Polarimetric and Photonic Properties of 2D Submicroparticle Arrays


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ABSTRACT

Self-assemblies of submicrometric sized particles in large area compact monolayers constitute a promising field with applications as new optical submicrostructured devices of macroscopic dimensions. These structured surfaces present a photonic band, directly associated to the self-assembled structure and to the nature of the used material. In this work, monodisperse silica submicrospheres with diameter sizes of about 300 nm and about 380 nm were synthesized by sol-gel process. They were arranged in monolayers showing hexagonal structure on 2.5 cm diameter glass disks by means of the Langmuir-Blodgett technique. Morphology and structural arrangements were determined by electron microscopy. The optical properties of the submicroparticle arrays were studied by optical transmittance measurements giving several photonic bands in the 340-440 nm region. Further measurements by phase-modulated transmission spectroscopic ellipsometry revealed optical anisotropy in the samples. This result suggests that the detected amount of birefringence and dichroism must be related to the periodical structure and to the presence of defects in the arrangement.

Keywords: silica particle, 2D crystal, Langmuir-Blodgett, birefringence.

1 INTRODUCTION

The field of photonic crystals (PC) has rapidly expanded in the last decades. These materials, due to the periodicity of their dielectric constant, are characterized by a photonic bandgap that forbids light propagation [1]. A complete photonic bandgap can only be theoretically achieved in 3D PC [2]. However, due to the simplicity of their fabrication, 1D and 2D PC are more developed [3]. 2D monolayer crystals which derive from 2D PC [4] possess interesting properties that allow a wide range of applications: from micrometric sized lenses [5], catalytic devices [6] to biological applications [7].

Concerning optical anisotropy in general, although linear birefringence is usually considered as an undesirable attribute in crystallography, the possibility of controlling and modifying this property is of great interest for photonic applications from reflection coatings to light confinement [8]. Linear birefringence is characterized by a difference in the speed of light for two orthogonal linear polarisation of light passing through a sample. Birefringence can be evidenced by placing the sample between two crossed polarizers. Recently, photoelastic modulators have been used to measure low levels of retardation and when used with a suitable optical setup, are also able to accurately measure the direction of the anisotropy fast axis [9,10].

In this work, we have synthesized silica particles by sol-gel method and used the Langmuir-Blodgett technique to organize them in compact monolayers on glass substrates. Our aim was focused on the optical properties of these 2D crystal monolayers or particle monolayer (PM), and more specifically on the photonic and optical properties related to the size and arrangement of the particles.

2 EXPERIMENTAL

2.1 Sample Production

The silica particles were synthesized by the Stöber method [11] from tetraethylorthosilicate (TEOS, high purity ≥99.0%, Fluka), absolute ethanol (Aldrich- 98%) and ammonia (NH₄OH, 25%, Merck). The solution was stirred for 24 h at ambient temperature to let the hydrolysis and condensation reactions of the alkoxide precursor to be completed. The excess reactant and by-products were eliminated by centrifugation before collection of the sol-gel particles and redispersion in fresh ethanol. The centrifugation cycle was repeated 5 times.

Glass substrates were cleaned in a Piranha solution, rinsed with Milli-Q water and immersed vertically inside the Langmuir-Blodgett trough filled with Milli-Q water. Meantime, the synthesized particles were diluted in a mixture of alcohol (ethanol or methanol) and chloroform (1:3) and sonicated for 5 min before spreading them on the water surface. The trough barriers were brought closer (with a constant rate of 10 mm/min) until a pressure of 5 mN/m was reached. The substrate was lifted from the trough with a speed of 2 mm/min at constant pressure, dragging on its surface a monolayer of silica particles.

2.2 Characterization techniques

The morphology of silica particles, their size and the assembly structure were determined by Environmental
SEM (ESEM Quanta 200 FEI). This apparatus allows non-destructive observations. An accelerating voltage of 15 kV, an emission current between 90-100 µA and a water vapour pressure of 0.5-0.9 Torr were used in this study.

Transmittance measurements were performed with a UV-2101 PC UV-Vis Scanning Spectrophotometer (Shimadzu), between 300 nm and 800 nm in normal incidence using unpolarized light. The reference of each sample was the bare glass substrate.

We used a standard phase modulated ellipsometry scheme (polarizer, photoelastic modulator, sample, and analyzer) in transmission mode (TSE), working in the UV-visible range, to measure the linear birefringence (LB) and the linear dichroism (LD) of the sample. In our setup, the sample could be rotated in its plane (azimuthal angle), describing a complete circle, with a minimum step of 1°.

The anisotropy axes of the samples were evaluated by performing several spectral measurements of LD and LB for different azimuthal angular positions of the sample (ϕ); thus, by rotating the sample, we performed a scan that allowed us to find LBmax and LDmax for every wavelength. More details of the transmission ellipsometer setup can be found in reference [12]. The Mueller matrix for a non-depolarizing linearly anisotropic uniaxial sample at normal incidence with its principal axis ϕ=0° is given by [12]:

\[
M = \begin{pmatrix}
\cosh\text{LD} & -\sinh\text{LD} & 0 & 0 \\
-\sinh\text{LD} & \cosh\text{LD} & 0 & 0 \\
0 & 0 & \cos\text{LB} & -\sin\text{LB} \\
0 & 0 & \sin\text{LB} & \cos\text{LB}
\end{pmatrix}
\]  

(1)

where  

\[
LB = \frac{2\pi d(n_u - n_e)}{\lambda} \quad \text{and} \quad LD = \frac{2\pi d(k_u - k_e)}{\lambda}
\]  

(2)

and \(d\) is the thickness of the sample, \(\lambda\) is the wavelength of light, \(n_u\) and \(n_e\) are the ordinary and extraordinary refractive indexes, and \(k_u\) and \(k_e\) are the ordinary and extraordinary extinction coefficients. When LB and LD are small (as those of the samples we have studied where they are not higher than 0.02 rad) equation (1) can be approximated as follows [12]:

\[
M = \begin{pmatrix}
1 & -\text{LD} & 0 & 0 \\
-\text{LD} & 1 & 0 & 0 \\
0 & 0 & 1 & -\text{LB} \\
0 & 0 & \text{LB} & 1
\end{pmatrix}
\]  

(2)

If the orientations of the polarizer, modulator and analyzer of the sample are strategically chosen (A = 45°, P-M = 45°, M = -45°) the Mueller matrix of the sample can be completely determined with a single phase-modulated ellipsometry measurement. In this configuration, the matrix elements \(m_{01}\) and \(m_{23}\) (that respectively are related to \(LD\) and \(LB\)) can be directly obtained from the fundamental and second harmonic amplitudes and phases of the detected signal. LB and LD were measured between 280 and 750 nm.

3 RESULTS AND DISCUSSION

Two kinds of samples were produced here: before Langmuir-Blodgett deposition a mixture of ethanol and chloroform was used for PM sample 1 (PM1), whereas ethanol was replaced by methanol for PM sample 2 (PM2). Moreover, slight differences introduced in the chemical synthesis made the particle size used for PM1 a bit smaller than the one used for PM2.

Figure 1: PM1 (a) and PM2 (b) observed by SEM
On figure 1, we observe that the particles are arranged in hexagonal structured domains. Many dislocations are present in the monolayer and could be the result of monolayer breaking due to the competition between gravitational and capillary forces during the particle arrangement on the substrate by the Langmuir-Blodgett process. Particle size calculation performed with ImageJ software gave $D = 297 \pm 5$ nm for PM1 and $D = 380 \pm 5$ for PM2.

$$k(\omega) = k_0 n_{eff} = k_d = \frac{2\pi}{a}$$  \hspace{1cm} (3)

where $k_0$ is the wave vector in vacuum, $n_{eff}$ is the effective refractive index of the 2D crystal and $a$ the interlinear distance between particles. The position of the gap contains information about the size of the particles. For instance if we consider the interlinear distance $a = \sqrt{3}/2 \cdot D$, typical of triangular lattices, with the assumption that the crystal is isotropic and we can apply the effective medium theory through a constant refractive index, with $n_{eff}=1.287$, we found a particle size of 305 nm for PM1 and 390 nm for PM2, which are closed to the values measured on the SEM pictures. The transmittance of fig.3 depends on the polarization of incident light according to the activation of the resonance associated to particular directions (hexagonal symmetry) in our 2D photonic crystal.

Figure 2: Normalized density correlations of PM1 (a) and PM2 (b). Positional order is greatly enhanced in (b) with respect to (a). The interparticle distance is represented on the horizontal axis.

In figure 2, peaks in the positional correlations correspond to the normalized probability of interparticle distances. The analysis has been performed in a region of size 50 x 50 particles for PM1 (a) and 200 x 200 particles for PM2 (b). Position correlations decrease rapidly with distance for PM1 as indicated by the amplitude of oscillations (a). This fast decay is related to the existence of dislocations that divide the monolayer in numerous ordered particle domains. As for PM2 (b), they decay significantly more slowly than PM1, and characteristic peaks are clearly resolved. For instance, the next-nearest neighbour ($\sqrt{3} D$) and the second neighbour ($2 D$) peaks can be distinguished only in PM2. This structural analysis illustrates the higher quality of PM2. Moreover this study shows that methanol is the best solvent to obtain large films of well ordered particles. It is actually well known that the bigger is the particle the better is the arrangement [13].

On transmittance spectra (figure 3), PM1 presents a gap at 340 nm while PM2 presents a gap at 435 nm and small non-well resolved gaps are noticeable at 340 and 360 nm. Light that propagates through the crystal is scattered by the individual particles of the crystal [14]. Photonic gaps are due to the coupling of the grazing scattered light, whose in-plane component $k_0$ is equal to the reciprocal network vector $G$ with the eigenmodes $k(\omega)$ of the 2D crystals [15, 16]:

$$k(\omega) = k_0 n_{eff} = k_d = \frac{2\pi}{a}$$  \hspace{1cm} (3)

The isotropy of a perfect 2D crystal having hexagonal symmetry implies null values for LB and LD. However peaks are found in the LB and LD spectra detected by ellipsometry (figure 4). Although their values are small, their presence and their evolution with the sample azimuthal rotation indicate that the monolayer is uniaxially anisotropic and that the anisotropy axis is on the plane of sample. The detected peak positions for PM1 and PM2 appear in the regions that coincide with the photonic gap locations found in the transmittance spectra (figure 3). The analogous positions are due to the fact that LD (eq. 2) is proportional to one polarization component value parallel to the anisotropy direction through $k$, which undergoes a variation at the wavelength resonance of the crystal.

A correspondence between every birefringent and dichroic peak is evident and the experimental dispersion relation for the real (LB) and imaginary (LD) parts of the anisotropy shows Lorentz oscillator characteristics [17]. The imaginary part of the anisotropy reaches its extreme values when the real part vanishes at energies slightly lower and higher than the absorption.

The presence of extra peaks (340 and 360 nm of PM2) found in TSE spectra confirms the existence of second-order photonic bands. Whispering gallery modes or Mie resonance of individual spheres may also be involved in
this phenomenon [18,19]. However, no significant change in the amplitude of anisotropy was found between PM1 and PM2 despite the differences of particle size and quality of the arrangement (PM1 on fig. 1 appears more disordered than PM2).

Figure 4: LB (a) and LD (b) spectra of PM1 (right scale) and PM2 (left scale) at 0º, 45º and 90º from bottom to top. Vertical axis scales are in radians.

The deposition technique could be responsible of the anisotropy found in the PM. Effectively the uniaxial birefringence can be related to the stretching of the monolayer in the extraction during deposition due to the competitive effect of capillary and gravitational forces, resulting in the formation of oriented phases in the 2D crystal. Within the lattice, the mismatches of the sample are not completely isotropically distributed (figure 1), and dislocations could be more frequent in one direction than in the others. We are taking further measurements here to prove whether the direction of the anisotropy is macroscopically introduced during the film transfer in the Langmuir process, so that the axis of the anisotropy is related with the dipping direction [20] or whether uniaxial birefringence is an intrinsic property of hexagonal 2D crystals.

4 CONCLUSION

Photonic gaps associated to uniaxial anisotropy were revealed in 2D hexagonal crystals of silica submicrosphere monolayer. This study showed the effect of order on the peaks appearance and the maintenance of anisotropy despite a high quality 2D crystal.

Possible applications of these anisotropic nanoparticle monolayer films are opal effect for application in jewellery, narrow-band polarizing filters and 2D-gratings in the UV-visible range for photonic applications.

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