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Measurements of Refractive Index of Liquids and Liquid Crystals Utilizing Opals with Interconnected Three-dimensionally Regular Array of Voids and Their Replicas

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Abstract

The optical stop band in the transmission spectrum and the diffraction peak in the reflection spectrum of opals with a three-dimensionally periodic structure shift markedly by the infiltration with various liquids and liquid crystals. Utilizing these phenomena, a new simple method to evaluate the refractive index of liquids and liquid crystals have been proposed.

Introduction

Recently, photonic crystals with a three-dimensionally periodic structure on the order of an optical wavelength have attracted much interest from both fundamental and practical points of view, because a new concept of photonic band gap has been theoretically predicted, and various novel properties and functionalities were expected in this new class of material [1, 2, 3].

We have demonstrated that a three-dimensionally periodic structure can be prepared by a self-assembly method, that is, by the sedimentation of mono-dispersed nano-spheres [4]. Such a three-dimensionally regular structure made of SiO_2 spheres is called also a synthetic opal. We have also proposed to realize new functionalities by infiltrating various materials into the percolated nanoscale voids of the synthetic opals and indicated interesting phenomena such as stabilization of photochromism and amplified spontaneous emission and lasing in opals infiltrated with fluorescent dyes and conducting polymers [4 – 6].

In this paper, we propose a new method to evaluate the refractive index of liquids and liquid crystals using the dependences of the stop band wavelength in the transmission spectrum through the opal and also the diffraction peak wavelength in the reflection spectrum on the refractive index of the infiltrated material.

Experimental

Three-dimensionally periodic structures in thin films were fabricated by the sedimentation of mono-dispersed SiO_2 spheres of 180 – 550nm diameter and films made of SiO_2 spheres of 300nm diameter were mainly used in this study. These thin three-dimensionally periodic structures of SiO_2 (synthetic opals) were confirmed to have a face-centered cubic (f.c.c.) structure and to contain interconnected nanoscale voids by measuring the optical diffraction and by the electron microscopic observation using a scanning electron microscope (Hitachi, S-2100C).

Polymer replicas of the synthetic opal were prepared by the infiltration with polymer or polymer precursor into nanoscale voids of the opal, followed by the removal of SiO_2 spheres by HF. In this paper, a UV curable prepolymer for polymer dispersed liquid crystals (Merck, PN393) was mainly used for polymer replicas.

The transmission and reflection spectra were measured using a spectrophotometer (Hitachi, 330) and a hand-made experimental setup with a W-lamp as a light source and a multi-channel analyzer (Hamamatsu Photonics, PMA-11) as a detector.

Various organic liquids, two types of liquid crystals, a nematic liquid crystal ZLI1132 (Merck) and a smectic liquid crystal (R)-4'-(1-metoxycarbonyl-1-ethoxy) phenyl - 4 - [4-(n-octyloxy) phenyl] benzoate (1MC1EPOPB), and also conducting polymers, poly(3-hexylthiophene) (PAT-6) and poly(3-octadecylthiophene) (PAT-18), were used for the infiltrations into the thin opal films and the polymer replicas.

Results and Discussion

Figures 1 (a) and (b) show the electron micrographs of the opal made of SiO_2 spheres of 300nm diameter and its polymer replica, respectively. As is evident from these figures, periodically regular structures were confirmed in both samples. Not only the synthetic opal but also its polymer replica exhibit a beautiful opalescent color and therefore it can also be named a polymer inverse opal. Corresponding to these opalescent colors, they exhibit the clear stop bands in the transmission spectra and also the clear diffraction peaks in the reflection spectra, as shown in Fig. 2 and Fig. 3.

These stop bands and diffraction peaks were confirmed to shift by the infiltration with liquids. Figures 4 and 5 show the transmission and reflection spectra of the synthetic opals infiltrated with various organic solvents, respectively. It should be noted that the stop band and diffraction peak wavelengths shift to a longer wavelength for the opal infiltrated with solvents with the larger refractive index. This relationship between the peak wavelength and the refractive index of the solvent is more clearly indicated in Fig. 6. These results indicate that the refractive index of a liquid can be evaluated by measuring the stop band wavelength in the transmission spectrum or the diffraction peak wavelength in the reflection spectrum of the opal infiltrated with the liquid.

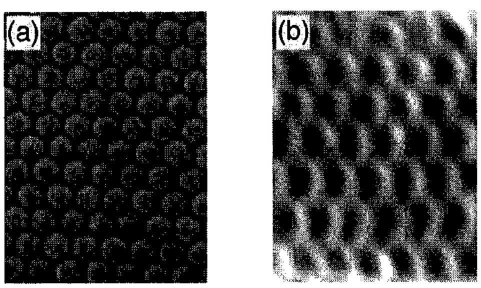

Fig. 1 Electron micrographs of (a) an opal and (b) a polymer replica.

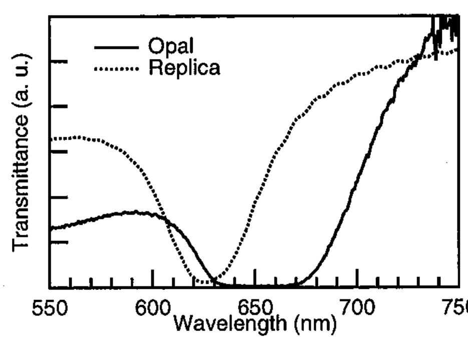

Fig. 2 Transmission spectra of an opal and a polymer replica infiltrated with water.

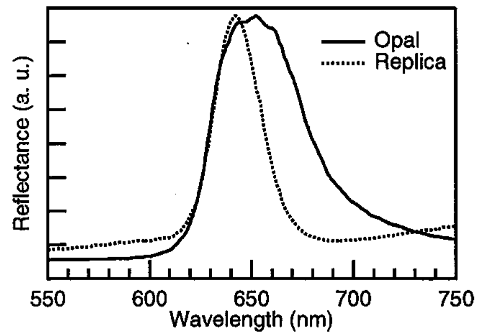

Fig. 3 Reflection spectra of an opal and a polymer replica infiltrated with water.

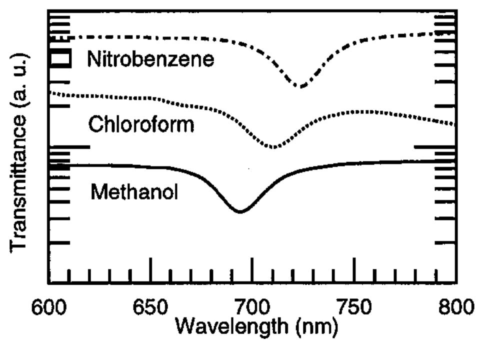

Fig. 4 Transmission spectra of opals infiltrated with various organic solvents.

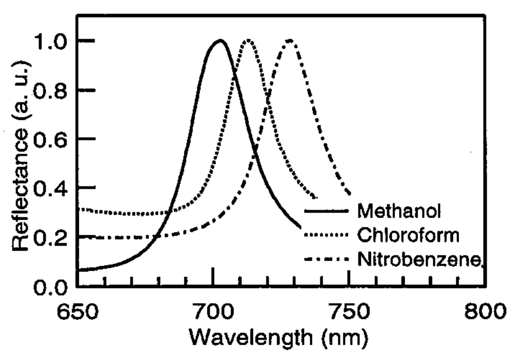

Fig. 5 Reflection spectra of opals infiltrated with various organic solvents.

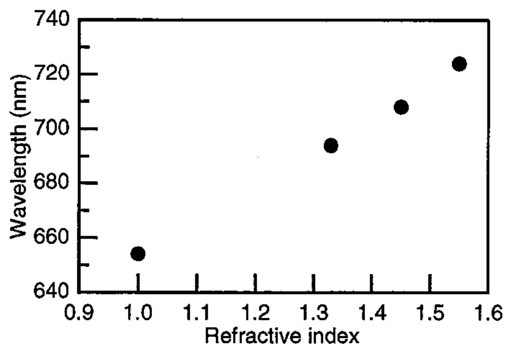

Fig. 6 Wavelength of diffraction peak as a function of the refractive index of the infiltrated material.

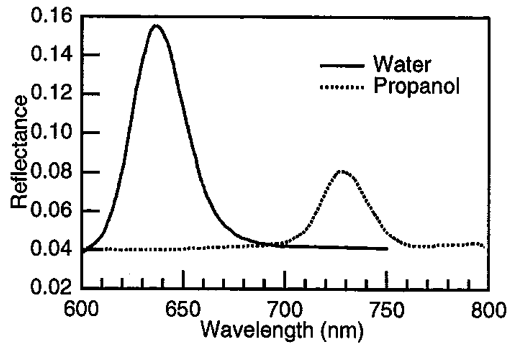

Fig. 7 Reflection spectra of polymer replicas infiltrated with water and 2-propanol.

It should also be noted that the opals made of SiO_2 spheres of a different diameter also exhibit the similar shifts of the stop band and the diffraction peak depending on the refractive index of the infiltrated liquids.

As is clearly shown in Fig. 7, the diffraction peak also shifts drastically by changing the liquid infiltrated into the polymer replica. That is, the polymer replica can also be used for the evaluation of the refractive index of liquids. Other replicas prepared with other materials can be also used for the same purpose.

Liquid crystals can also be well infiltrated into the opal and the polymer replica. Accompanying with the infiltration with liquid crystals, the diffraction peak wavelength changes drastically. It should be noted that it also shifts with changing temperature, which can be interpreted in terms of the temperature dependence of the refractive index of the liquid crystal.

Using this phenomenon, we can evaluate temperature dependence of the refractive index of the liquid crystal. Figure 8 shows the temperature dependence of the evaluated refractive index of 1MC1EPOPB. It should be noted in this figure that the refractive index changes step-wise at the phase transition points.

Furthermore, we used conducting polymers, PAT-6 and PAT-18, for the infiltration into the synthetic opal. Figure 9 shows the shift of the diffraction peak wavelength by the infiltration with PAT-6. The evaluated refractive index of the infiltrated PAT-6 from this experiment, however, was smaller than that evaluated by the Brewster angle measurement, and depended on the measured spot of the sample. This means that PAT-6 filled partially the voids of the opal. In the case of the infiltration with the PAT-18, the partial infiltration was also observed. These unsatisfied infiltrations should be improved by the melting of the infiltrated conducting polymer using heat.

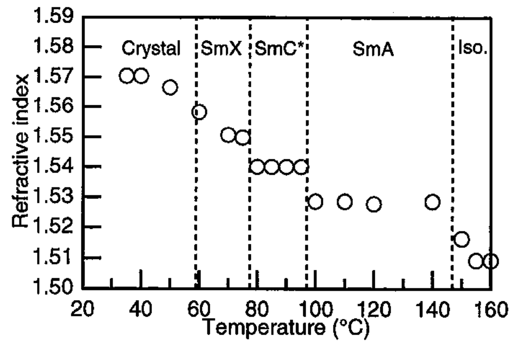

Fig. 8 Temperature dependence of the evaluated refractive index of smectic liquid crystal (1MC1EPOPB).

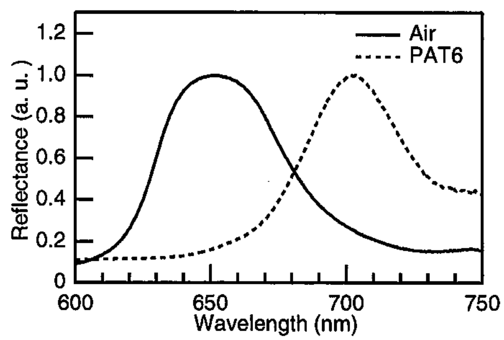

Fig. 9 Reflection spectra of an opal and an opal infiltrated with PAT-6.

Summary

The stop band in the transmission spectrum and the diffraction peak in the reflection spectrum depend strongly on the refractive index of the liquid or the liquid crystal infiltrated into the opal or the polymer replica of the opal. New simple method to evaluate the refractive index of liquids and liquid crystals precisely were proposed using the above phenomena in the infiltrated opal.

Acknowledgement

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