$(2+1)$-dimensional photonic crystals from Langmuir-Blodgett colloidal multilayers

S. G. Romanov, M. Bardosova, M. Pemble, and C. M. Sotomayor Torres

Citation: Appl. Phys. Lett. **89**, 043105 (2006); doi: 10.1063/1.2234568
View online: http://dx.doi.org/10.1063/1.2234568
View Table of Contents: http://aip.scitation.org/toc/apl/89/4
Published by the American Institute of Physics

(2+1)-dimensional photonic crystals from Langmuir-Blodgett colloidal multilayers

S. G. Romanov,[a] M. Bardosova, M. Pemble, and C. M. Sotomayor Torres
Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland

(Received 19 April 2006; accepted 19 June 2006; published online 24 July 2006)

Angle-resolved transmission spectra of multilayers of two-dimensional colloidal crystals prepared by the Langmuir-Blodgett technique have been studied. In contrast to the light diffraction in three-dimensional colloidal crystals, optical spectra revealed only very weak correlation between layers in the Langmuir-Blodgett multilayers. Two reasons for the observed transmission minima have been identified: the diffraction at a stack of layers and the scattering of the incident beam by guided modes of the two-dimensional colloidal crystals. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2234568]

Colloidal crystallization represents a convenient approach to prepare templates for three-dimensional (3D) photonic crystals (PhCs).[1] The major drawback of this method is the inflexibility of the self-assembly, which generally results in the crystallization of opals with face-centered cubic (fcc) lattices of spheres. Because the fcc lattice is not the most efficient configuration for opening the PBG, the recent trend is to build up the colloid-based architectures in more deterministic way, for example, to control the growth direction,[2] the crystal size,[3] the free volume,[4] and the crystal symmetry.[5] The Langmuir-Blodgett (LB) method realizes such control at the level of assembling two-dimensional (2D) colloidal crystals and depositing them in a one-dimensional (1D) stack.[6] Advantages, such as control over the formation of individual 2D lattices and the precision in counting the number of 2D layers, are counterbalanced in LB packages by the lack of forces, which can provide lateral alignment of 2D crystals in the 1D stack.

Thus far, optical spectra of LB colloidal multilayers were studied from the point of view of similarity to opals.[6–8] The reported optical studies of LB multilayers dealt with wavelengths, which are larger than the sphere diameter by a factor of 2. Moreover, no spectroscopic evidence has been demonstrated to prove the formation of a 3D lattice in LB multilayers.[9] On the other hand, optical spectra of 2D hexagonal sphere crystals were studied only at wavelengths shorter than the sphere diameter,[10,11] i.e., in the range of their 2D PBG.

In this letter we report a study of optical transmission of colloidal mono- and multilayers prepared by the LB technique across a wide spectral range and demonstrate the coexistence of transmission minima from the 2D sphere grating and the 1D stack of sphere layers. This observation allows us to consider LB multilayers as (2+1)-dimensional [(2+1)D] PhCs and pin down their unique optical properties.

Silica spheres of 519 nm in diameter from Microparticles GmbH were hydrophobized using 3-(trimethoxysilyl)propyl methacrylate and then they were deposited on a glass substrate using a LB technique from doubly distilled de-ionized water subphase.[12] A low barrier speed of 6 cm^2/min and pressure of 4 mN/m were used for the monolayer compression. LB monolayers of spheres crystallize in a hexagonal lattice.[7] Subsequent layers were deposited after drying the deposited ones. Monolayer (1L) and up to ten-layer (10L) films were prepared.

Angle-resolved transmission spectra were acquired at different angles of incidence θ from 0 to 80° with respect to the film normal. The collimated light beam of 1 mm in diameter from a tungsten halogen lamp was delivered through a prism polarizer to study the polarization anisotropy. The transmitted light was collected from a solid angle of 2°. A quarter-wavelength plate was used to transform the linearly polarized transmitted signal into circularly polarized light.

Figure 1(a) shows transmission spectra of 1L and 10L films in *s*-polarized light at $\theta=0$ and 70°. Along the normal to the film these spectra demonstrate similar structure showing the minima centered at 545 and 1096 nm and accompanied by Fabry-Pérot oscillations. At 70° the similarity between the spectra is lost because the 1L film shows a maximum at 542 nm and Fabry-Pérot minimum at 750 nm, whereas the 10L film shows the spectrum with minima at 718 and 919 nm and several Fabry-Pérot oscillations.

With increasing number of layers N, the central wavelength of the 545 nm minimum remains at the same position [Fig. 1(b)] and the relative attenuation at the minimum, $\Delta I/I_0$, which is the ratio of the attenuation ΔI to the extrapolated undisturbed transmission I_0, increases [Fig. 1(b), inset]. Being normalized to the number of layers, the specific attenuation reduces nearly linearly with the number of layers.

The transmission of 1L and 10L samples at wavelengths comparable to the sphere diameters is similar (Fig. 2). The difference in this range is the threefold lower transmission background for the latter, which can be attributed to the result of stronger diffuse light scattering in multilayers.

Considering in the wide spectral and angular range, the transmission of 1L and 10L LB films in the *s*-polarized light as a function of the angle and the wavelength differs significantly (Fig. 3). The main feature of the latter is the intense diffraction minimum observed over the whole range of explored angles that arises due to the presence of a well-ordered multilayer structure. According to the best fit of the dispersion of this diffraction minimum [Fig. 4(a)] to the Bragg law $\lambda^2=2d\sqrt{n_{eff}^2-\sin^2\theta}$, where n_{eff} is the effective refractive index (RI) of the film and d is the distance between planes, $d=440$ nm and $n_{eff}=1.238$ apply. Setting the sphere

[a]Author to whom correspondence should be addressed; electronic mail: sergei.romanov@tyndall.ie

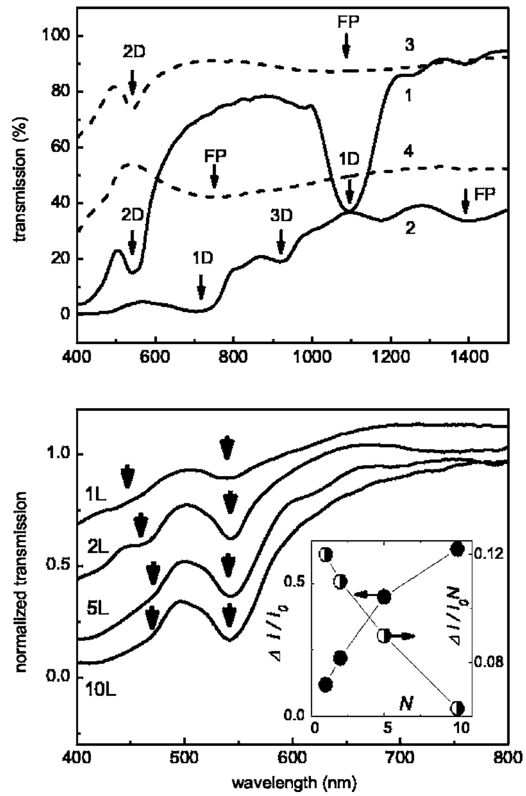

FIG. 1. (a) *s*-polarized transmission spectra of 1L (dash) and 10L (solid) LB films at $\theta=0°$ (curves 1 and 3) and 70° (curves 2 and 4). The arrows indicating the minima are labeled according to their origin. (b) Normalized transmission spectra of LB multilayers. The curves are shifted for clarity. The arrows are to guide the eye. Inset: relative attenuation $\Delta I/I_0$ at 545 nm minimum and the specific relative attenuation $\Delta I/NI_0$ per layer as the function of the number of layers *N*.

diameter to $D=492$ nm obtained from the Bragg fit of the transmission minimum dispersion of the fcc opal assembled from the same spheres, the interlayer distance is found to be $d=0.89D$. The factor 0.89 points to a looser packing of layers in the LB film compared to distance between (111) planes

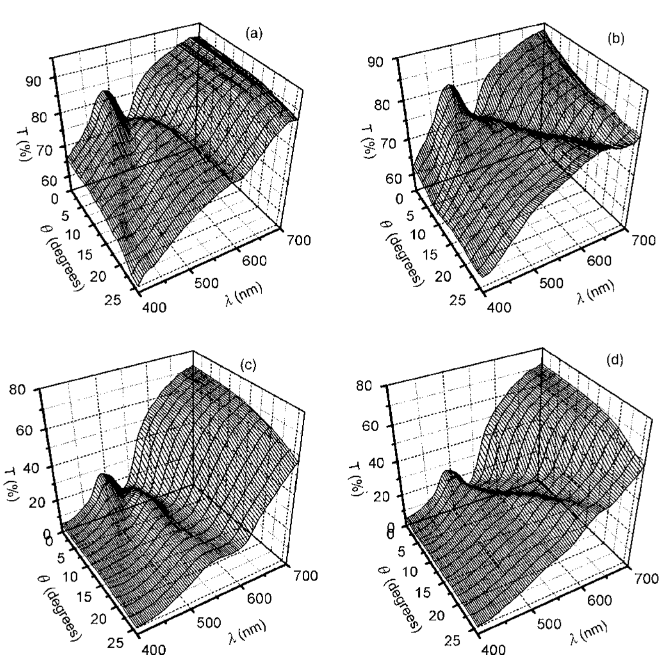

FIG. 2. 3D transmission plots of [(a) and (b)] 1L and [(c) and (d)] 10L films in the *s* and *p* polarizations, panels (a) and (c) and (b) and (d), respectively.

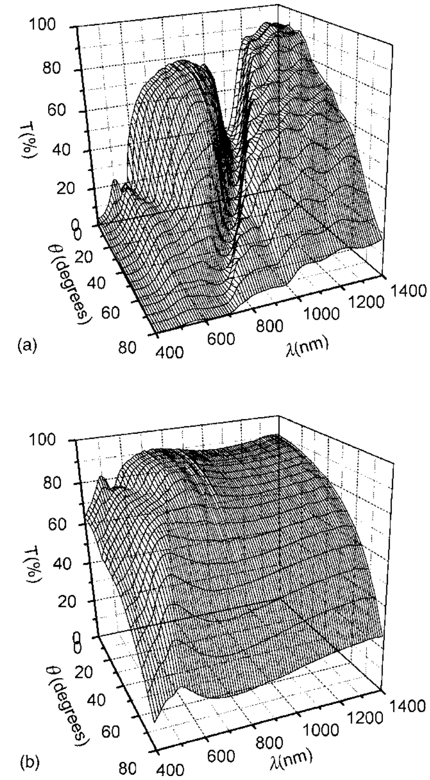

FIG. 3. 3D transmission plots of (a) 10L and (b) 1L films in the *s*-polarized light.

in the fcc lattice. This conclusion is supported by the lower n_{eff} compared to that of opal of similar RI contrast.

The weak minimum observed at $\theta > 60°$ in the wavelength range of 880–935 nm for both polarizations can be also interpreted as the result of diffraction. The Bragg fit specifies a set of planes separated by 387 nm and oriented at 66° with respect to LB layers. This result is not far from the

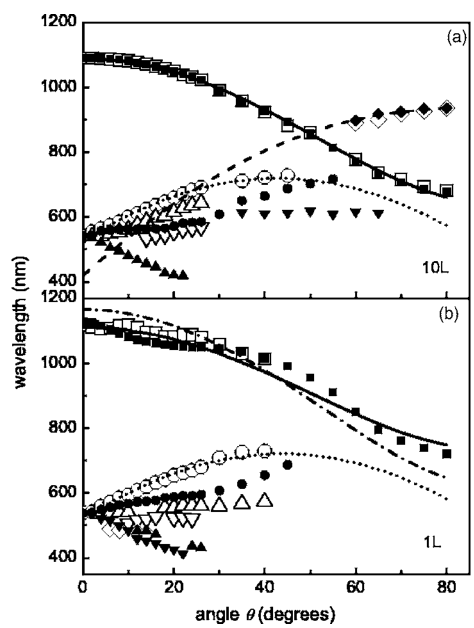

FIG. 4. (a) Dispersion of transmission minima of 10L film in *s* (solid symbols) and *p* (open symbols) polarizations. The solid and dashed lines denote Bragg fits to the diffraction at 1D stack of LB monolayers and 3D diffraction, respectively. The dotted line is a fit to diffraction of a 2D grating. (b) The same for 1L film. The solid and dashed lines denote Bragg fits to the diffraction at 1D stack of LB monolayers using two and one free parameters, respectively.

diffraction at $(\bar{1}11)$ planes of the fcc lattice, which is described by the 401 nm distance and the 70.52° angle. This diffraction branch, which is repeatedly observed in LB multilayers is an argument in favor of weak 3D correlation existing between layers of spheres. Extrapolation of this fit to lower angles indicates that none of the short wavelength transmission minima can be associated with 3D ordering [Fig. 4(a)].

The 1096 nm minimum in transmission of the 1L film is the Fabry-Pérot resonance expected for a monolayer of spheres,[13] to which the same functional dependence upon the angle as for the Bragg resonance applies [Fig. 4(b)]. Two fits were explored. The first one assumes the fixed sphere diameter $D=492$ nm. In spite of the realistic $n_{\mathrm{eff}}=1.18$, it does not approximate the dispersion. The second fit, which leaves d and n_{eff} as free parameters, reproduces more closely this dispersion branch with $d=417$ nm and $n_{\mathrm{eff}}=1.33$. Thus, the optical behavior of the 1L film corresponds to that of the thinner than the sphere diameter slab.

The short-wavelength transmission minima of 1L and 10L films split into several branches with increasing incidence angle (Figs. 2 and 4). The dispersion of the longer wavelength branch in the p polarization (Fig. 4) satisfies the standard expression for a planar diffraction grating $\lambda = d[\sin\theta + \sin(2\alpha - \theta)]$, with parameters $d=521(529)$ nm and $\alpha = 88°(86°)$, for 1L (10L) films. This resembles a grating with, approximately, 45° blazing angle and the period of the sphere diameter.

The transmission across the LB monolayer in the range below 700 nm can be interpreted in two ways. One approach is based on consideration of 2D PhC, the PBG of which is calculated by coupling of whispering gallery mode resonances of individual spheres in the 2D crystal.[10] The lowest wavelength resonance in this model appears at $D/\lambda \approx 0.9$, which corresponds to the 545 nm minimum in our case (Fig. 1). The dispersion of the transmission minima follows the calculated PBG structure of 2D PhC in the range of 720–400 nm (Fig. 4). Another approach, based on the rigorous coupled-wave analysis[14] or vector-coupled-mode theory,[15] explains these transmission minima as resonant scattering due to coupling of the incident light and guided modes supported by the 2D PhC.

Both approaches describe the splitting of resonances for oblique light incidence, the lower coupling efficiency at high angles, and their polarization anisotropy. The spectral position and resolution of scattering resonances depend on the RI of substrate.[14,16] In our case the RI of the substrate exceeds the effective RI of the sphere monolayer. In order to use the waveguiding model, we have to assume that a monolayer of spheres is optically isolated from the substrate. It is noteworthy that the contact area between spheres and substrate is very small and the RI of the monolayer approaches its maximum at the distance of the sphere radius from the substrate. This view is supported by the parameters of the dielectric slab, which approximates the 1L film according to the second fit to the Fabry-Pérot resonance dispersion. The large width of the resonance minima observed in transmission compared to theoretical calculations points to the leaky character of the guided modes in the film.

The spectral location of the transmission minimum at normal light incidence corresponds to the scattering of the incident wave by either TE or TM waveguide modes. This gives an explanation to the resonances at 542 and 445–465 nm [Fig. 1(b)]. In our spectra the latter resonance is much weaker and more sensitive to the destructive influence of disorder. At the oblique incidence the degeneracy condition of the resonance is lifted, leading to splitting of guided resonances[14] thereby explaining resonance dispersion and polarization anisotropy.

Summarizing, a comparative investigation of the transmission of LB multilayers has revealed the absence of the 3D coordination between monolayers. The observed transmission minima are interpreted as the Bragg diffraction of a 1D PhC consisting of monolayers of spheres and scattering by eigenmodes of 2D PhCs. The coexistence of resonances associated with PhCs of different dimensionalities makes optical properties of LB multilayers qualitatively different from that of 3D colloidal crystals (opals) and allows classifying them as (2+1)D colloidal PhCs. Therefore, LB multilayers cannot be considered as 3D crystals with stacking faults, as with LB stacks the interplanar distance is increased and the bilayer correlation is lost. Several effects, such as the polarization anisotropy, the absence of the second harmonic of the Bragg resonance, and the transmission maximum observed in the 1L film at high incidence angles, remain to be explained by rigorous modeling.

The authors acknowledge the support of the Science Foundation Ireland, the EU IST projects "PHAT" and "PHOREMOST" and thank D. Whitehead for help in sample preparation and I. Povey for helpful discussions.

[1]Y. Xia, B. Gates, Y. Yin, and Yu Lu, Adv. Mater. (Weinheim, Ger.) **12**, 693 (2000).
[2]A. van Blaaderen, R. Ruel, and P. Wiltzius, Nature (London) **385**, 321 (1997).
[3]P. Ferrand, M. Egen, B. Griesebock, J. Ahopelto, M. Mьller, R. Zentel, S. G. Romanov, and C. M. Sotomayor Torres, Appl. Phys. Lett. **81**, 2689 (2002).
[4]H. Míguez, F. Meseguer, C. Lopez, A. Blanco, J. S. Moya, J. Requena, A. Mifsud, and V. Fornes, Adv. Mater. (Weinheim, Ger.) **10**, 480 (1998).
[5]F. Garcia-Santamaria, H. T. Miyazaki, A. Urrquia, M. Ibisate, M. Belmonte, N. Shinya, F. Merseguer, and C. Lopez, Adv. Mater. (Weinheim, Ger.) **14**, 1144 (2002).
[6]S. Reculusa, P. Masse, and S. Ravaine, J. Colloid Interface Sci. **279**, 471 (2004).
[7]M. Bardosova, P. Hodge, L. Pach, M. E. Pemble, V. Smatko, R. H. Tredgold, and D. Whitehead, Thin Solid Films **437**, 276 (2003).
[8]S. Reculusa and S. Ravaine, Chem. Mater. **15**, 598 (2003).
[9]S. G. Romanov, T. Maka, C. M. Sotomayor Torres, M. Müller, R. Zentel, D. Cassagne, J. Manzanares-Martinez, and C. Jouanin, Phys. Rev. E **63**, 056603 (2001).
[10]H. T. Miyazaki, H. Miyazaki, K. Ohtaka, and T. Sato, J. Appl. Phys. **87**, 7152 (2000).
[11]Y. Kurokawa, H. T. Miyazaki, and Y. Jimba, Phys. Rev. B **65**, 201102 (2002).
[12]M. Bardosova, P. Odge, V. Smatko, R. H. Tredgold, and D. Whitehead, Acta Phys. Slov. **54**, 1 (2004).
[13]Shanhui Fan and J. D. Joannopoulos, Phys. Rev. B **65**, 235112 (2002).
[14]Song Peng and G. Michael Morris, J. Opt. Soc. Am. A **13**, 993 (1996).
[15]A. R. Cowan, P. Paddon, V. Pacradouni, and J. F. Young, J. Opt. Soc. Am. A **18**, 1160 (2001).
[16]Y. Kurokawa, H. Miyazaki, and Y. Jimba, Phys. Rev. B **65**, 201102 (2002).