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Self-assembling three-dimensional colloidal photonic crystal multilayers from aqueous ethanol mixture solutions*

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Vertical deposition technique to fabricate thin film solid artificial opals is becoming widely used. In the present work, we report our research on solvent modification and its effect on the quality of colloidal crystals. We used aqueous ethanol mixture solution to replace the ethanol solution, and used the vertical deposition technique to pack the spherical colloids into close-packed arrays. High quality samples can be prepared with thickness up to 20μm in one step. Furthermore, large spheres (diameters greater than 500nm) were successfully crystallized. Scanning electron microscopy (SEM) and optical methods were used to measure sample thickness and uniformity. The number of layers was calculated from the spectral separation of the Fabry–Perot fringes.

Keywords: colloid crystal multilayers, solvent modification, Fabry- Perot fringes, layer number
PACC: 4270Q, 6480G, 8110D

1. Introduction

Photonic crystals with three-dimensional periodicity have been fabricated using a variety of lithographic and selective etching techniques,[1−9] holographic methods,[10,11] and colloidal self-assembly and templating techniques.[12−16] Unlike most other techniques, self-assembly and templating techniques offer an impressive versatility with respect to the materials used in fabricating the crystals as well as their structural morphology.[17,18] In 1999 Jiang *et al* published a novel self-assembly method to fabricate thin film solid artificial opals.[12] This method, known as vertical deposition, is becoming widely used and has surpassed other methods due to its many advantages, for example, good control over sample thickness, samples attached to a substrate and thus facilitates its manipulation, etc. The main drawbacks of this method are that it can only produce three-dimensional crystal films of up to 50 layers in one step, and large spheres (diameters more than 500nm) fail to crystallize because the sedimentation velocity of the spheres is higher than the solvent evaporation. Jiang *et al* attempted to deposit silica colloids from aqueous solutions for getting thicker films, but the obtained samples had poor quality. Vlasov *et al* have been successful in fabricating the colloidal crystals with larger sphere diameter by placing the vial in a temperature gradient.[19] In this case, the temperature at the surface of the suspension was low enough to give a valid evaporation rate. Meanwhile, the temperature gradient caused convection forces and a continuous flow of spheres was directed towards the surface.

Many types of fascinating applications have been proposed or demonstrated for colloidal crystals. For example, 3D opaline lattices of colloidal spheres have been exploited as diffractive elements to fabricate sensors, filters, switches, photonic bandgap (PBG) crystals and other types of optical and electro-optical devices, and has also been used as a directly observable (in 3D real space) model system to study a wide variety of fundamental phenomena such as crystallization, phase transition, melting, and fracture mechanics. The success of all these applications strongly depends on the availability of colloidal spheres with

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tightly controlled sizes and surface properties, and on the ability to self-assemble into ordered arrays with well-defined structures and sufficiently large domain sizes.[13]

In this paper, we report on solvent modification and its effect on the quality of colloidal crystals. We used aqueous ethanol mixture solution to replace the ethanol solution. The colloidal crystal multilayers were prepared with larger sphere diameter (over 500nm) and thickness up to 20μm in one step by the vertical deposition technique. The resulting planar colloidal crystals have higher quality and fewer dislocations and vacancies. The optical properties of these samples were measured at normal incidence and the number of layers was calculated from the Fabry–Perot fringes. The effect of the solvent on the crystalline quality of colloidal crystals was confirmed.

2. Experimental methods

In our experiment, a self-assembled lattice of silica spheres was formed on a glass substrate by vertical deposition. The diameters of the silica spheres were 200, 300 and 600nm with a relative standard deviation of about 4% (prepared at the Technical Institute of Physics and Chemistry of Chinese Academy of Sciences). Clean glass substrates were vertically placed into a vial containing aqueous ethanol mixture solutions. The mixture solutions with volume fraction of ethanol from 80% to 5% respectively were used. The above solutions contained silica spheres around 0.5% to 8% volume fraction respectively. The vial was kept in a temperature-controlled oven at 55°C[14] and free of vibration and noise. The solution contained in the vial had a temperature gradient since the vial was placed directly on the bottom of the oven. After 20 hours, colloidal crystal multilayers with high crystalline quality over areas as large as 25 mm $\times$10 mm were grown from solutions with volume fraction of 10% ethanol.

The morphology of the samples was characterized by scanning electron microscopy (LEO1530 VP). Transmission and reflection spectra were obtained by the UV–near-IR spectrometer (UV-3130 PC).

3. Results and discussion

Crystalline quality is among the most important parameters in determining the performance of colloidal crystals in optical applications. The crystal growth process consists of nucleus formation, transport of particles towards the ordered nucleus, and crystallization. The sample fabricated at a higher temperature has the tendency to have fewer defects, but the too fast solvent evaporation inevitably spoils the balance of nucleus formation, particle transport, and crystallization. Moreover, faster evaporation speed also increases the drying tension in thin colloidal films, which cause cracks in the colloidal crystal multilayers. So the compromise between a higher evaporation temperature and a slower crystal growth rate is very important. Thus an important issue in this vertical deposition method is the role that the solvent plays in controlling the deposition of colloidal multilayers. The growth of colloidal crystal from aqueous solution needs higher evaporation temperature (T) than that from ethanol solution. Moreover, solvents such as water, which have large surface tensions and even lower contact angles, should deposit thicker films than the corresponding ethanol solutions. Unfortunately the film usually cracks and falls of as a result of faster drying speed and larger surface tension. To avoid cracking and peeling and achieve faster evaporation of the solvent, dilute ethanol solvent (the volume fraction of ethanol is about 10%) is used. Using these parameters, with the above mechanism we succeeded in fabricating colloidal crystal multilayers in aqueous ethanol mixture solutions. Fig.1. shows a typical SEM image of the single crystal of colloidal silica with a 600nm diameter. This sample exhibits an ordered closed-packed arrangement of the spherical colloids in planes parallel to the substrate over a large area and has few dislocations and vacancies. The temperature gradient plays an important role in our solvent system, too. The temperature at the surface of the suspension was low enough to maintain a valid evaporation rate of

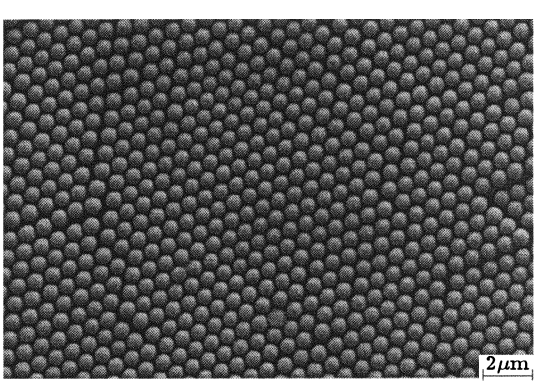


Fig.1. Typical scanning electron micrograph (SEM) of a sample (top view) from aqueous ethanol mixture solutions with spheres of 600 nm diameter.

the water-ethanol mixture, and the temperature gra-

dient causes convection forces and a continuous flow of spheres is directed towards the surface. So enough spheres are always present in the meniscus to sustain crystallize.

Figure 2 shows a SEM cross-sectional images of sample of 88 layers with 200nm sphere diameter (a) and 64 layers with 300nm sphere diameter (b). It demonstrates that vertical deposition from aqueous ethanol mixture solutions did give thicker films in one step, and the samples are planar and uniform.

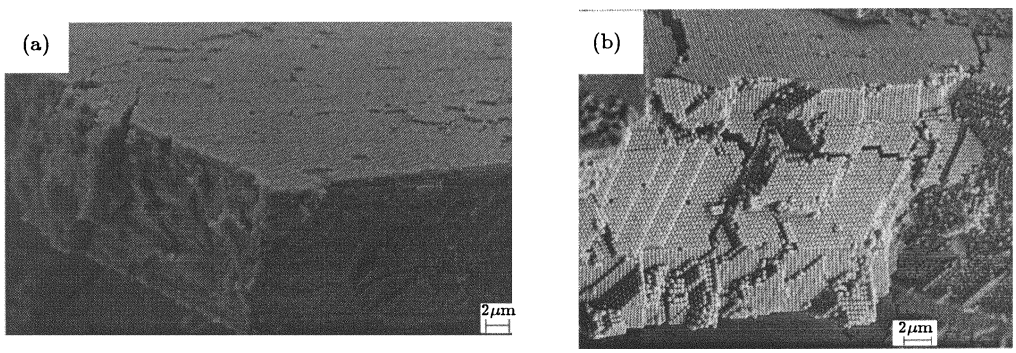


Fig.2. SEM cross-sectional image of the SiO_2 colloidal crystal thick films with 200nm (a) and 300nm sphere diameter (b).

Thin film opals present some special characteristics in their optical properties, which cannot be observed on thicker opals. The interference of light reflected by the top and bottom surfaces causes the well known Fabry–Perot (FP) interferences. As a matter of fact these interferences are always present in opals. In the case of film of thickness less than 8μm under visible light, intensity oscillations can be clearly observed. The FP fringes can be seen at both sides of the Bragg peak (Fig.3(a)). The observation of well-defined fringes demonstrates that the film is uniform. If the thickness of the sample in the optical path varies by more than $\pm 10\%$, then well defined maxima and minima will not be observed. However, opals are too thick and fringes form a continuous background (Fig.3(b)).

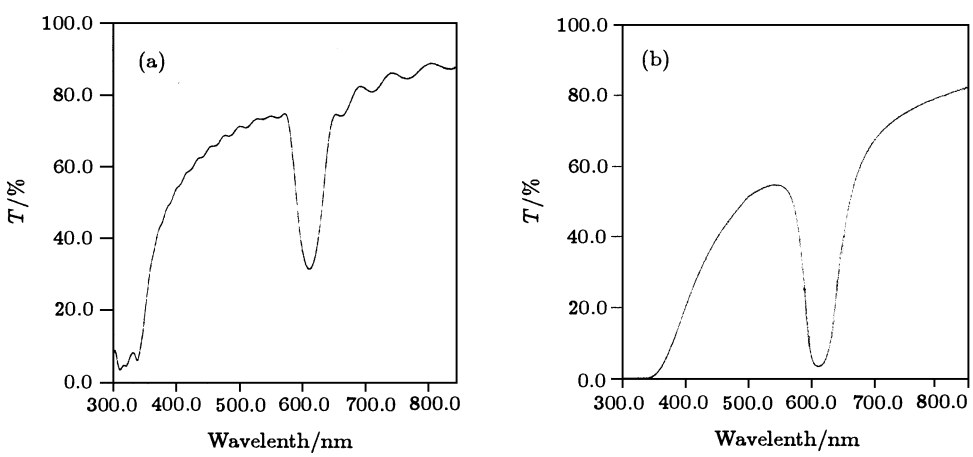


Fig.3. Optical transmission spectra for colloidal crystal multilayers made up of 17 layers (a) and 64 layers (b) of spheres of 300nm diameter.

The number of layers and therefore the thickness of the sample is an interesting parameter to be considered when studying the optical properties of the thin film opal. While SEM provides a measure of this parameter, it is a destructive method as it requires a thin gold coating on the sample. In fact, the number of layers can be calculated from the spectral separation of the FP fringes.

At normal incidence, one particular FP minimum

occurs at a longest wavelength, λ_0 given by

$$p_0\lambda_0 = 2n_{\text{eff}}T, \tag{1}$$

where p_0 is an integer, n_{eff} is the effective refractive index of the medium and T is the film thickness. Subsequent minima appear at shorter wave wavelengths:

$$(p + p_0)\lambda_{\text{p}} = 2n_{\text{eff}}T. \tag{2}$$

Here p is a positive integer numbering consecutive minima from the fringe p_0.

Combining Snell's law and Bragg's law, we obtain the Bragg diffraction wavelength, λ_{c}, at normal incidence:

$$\lambda_{\text{c}} = 2n_{\text{eff}}d_{hkl}, \tag{3}$$

where d_{hkl} is the distance between two adjacent diffracting (hkl) planes.

Rearranging Eqs.(1), (2) and (3) gives the number of layers, L (T/d_{hkl}):

$$L = \frac{T}{d_{hkl}} = \frac{p\lambda_{\text{p}}\lambda_0}{\lambda_{\text{c}}(\lambda_0 - \lambda_{\text{p}})}. \tag{4}$$

Using the above equation, we can obtain the number of layers from diffraction spectra independently. We come to the conclusion of 17 layers for Fig.3(a) and it is in excellent agreement with the thickness found from SEM (Fig.4).

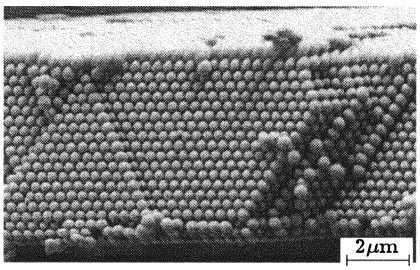


Fig.4. SEM cross-sectional image of the 17-layer SiO_2 colloidal crystal film with 300nm sphere diameter.

4. Conclusion

Using the aqueous ethanol mixture solutions and the vertical deposition technique to pack the spherical colloids into close-packed arrays, high quality colloidal crystalline multilayers were prepared with thickness more than 18μm in one step. Large spheres (diameters over 500nm) are crystallized. The sample exhibited planar form, uniformity and was crackless as a result of an appropriate drying rate. From the spectral separation of the Fabry–Perot fringes the number of layers can be calculated. The advantages of this technique are improved processing speed, efficiency and reduced material consumption relative to the growth of colloidal crystal from ethanol solution.

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