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SHORT COMMUNICATION

Effects of stretching on microstructures of polymer-immobilized non-close-packed colloidal crystalline array

Hiroshi Nakamura · Masahiko Ishii

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Abstract Non-close-packed silica colloidal crystalline array was immobilized by polymer, and effects of stretching on the change of the optical properties and microstructure of the colloidal crystalline arrays have been demonstrated. The immobilization was a two-step polymerization process: the first step was with hydrophilic polyethylene glycol acrylate (PEGA) polymer gel, and the second step was with 2-hydroxyethyl acrylate polymer matrix. The structure of the three-dimensional array was maintained during the immobilizing process with lock in periodic order. The peak wavelength of Bragg diffraction of the polymer-immobilized colloidal crystalline array shifted to shorter wavelength with stretching. The peak shift was caused by the compression of the polymer proportional to the stretching ratio, and the compression was homogeneous throughout the polymer-immobilized colloidal crystalline arrays. These results show that by using polymer-immobilized non-close-packed colloidal crystalline array, mechanically tunable photonic crystals can be realized, and they open the possibility of tuning the microstructure of colloidal crystalline array for photonic crystal.

Keywords Polymer-immobilized · Non-close-packed colloidal crystalline array · Stretching · Microstructures · Compression

H. Nakamura (✉) · M. Ishii
Toyota Central Research and Development Laboratories, Inc.,
41-1, Yokomichi, Nagakute, Aichi-gun,
Aichi 480-1192, Japan
e-mail: nakamura@mosk.tytlabs.co.jp

M. Ishii
e-mail: m-ishii@mosk.tytlabs.co.jp

Introduction

Colloidal crystalline arrays, which are three-dimensionally periodic lattices of self-assembled, monodispersed colloidal spheres, most commonly amorphous silica or a polymer latex, diffract ultraviolet, visible, and near-infrared light, depending on the lattice interplanar spacing, just as atomic crystals diffract X-rays that meet the Bragg condition. These periodic structures have been actively explored as functional components in fabricating new types of diffractive devices, such as optical filters and chemical sensors, and photonic bandgap structures. Recent studies on the unique optical properties of these materials, often referred to as photonic bandgap crystals, have now evolved into a new, exciting field of research [1–4].

Two methods of fabricating monodispersed colloidal spheres for the generation of colloidal crystals have emerged. One approach involves assembly of the spheres into close-packed crystalline arrays through sedimentation or solvent evaporation [5–11], and the second utilizes the long-range electrostatic interactions of charged colloidal spheres dispersed in a liquid medium to make non-close-packed crystalline arrays [12–18]. The second method, based on electrostatic interactions, seems to be the most powerful and successful method for generating multilayer assemblies of mesoscale spheres. In this method, however, the low elastic modulus exhibited by a liquid dispersion results in weak shear, gravitational, electric, or thermal forces having the propensity to disturb the crystalline order, which is a severe drawback to the practical application of colloidal crystalline arrays in photonic devices. Due to the free spaces inside the non-close-packed colloidal crystalline arrays, the photonic bandgap energy and the dispersion relation of the refractive index of the charged colloidal crystal can be tuned by mechanical stress. However, for the

crystals to be of practical use, the structure must be fixed in a flexible matrix.

Recently, approaches to develop robust network matrices have been pioneered for stabilizing both organic and inorganic arrays through in situ polymerization of monomers around non-close-packed colloidal crystalline arrays. Asher and coworkers [19–21] have achieved the formation of a solid colloidal crystalline array matrix using highly purified acrylamide and have used polymer-immobilized colloidal crystalline arrays in optical filtering and sensing applications. Foulger and coworkers have shown that polyethylene glycol derivatives are suitable matrices for polymer-immobilized colloidal crystalline arrays [22–25]. In addition, mechanically robust composite films composed of silica particles in acrylate polymers have been presented by Ford and coworkers [26–28], which exhibited a mechanochromic response.

In this paper, we describe the immobilization of non-close-packed colloidal crystalline arrays by a two-step polymerization process with a PEGA polymer and a 2-hydroxyethyl acrylate polymer, in a similar manner to that reported by Foulger et al., and we also describe the change of optical properties and microstructures of polymer-immobilized colloidal crystalline arrays with stretching and determine the change of the optical properties and microstructure with mechanical stress.

Experimental

Polymer immobilization of non-close-packed colloidal crystalline arrays

Monodispersed colloidal silica spheres SI-80P (diameter 74 nm) were purchased from Catalyst & Chemicals Industries, Japan. The spheres were shaken with an excess of mixed-bed ion-exchange resin [AG501-X8 (D), Bio–Rad Laboratories, Hercules, CA, USA] in an aqueous dispersion to reduce ionic impurities and form non-close-packed colloidal crystalline arrays.

The non-close-packed colloidal crystalline arrays were immobilized with a two-step polymerization. The first step is immobilized with a polymer hydrogel matrix prepared by an in situ photopolymerization procedure. The volume fractions of the silica spheres were 5 vol.%. The matrix materials included a monomer of PEGA (number of ethylene glycol chain=9, Mn=482, 13.5 wt%), a cross-linker of polyethylene glycol diacrylate (PEGDA, number of ethylene glycol chain=14, Mn=726, 1.5 wt%), and a photoinitiator of 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Ciba Specialty Chemicals DAROCUR 1173). The colloidal crystalline array and PEGA/PEGDA mixture in an aqueous dispersion were injected into a glass cell composed of two glass plates separated by a 1-mm silicone rubber spacer and then polymerized through exposure to a UV source for 5 min. The resulting gel had 10–20 vol.% polymer networks. The second step is immobilized with a polymer matrix prepared by an in situ photopolymerization procedure after substituting water contained in gel to 2-hydroxyethyl acrylate monomer.

Measurements of optical properties and microstructures

The microstructure of the polymer-immobilized colloidal crystalline array was observed by scanning probe microscopy (SPM) as viscoelastic images in the tapping mode using a Digital Instruments SPM D3100 (Nanoscope IIIa). The optical properties of the polymer-immobilized colloidal crystalline arrays were evaluated by measuring their reflection spectra at normal incidence using a multichannel spectrometer (Soma Optics, Fastevert S-2650). Structural analysis was then performed by angle-resolved reflection spectroscopy using the multichannel spectrometer. Angle-resolved reflection spectra were measured by changing the angle of incidence θ between the beam and the normal of the sample surface from 9 to 34° and by collecting the light scattered in the Bragg configuration. The Bragg equation is given by

$$m\,\lambda_{peak} = 2d_{111}\left(n_{eff}^2 - \sin^2\theta\right)^{1/2}, \quad (1)$$

where m is the order of diffraction, λ_{peak} is the wavelength of the diffraction peak, d_{111} is the interplanar spacing between the (111) planes, θ is the angle between the incident light and the normal to the diffraction planes (θ=0 at normal incidence), and n_{eff} is the mean effective index of the crystalline lattice.

The polymer-immobilized non-close-packed colloidal crystalline array was stretched by using a vise placed on the array. The effects of the stretching on the optical properties and microstructures were evaluated by measuring their reflection spectra and stretching ratio, respectively.

Results and discussion

Optical properties and microstructures

Figure 1 shows the appearance and SPM viscoelastic images of polymer-immobilized non-close-packed colloidal crystalline array of silica spheres. The array indicates a green range reflected light caused from Bragg diffraction from ordered arrays (Fig. 1a). SPM viscoelastic images indicate ordered array formed with silica particles directly and interparticle distance a about 230 nm.

Figure 2a illustrates the angle-resolved reflection spectra of polymer-immobilized colloidal crystalline arrays made

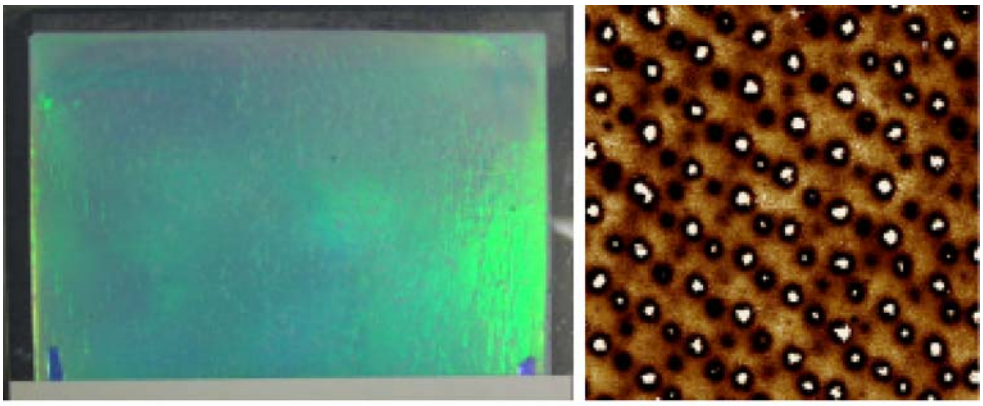

Fig. 1 **a** Appearance and **b** SPM viscoelastic image of polymer-immobilized non-close-packed colloidal crystalline arrays made of 5 vol.% silica particles

of 5 vol.% silica spheres. The wavelength λ_{peak} of each reflection peak is plotted against θ (Fig. 2a). The spectra evolve gradually with increasing θ. In each case, the diffraction peak shifts to lower wavelengths with an increase in θ. This behavior can be explained by the Bragg Eq. (1), which applies to the diffraction of light from a crystalline lattice of colloidal spheres. The (111) planes of the colloidal crystalline array are oriented parallel to the surface of the supporting substrate. In the measurements, the incident light and detector were both oriented perpendicular to the (111) plane of this lattice. The relationship between the incident angle and the peak of the reflection spectra with compression and shearing stress is shown in Fig. 2b. The very smooth fits further suggest that these structures diffract based on the Bragg law. The results of fits of Eq. (1) giving n_{eff} and d_{111} are 1.40 and 191 nm, respectively. n_{eff} and d_{111} of nonimmobilized colloidal crystalline arrays derived from the same way were 1.37 and 204 nm, respectively. n_{eff} increased and d_{111} decreased; however, the amounts of both changes were little. It is apparent that the structure of the three-dimensional array was maintained during the immobilizing process. Hence, a colloidal crystalline array forms a polymer network that locks in periodic order; the colloidal crystalline array remains stable in the presence of polymerizable species provided that the monomers do not contain ionic impurities. On the assumption that the colloidal crystalline array has an fcc structure, a relationship between the interparticle distance a and the interplanar spacing d_{111} was given by $a=(3/2)^{1/2}d_{111}$. This result derived a as 234 nm. This corresponds closely to the values determined by SPM.

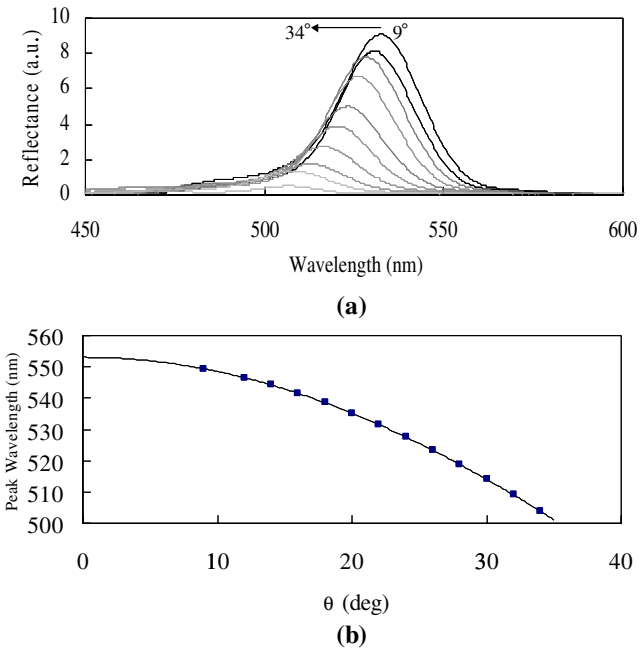

Fig. 2 **a** Angle-resolved reflection spectra and **b** relationship between incident angle and peak of reflection spectra of polymer-immobilized non-close-packed colloidal crystals made of 5 vol.% silica particles

Effects of stretching on optical properties and microstructures

Figure 3a shows the appearance and reflection spectra of the polymer-immobilized colloidal crystalline arrays under stretching. With stretching, the visible light reflection from the array changes from green to blue, and the diffraction peak shifts to lower wavelengths with stretching. The color of the polymer-immobilized colloidal crystalline arrays does not change uniformly because of partially inhomogeneous polymer network in the substrate with nonuniform monomer substitution or photopolymerization. When the stress was removed, the peak wavelength returned to the initial value immediately. It should also be mentioned that the reflection peak shows a blue shift with increasing strain with stretching, that is, with elongation. The decrease of lattice constant must be caused by the decrease of thickness of the polymer-immobilized colloidal crystalline array with elongation (Fig. 3b). In the proposed mechanism, a tensile deformation along the y-axis results in a decrease in the interplanar spacing of the spheres along the z-axis. We attribute this response to the compression of the lattice, where in "Optical properties and microstructures", the nearest neighbor distance for the spheres in the polymer-

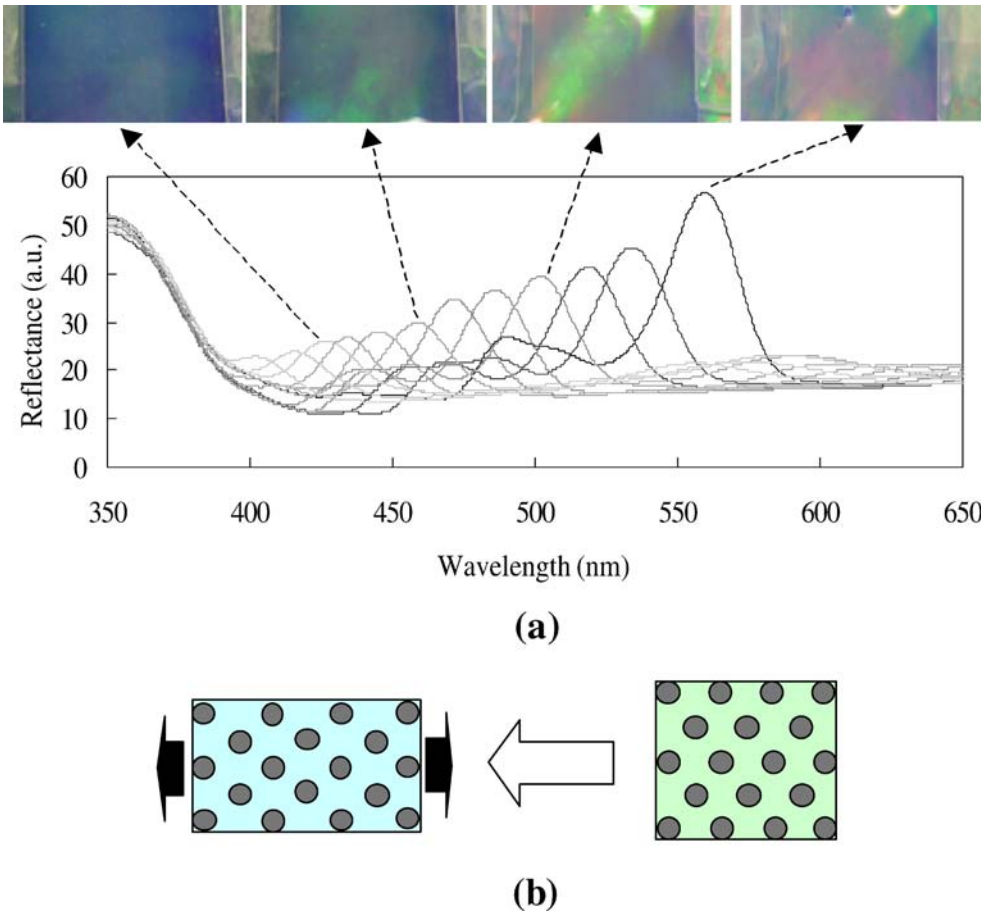

Fig. 3 **a** Appearance and reflection spectra and **b** schematic illustration of polymer-immobilized non-close-packed colloidal crystalline arrays made of 5 vol.% silica particles with stretching

immobilized array was calculated to be 3.4 times greater than the distance based on the intimate contact of the particles. Obviously, there is sufficient volume between particles to allow for the compression of the lattice while maintaining their long-range order. This large free space enabled a large deformation of the crystal without particle collision, resulting in the peak shift covering almost all wavelengths of visible light.

Figure 4a shows the shift of the peak wavelength and interplanar compression ratio as a function of stretch ratio. As the stretch ratio increases, the peak wavelength gradually shifts to shorter wavelength, suggesting that the (111) spacing parallel to the film surface decreases upon stretching. This result shows that the stop band shifts to short wavelength in proportion to a decrease in the interplanar spacing of the spheres along the *z*-axis. The degree of peak shift was calculated. In this study, it was assumed that a basic lattice was compressed along the direction perpendicular to the (110) plane under a constant lattice volume. Solid line in Fig. 4b predicted a roughly linear relation between t/t_0 and d/d_0. This means that the peak shift of Bragg diffraction was caused by the compression of the polymer proportional to the stretching ratio. By the way, this implies that the crystalline grain of a submillimeter size changed in shape uniaxially along the

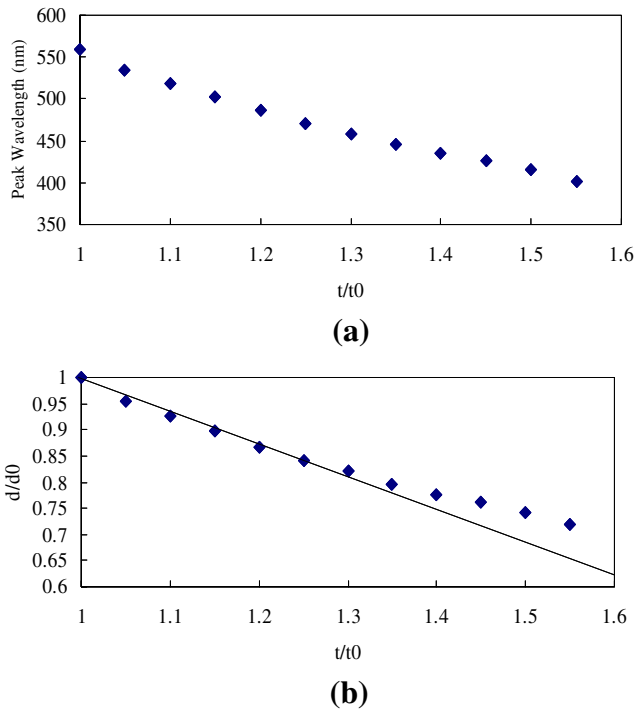

Fig. 4 Relationship between stretch ratios (t/t_0) and **a** peak wavelength of Bragg diffraction and **b** interplanar compression ratio (d/d_0) with stretching of the polymer-immobilized colloidal crystalline

same direction and with the same ratio as the macroscopic deformation of the polymer. Although so far we focused on single grains near the polymer surface, the linearity between t/t_0 and d/d_0 still holds for the spectrum optically averaged over the grains inside the polymer matrix. This suggests that the compression was homogeneous throughout the polymer-immobilized colloidal crystalline arrays.

Conclusions

We have examined the change of the optical properties and microstructure of polymer-immobilized non-close-packed colloidal crystalline arrays with stretching. The peak wavelength of Bragg diffraction shifted to shorter wavelength with stretching. The result was caused from the decrease in the interplanar spacing with stretching. These results show that by using polymer-immobilized non-close-packed colloidal crystalline array, mechanically tunable photonic crystals can be realized, and they open the possibility of tuning the microstructure of colloidal crystalline array for photonic crystal. These systems may be useful in optical sensor or switching applications.

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