Transactions of the Materials Research Society of Japan 30[2] 381-384 (2005)

Preparation of Self-organized Regular Arrangement of Monodispersed Polystyrene Microparticle Layer

Atsushi Kato[1,2*] and Takatoshi Kinoshita[1]
[1]Graduate School of Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya-shi Aichi 466-8555, JAPAN
Fax: +81-52-731-5267, E-mail: kinoshita.takatoshi@nitech.ac.jp,
[2]Tokai Optical Co., Ltd,
5-26 Shimoda, Eda-cho, Okazaki-shi Aichi 444-2192, JAPAN

Photonic crystal is a kind of dielectric structures with a period of the order of optical wavelength. Sub-micro sized spherical particles in opal-like structure have been demonstrated to build photonic crystal. In this study, polystyrene (PS) monodispersed particle layer, which build the opal-like structure, were obtained on the substrate by Langmuir-Blodgett (LB) method. The particle monolayer was found to be in the hexagonal structure. The reflective spectra of the particle multilayer (5 layers) were measured with several incident angles. The peaks of wavelength were gradually shifted to the low wavelength with increase in the incident angle. Then, the regular arrangement and refractive index of the particle multilayer could be analyzed by the equation that was derived from Bragg's law using the reflective spectrum. As a result, the refractive index and diameter of polystyrene particle obtained were 1.43 and 273 nm by postulating the particles were in the face-center-crystal in the particle multilayer. Moreover, we prepared the multilayer of the sulfonated PS particle layer with nickel ion and the multilayer of the alternating PS and sulfonated PS particle with nickel ion layers. These refractive indexes were found to be increased by the surface modification of PS with nickel ion.

Key words: Polystyrene particle, LB method, Multilayer, Reflective spectra, Surface modification

1. INTRODUCTION

The structural color[1,2], such as opal, morpho butterfly, feather of peacock and so on, is originated from the interference of light. For example, opal was made by the deposition of layer of monodispersed spherical silicon particles. When this regular array of particle layer interferes with visible light, it show the color corresponding with the particle size and its arrangement. Colloidal crystals with three-dimensionally periodic lattices had been studied[3-6] in the fields of physics and colloid science. Recently, a photonic crystal has been investigated[7,8] in the infrared wavelength region for the application for optical circuits, computing systems and so on. There have been few studies about ordered structure of particle multilayer, which interacts with visible light wavelength.

Several construction methods of colloidal crystals were proposed such as evaporation[6], sedimentation[9], centrifugation[10] and substrate dipping[4,5]. However, it was difficult to produce a colloidal crystal with large scale.

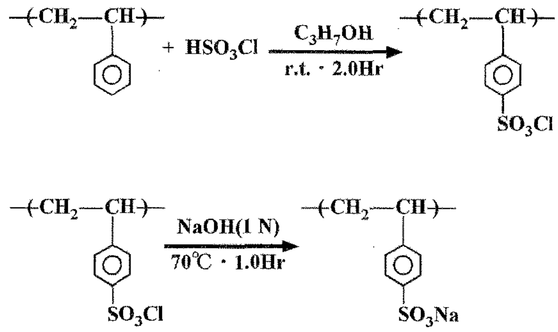
In this study, we prepared that ordered array of sub-micro sized polystyrene particle layer on the substrate by Langmuir-Blodgett (LB) method. We estimated the structure and optical properties of the PS particle multilayer obtained. And the addition of metal ion into polymer was reported to be able to increase the refractive index[11]. The metal ions, which have high refractive index, are Ni, Pb, Fe and etc. Among these metals, we have focused on nickel ion because of its high transparency and readily handling. Thus, it was prepared and calculated the refractive index of particle multilayer with nickel ion.

2. EXPERIMENTAL

2.1 Materials

Monodispersed polystyrene (PS) spherical particle

(D= 300 nm), purchased from Seradyn, Inc, was used with dialysis by Milli-Q water. Sulfonated PS particle was synthesized by using this PS particle and chlorosulfonic acid in *n*-propanol at room temperature for 2 hours. And the obtained particles were agitated in NaOH aqueous solution (1 N) at 70 ℃ for an hour (Scheme 1).



Scheme 1. Preparation of sulfonated PS.

2.2 Hydrophobic silicon wafer substrate

Silicon wafer (Nilaco) was used as substrate. The surface of silicon is known to be hydrophilic owing to the hydroxyl groups. So the silicon was modified with silane-coupling agent to produce the hydrophobic surface. First, substrate cleaned by acetone, nitric acid and then the ozone cleaner (NL-UV253, Nippon Laser and Electronics Lab.) An octadecyltriethoxysilane in benzene solution was spread on a Teflon trough filled with an aqueous solution. The deposition of the monolayer on the silicon wafer substrate was performed at 11 mN/m by LB method.

2.3 Deposition of particle layers

The PS and the sulfonated PS particle were dispersed in ethanol and *n*-butanol (1:1) mixed solvent. The dispersion of the mixed solvent was gently added drop way on the surface of an aqueous solution in Teflon trough using a micro-syringe. The spread particles were allowed to stand on the water surface for 30 min, and then surface compression was carried out at a speed of 5 mm/min by LB film deposition apparatus (NL-BIO40s-MWC, Nippon Laser and Electronics Lab.). During the compressing, the surface pressure was measured using Wilhelmy plate. And the PS particle monolayer at 11 mN/m was transferred in the vertical mode method onto the hydrophobic silicon wafer substrate. The particle multilayer was prepared by repeating the same process. The sulfonated PS particle layer was immersed into nickel chloride aqueous solution to produce nickel ion-sulfonic acid complex formation. The alternative multilayer of PS and sulfonated PS particle layer with nickel ion was also prepared.

2.4 Measurements

Reflective spectrum measurements were performed by use of a UV/VIS spectrophotometer V-550 (JASCO) together with an attachment, ARV-474 (JASCO) with incident angles with 5 degree intervals of 5 to 55 degree.

AFM image of the layer on silicon wafer was measured by NanoScopeIV (Digital instruments).

3. RESULTS AND DISCUSSIONS

3.1 PS particle monolayer

Figure 1(a) shows the PS particle monolayer on the substrate. This PS particle monolayer was a long-range ordered layer. We also show the AFM image of the surface of the PS particle monolayer (Figure 1(b)). This image suggests that opaline lattice of the PS particle monolayer exhibited the hexagonal structure. And the average distance between the top positions of particles was 281 nm.

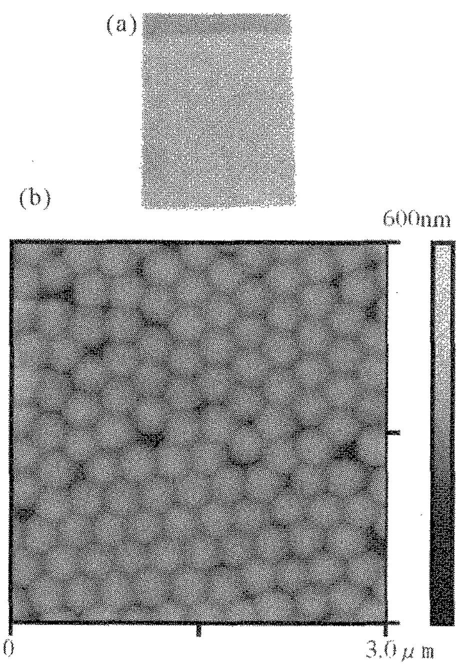


Figure 1. Photograph (a) and AFM image (b) of the PS particle monolayer on the substrate by LB method.

3.2 PS particle multilayer

We prepared the PS particle multilayer on the hydrophobic silicon substrate. Figure 2(a) shows the PS particle multilayer with 5 layers. We measured reflective spectra of the particle multilayer at different incident

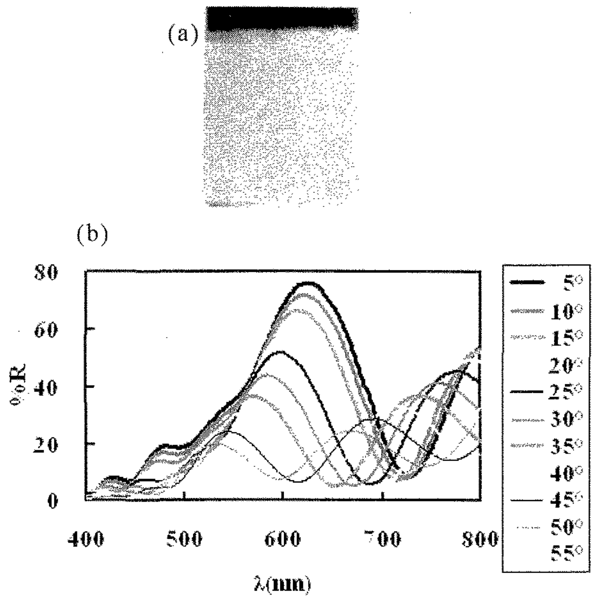


Figure 2. Photograph (a) and reflective spectrum (b) of the PS particle multilayer with 5 layer at incident angle from 5 to 55 degree.

angle (Figure 2(b)). We found that the peak wavelength was gradually shifted to the low wavelength with increase in the incident angle. And this particle multilayer has high reflectance value, 76 %, at incident angle of 5 degree. This showed that the particles are highly arranged in the multilayer.

The structural regularity and the optical properties of the PS particle multilayer could be analyzed by the reflective spectra. In general, the wavelength of light diffracted from a colloidal crystal is determined by the Bragg's equation[9].

$$\lambda = 2d \cdot (n^2 - \sin^2\theta)^{1/2} \quad (1)$$

$$d = a_{[hkl]} / (h^2+k^2+l^2)^{1/2} \quad (2)$$

$$a_{[111]} = 2^{1/2} \cdot D \quad (3)$$

where λ is the peak wavelength of the diffracted light, n is the mean refractive index of the particle layer, d is the inter-planar spacing between the particle layers, θ is the incident angle, $a_{[hkl]}$ is the unit cell parameter, [hkl] is the direction of unit cell and D is the diameter of particle. Eq.(1) suggests that the wavelength of light diffracted from the particle layer is directly proportional to the reflective spectra. Thus, it is appropriate to verify the ordered array of particles from the reflective spectra.

The inter-planar spacing d and the refractive

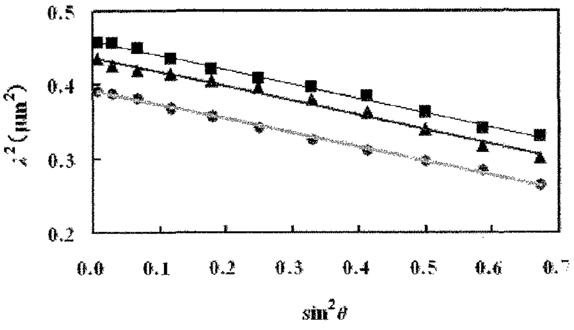


Figure 3. Plot of incident angle VS wavelength of maximum light (■: sulfonated PS particle multilayer with nickel ion, ▲: alternated PS particle layer and sulfonated PS particle layer with nickel ion ●: PS particle multilayer).

index n were calculated by the slope and the intercept of Figure 3. As a result, the diameter of particle was 273 nm, by postulating the particle arrangement was in the face-center-crystal (FCC) structure (Figure 4(a)). This diameter of particle is almost consistent with the distance between the top positions of particles, 281 nm, by the AFM image (Figure 1(b)). And the refractive index of the PS particle multilayer was estimated to be 1.43.

3.3 Refractive index of the surface modification of the particle

The refractive index of the PS particle multilayer with nickel ion (Figure 4(b)) and the apparent refractive index of alternated PS particle multilayer (Figure 4(c)) were estimated to be 1.55 and 1.50, respectively, using Figure 3. It may say, therefore, that the refractive index of the layer can be controlled by the surface modification of

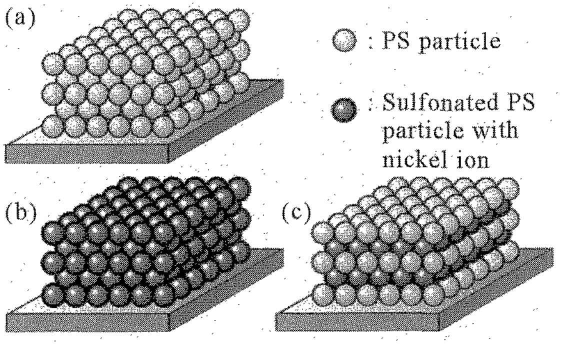


Figure 4. Schematic illustration of the particle multilayer with 5 layers [(a): PS particle layer, (b): sulfonated PS particle layer with nickel ion, (c): alternating PS and sulfonated PS particle layer with nickel ion].

PS particle. And the slopes in Figure 3 of sulfonated and alternated particle multilayers with nickel ion were similar to that of the PS particle multilayer. The diameters of particle were 271 nm and 272 nm, respectively. Therefore, the particle arrangements of these particle multilayers were suggested to form FCC structure.

4. CONCLUSION

This paper reported the regular arrangement of the particle layer, which was prepared at air/water interface by LB method. First, we showed PS particle layer formed in the FCC manner on the substrate. The quality of array was investigated by AFM and reflective spectra. Refractive index of the particle multilayer was increased with nickel ion complexation on the surface of the particle.

This way might be a new approach for the preparation of colloidal crystals with three-dimensionally systematic structure.

REFERENCES

[1] H.Tabata, K.Kumazawa, M.Funakawa, J.Takimoto and M.Akimoto, *Opt.Rev.*, **3**, 139 (1996).
[2] P.Vukusic, J.R.Sambles, C.R.Lawavence and R.j.Wootton, *Nature*, **410**, 36 (2001)
[3] K.Dou, Z.Xu, X.J.Wang, Y.Chen and T.Collins, *J. Lumin.*, **102/103**, 476, (2003).
[4] Z-Z.Gu, H.Uetsuka, K.Takahashi, R.Nakajima, H.Onishi, A.Fujishima and O.Sato, *Angew. Chem .Int .Ed.*, **42(8)**, 894, (2003).
[5] H.Fudouzi and Y.Xia, *Langmuir*, **19**, 9653 (2003)
[6] L.M.Goldenberg, J.Wagner, J.Stumpe, B.-R. Paulke and E.Gornitz, *Mater. Sci. Eng.*, **C22**, 405 (2002).
[7] A.Chutinan and S.Noda, *Appl. Phys. Lett.*, **75**, 3739,(1999).
[8] B.Song, S.Noda, and T.Asono, *Science*, **300**, 1537, (2003).
[9] R.Mayoral, J.Requena, J.S.Moya, C.Lopez, A.Cintas and H.Miguez, *Adv.Mater.*, **9**, 257, (1997).
[10] N.P.Johnson, D.W.McComb, A.Richel, B.M.Treble and R.M.De.La Rue, *Synth. Mater.*, **116**, 469 (2001).
[11] Q.Lin, B.Yang, J.Li, X.Meng and J.Shen, *Polymer*, **41**, 8305, (2000).

(Received December 24, 2004; Accepted February 24, 2005)