interested in the possible technological applications of this work. The yield from a standard MLM coated with a thin amorphous TiO2 film is even higher than that detected for the bulk sample TiO2(011) (Table I). In the following sections, we discuss this phenomenon and factors controlling the TEY from TiO2-MLMs.

B. TEY of a TiO2-capped MLM as a function of photon energy

Figure 3 illustrates the total electron yield for a standard TiO2-capped MLM for photon energies in the range of 50 to 250 eV. At energies between 95 and 120 eV, the spectrum exhibits the strong Si L3,2 absorption feature.26 Our XPS measurements (not shown) did not reveal Si on top of the TiO2 film, and thus we conclude that the signal comes solely from the SiO2/Si layer beneath the TiO2 cap. This is consistent with earlier work27 reporting that a typical sampling depth of the TEY in the vicinity of Si L absorption is somewhat larger than the thickness of the terminating oxide layer.

In the photon energy range of 90–95 eV, the region of resonantly enhanced reflectivity, the spectrum of Fig. 3 reveals a strong maximum. Here the TEY varies between ~0.02 and ~0.06 electrons per incident photon (compare this to the value of ~0.03 electrons per incident photon for the TiO2 single crystal shown in Table I). The inset in Fig. 3 zooms in on the narrow energy region of 87 to 102 eV. The yield exhibits fringes similar to those observed in the mirror reflectivity curves, indicating a correspondence between photoelectron emission and electric field intensity within an escape depth of the mirror.

The amplitude of the TEY curve is very sensitive to the position of the solid/vacuum interface with respect to the electric field intensity. Figure 4(a) illustrates the dramatic change of the TEY curve when the thickness of the terminating Si layer expands from 2.3 to 7.8 nm (N.B. for these mirrors, the “standard” thickness of Si in MoSi bilayers is 4.15 nm). This expansion does not change the intensity distribution of the electric field throughout the multilayer stack but places the TiO2 surface of the MLM at different locations within the standing wave of the electric field. The inset illustrates the surface coincident with the antinode for a Si thickness of 4.7 nm and with the node for a Si thickness of 7.8 nm. The two other thicknesses, 2.3 and 3.3 nm, of Si represent intermediate cases. At the same time, the photoemission at the Si L3,2 absorption line that is off resonance remains virtually unaltered. The influence of the relative positions of the SW and the surface on the amplitude and structure of the...
The photoelectron yield is also demonstrated in Fig. 4(b). Here, the effect is achieved by increasing the carbon overlayer thickness from 0 to 7 nm (varC-TiO₂-MLM), which is a representative thickness range observed in EUV MLM lifetime tests. The appearance and growth of "foreign" material (carbon) on the surface of the TiO₂ cap has an additional effect on the yield: the span of the TEY curve (min-to-max value) decreases with the overlayer thickness, presumably due to the weaker photoemission properties of the carbon film (see Table I).

The effect of changing the angle of incidence of the EUV is illustrated in Fig. 5. Tilting the sample leads to an energy shift of the resonant portion of the spectrum due to the standing wave properties, but it has no effect on the adjacent Si L absorption line. We see that tilting the sample from 0° to 11° changes the wavelength near resonance from 13.48 nm (92 eV) to 13.23 nm (93.7 eV). Finally, the yield as a function of two parameters, energy and angle of incidence, is shown in Fig. 6 for a series of samples studied. The data presented are consistent with the relationship of the resonant wavelength $\lambda$ to the angle of incidence $\phi$ given by the equation $\lambda = 2n d \cdot \cos \phi$, where $n$ is the index of refraction of the material (slightly less than 1) and $d = 6.91$ nm, the periodicity of the multilayer.

IV. DISCUSSION

A. Earlier modeling of photoemission from a MLM

Formulating a comprehensive model of radiation-induced carbon contamination of EUV optics, Hollenshead and Klebanoff derived a semiempirical expression for the secondary electron flux leaving the surface of the MLM under monochromatic irradiation. The expression succeeds in reproducing the general trend of the experimental yield measured as a function of carbon overlayer thickness, but it does not account for the resonant structure of the MLM. Even a lower intensity planes of the standing wave field within the

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**FIG. 5.** (Color online) The total electron yield $Y$ measured as a function of the photon energy $h\nu$ at normal incidence (black curve) and at 11° (gray curve) for TiO₂-MLM with the thickness of the last silicon layer at 2.3 nm. The data are obtained at beamline U3C (NSLS). They demonstrate a $\Delta E \approx 1.7$ eV energy shift of the resonance structure of the electron yield curves with changing angle of incidence. The fundamental Si L absorption line is not affected by the tilt.

**FIG. 6.** The total electron yield $Y$ measured as a function of the photon energy $h\nu$ and the angle of incidence $\phi$ for TiO₂-MLM with (a) increasing thickness of the top silicon layer from 2.3 to 7.8 nm and (b) increasing thickness of the carbon overlayer from 0 to 7 nm. The yields are measured at beamline USUA, at NSLS at BNL, and are given in a linear grayscale. The increase of the yield is reflected by the pattern brightness, so white shading corresponds to the maximum yield, whereas black shading is associated with the minimum yield. The span of yields is different in each pattern and can be determined by comparing the brightness along the $\phi = 0$ line with the plots in Fig. 4.
MLM produced by the coherent superposition of the incoming and Bragg-reflected waves have the periodicity of the multilayer structure. Ejima\textsuperscript{12} calculated the TEY for a multilayer film by extending the single-layer model developed by Pepper\textsuperscript{30} to calculate the angular dependence of the photoemission from a thin film on a substrate. Within this model, the number of excited photoelectrons is proportional to the number of absorbed photons per unit volume given by the divergence of the time-averaged Poynting vector. To account for electron transport within the multilayer, Ejima\textsuperscript{12} introduced an attenuation length of the primary photoelectrons and a transmission factor for each interface. The method was applied to simulate spectra of a LiF/Si multilayer film on a Si substrate measured around the Si L\textsubscript{3,2} absorption edge.\textsuperscript{12} The author concluded that due to the low electron transmission rate at the interface between Si and LiF and to the short electron mean free path, the TEY of this multilayer film was mostly determined by the characteristics of the topmost layer, with interference introducing only a small effect.

In the following section, we describe a model similar to one reported by Ejima\textsuperscript{12} and use it to simulate the TEY curves measured for TiO\textsubscript{2}-MLMs and the effect of finite bandwidth.

B. Model for present TiO\textsubscript{2}-capped Mo/Si MLMs

The probability of a photoelectron’s being generated by the absorption of an incoming photon in species \(i\) is described by the total photoionization cross section \(\sigma_i(h\nu)\). Even though we are dealing with a solid, we use tabulated atomic cross sections\textsuperscript{31} because the high photon energies of the EUV favor inner-shell ionization that retains its atomic character. The electron current density produced by species \(i\) at depth \(z\) is proportional to the number density \(n_i(z)\) and to the electric field intensity \(|E|^2(h\nu,z)\), varying with the photon energy \(h\nu\) and the depth \(z\). The electric field strength is calculated using IMD software\textsuperscript{20} that implements a recursive approach to compute the field amplitudes throughout the MLM stack starting at the bottom-most layer.\textsuperscript{32} Thus, the number of primary photoelectrons generated at a depth \(z\) below the surface by species \(i\) is represented by the product of the electric field intensity \(|E|^2(h\nu,z)\), the photoionization cross section \(\mu_i(h\nu)\), and the number density \(n_i(z)\) of species \(i\) at this depth. The probability that an electron generated at depth \(z\) will reach the surface is given by the exponential term \(\exp(-z/\Lambda)\), where \(\Lambda\) is an effective electron attenuation length.

The final dependence of the TEY on the photon energy \(h\nu\) is given by the following equation:

\[
Y'(h\nu) \propto \int_0^\infty \sum_i |E|^2(h\nu,z) n_i(z) \sigma_i(h\nu,z) e^{-z/\Lambda} dz. \tag{1}
\]

To arrive at an appropriate value of \(\Lambda(z)\), we start with the material specific inelastic electron mean free path (IMFP), \(\lambda\), taken from the NIST Standard Reference Database\textsuperscript{33} at the lowest available electron energy, 50 eV. This energy is close to the minimum of the IMFP \(\lambda(E)\) as a function of the electron energy \(E\) for various inorganic compounds.\textsuperscript{34} In the preceding sections we have shown that most of the photoelectrons are secondaries emitted with energies below 20 eV, and hence the tabulated value of the IMFP at 50 eV, \(\lambda_{50}\), represents a lower limit of the distance a secondary electron can travel through the solid. We introduce a fitting parameter \(\beta\) in \(\Lambda = \beta \cdot \lambda_{50}\) to correct the electron attenuation length and to include empirically the probability of electron transmission through an interface. By choosing a \(z\)-independent \(\beta\), we make a simplifying assumption that the probabilities are similar for all interfaces in the stack. Because \(\lambda_{50}\) is several times less than the typical MLM layer thickness, it is unlikely that an electron will pass through more than two interfaces.

C. Simulation of experimental TEYs

In Fig. 7 we compare several experimental (symbols) and calculated (lines) yields \(Y'(h\nu)\) for (a) the clean TiO\textsubscript{2}-MLM and (b) the two mirrors covered with 3.5 and 6.2 nm of carbon, respectively. The calculated curves are obtained using Eq. (1). Figure 7 shows good agreement between calculated and measured data. This agreement is achieved by a
sequential fitting of the reflectivity $R(h\nu)$ [similar to the one shown in Fig. 7(a)] and the photoelectron yield $Y'(h\nu)$ curves. The fitting of the reflectivity curves using $R_1$-factor\(^{32}\) helped us to set the thickness and the stoichiometry of the silicide layers. During the fitting of the photoelectron yields, we adjusted sequentially the basal multilayer structure, the thicknesses of the top mirror layers (carbon, TiO\(_2\)), and, finally, the parameter $\beta$. The best fits of all the parameters were within the fabrication and experimental uncertainties. The optimization criteria for $Y'(h\nu)$ were determined by a reliability factor analysis using $R_1$-factor\(^{32}\) as defined by van Hove\(^{36}\) to quantify the similarities in the positions, widths, and relative heights of peaks and troughs.

Figure 8 shows an example of the $R_1$-factor for air-exposed TiO\(_2\)-MLM with no predeposited carbon as a function of two variables: (1) the thickness of adventitious carbon $d_C$ on the surface of the MLM and (2) the electron attenuation fitting parameter $\beta$. The absolute minimum of the $R_1$-factor is observed at $d_C \approx 0.5$ nm and $\beta \approx 1$. The thickness $d_C \approx 0.5$ nm for the adventitious carbon is reasonable. Measurements on other MLMs also indicated $\beta$ parameters close to 1. This indicates that the experimental TEY is determined not solely by the electric field at the surface (as would be the case for $\beta \to 0$) but also by the combined effect of photoelectrons generated at different depths.

D. Effect of the EUV light spectrum on the photoelectron yield

Equation (1) gives the yield $Y'(h\nu)$ for a monochromatic EUV source. If we wish to see what the effect would be with a source in a commercial stepper, we must integrate over a finite bandwidth centered at 13.5 nm. As was mentioned, we expect that such a source will be similar to the source used in the EUV optics lifetime testing facility at SURF III. For this source, the spectrum of the incident light $S(h\nu)$ is determined by convolution of the SURF III synchrotron radiation spectral power density $dN(h\nu)/dv$, the measured reflectivity $R(h\nu)$ of the focusing mirror [similar to the one shown in Fig. 7(a)], and the known transmission $T(h\nu)$ of the Be filter:\(^{23}\)

$$S(h\nu) = R(h\nu)T(h\nu)\frac{dN(h\nu)}{dv}.$$

The yield of photoelectrons $Y$ from the nonmonochromatic irradiation is found integrating the product of the TEY spectrum $Y'(h\nu)$ from Eq. (1) and the spectrum $S(h\nu)$ of the incident light over the appropriate range of photon energies:

$$Y \propto \int Y'(h\nu)S(h\nu)dv.$$

Figure 9(a) shows the relative photoelectron yield $Y$ (open circles) measured at SURF III for the set of mirrors as a function of increasing thickness $d_C$ of the carbon overlayer. The calculations are normalized to the maximum yield detected for the clean TiO\(_2\)-MLM. Figure 9(b) illustrates similar data obtained for the set of mirrors with increasing thickness $d_{Si}$ of the top silicon layer.

Directly measured yields $Y$ at SURF III and the yields calculated from the NSLS measurements using Eq. (2) reveal similar trends. Both of these measured values are in agreement with the model predicted yields. This supports the suggested picture of a photoemission process in the vicinity of the resonant energy of the multilayer structure. Our model is able to reproduce the relative change of the cumulative phot-electron yield with an acceptable level of accuracy. Overall, the result demonstrates that during resonant irradiation of...
a MLM, the yield can vary up to a factor of 3 as contamination grows and the solid/vacuum interface “moves” through the standing wave. This yield variation is somewhat smeared out due to photon energy spread in the incident light spectrum and contributions from electrons from different depths. The photoemissive efficiency of the topmost layer, where most electrons come from [e.g., C in Fig. 9(a) and TiO$_2$ in Fig. 9(b)], is also important for the absolute yields.

V. CONCLUSION

In this paper, we have discussed photoelectron emission from TiO$_2$-capped MLMs designed for EUV lithography. The work is motivated by the importance of low energy electrons in the chemical transformation of molecular adsorbates on surfaces and, specifically, in the conversion of adsorbed hydrocarbons into carbonaceous deposits contaminating EUVL optics. The conclusions that come from this study are as follows:

Photoelectron emission measured as a function of the angle of incidence and the energy of EUV photons exhibits a resonance pattern that originates from the coherent scattering of the incoming light. Large modulations occur when the light satisfies the Bragg condition of the MLM stack, thus producing a standing wave. The production of photoelectrons is a strong function of the position of the antinode in the near surface region of the optic, a condition that results in a dramatic variation of measured TEY near the Bragg condition (energy/angle).

The theoretical analysis of experimental TEYs requires accounting for electrons generated by EUV light within one electron attenuation depth below the surface. We show that a simple model that takes this assumption into account can reproduce the experimental data reasonably well.

The photoelectron energy spectrum generated by 92 eV photons (the energy used in EUVL stepper prototypes) is dominated by electrons produced in the top layer of the surface. Approximately 90% of electrons emitted from a multilayer sample have energies below 15 eV. Such low energy electrons are known to play major roles in all aspects of radiation damage in solids and liquids, which in many such cases occurs via dissociative electron attachment (DEA). The DEA can be assumed as a probable mechanism of electron mediated surface reactions on UV optics.

The effect of the top layer material and of the position of the surface with respect to the maxima and minima of the electric field was also studied. We found that the TEY from a TiO$_2$-MLM surface can vary by a factor of 3 in the carbon thickness range 0 to several nm, and that the photoemissive properties of the top layer (C vs TiO$_2$) can substantially change the absolute yield. The bandwidth of the incident light also determines the span of the TEYs.

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