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Optical constants of magnetron-sputtered magnesium films in the 25–1300 eV energy range

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The transmittance of dc magnetron-sputtered Mg thin films was measured in the 25–1300 eV spectral range. Freestanding Mg films protected with Al layers were characterized *ex situ*. Transmittance measurements were used to obtain the extinction coefficient k of Mg films. The obtained k values along with the data available in the literature, and with interpolations and extrapolations for the rest of the spectrum, were used to obtain the real part of the index of refraction n by the Kramers–Krönig analysis. Sum-rule tests indicated a good consistency of the data. © *2010 American Institute of Physics*. [doi:10.1063/1.3481457]

I. INTRODUCTION

The growing interest in fields such as extreme ultraviolet (EUV) lithography, synchrotron radiation, solar physics, and plasma diagnostics, involves the need of a good knowledge of the optical constants of materials in the EUV ($\sim$10–120 eV) and soft x-rays ($\sim$120 eV to a few kiloelectron volt) spectral regions. The development of high-performance coatings for these applications is limited by the high absorption of most materials, particularly for small energies in the EUV. Magnesium is an interesting material for the EUV because it has a low absorption band below the L_3 edge (49.50 eV). This makes Mg a promising material for filters and multilayer coatings in energies below the L_3 edge. In fact, several groups have recently developed multilayers based on Mg.[1–7]

The EUV properties of Mg films have been investigated by several authors. Sabine[8] measured the reflectivity of magnesium films evaporated over a film of chromium in the 2.6–31.0 eV energy range. Townsend[9] determined the absorption coefficient of self-supported Mg films in the 35.4–155.0 eV range. Kroger and Tomboulian[10] determined the absorption coefficient of Mg films from transmittance measurements over the spectral range from 16.5 to 56.4 eV. Daudé *et al.*[11,12] determined the optical constants of thin films of Mg evaporated in ultrahigh vacuum conditions, in the 5–24.8 eV range; the optical constants were calculated from reflectance measurements. Hagemann *et al.*[13] calculated the absorption coefficient of Mg thin films through transmittance measurements in the 45–154 eV energy range. They also used literature data and interpolated data in order to obtain a complete set of optical constants of Mg from 0.07 to 50 000 eV. Gullikson *et al.*[14] measured the absorption coefficient of Mg deposited by dc magnetron sputtering from 25 to 50 eV. Due to the high reactivity of Mg in contact with air, the Mg films, in the Gullikson measurements, were protected on both sides with 5-nm-thick Si capping layer. Regarding the evaluation of the energy position of an absorption edge, Seely *et al.*[15] determined the energy of the Mg $L_{2,3}$ attenuation edge by a careful measurement of the transmittance through thin filters based on Mg, with an Al capping layer on each side.

This paper presents novel experimental data and Kramers–Krönig (KK) evaluation that provides more accurate optical constants of Mg in the 25–1300 eV spectral range. Section II describes the experimental techniques. Section III presents the transmittance measurements for various Mg film thicknesses, the extinction coefficient of Mg from transmittance, and the index of refraction calculated using KK analysis. The consistency of the data gathered is evaluated through the inertial and f sum rules.

II. EXPERIMENTAL TECHNIQUES

Mg films were deposited using dc magnetron sputtering in a vacuum system located at Lawrence Berkeley National Laboratory (LBNL). The base pressure of the system was 10^{-5} Pa, and Ar gas was used as the sputtering gas at a pressure of 0.133 Pa during deposition. Sample fabrication process was as follows. We used Si wafers as substrates which had been spin coated with photoresist. First a 25-nm-thick Al film was deposited by dc magnetron sputtering. Over the Al capping layer, we deposited the Mg film of a desired thickness. The Mg film was then overcoated with a 25-nm-thick Al film. The Al films were deposited on both sides of the Mg film to prevent Mg oxidation. The Al/Mg/Al sandwiches were deposited without breaking vacuum. After deposition, stainless steel support rings were glued onto the coated substrates, and then the films were removed from the wafer by soaking in acetone to dissolve the photoresist. This method is a successful procedure often used to produce freestanding films.[14,16,17]

Transmittance measurements on Mg films from 25 to 1300 eV were performed *ex situ* at beamline 6.3.2 at the Advance Light Source synchrotron, at LBNL. The character-

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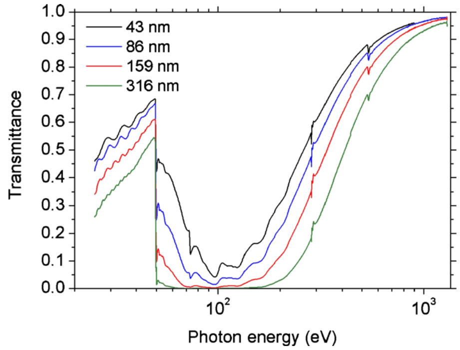

FIG. 1. (Color online) The transmittance vs photon energy (log scale) for four Mg films with different thicknesses.

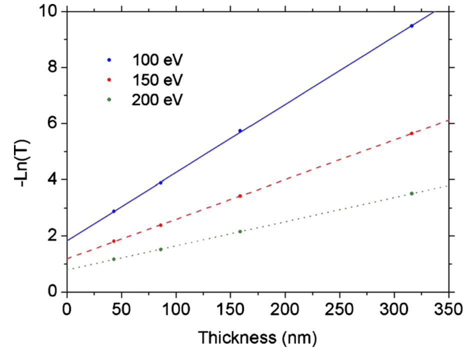

FIG. 2. (Color online) The logarithm of transmittance as a function of Mg film thickness for several photon energies.

istics of the beamline and the measurement chamber have been described elsewhere.[18,19]

Four samples with Mg film thicknesses of 43, 86, 159, and 316 nm were prepared. The deposition rate for Mg was 1.5 nm/s. In order to verify the film thickness, the reflectance versus incidence angle at 48.6 eV was measured on each sample prior to removing the Al/Mg/Al sandwiches from the substrate. Mg film thicknesses were obtained by fitting the Kiessig interference fringes which are produced by the interference of radiation reflected from the top and the bottom of the film.

III. RESULTS AND DISCUSSION

A. Transmittance and extinction coefficient data

Figure 1 shows the transmittance of the Al/Mg/Al sandwiches measured *ex situ* from 25 to 1300 eV. The thickness of each Mg film is indicated. The figure displays the high transmittance below the $L_{2,3}$ absorption edge at 49.8 and 50.1 eV. The oscillations at ~280 eV C *K* edge and 541 eV O *K* edge are attributed to the presence of some hydrocarbon contamination on the sample surfaces. The transmittance of 43-nm-thick Mg layer above 900 eV was found inconsistent with that of the other samples and hence it was discarded. This inconsistence was attributed to the weak flux and noisy measured signal at these higher energies.

If we assume that the contribution to the transmittance coming from multiple reflections inside the film is negligible, the extinction coefficient *k* can be calculated through the following expression:

$$Ln(T) \approx A + \left(-\frac{4\pi k}{\lambda}\right)d, \quad (1)$$

which is a straightforward derivation of the well-known Beer–Lambert law. *d* stands for the Mg film thickness, λ stands for the radiation wavelength, and *A* is a constant assuming that the reflectance variation over the samples is negligible; *A* involves the presence of Al and of a native oxide or hydrocarbon layer on the surface of all the samples.

In Fig. 2 we plot the logarithm of transmittance versus *d* and a fitting with Eq. (1) for some selected photon energies. *k* can be obtained from the slope of each linear fit.

In Fig. 1, all the curves display oscillations between 25 and 50 eV due to the interferences of the multiple reflections at the Al/Mg and Mg/Al interfaces. These oscillations may be transferred to *k* when we follow the above calculation method, resulting in unphysical oscillations at *k*. In order to avoid this, we modified the transmittance data in the following way. For each curve, two polynomial envelopes were constructed: one envelope for the maxima and one envelope for the minima of the oscillations. New transmittance data were generated by averaging the two envelopes for each curve; the generated transmittance data were used in the calculation of *k*.

Figure 3 shows the calculated extinction coefficient in the whole spectral range from 25 to 1300 eV in log-log scale. The absence of any features at the C *K* and O *K* edges indicates that the effects of hydrocarbon contamination on the samples were correctly accounted for by the fitting procedure. The data from literature in the coincident range are also displayed.

Figure 4 shows in more detail the extinction coefficient near the Mg $L_{2,3}$ absorption edge, along with the data of Gullikson *et al.*,[14] Henke *et al.*,[20] Hagemann *et al.*,[13] and Townsend.[9] The data of Henke were calculated with a density of 1.738 g/cm^3.

B. Refractive index calculation with the dispersion relations

The refractive index *n* of Mg was calculated using KK dispersion relations:

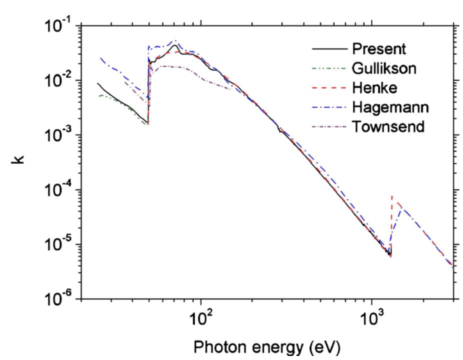

FIG. 3. (Color online) Log-log plot of the extinction coefficient of Mg vs photon energy, along with the data of Gullikson *et al.* (Ref. 14), Henke *et al.* (Ref. 24), Hagemann *et al.* (Ref. 13), and Townsend (Ref. 9).

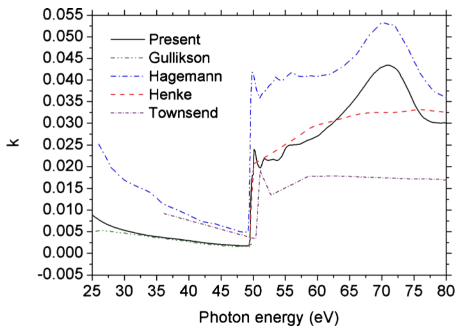

FIG. 4. (Color online) Log-log plot of the extinction coefficient of Mg in the spectral region close to the $L_{2,3}$ absorption edge, represented along with Gullikson *et al.* (Ref. 14), Henke *et al.* (Ref. 20), Hagemann *et al.* (Ref. 13), and Townsend (Ref. 9) data.

$$n(E)-1=\frac{2}{\pi}P\int_0^{\infty}\frac{E'k(E')}{E'^2-E^2}dE', \quad (2)$$

where P is the Cauchy principal value. In order to calculate n though Eq. (2) it is necessary to have a complete set of k data over the whole electromagnetic spectrum. So we extended the present data with the available data in the literature and extrapolations in the following way: Daudé *et al.*[11] k values were used from 6.36 to 8.87 eV. Between 8.89 and 24.63 eV we used the data of Daudé *et al.*[12] The data sets were coupled with a smooth connection. For large energies, Henke data from the center for x-ray optics (CXRO) web page[20] were used. Gesell *et al.*[21] measured the reflectance of evaporated Mg films *in situ* for energies from 2 to 12 eV. They fitted the reflectance measured with a Drude model with the following parameters values: $\lambda_p=118.2$ nm and $\tau_p=1.64\times10^{-15}$ s; in the fit they accounted for the effect of surface roughness on reflectance. We used the Drude model obtained by Gesell *et al.*[21] to perform the extrapolation of k data from 6.3 to 0 eV energy. The extrapolation to infinity was performed by keeping constant the slope of the log-log plot of Henke k data[20] as function of photon energy.

Figure 5 displays the extinction coefficient data that were gathered for the KK analysis.

Figure 6 shows $\delta=1-n$ calculated with Eq. (2) in the 20–1700 eV energy range, along with the data from the literature.

In Fig. 7 $\delta=1-n$ of Mg is plotted in the spectral range close to the $L_{2,3}$ absorption edge. The results are in a reasonable agreement with Henke data, although we found more structure, similar to what was found for k. A larger difference with the data of Hagemann *et al.* is observed.

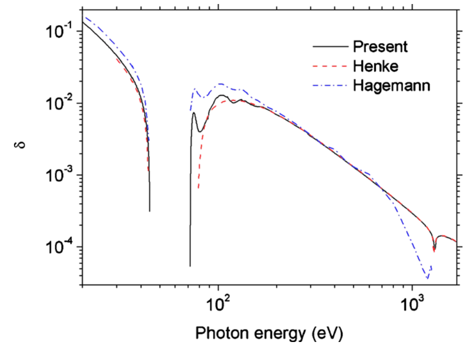

FIG. 6. (Color online) Log-log plot of $\delta=1-n$ in the 20–1700 eV energy range, along with the data of Henke *et al.* (Ref. 20) and Hagemann *et al.* (Ref. 13).

C. Consistency of optical constants

Sum-rule tests provide a guidance to evaluate the accuracy of the optical constants n and k. The f-sum rule relates the number density of electrons to k integrated in the whole energy range. It is useful to define the effective number of electrons contributing to the optical properties up to a given energy as follows:

$$n_{eff}(E)=\frac{4\varepsilon_0 m}{\pi N_{at}e^2h^2}\int_0^E E'k(E')dE', \quad (3)$$

where N_{at} is the atom density, e is the electron charge, ε_0 is the permittivity of vacuum, m is the electron mass, and h is Planck's constant. In the limit of high energies n_{eff} must be equal to the atomic number of Mg, $Z=12$. When the relativistic correction on the scattering factors is taken into account, Z is modified in the following way:[22] $Z^*=Z-\Delta,\Delta\approx(Z/82.5)^{2.37}$. Hence, in the case of the Mg $Z^*=11.99$. The high-energy limit of n_{eff} obtained through Eq. (3) was 11.84, which is about 1.2% smaller than Z^*. The consistency of the set of optical constants gathered by Hagemann[13] was also evaluated and gave a high-energy limit of n_{eff} of 13.58, which is ~12% higher than the Z^* value. This result suggests an improved accuracy of the present data.

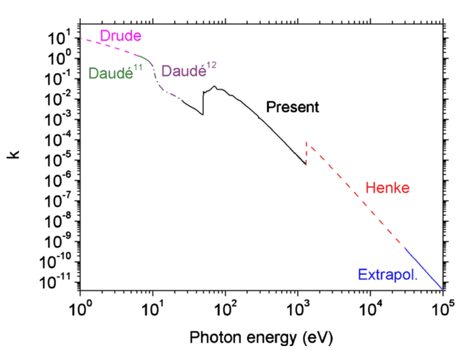

FIG. 5. (Color online) Log-log plot of the extinction coefficient data set used in the KK analysis. The data from Daudé *et al.* (Refs. 11 and 12) and Henke *et al.* (Ref. 20) are also represented.

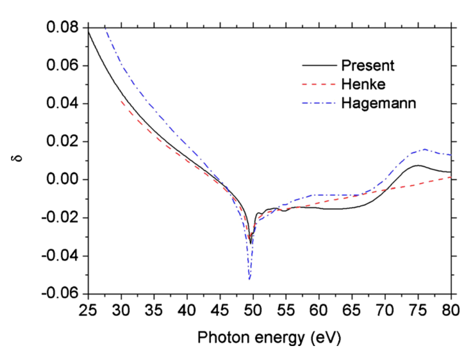

FIG. 7. (Color online) $\delta=1-n$ in the spectral region close to the Mg $L_{2,3}$ edge. The data from Henke *et al.* (Ref. 20) and Hagemann *et al.* (Ref. 13) are also displayed.

Another useful test to evaluate the accuracy of KK analysis is obtained with the inertial sum rule:

$$\int_0^\infty [n(E) - 1] dE = 0, \tag{4}$$

which expresses that the average of the refractive index in all the spectrum is unity. According to Shiles *et al.*,[23] the following parameter is defined to evaluate how close to zero is the integral of Eq. (4):

$$\zeta = \frac{\int_0^\infty [n(E) - 1] dE}{\int_0^\infty |n(E) - 1| dE}. \tag{5}$$

Shiles *et al.*[23] suggest that a good value for ζ, stands within ± 0.005. We obtained through the inertial sum-rule test an evaluation parameter of $\zeta = 0.000\,18$ for the present experimental data. This result, along with the above one on the f sum-rule, suggests that the accuracy of the present experimental and extrapolated data is higher than older data.

IV. CONCLUSIONS

Optical constants of Mg films deposited by dc magnetron sputtering have been obtained from transmittance measurements in the 25–1300 eV photon energy range. The extinction coefficient has been directly calculated from transmittance measurements. Due to the high reactivity of Mg in contact with atmosphere, it was necessary to protect the Mg film with Al protective layers on the two sides. The refractive index was obtained with KK analysis. We checked the consistency of the optical constants with both inertial and f sum rules and very good evaluation parameters were obtained, which suggests a higher accuracy of the present data compared with older data. The new optical constants may allow a more precise design of multilayers involving Mg films, particularly right below the $L_{2,3}$ edge (49.8 eV).

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