

# Nanocrystallization of Single Crystal Opal Films and the Spectral Characteristic of Related Photonic Structures

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The prospects for using thin single crystal films of opal structures consisting of monodisperse spherical silica particles (MSSPs) in microphotonic devices make it necessary to investigate comprehensively their single crystal growth mechanism. The fact that the growth of such films involves interaction between MSSPs and the nanocrystallization process has not been discussed in the literature, the investigations were mainly empirical [1–5], and the appearance of regular structures was explained merely by their self-assembling. Meanwhile, it is impossible to obtain high-quality single crystal opal films without a clear notion of the essence of phenomena occurring during their growth.

Coagulation-resistant nanosize MSSP suspensions are obtained by the hydrolysis of tetraethoxysilane ( $\text{Si}[\text{OC}_2\text{H}_5]_4$ ) in an alcohol solution in the presence of ammonia [6] playing the role of the process catalyst and, then, of an electrolyte, which is a potential-forming and suspension-stabilizing factor. In the suspension, negatively charged MSSPs are surrounded with a double diffusion layer of  $\text{NH}_4^+$  counterions with a thickness  $\tau$  and form with this layer a structural unit (SU) for nanocrystallization [7–9]. The value of  $\tau$  depends on the total electrolyte concentration in the suspension expressed through the Debye parameter  $\chi$  as  $\tau = \frac{1}{\chi}$ .<sup>1</sup> In turn, the ratio between the MSSP radius  $r$

and  $\tau$  is a key parameter of the particle interaction and nanocrystallization (this ratio is more conveniently expressed as the product  $\chi r$ ).

The DLVO (Deryagin, Landau, Verwey, and Overbeek) theory considers the pair interaction energy of negatively charged MSSPs in a suspension. During volume spontaneous nanocrystallization in a concentrated suspension under constrained conditions, there are the molecular attraction  $U_m$  of particles and the electrostatic repulsion  $U_i$  of their counterion atmospheres. Differentiating the energies  $U_m$  and  $U_i$  with respect to a distance  $H$  between MSSPs in the suspension or in the growing nanocrystal, we can pass to counteracting molecular and ion forces  $P_m$  and  $P_i$ , respectively:

$$P_m = \frac{Ar}{12H^2}, \quad (1)$$

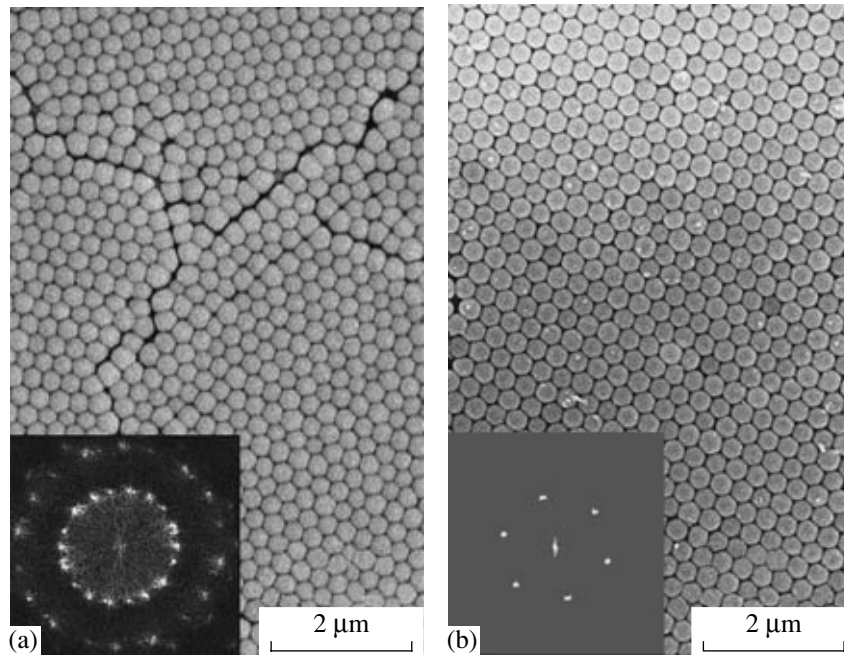
$$P_i = \frac{\varepsilon\phi_0^2 r \chi e^{-\chi H}}{2(1 + e^{\chi H})}, \quad (2)$$

where  $A$  is the Hamaker constant,  $\varepsilon$  is the permittivity of the dispersion medium (water, ethyl alcohol, diethyl ether, acetone, etc.), and  $\phi_0$  is the surface potential [9].

The sum of counteracting forces between particles in equilibrium growing crystal should be equal to zero [10, 11]. Under the conditions of spontaneous crystallization from a concentrated suspension under constrained conditions, nanocrystals are a result of the balance of forces acting between SUs:  $P_m$ ,  $P_i$ , and gravitational forces  $P_g$  as an equivalent of  $P_m$  [9]. In freshly prepared alkaline stabilized  $\text{NH}_4\text{OH}$  (pH 9.5–10,  $\chi r \gg 1$ ) suspensions,  $P_i > P_m$  during crystallization under constrained conditions, and an additional force  $P_g$  ( $P_i = P_m + P_g$ ) is necessary to provide for the balance of forces. The situation is different when growing thin-film nanocrystals.

A mechanism realized in the most promising method of growing thin-film structures, which is close

<sup>1</sup> The Debye parameter is defined as  $\chi = \left(\frac{8\pi e^2 z^2 n}{\varepsilon kT}\right)^{1/2}$ , where  $e$  is the elementary charge,  $z$  is the counterion valence,  $n$  is the ion concentration, and  $\varepsilon$  is the permittivity of a dispersion medium.



**Fig. 1.** SEM images of (a) an opal film surface with a domain structure grown for  $P_i > P_m$ ,  $\chi r \leq 1$ , and (b) single crystal opal film grown for  $P_i \approx P_m$ ,  $\chi r \gg 1$ . The insets show the results of two-dimensional discrete Fourier transform of the images, demonstrating the degree of ordering of the structure.

to the methods described in [1–4], was considered recently in [12]. The main idea is that the film grows in the vicinity of a meniscus in the dispersion medium (ethyl alcohol, water, diethyl ether, or acetone), but the formation of a regular structure is also the result of nanocrystallization. This method rules out the manifestation of  $P_g$  forces, so that only the surface tension of the dispersion medium acts as a macroscopic force with respect to the particle interaction forces, which provides the constrained conditions necessary for the nanocrystallization process. If nonequilibrium nanocrystallization ( $P_i \gg P_m$ ) proceeds on a flat substrate, the result can be a fragmentary character of crystallization and the polycrystalline structure of the film (Fig. 1a) instead of the desired single-crystalline structure. Therefore, to ensure the high quality of a thin-film photonic crystal, it is necessary, first of all, to reduce the particle interaction forces in the suspension to a state close to equilibrium ( $P_i \approx P_m$ ). This problem has been formulated and solved for the first time.

Previously, we investigated the MSSP sedimentation rate and the spontaneous nanocrystallization rate depending on a decreasing concentration of the potential-forming  $\text{NH}_4\text{OH}$  electrolyte [13], which was removed from the suspension until reaching the neutral state using an ion-exchange resin. In this case, the value of  $\tau$  considerably increases ( $\chi r \approx 1$  or  $< 1$ ). Nevertheless, the magnitude of  $P_i$ , which is dependent on the surface potential  $\phi_0$ , exceeds  $P_m$  more than 20 times.

These conditions cannot be considered as ideal for growing films.

At the partial deionization and subsequent neutralization of the freshly prepared alkaline ( $\text{pH} \approx 10$ ) MSSP suspension with an HCl solution and the replacement of  $\text{OH}^-$  groups by  $\text{Cl}^-$ , the total counterion concentration remains high while  $\tau$  is small (i.e.,  $\chi r \gg 1$ ). However, because the new  $\text{NH}_4\text{Cl}$  electrolyte is indifferent rather than potential forming, the particle charge  $\theta$  decreases and, accordingly, the surface potential  $\phi_0$  decreases

(since  $\phi_0 = \frac{\theta}{\epsilon r(1 + \chi r)}$ ) [14] down to a value of about

50 mV (at  $\text{pH} 4\text{--}4.5$ ). Then, according to Eq. (1), the magnitude of  $P_i$  decreases to approach  $P_m$ . This state is close to equilibrium and favors the nanocrystallization of MSSPs in the meniscus region with the formation of a homogeneous film structure that has a long-range order and is free of domains. The uniformity of stacking of the MSSP rows (single crystal structure) is maintained over a large film area (Fig. 1b). The above considerations refer to the direct interaction of particles at small distances of about  $2r$  when the MSSPs approach each other at these distances in the region of nanocrystallization.

A serious problem in growing single crystal opal films is related to cracks, which appear when the thin-film nanocrystals are drying and the structure is compressed under the action of capillary forces. This “shrinkage” is proportional to the initial distance

between MSSPs in a nanocrystal, which is equal to  $\sim 2\tau$ . Therefore, the smaller  $\tau$ , the lower the probability of cracking; hence, the best growth conditions correspond to  $\chi r \gg 1$ , which takes place either in a strongly alkaline region or in the acid region with  $\text{pH} \sim 4\text{--}5$ .

In view of the aforesaid, nanocrystalline opal films grown on a flat substrate are transparent, have a brilliant “varnish” appearance, and cause a bright homogeneous diffraction of incident light. Their thickness can be controlled from 0.5 to 2–8  $\mu\text{m}$  (from 2–3 to 10–15 MSSP layers) by varying the MSSP concentration in the suspension. Such a film represents a single crystal over the entire area, which is corroborated by scanning electron microscopy (SEM) examination. The MSSPs in the film are stacked in hexagonal close-packed layers corresponding to the [111] plane of the face-centered cubic lattice (fcc) and are parallel to the substrate surface. The film surface area reaches 1–2  $\text{cm}^2$ .

The inset to Fig. 1b shows the results of the two-dimensional discrete Fourier transform

$$F(k_x, k_y) = \sum_{x=0}^{x_{\max}} \sum_{y=0}^{y_{\max}} f(x, y) \exp\left[-2\pi i \left(\frac{k_x x}{x_{\max}} + \frac{k_y y}{y_{\max}}\right)\right]$$

for a SEM image of a  $40 \times 40\text{-}\mu\text{m}$  surface area of a single crystal opal film. Here, zero values of the  $k$  modulus are attained at the center of the Fourier image. This pattern shows a strictly ordered hexagonal structure of the film. At the same time, the Fourier transform of an image of the same area of a film obtained under non-equilibrium nanocrystallization conditions shows the presence of domains with hexagonal and cubic packing (see inset in Fig. 1a). The major fraction of particles in 10–30  $\mu\text{m}$  domains is packed in the hexagonal structure, while cubic packing appears at the boundaries of domains. Differences in the orientation of domains, their structure, and minor alterations in the periodicity lead to the appearance of many axisymmetric maxima and overtones in the Fourier image, and the “background” appears because of the presence of film defects in the form of cracks.

The spectral dependences of the transmission and reflection coefficients measured at various incidence angles  $\psi$  for various polarizations of light can provide information about the degree of crystallinity of a film. In our case, the film surface area amounted to  $\sim 3\text{ mm}^2$ , and the incident monochromatic light beam had a divergence of  $\sim 2^\circ$ . Experiments showed that the depth of a minimum in the transmission spectrum near the diffraction resonance (stop band), as well as the value of the reflection coefficient, increase with the size of single-crystalline domains for the same film thickness. Therewith, the degree of long-range correlation of the crystal structure of domains increases.

Figure 2 shows the transmission and reflection spectra of a single crystal opal film measured at an incidence angle of  $\psi = 5^\circ$  for the  $s$ -polarization of light. The

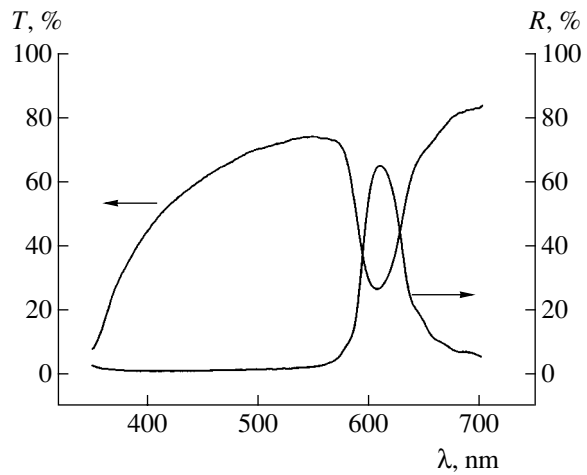


Fig. 2. Transmission ( $T$ ) and reflection ( $R$ ) spectra of a single crystal opal film measured at an incidence angle of  $5^\circ$  for the  $s$  polarization. The film thickness is 2  $\mu\text{m}$ .

presence of an ordered structure results in a high reflection coefficient ( $\sim 70\%$ ) and a low transmission coefficient ( $\sim 30\%$ ) at the center of the stop band with the wavelength  $\lambda_B$ . Measured in the reflection spectrum, the relative width of the stop band (full width at half

maximum) amounts to  $\frac{\Delta\lambda}{\lambda_B} = 6.2\%$ , which agrees well

with the value of 6.3% calculated for the diffraction on the [111] planes of the opal fcc lattice [15]. Determined from the measured position of the stopband, which is given by the Bragg condition

$$\lambda_B = 2d_{[111]}\sqrt{n_{\text{eff}}^2 - \sin^2\psi}$$

(where  $d_{[111]}$  is the distance between the [111] planes,  $n_{\text{eff}}^2 = fn_{\text{SiO}_2}^2 + (1-f)n_{\text{Air}}^2$  is the effective refractive index,  $f = 0.74$  is the filling factor, and  $n_{\text{SiO}_2} = 1.46$  and  $n_{\text{Air}} = 1.0$  are the refractive indices of MSSP and air, respectively), the lattice parameter proved to be  $d_{[111]} = 229\text{ nm}$ , which agrees with the MSSP size of  $2r = \frac{d_{[111]}}{0.816} = 280\text{ nm}$  determined from the electron-microscopic data. The calculated effective refractive index  $n_{\text{eff}} = 1.356$  agrees well with the measured Brewster angle  $\psi_B$  for the  $p$  polarization ( $\psi_B = 53.6^\circ$ ).

Thus, correct allowance for the mechanisms of the photonic crystal film growth in the vicinity of the meniscus in the dispersion medium leads to the formation of a regular structure, which is the result of a nanocrystallization process. Using this method, it is possible to grow single crystal opal films of a desirable size on a flat substrate, which opens to investigations into the optical effects characteristic of three-dimensional photonic structures and the creation of device structures with the preset functionality.

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