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Studies of optical anisotropy in opals by normal incidence ellipsometry

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ABSTRACT

Anisotropy of thin opal films was studied by ellipsometric technique in a visible spectral range. At normal light incidence, the ellipsometric data were directly related to anisotropy parameters measured by polarization modulation technique. In the (111)-oriented thin films, the optical anisotropy was mainly caused by internal strain-induced birefringence with anisotropy axes oriented along [110] and [-112] directions. The deviation from 180°-symmetry, which has been observed for ellipsometric parameters in the in-plane sample rotation experiments at normal incidence, was enhanced at oblique incidence and assigned to particular properties of opal. Experimental data were discussed in the model of stacked anisotropic layers.

1. Introduction

Study of anisotropic and complex media is one of the topics in modern spectroscopic ellipsometry [1]. In general case, the optical anisotropy results in appearance of the off-diagonal elements in reflection/transmission matrix [2]. Several solutions of this problem are used. A conventional method to determine the optical constants of crystals is to perform the measurements under symmetric configurations [2], at which the off-diagonal components in reflection matrix vanish. Using this method, the components of dielectric function tensor in a series of crystals of symmetry not lower than orthorhombic were determined [3–5] by spectroscopic ellipsometry technique.

Extension of spectroscopic ellipsometry to generalized ellipsometry [6] allowed one to determine the elements of the optical Jones reflection (or transmission) matrix or all components of the Mueller matrix (see, e.g., [7]). The experiments have been performed for arbitrary oriented anisotropic and homogeneous layered structures [8–10].

In generalized ellipsometry a particular attention is paid to the studies of in-plane sample rotation, which shows anisotropic nature of the dielectric response [11,12]. It was found [13] that Mueller matrix elements are to be defined over a full turn in azimuth-resolved measurements in order to characterize completely the optical properties of highly anisotropic structures. The generalized ellipsometry parameters related to the ratios of elements in the Jones reflection matrix clearly demonstrate the optical anisotropy in the in-plane sample rotation experiments [9,14].

Recently, spectroscopic ellipsometry technique was applied for investigations of new structures, e.g., the system of Si nanorods [15] and thin monoclinic films composed of slanted titanium nanocolumns [13]. Ellipsometric investigations of photonic crystals are to be particularly noticed. The two-dimensional photonic crystals composed of dissymetric metal-coated oxide submicrospheres were studied [16] by ellipsometric technique in transmission mode. The azimuthal rotation of the sample revealed the birefringent and dichroic bands originated from the formation of oriented phases in the 2D crystal. All the components of Mueller matrix were determined by variable-angle ellipsometry and by in-plane sample rotations. The studies of the polarization state in the specular beam were shown to be a useful tool for a characterization of the band gaps in photonic crystals.

The optics of opals, 3D photonic crystals composed of SiO_2 spheres regularly arranged in the cubic structure of the *fcc* symmetry, was widely studied. The main features of ellipsometric spectra of photonic crystals were well understood [17,18] in the model of stacked layers of different refractive index. However, a weak optical anisotropy was observed in synthetic opals due to the symmetry of the photonic bands [19] and the strain, which has been induced during a growth process [20,21]. The optical anisotropy of opals was indicated in diffraction [22] and in the azimuth-resolved transmission spectra, which have shown a rotational symmetry at oblique [23] and normal [24] light incidence.

In this work the optical anisotropy of (111)-oriented thin films of synthetic opals was studied by normal incidence ellipsometry in the region of the stop band which occurred due to the Bragg diffraction. In

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the sample in-plane rotation experiments, the azimuth dependence of ellipsometric parameters in transmission was measured and analyzed. The mechanisms of the observed effect were discussed.

2. Experimental

Thin films of synthetic opals deposited on glass/quartz substrates were investigated. The films composed of ~15 layers of SiO_2 spheres (∅ 250–280 nm for samples of different series) were grown from suspension of SiO_2 particles. Self-assembly of SiO_2 spheres were produced by using the vertical deposition method [25].

The ellipsometric measurements have been carried out in polarizer-sample-analyzer (PSA) configuration in the spectral range of 400–700 nm by means of photometric ellipsometer with rotating analyzer. A standard system composed of light source (100-W halogen lamp), chopper (300 Hz), monochromator (SPM 2, f 0.4 m), Glan prisms, photomultiplier (Hamamatsu H7732) and lock-in amplifier (Unipan 232B) was used. The experiment was controlled by means of CAMAC system units.

At polarizer azimuth $P = 45°$, the light intensity measured by a detector is as follows [26]:

$$I = I_o(1 - \cos 2\Psi \cos 2A + \sin 2\Psi \cos\Delta \sin 2A), \qquad (1)$$

where Ψ, Δ are the ellipsometric parameters and A is the analyzer azimuth. The detector signal was measured at constant wavelength as a function of analyzer azimuth, which has been scanned with a constant step from the range of 0.5–3.0°. The Ψ- and Δ-values were determined by fitting Eq. (1) to the experimental data. In the in-plane sample rotation experiments, the spectra of ellipsometric parameters were measured at fixed sample azimuth values. Then, at constant wavelength, the Ψ- and Δ-values were determined as a function of sample azimuth. The test measurements with isotropic Si wafer have shown that the accuracy in determination of ellipsometric parameters Ψ and Δ was better than 0.001 rad.

Experimental Ψ, Δ data were compared to the calculations in the opal model of stacked homogeneous anisotropic layers [17,18]. In terms of generalized ellipsometry, the complex reflection ratio ρ is [7]

$$\rho = \frac{R_{pp} + R_{sp}\chi^{-1}}{1 + R_{pp}R_{ps}\chi} \equiv \tan\Psi \exp(i\Delta), \qquad (2)$$

where R_{ij} is the ratio of the correspondent components in the Jones reflection matrix and χ is the ratio of the incident wave amplitudes $\chi = A_p/A_s$. The optical response of the multilayer structure was calculated by a transfer-matrix technique modeling the propagation of the electromagnetic wave by introduction a 2D vector for electric and magnetic fields and taking into account the boundary conditions [27].

3. Results and discussion

Ellipsometric investigations have shown that the spectra of ellipsometric parameters for thin opal films correlate with those of anisotropic parameters determined directly by polarization modulation technique [24]. Fig. 1 illustrates this correspondence presenting, on the one hand, the spectra of ellipsometric parameters Ψ and Δ, and on the other hand, the spectra of linear dichroism (LD), *i.e.*, the difference between the absorption coefficients $\Delta K_L d$ for light polarized with respect to anisotropic axis, and linear birefringence (LB) defined as the phase difference ΔΦ induced by the sample of thickness *d*. In these measurements, the optical response of the samples was analyzed in transmission mode at normal light incidence. A particular spectral feature of dissipative lineshape for Ψ(λ) and dispersive lineshape for Δ(λ) has been observed at the opal photonic crystal stop band, which manifests itself as transmission dip and reflection peak (at ~525 nm for sample GV2L121 in Fig. 1). In Fig. 1a, the inset shows the sketch of opal lattice in the in-plane sample rotation experiment.

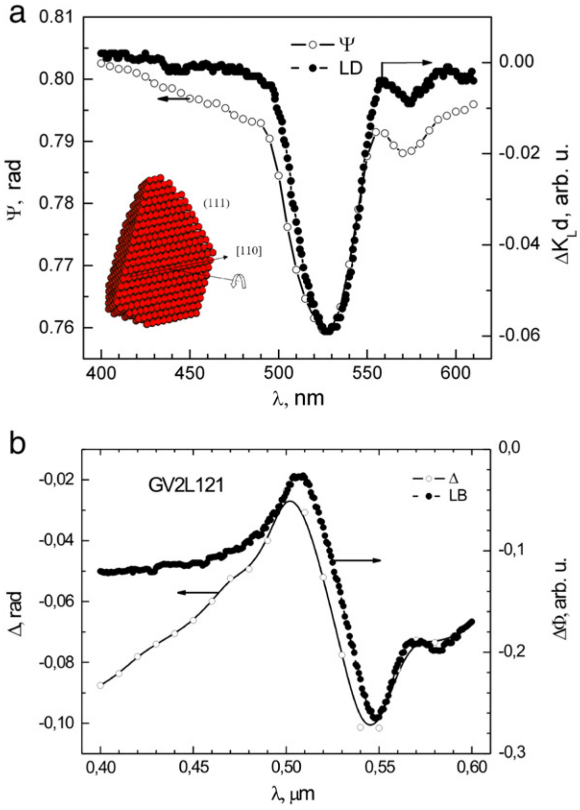

Fig. 1. Spectral dependence of ellipsometric parameters Ψ (a) and Δ (b) as compared to linear dichroism (LD) $\Delta K_L d$ and the phase difference ΔΦ related to linear birefringence (LB) determined in transmission mode at normal incidence for opal thin film (sample GV2L121). In (a) the inset shows the sketch of opal lattice in the in-plane sample rotation experiment. In (b) the curves (spline functions) are guides for eye.

The ellipsometric measurements have confirmed that opal thin films do possess a small optical anisotropy with birefringence of order 4×10^{-3} with anisotropy axis oriented along [110] and [−112] directions. The anisotropy axes were indicated by in-plane sample rotation experiment and correlated to structural AFM data. Fig. 2 illustrates the data obtained from in-plane sample rotation experiments at light incidence normal to (111)-oriented opal thin film. The azimuth dependences of ellipsometric parameters were analyzed by a series of harmonics as

$$\xi(\varphi) = \sum_m a_m^{\xi} \cos(m\varphi), \qquad (3)$$

where $\xi = \Psi,\ \Delta$. The second harmonic ($m = 2$) is dominating whereas the contribution of other terms in Eq. (3) is of order 10%.

As seen from Fig. 2, the azimuth dependences are wavelength dependent. In the spectra of harmonic amplitudes (Fig. 3), particular features are observed in the region of the photonic stop band (at 525 nm for sample Q5). The spectral dependences of amplitudes for dominating harmonic a_2^{Ψ}, a_2^{Δ} correspond to those (Fig. 1) for Ψ(λ) and Δ(λ), respectively, as the 2nd harmonic represents the 180°-anisotropy due to linear birefringence determining the main contribution to optical anisotropy of artificial opals. It should be emphasized that the spectra of a_2^{Ψ}, a_2^{Δ} and a_3^{Ψ}, a_3^{Δ} are correlated indicating that both are related to the particular feature of photonic crystal.