Determination of optical constants in DUV/VUV

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An approach for determining the optical constants of the weakly absorbing substrate is developed and applied to obtain the parameters of CaF_2 and fused silica substrates in deep ultraviolet (DUV) and vacuum ultraviolet (VUV) range. A method for extracting the optical constants of thin films deposited on strongly absorbing substrate, which is based on the reflectance spectra measured at different angles of incidence, is also presented. The optical constants are determined by fitting the measured spectra to the theoretical models. The proposed method is applied to determine the refractive index and extinction coefficient (n, k) of MgF_2 film deposited on silicon substrate by electron beam evaporation with substrate temperature 300 °C and deposition rate 0.2 nm/s. The determined n, k values at 193 nm are 1.433 and 9.1×10^{-4}, respectively.

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CaF_2, fused silica, and MgF_2 are optical materials commonly used for optical coatings in precision optical applications owing to their high transparency in deep ultraviolet (DUV) and vacuum ultraviolet (VUV) range. The design and preparation of high quality optical coatings at DUV/VUV spectral range require the accurate determination of the optical constants of the optical materials. In the past, several methods have been developed for the determination of the refractive indices of transparent substrates. Among them a widely used approach is determining the refractive index n_1 of a substrate from the measured transmittance spectrum T via the following formula[1,2]: $n_1 = 1/T + (1/T^2 - 1)^{1/2}$. Practically, this method is valid only for substrates with no or negligible bulk or interfacial absorption. As applications extended to DUV/VUV spectral range, the optical loss (including absorption and scattering losses) of the substrate is no longer negligible and its influence on the optical constant determination has to be taken into consideration.

For the determination of the optical constants of thin film deposited on transparent substrate, the existing methods included spectrophotometry[3], spectroscopic ellipsometry (SE)[4], guided-wave[5], surface plasmon resonance[6], and polarization conversion[7], etc. On the other hand, currently the optical constants of thin film deposited on strongly absorbing substrates were determined mainly from ellipsometric measurements. The determination from spectrophotometric measurements was scare in literature. Up to now, Bridou *et al.*[8] had developed an iso-reflectivity graphic method to determine the optical constants of ZnSe film deposited on aluminum layer under normal incidence. The procedure was tedious as three or more samples with different top layer thicknesses had to be prepared under the same coating process for the (n, k) determination.

In this letter, an approach is developed to determinate the optical constants of the weakly absorbing substrate via a numerical optimization algorithm. Another method for extracting the optical constants of thin film deposited on strongly absorbing substrate, which is based on the reflectance spectra of coating samples measured at different angles of incidence, is also presented in detail. Experimentally, the proposed methods are employed to extract the optical constants of CaF_2 and fused silica substrates as well as a MgF_2 film deposited on a silicon wafer by electron beam evaporation with substrate temperature 300 °C and deposition rate 0.2 nm/s. Very high precision for the optical constant determination is experimentally achieved.

For a weakly absorbing substrate, the transmission and reflection of light is shown in Fig. 1(a). The substrate has thickness t and complex refractive index $\boldsymbol{n}_1 = n_1 - \mathrm{j}k_1$, where n_1 is refractive index and k_1 is the extinction coefficient which can be expressed in terms of the absorbance A, $A = \exp(-4\pi k_1 t/\lambda)$. The refractive index of the surrounding air is assumed to be $n_0 = 1$. When calculating the transmittance and reflectance of the weakly absorbing substrate, all multiple reflections, transmissions, and absorption have to be taken into account. According to incoherent multiple-beam summation, the transmittance T and reflectance R of the substrate can be written as

$$\begin{cases} T = \dfrac{AT_\mathrm{s}^2}{1 - A^2R_\mathrm{s}^2} \\ R = \dfrac{R_\mathrm{s}[1 + A^2(T_\mathrm{s}^2 - R_\mathrm{s}^2)]}{1 - A^2R_\mathrm{s}^2} \end{cases}, \tag{1}$$

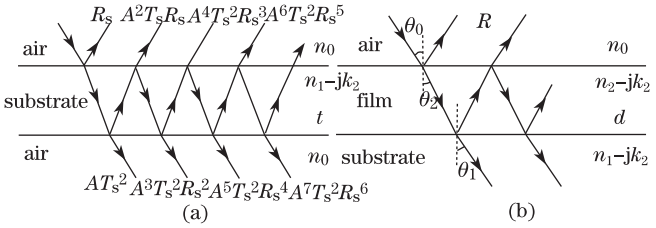

Fig. 1. (a) Transmission and reflection of light by a weakly absorbing substrate; (b) reflection of light by a thin film coated on a strongly absorbing substrate.

where T_s and R_s are the interfacial transmittance and reflectance of the substrate, which can be describes as $T_s = 4n_0n_1/|n_0+n_1-jk_1|^2$ and $R_s = |n_0-n_1+jk_1|^2/|n_0+n_1-jk_1|^2$, respectively. Once T and R are experimentally measured with a spectrophotometer, from Eq. (1) the n_1 and k_1 values can be determined via an iterative procedure.

For a thin film deposited on a strongly absorbing substrate, the reflection of light is shown in Fig. 1(b). With thickness d and complex refractive index $\boldsymbol{n}_2 = n_2 - jk_2$, where k_2 relates to optical loss of thin film (both absorption and scattering), the film can be described by a characteristic matrix[9]

$$\begin{pmatrix} \cos\delta & j\sin\delta/\eta_2 \\ j\eta_2\sin\delta & \cos\delta \end{pmatrix}, \tag{2}$$

where δ is the phase thickness of the thin film given by $\delta = 2\pi(n_2 - jk_2)d\cos\theta_2/\lambda$, and η_2 is the optical admittance. When both p and s polarization states (i.e., polarization of the electric field parallel and perpendicular to the plane of incidence) are taken into account, we have $\eta_{2p} = (n_2 - jk_2)/\cos\theta_2$ for p polarization, and $\eta_{2s} = (n_2 - jk_2)\cos\theta_2$ for s polarization, with θ_2 the angle of incidence inside the film.

Defining parameters B and C with the following formula

$$\begin{bmatrix} B \\ C \end{bmatrix} = \begin{pmatrix} \cos\delta & j\sin\delta/\eta_2 \\ j\eta_2\sin\delta & \cos\delta \end{pmatrix} \begin{bmatrix} 1 \\ \eta_1 \end{bmatrix}, \tag{3}$$

where η_1 is the optical admittance of the substrate for the two polarization states, i.e., $\eta_{1p} = (n_1 - jk_1)/\cos\theta_1$ for p polarization, and $\eta_{1s} = (n_1 - jk_1)\cos\theta_1$ for s polarization, with θ_1 the angle of incidence inside the substrate.

Reflectance for both polarizations is given by

$$R = \left(\frac{\eta_0 B - C}{\eta_0 B + C}\right)\left(\frac{\eta_0 B - C}{\eta_0 B + C}\right)^*, \tag{4}$$

where η_0 is the optical admittance of the entrance medium. That is, $\eta_{0p} = n_0/\cos\theta_0$ for p polarization, and $\eta_{0s} = n_0\cos\theta_0$ for s polarization, θ_0 is the angle of incidence inside the corresponding medium. When θ_0 is known, the incident angles θ_1 and θ_2 can be also determined with Snell's law. Furthermore, if optical constants of substrate n_1 are also given, it is convenient to write the reflectance R as function of $n_2(\lambda)$ and d:

$$R = R(n_2(\lambda), d). \tag{5}$$

Afterward, the optical constants of the thin film can be determined with high precision from the measured reflectance spectra at different angles of incidence.

The samples used for the determination of the optical constants of substrates in DUV/VUV range were CaF_2 (size: Φ25.4×3 (mm), with a root mean square (RMS) roughness 0.3 nm by atomic force microscopy (AFM)) and fused silica (size: Φ25.4×4 (mm), with a RMS roughness 0.5 nm). Before spectral measurements, the samples were cleaned manually with alcohol and acetone, and then irradiated by a commercial ultraviolet (UV) photocleaner for 40 min to remove hydro-carbon contaminations at the substrate surfaces[10].

On the other hand, for the determination of the optical constants of thin film, single-layer MgF_2 film prepared by electron beam evaporation without plasma assistance was used as the sample. In the coating process, the vacuum chamber was pumped down to a base pressure of 3.0×10^{-4} Pa by a cryopump set, the substrate temperature was heated to 300 °C with ceramic heaters, and the deposition rate and physical thickness of the thin films were set to 0.2 nm/s and 200 nm, respectively, as controlled by a quartz crystal monitor. As the starting material, MgF_2 grains (Merck) were used. Conventionally polished silicon wafer (size: Φ25.4×3 (mm), with RMS roughness 0.5 nm) was used as the substrate. The silicon substrate was cleaned manually with alcohol and acetone. Before coating started, the substrate and deposition chamber were pretreated with advance plasma source (APS) for cleaning.

A high-precision DUV/VUV spectrophotometer (VUVaS 2 000, McPherson, USA) operated under vacuum environment (with a pressure $p<1.0\times10^{-2}$ Pa) was used to measure the transmittance and reflectance spectra of CaF_2 and fused silica substrates in the spectral range from 160 to 300 nm. Transmittance measurements were performed at normal incidence and reflectance at incident angle of 10°. Meanwhile, the reflectance spectra of the bare silicon wafer and of the single-layer MgF_2 film deposited on the silicon substrate were measured at incident of 10° and 20°, respectively. In addition, an ultraviolet/visible/infrared (UV/VIS/IR) spectrophotometer (Lambda 1050, Perkin-Elmer, USA) was used to measure the reflectance spectrum of the single-layer MgF_2 film deposited on silicon wafer in the spectral range of 250–500 nm, and a variable angle SE (VASE, J. A. Wollam Co., Inc., USA) was utilized to analyze the native oxide layer of the bare silicon wafer by measuring the reflectance spectra of the bare silicon substrate at incident angles of 65° and 75°, respectively.

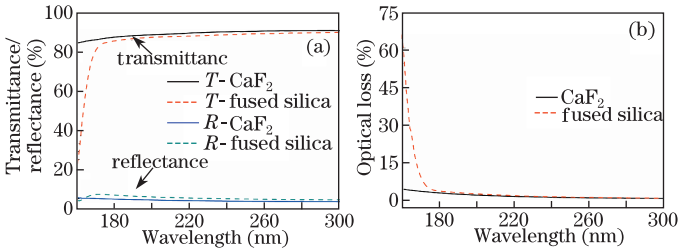

Fig. 2. (Color online) (a) Measured spectra of fused silica and CaF_2 substrates; (b) optical loss of substrates determined from the spectral measurements.

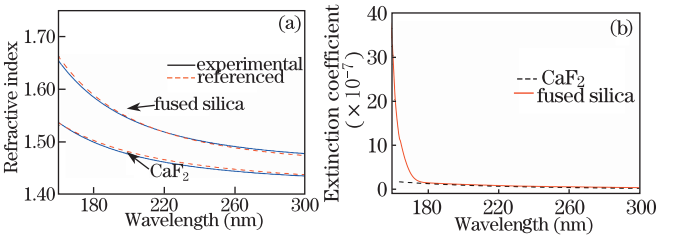

Fig. 3. (Color online) Optical constants of CaF_2 and fused silica substrates. (a) Experimental refractive index (solid lines) and referenced data (dashed lines); (b) experimental extinction coefficient.

Figure 2(a) showed the measured transmittance (T) and reflectance (R) spectra of CaF_2 and fused silica substrates in the spectral range of 160–300 nm. Correspondingly, the optical losses of the substrates, defined as $1 - T - R$, were presented in Fig. 2(b). The optical loss of the 3-mm-thick CaF_2 substrate was approximately 3.6% at 160 nm, and decreased monotonically to approximately 0.1–0.2% at 300 nm. On the other hand, for the 4-mm-thick fused silica substrate, the optical losses at 180 and 300 nm were approximately 2.9% and 0.1–0.2%, respectively. Below 180 nm, the optical loss increased rapidly with the decreasing wavelength. The optical loss of the fused silica substrate was approximately 65.5% at 160 nm.

It is learned from Eq. (1) that, the optical constants of the substrates can be determined once the transmittance/reflectance spectra and the thicknesses of the substrates are known or measured. Unfortunately, the expressions for transmittance and reflectance in Eq. (1) are transcendental equations. That means no explicit expressions for the optical constants (n, k) can be given, and the n, k values cannot be directly calculated. In this case, the optical constants of the substrate can still be calculated via a numerical computation method. In this letter, a least-square minimization based simulated annealing algorithm is used in the calculations. The calculated refractive indices and extinction coefficients of CaF_2 and fused silica substrates are presented in Fig. 3, and corresponding refractive index of CaF_2 and fused silica referenced from other work are also shown in Fig. 3(a)[11]. For both substrates, the difference between the experimental results and the referenced refractive indices is smaller than 0.006. The calculated extinction coefficients are of the same order of magnitude in the spectral range from 180 to 300 nm. Below 180 nm, the extinction coefficient of the fused silica increases rapidly with the decreasing wavelength, in consistent with the measured optical loss as mentioned above.

The reflectance spectrum of the silicon substrate is measured by the high-precision DUV/VUV spectrophotometer at incident angle of 10° before coating process and the measured result is shown in Fig. 4 with a solid line. The dashed line in Fig. 4 represents the theoretical reflectance spectrum with the optical constant values of silicon in Ref. [11] Clearly, below 250 nm there is a significant deviation between the measured and theoretical spectra. This deviation is caused by a native oxide layer formed on the silicon wafer surface. To analyze its influence on the reflectance spectrum of the silicon substrate, the thickness of the native oxide layer is determined by measuring the SE data at incident angles of 65° and 75° in the spectral range of 300 –1 000 nm. By fitting the measured SE data to an optical model consisting of a silicon dioxide layer and a silicon substrate layer, the physical thickness of the native oxide layer is determined to be 2.8 nm.

Figure 5 shows the experimental reflectance spectra of the single-layer MgF_2 film in the spectral ranges from 160 to 230 nm, measured by the DUV/VUV spectrophotometer, and from 250 to 500 nm, measured by the UV/VIS/IR spectrophotometer. The reflectance spectrum measured from 250 to 500 nm is used to determine the physical thickness of the MgF_2 film. As in the spectral range from 250 to 500 nm the extinction coefficient of the MgF_2 film is very small and its influence on the reflectance is negligible, the MgF_2 film is treated as non-absorbing material in the thickness determination. In the reflectance calculation, it is assumed that the refractive index versus the wavelength follows the Cauchy law,

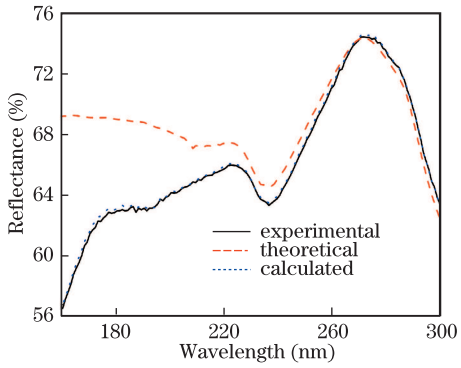

Fig. 4. (Color online) Theoretical, experimental, and fitted reflectance spectra of silicon wafer.

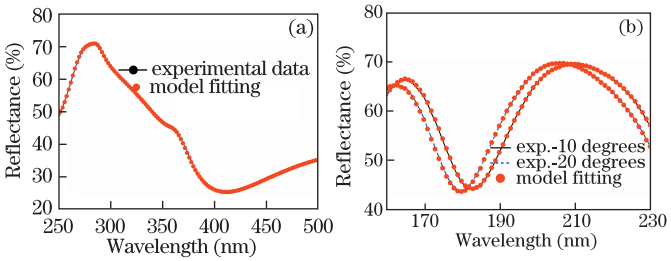

Fig. 5. (Color online) The measured and calculated reflectance spectra of MgF_2 film in the spectral range of (a) 250–500 nm and (b) 160–230 nm.

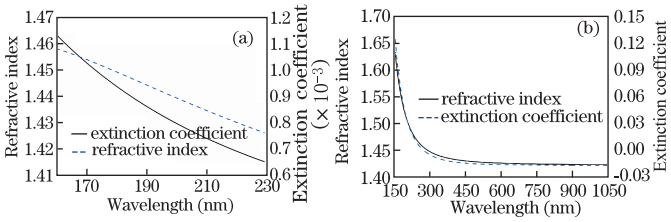

Fig. 6. Optical constants of (a) the MgF_2 film and (b) the native oxide layer determined from the reflectance spectrum measurements.

$$n(\lambda) = A_1 + \frac{A_2}{\lambda^2} + \frac{A_3}{\lambda^4}, \tag{6}$$

where A_1, A_2, and A_3 are the Cauchy parameters. Then the physical thickness of the MgF_2 film is determined by fitting the calculated reflectance to the measured spectra to be 214.4 nm. The corresponding best fit is also presented in Fig. 5(a). Worthy mentioning that the impact of the 2.8-nm-thick native oxide layer on the reflectance calculation and thickness determination is also taken into account.

In DUV/VUV spectral range, significant absorption exists in the coating materials (both MgF_2 film and the native oxide layer). Therefore the influence of the extinction coefficient on the reflectance must be taken into

account. It is assumed that the extinction coefficients of both materials versus wavelength also follow the Cauchy law,

$$k(\lambda) = B_1 + \frac{B_2}{\lambda^2} + \frac{B_3}{\lambda^4}, \quad (7)$$

where B_1, B_2, and B_3 are the Cauchy parameters. To determine the optical constants of the MgF_2 film deposited on silicon substrate, set n, k values of the MgF_2 film and of the native oxide layer as free parameters to minimize a merit function defined as the squared difference between the measured and calculated reflectance spectra of the single layer MgF_2 film sample. In the multi-parameter fitting, the physical thicknesses of the MgF_2 film and of the native oxide layer have been determined previously. The reflectance spectra measured at incident angles of 10° and 20° in DUV/VUV spectral range are fitted to the theoretical reflectance spectra. The measured and the corresponding calculated spectra of the MgF_2 film sample are presented in Fig. 5(b). Clearly, excellent agreement between the measurements and theoretical calculations is obtained.

The fitted optical constants of the MgF_2 film and of the native oxide layer are presented in Fig. 6. The optical constants of both films present significantly dispersion in DUV/VUV spectral range. The refractive index and extinction coefficient of the MgF_2 film at 193 nm are determined to be 1.433 and 9.1×10^{-4}, respectively. On the other hand, once the thickness and extinction coefficient are determined, the influence of the native oxide layer on the reflectance spectrum of the silicon substrate can be calculated and the results are also presented in Fig. 4. As expected, much better agreement between the experimental and calculated reflectance spectra is obtained.

In conclusion, approaches for determining the optical constants of weakly absorbing substrates and of thin films deposited on strongly absorbing substrates in DUV/VUV spectral range are developed. For the bare substrates, the determination is fulfilled by fitting the measured transmittance and reflectance spectra via simulated annealing algorithm. For the thin film samples, on the other hand, the determination is realized by fitting the experimental reflectance spectra measured at different angles of incidence to the corresponding theoretical model. The proposed methods are applied to determine the optical constants of CaF_2 and fused silica substrates in the wavelength range from 160 to 300 nm and the refractive index and extinction coefficient of MgF_2 film deposited on silicon substrate in the spectral range of 160–230 nm. The proposed approaches are expected to find applications in the optical characterization of thin films and optical materials in DUV/VUV spectral range.

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