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Preparation and Characterization of Porous Polymethylmethacrylate Film Showing Optical Reflectivity

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This paper describes a method for the preparation of porous polymethylmethacrylate showing optical reflectivity from the porous silicon template. A porous polymethylmethacrylate showing optical reflectivity was prepared by replicating porous silicon template which was obtained by applying a computer-generated periodic square current density and resulted in a mirror with high reflectivity in a specific narrow spectral region. A porous polymethylmethacrylate showing an excellent reflectivity was successfully obtained by dissolving the Porous silicon template from the porous polymethylmethacrylate composite film. A porous polymethylmethacrylate exhibited a sharp reflection resonance in the reflectivity spectrum. Surface image of the porous polymethylmethacrylate indicated that the surface of the porous polymethylmethacrylate film had a porous structure. These porous polymethylmethacrylate films in aqueous solutions were stable for several days without any degradation.

Key words: Reflection, Porous Polymer, Porous Silicon, Polymethylmethacrylate

1. Introduction

Discovering of new optical materials based on novel physical and chemical properties represents one of the most interesting challenges in modern materials science. Especially, flexible optical polymethylmethacrylate thin films having porosity are particularly attractive[1]. Recently, the addition of functionalities to polymer materials has led to markedly enhanced control of a wide range of technically important material properties from optoelectronic to mechanical properties[2]. The optical polymer thin films having porosity have advantages of flexible possibilities. However, studies on the porous polymethylmethacrylate exhibiting the reflection optical properties are very limited.

Since the discovery of porous silicon by Cahnam[3], porous silicon has been investigated for various applications, such as biological and chemical sensors, medical diagnostics, optical filters, micro chemical reactors, and fuel cells. Optical devices based on porous silicon have been brought to the attention of scientists[4-15]. Porous silicon has advantages for building optical structures as well as very high surface area with various surface chemistry and unusual optical properties. The porosity and pore size of porous silicon can be controlled by modulating the applied current densities[16-20]. Porous polymer materials showing optical properties could be an alternative, since porous silicon has the limitation for chemical and mechanical stability for many applications. This provides the means to construct complex porous structures of polymer thin film that are compatible with harsh environments and to improve chemical and mechanical stability.

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2. Experimental Section

2.1. Preparation of Porous Silicon

The porous silicon samples were prepared by electrochemically etching heavily-doped p^{++}-type silicon wafers (boron doped, polished on the <100> face, resistivity of 0.8-1.2 mΩ·cm, Siltronix, Inc.). The etching solution consisted of a 3:1 volume mixture of 48% aqueous hydrofluoric acid (ACS reagent, Aldrich Chemicals) and absolute ethanol (ACS reagent, Aldrich Chemicals). A galvanostatic etch was carried out in a Teflon cell by applying 20 cycles of a two-electrode configuration with a Pt mesh electrode. DBR porous silicon was prepared by using periodic square wave currents between 5 $mA \cdot cm^{-2}$ for 75 s and 50 $mA \cdot cm^{-2}$ for 2 s. The anodization current was supplied by a Keithley 2420 high-precision constant current source controlled by a computer to allow the formation of porous silicon

multilayers. To prevent the photogeneration of carriers, we performed the anodization in the dark. All the samples were then rinsed several times with ethanol and dried were under an Ar atmosphere prior to use. Free-standing porous silicon films were obtained from the silicon substrate by applying as electropolishing current of 360 mA·cm^{-2} for 1 min in an ethanoic 37.5% aqueous HF solution and of 24 mA·cm^{-2} for 2 min in an ethanoic 3.3% aqueous HF solution.

2.2. Preparation of Porous Polymethylmethacrylate Thin Film

Prepared free-standing porous silicon films were thermally oxidized in a furnace at 300°C for 3 hrs. For the replicating solution, 3 g of polymethylmethacrylate (Aldrich, Mw = 120,000) was dissolved in 20 mL of toluene (Fisher Scientific). The resulting mixtures were cast onto porous SiO_2 film and the samples were annealed in an oven at 95°C for 1 hr. Then, the oxidized porous silicon was removed in 0.1 M aqueous NaOH for 3 hrs.

2.3. Instrumentation and Data Acquisition

The optical reflectivity spectra were measured using a tungsten-halogen lamp and an Ocean Optics S2000 CCD spectrometer fitted with a fiber optic input. The reflected light collected at the end of the fiber optic was positioned at the focal plane of an optical microscope. FT-IR spectra were acquired with a Nicolet model 5700 FT-IR instrument in the diffuse reflectance mode (Spectra-Tech diffuse reflectance attachment). The FT-IR sample compartment was purged with nitrogen before each acquisition. The morphology of sample was observed with FE-SEM (S-4700, Hitachi)

3. Results and Discussion

Schematic diagram for the preparation of porous polymethylmethacrylate thin films are shown in Figure 1. A porous polymethylmethacrylate showing optical reflectivity was prepared by replicating porous silicon template which was obtained by applying a computer-generated periodic square current density. Porous silicon exhibits a high reflectivity band with a Bragg wavelength λ_{Bragg} that depends on the thicknesses of the layers (d_1, d_2) and the corresponding refractive indices (n_1, n_2). The mth order of the Bragg peak is given by

$$m\lambda_{Bragg} = 2(d_1 n_1 + d_2 n_2).$$

Typical etch parameters for the porous silicon structure involve a periodic square wave current between low and high current densities. For the fabrication of porous silicon, an applied current densities used between 5 and 50 mA·cm^{-2}. The etching times for a $\lambda/4$ layer of a Bragg structure were typically 75 s for a low current and 2 s for a high current. The reflection peak shown in Fig. 2 in the reflection spectrum showed a narrow full width at half maximum ca. 22 nm at 610 nm. The resulting porous silicon films were lifted off from the silicon wafer to obtain porous silicon films

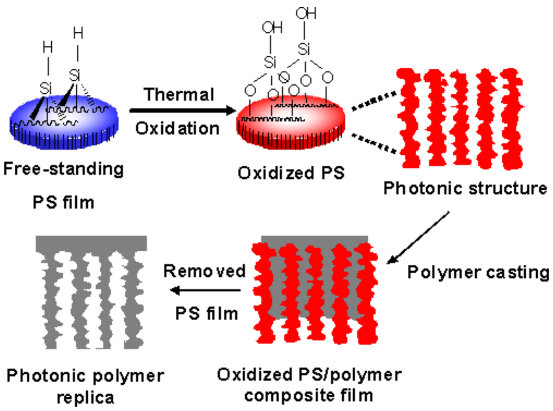

Fig. 1. Schematic diagram for the preparation of porous polymethylmethacrylate thin film.

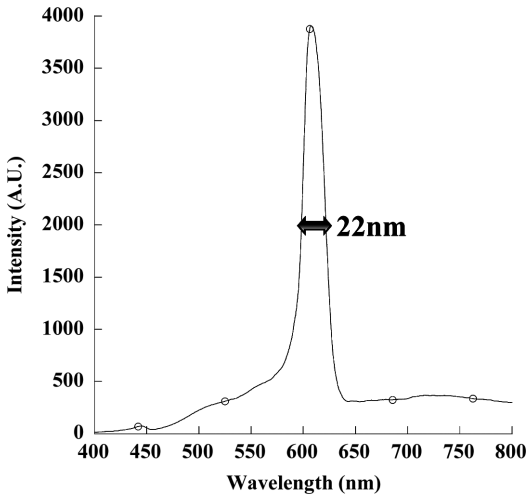

Fig. 2. Optical reflectivity spectrum of porous silicon films.

by applying of electropolishing current in a solution of HF and ethanol. The reflection peak of porous silicon film was observed at 610 nm. Oxidation of porous silicon film was thermally carried out in a furnace at 300°C for 4 hrs. The reflection peak for the oxidized porous silicon film displayed reflectivity at 570 nm, which were shifted to shorter wavelengths. This is due to a decrease of the average refractive index from that for silicon to that for silicon dioxide.

After the thermal oxidation of the porous silicon film, the presence of silicon oxide was determined by using FT-IR measurement, as shown in Figure 3. The FT-IR spectrum of a fresh porous silicon film displayed vibrational bands in the fingerprint region of the spectrum. $\upsilon_{(Si-H)}$ and $\delta_{(Si-H)}$ vibrations associated with surface Si-H species were also apparent at 2117 and 941 cm^{-1}, respectively. Thermal oxidation of the porous silicon layer resulted significant loss of intensity of the υ (Si–H) modes in the infrared spectrum at 2150 cm^{1}, but vibrational bands due to oxygen-back-bonded silicon hydride, υ (OSi–H) and δ (OSi–H) modes, grew at 2300 and 850 cm^{1}, respectively. Multiple silicon oxide species, Si–O–Si, displayed a strong, very broad absorption band between 1000 and 1250 cm^{1}.

The surface morphology of porous silicon was obtained with cold FE-SEM and shown in Figure 4. FE-SEM image of porous silicon surface indicated that the porous silicon exhibited very stable and even surface. FE-SEM image of porous silicon indicates that the prepared porous silicon has cylindrical mesopores with the pore size of few nanometers and the depth of few microns.

To obtain the porous polymer thin films, the polymethylmethacrylate solution was cast on the top surface of the oxidized porous silicon film. After drying in an room temperature, the resulting composite film was annealed in an oven at 95°C to fill the pores of porous silicon with the polymethylmethacrylate. Since top side of the oxidized porous silicon films were coated with the polymethylmethacrylate, the silicon oxide of oxidized porous silicon matrix can be easily removed from the composite films in a dilute aqueous sodium hydroxide solution. X-ray diffraction pattern of the porous polymethylmethacrylate thin film indicates that the oxidized porous silicon template was completely removed from the composite films and that no crystalline silicon was remaining. The surface morphology of porous polymethylmethacrylate thin film was obtained with cold FE-SEM and shown in Figure 5. FE-SEM image of surface of porous polymethylmethacrylate thin film indicated that the prepared porous polymethylmethacrylate thin film has cylindrical mesopores with

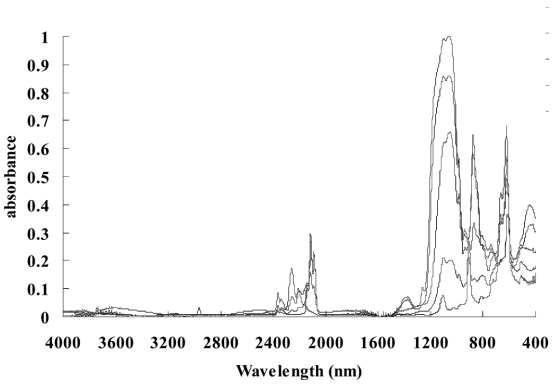

Fig. 3. FT-IR spectra of oxidized porous silicon films.

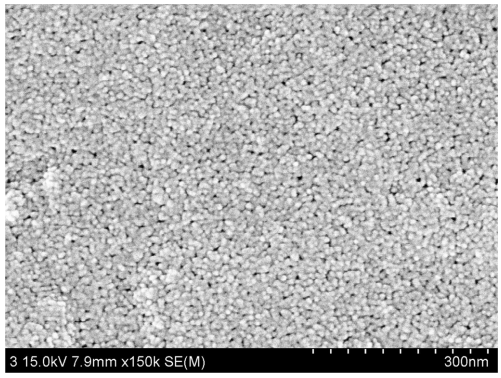

Fig. 4. Surface SEM image of porous silicon

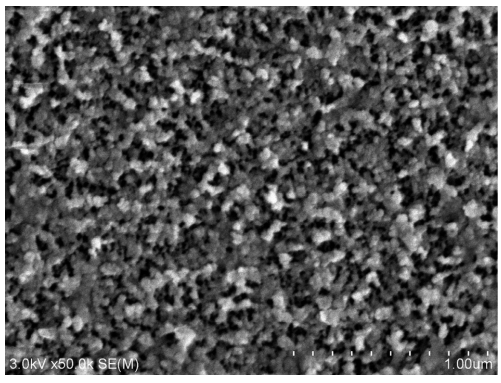

Fig. 5. Surface SEM image of porous polymethylmethacrylate thin film.

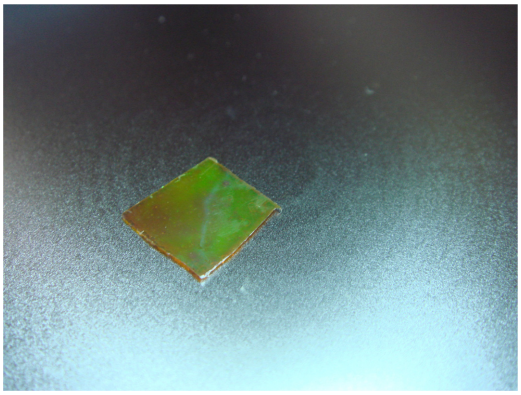

Fig. 6. Photo image of porous polymethylmethacrylate thin film.

the pore size of 100 nm and the depth of few microns.

After removal of the oxidized porous silicon from the composite film, the porous polymethylmethacrylate thin film exhibited a reflection peak at 570 nm. Porous polymethylmethacrylate thin film shown in Figure 6 exhibits a green color due to the reflection peak of the porous polymethylmethacrylate. The polymethylmethacrylate replica was also highly flexible and displayed a significantly improved mechanical stability without apparent degradation. Its optical properties were retained upon flexing. This method provides a general means of fabricating the photonic porous polymer thin films. The photonic porous polymer thin films possessed stable spectral features and increased stability to corrosion.

4. Conclusion

Porous polymer thin films showing high reflectivity were prepared by casting a polymer solution onto the oxidized porous silicon and then removing silicon dioxide of the oxidized porous silicon template from the polymethylmethacrylate composite film. The porous polymer thin films were robust and flexible. They exhibited excellent reflectivity in the reflection spectrum. The methods based on porous silicon have been provided for the preparation of photonic polymer having porous structures.

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