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Ellipsometric and Spectrophotometric Investigations of Porous Silica Thin Films Produced by Sol–Gel Method

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The work presents the optical properties of porous silica thin films prepared by TEOS sol–gel method. The films were deposited onto glass substrate using dip-coating technique. The spectroscopic ellipsometry measurements have been performed to determine the optical constants of the films. This technique also enabled evaluation of the depolarization for the investigated layers. Additionally, the spectrophotometric measurements of transmittance and reflectance by the use of integrating sphere and reflectance probe have been made with the aim of possible application of the films as antireflective coatings.

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1. Introduction

The sol–gel method is a chemical means of the production of glass and ceramics from liquid phase. This method can be used to produce various materials whereof structure and consequently physical properties can be transformed within a wide range [1]. This is a principal advantage of sol–gel method. The structure of the fabricated material, depending on the applied technological process, can be compact or porous, in which the pore size can vary from a few nanometers to dozens of nanometers. In sol–gel method bulk materials can be produced as well as films on the different substrates [1]. The porous silica films can offer various application in optoelectronics [2–4]. Due to low refractive index, the porous silica layers can be applied in optical systems to reduce the light reflection coefficient [5, 6].

1.1. *Coherent and incoherent scattering in porous films*

Ellipsometry is efficient technique for optical constants and thickness determination. It employs the Fresnel relation in basic formula of ellipsometry. Therefore in ellipsometric analysis only coherent part of reflected radiation is regarded. Although in general intensity of reflected radiation from the real surfaces are a sum of the coherent R_{c} and incoherent R_{i} scattering. These two components R_{c} and R_{i} cannot be separated in single measurement. However, in some experimental studies we may assume that the incoherent component is negligible, thus the specular reflected radiation is nearly coherent. Specular part of scattered radiation is identified with the coherent component. As well, according to coherence theory [7], we may accept the diffuse part of scattered radiation spread uniformly in hemisphere is completely incoherent. If we make some assumption the expression for the total reflection at angle of incidence $\theta_{\mathrm{i}} = 0$ may be shown as following [8]:

$$R_{\mathrm{tot}} = R_0 \exp\left(-\left(\frac{4\pi\sigma}{\lambda}\right)^2\right) + R_0 \frac{(2\pi)^4\sigma^2 T^2}{\lambda^4}\Delta\omega, \quad (1)$$

where first and second components represent specular and diffuse part of scattered radiation. R_0 is the Fresnel reflection coefficient, λ is light wavelength, σ — surface roughness, T — autocorrelation length, $\Delta\omega$ — solid angle of scattered radiation. Also light scattering in a case of thin film or stack of thin films depends on roughness of interfaces, optical inhomogeneities as refractive index variation in the bulk and porosity of layers.

The goal of this work is to present phenomena of coherent and incoherent scattering in porous silica films used as antireflective layers in optical devices observed in ellipsometric and spectrophotometric measurements.

2. Experimental details

2.1. *Sol–gel processing*

In the research presented here, the starting solutions were prepared with the application of the following solutions: tetraethyl orthosilicate (TEOS), water, ethyl alcohol C_2H_5OH (EtOH) and hydrochloric acid as catalyst with the following molar ratios being applied: TEOS:EtOH:H_2O:HCl = 1:4:4:0.02. A non-polar surfactant Triton X-100 (TX) was added to the starting solution in volumetric ratio TX:TEOS = 0.7. After mixing the components, the sol formation was carried out

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for 3 h in a closed glass vessel at temperature 50 °C, using ultrasonic mixing. Then, after cooling up the solutions, they were filtered with the application of syringe filters of the pore size of 0.2 μm. In the research we applied microscopic soda-lime glass substrate plates (Menzel–Glaser) of the dimensions $76 \times 25 \times 1$ mm^3. The substrate glass plates were washed following the procedure which included: mechanical cleaning in water with detergent, rinsing in deionized water, soaking in 5% ammonia water solution, rinsing in deionized water, rinsing in acetone and drying.

The fabricated structures were finally annealed at temperatures 400 °C over 40 min. In annealing processes the final properties of fabricated films are establishing. In the annealing process the removal of solvent remains was taking place as well as the condensation and the collapse of the structure caused by the action of capillary pressure.

2.2. Measurement methods

The complex refractive index and depolarizing ability of the porous silica films have been determined by ellipsometric way [9]. Ellipsometry technique uses the light of known polarization incidenting on the surface under study and detects the polarization state of the reflected light. Incident light is usually linearly polarized and the reflected light has elliptical polarization. Spectroscopic ellipsometry directly determines two angles Ψ and Δ, with

$$\rho = \tan \Psi = \frac{r_p}{r_s} \mathrm{e}^{\mathrm{i}\Delta}, \tag{2}$$

where Ψ represents the angle determined from the amplitude ratio between p- and s-polarizations and Δ is the phase shift between the polarized waves. r_p and r_s are the complex Fresnel reflection coefficients for p- and s-polarizations, respectively. Knowledge of ellipsometric angles allows us to determine dispersion of the refractive index n and the extinction coefficient k of the films.

The studies were carried out in the wavelength range from 190 nm to 1700 nm, with the application of a spectroscopic ellipsometer Wollam M2000 (manufactured by J.A. Wollam Co.). The measurements of refractive indices in ambient conditions have been performed for three angles of incidence, namely: 60°, 65° and 75°. To analyze the data, we have combined all angular spectra and performed the fitting to all the data simultaneously.

Reflectance and transmittance measurements for investigated samples were performed with application of spectrophotometer PC 2000 with an optical fiber waveguide reflection probe R200-7 Ocean Optics and integrating sphere.

3. Results and discussion

In Fig. 1 we show spectral dependence of ellipsometric angles for one chosen angle of incidence, namely $\theta_{\mathrm{i}} = 0$. The dotted line represents fittings obtained from a simple model where the geometry of the sample is assumed as consisting of a substrate (glass) and silica based thin film.

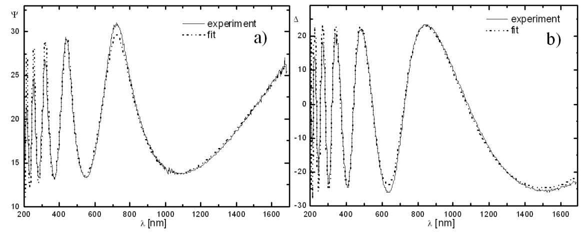

Fig. 1. The spectral dependence of ellipsometric angles.

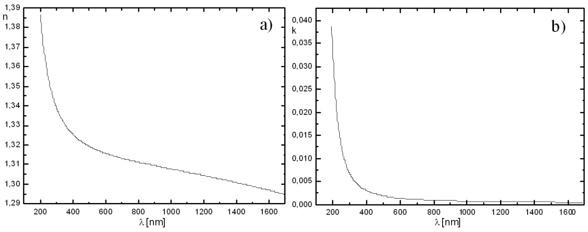

Fig. 2. Optical dispersion of (a) refractive index and (b) extinction coefficient.

As can be seen, the choice of the Sellmeier model [10] very well fits experimental data. In Fig. 2 the spectral dependence of refractive index n and extinction coefficient k have been shown.

Dispersion relations have been obtained from the above mentioned fitting of the Sellmeier model to the ellipsometric data. As one can see, refractive index of the porous silica layer is low (≈ 1.30 for wavelength 633 nm) compared to n of fused silica (1.45). The low value of n of porous SiO$_2$ can be explained by the porosity. Assuming that the pores of this layer are filled up solely with air, their porosity P can be calculated on the basis of the simplified effective medium approximation [11]:

$$\frac{n^2 - 1}{n^2 + 2} = (1 - P) \frac{n_{\mathrm{d}}^2 - 1}{n_{\mathrm{d}}^2 + 2}, \tag{3}$$

where n_{d} is the refractive index of dense silica, $n_{\mathrm{d}} \approx 1.4585$. It is easy to calculate that the porosity of presented layer is about 32%. In Fig. 3 we illustrated refractive index as a function of porosity obtained from formula (3).

The dependence shown in Fig. 3 is particularly important in projection of antireflective layers for common optical glass devices.

Namely, if we take into account the well known expression for the antireflective coatings, the best antireflective properties exhibit the layers with refractive index $n_{\mathrm{coating}} = \sqrt{n_{\mathrm{substrate}}}$. For most glasses ($n = 1.52$) a coating with refractive index of 1.23 is required. It is clear that the porous silica layer with high value of porosity could fulfill this condition.

Light scattering in forward direction does not influence on wavefront and also does not change its polarization state. So well transmission measured with the use of

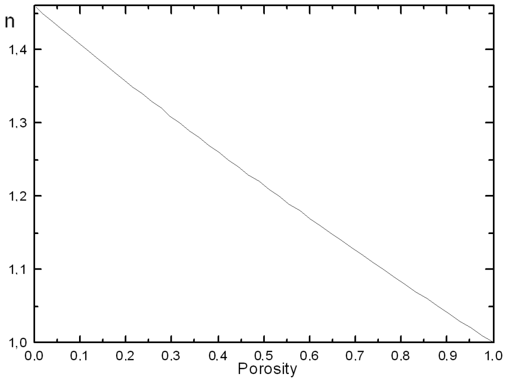

Fig. 3. Refractive index as a function of porosity obtained from formula (3).

ellipsometer with fixed polarization should give the same results as measured with the use of spectrophotometer employing depolarized light. It may be concluded from Fig. 4 which presents transmission spectra obtained by M2000 ellipsometer and PC 2000 spectrophotometer.

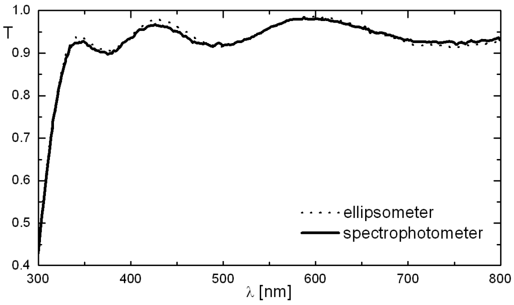

Fig. 4. Transmission spectra of porous SiO_2 film measured by the means of M2000 ellipsometer and PC 2000 spectrophotometer.

In Fig. 5 we present the spectral dependence of specular reflection coefficient for incidence angle $\theta_{\mathrm{i}} = 0$ determined from reflection probe measurements and calculated from the Fresnel equation for one layer on glass optical system. In equation we used thickness d and optical constants n and k calculated from fitting these parameters of film optical model to ellipsometric data.

As it is easy to notice, the reflectance obtained from reflection probe measurements and calculated from the Fresnel formula are nearly the same. That is study of specularly reflected radiation measuring reflected beam intensity or its polarization state should give the same Fresnel parameters if film roughness is reasonably small. Then first component of sum in (1) describing specular and coherent part of scattered light approach to R_0. This condition for our films is fulfilled because roughness found from atomic force microscopy (AFM) studies give values less than 1 nm.

There was mentioned already in introduction that the porous silica layer are applied as antireflective ARC coatings on glass optical devices therefore such important factor as total reflectance on porous SiO_2 films were done.

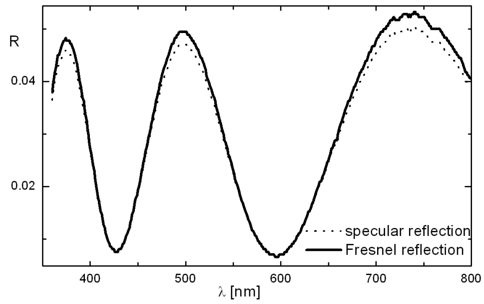

Fig. 5. Reflection from porous SiO_2 film on the Menzel glass substrate (solid line — theoretical Fresnel reflection coefficient, dotted line — measured data).

The total reflectance measurements were performed by the means of integrating sphere ISFP-REF [12]. In Fig. 6 there is shown the total, specular and diffuse reflectance on 587 nm thick porous SiO_2 film.

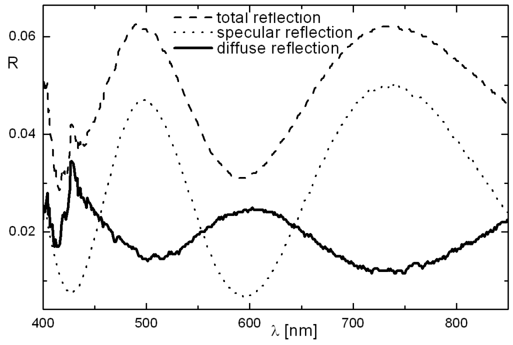

Fig. 6. Total, specular and diffuse reflectance determined from integrating sphere measurements.

Diffuse reflectance is equal to difference between total and specular component. As may be noticed, contribution of diffuse part to total reflectance is relatively large. Diffuse scattering is not produced by roughness which is very small.

So well we added to analysis of ellipsometric and reflectometric results the depolarization. Figure 7 shows depolarization coefficients for light reflected from 587 nm thick porous silica film on soda-lime glass substrate.

Presence of depolarization in light reflected from porous SiO_2 films (Fig. 7) may partly result from anisotropy arising from columnar-like spatial distribution of pores upon the normal to the film axis and due to nonuniformity of pore size in volume of films [11]. The visible extrema in spectral dependence of depolarization coefficient are related with interference phenomena in a film. Depolarization is effect of appearing of incoherent light component in specular reflectance. Therefore one must be careful because optical constants found by the use of ellipsometry are determined from coherent part of

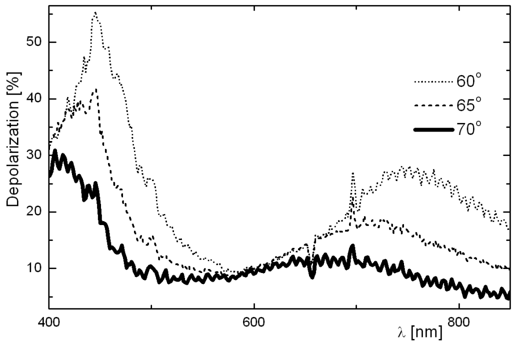

Fig. 7. Depolarization of reflected beam from porous SiO_2 film for incidence angle 60°, 65° and 70°.

reflected light only (the Fresnel assumptions).

For deeper analysis of the refractive index the optical inhomogeneity should be assumed particularly for porous SiO_2 layer with thickness less than 100 nm and for more than 1000 nm films. Although the porous SiO_2 films have very useful properties as ARC, there are still many problems to solve in order to apply them as efficient glass covers.

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