Fabrication and Optical Characterization of Rugate-structured Polymer Replicas†

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Photonic crystals containing rugate structure result in a mirror with high reflectivity in a specific narrow spectral region and are prepared by applying a computer-generated pseudo-sinusoidal current waveform. Well defined 1-dimentional photonic polymer replicas showing a reflectivity at 534 nm have been successfully obtained by the removal of rugate porous silicon (PSi) template from the polystyrene composite film. XRD measurement indicates that the oxidized rugate PSi has been completely removed from the composite films. Polymer replicas exhibit a sharp resonance in the reflectivity spectrum. Optical characteristics of photonic polymer replicas indicate that the surface of polymer film has a negative structure of rugate PSi. These replicas are stable in aqueous solutions for several days without any degradation. The methods have been provided for the construction of photonic structures with polymers.

Key Words : Rugate filter, Porous silicon, Photonic structure, Polymer replica

Introduction

The development of new methods to build photonic structures in a device is of great interest, since conventional lithographic method is too complex to fabricate. An electrochemical etch is one of lithographic methods to fabricate a photonic structures into the materials. Since the discovery of porous silicon,[1] multilayer-structured PSi has been intensively investigated for a variety of applications such as chemical[2,3] and biological sensors,[4] medical diagnostics,[5] optical band pass filters,[6] micro chemical reactors,[7] and micro fuel cells.[8,9] Its importance is due to very high surface area as well as their unique photonic properties. Multilayered PSi is an attractive candidate for building photonic structure, because the porosity and average pore size can be tuned by adjusting the electrochemical preparation conditions that allow the construction of photonic crystals.[10,11] Multilayer PSi such as distributed Bragg reflectors (DBR) PSi[12] or rugate PSi[13] exhibit unique optical properties providing a reflection band at specific wavelength in the optical reflectivity spectrum. However porous silicons are limited by their chemical and mechanical stability for many applications, because these films are very brittle.[14] In addition, they are not suitable for the application of biological sensors *in vivo* due to the presence of silicon metal of the PSi films. To overcome these issues, polymer materials showing identical optical properties might be an alternative.[15,16] In the present work, we have prepared polystyrene replicas showing rugate photonic structure by casting of polystyrene solution onto an oxidized rugate PSi films, where the PSi films are used as templates for building nanostructured materials. Replication process and photonic features of the polymer replicas are presented. This provides the means for the construction of complex photonic structures of polymers that are compatible with harsh environments and improves chemical and mechanical stability.

Experimental

Preparation of Rugate PSi Samples. Rugate PSi samples were prepared by an electrochemical etch of heavily doped p^{++}-type silicon wafers (boron doped, <100> oriented, resistivity of 0.8-1.2 mΩ-cm, Siltronix, Inc.). The etching solution consisted of a 3:1 volume mixture of aqueous 48% hydrofluoric acid (ACS reagent, Aldrich Chemicals) and absolute ethanol (ACS reagent, Aldrich Chemicals). Rugate PSi samples were prepared by using a computer-generated sinusoidal current waveform with limits of 11.5 to 34.6 mA/cm^2, 100 repeats, and periods on the order of 8 sec depending on the desired wavelength of maximum reflectivity. The porous layers generated in the electrochemical etch were smooth enough to create high-quality 1D photonic crystals. Free-standing rugate PSi films were obtained from the silicon substrate by an applying of electropolishing current at 460 mA/cm^2 for 2 min in an ethanoic 37.5% aqueous HF solution, and then at 22 mA/cm^2 for 2 min in an ethanoic 3.3% aqueous HF solution.

Preparation of Photonic Polymer Replicas. Free-standing rugate PSi films were thermally oxidized in the furnace at 450 °C for 2 h. In a typical preparation, 4 g of polystyrene (Aldrich, Mw = 280,000) are dissolved in 20 mL of toluene (Fisher Scientific). The toluene solution was cast into the porous SiO_2 films and the samples were annealed in an oven at 95 °C for 20 min. Then oxidized rugate PSi matrix from the composite films were removed in aqueous 8% HF solution for 12 h. After the removal of the oxidized rugate

†This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

PSi template by chemical dissolution, the polymer castings replicate the photonic features and the nanostructure of the master.

Instrumentation and Data Acquisition. The anodization current was supplied by a Keithley 2420 high-precision constant current source which was controlled by a computer to allow the formation of PSi multilayers. 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 collection end of the fiber optic was positioned at the focal plane of the optical microscope. The morphology of rugate PSi film and polymer replica were observed with cold field emission scanning electron microscope (FE-SEM, S-4700, Hitachi). The surface characterization of fresh and oxidized rugate PSi samples for chemical properties was achieved by fourier-transform infrared (FT-IR, Nicolet 5700, Thermo Electron Co.). Rugate PSi film and polymer replica were characterized by X-ray diffractometer (XRD, D/MAX-3C, Riguku Co.) with CuKα radiation (0.15406 nm). The XRD patterns were collected in the 2θ range of 3-90° at room temperature.

Results and Discussion

Multilayered porous silicon has been successfully prepared using a periodic galvanostatic electrochemical etch of crystalline silicon by applying a sine wave current. The applied current density is modulated with a pseudo sine wave to generate a periodically varying porosity gradient. Rugate PSi samples display a very sharp reflection line at 585 nm without sidelobes around the reflectance peak in the optical reflectivity spectrum as shown in Figure 1. The spectral band of rugate PSi sample has a full-width at half-maximum (FWHM) of about 17 nm, which is much narrower than that of fluorescence spectrum obtained from a fluorescent organic molecules or quantum dot.[17]

An electrochemical etching offers the opportunity to modulate the porosity in depth and allows the fabrication of structures with any refractive index profile. When the current is gradually modulated, a smooth index profile of rugate PSi can be achieved. An effective refractive index of rugate PSi depends directly on porosity. The shape, size, and orientation of pores of PSi layers depend on surface orientation and the dopant level of the crystalline silicon

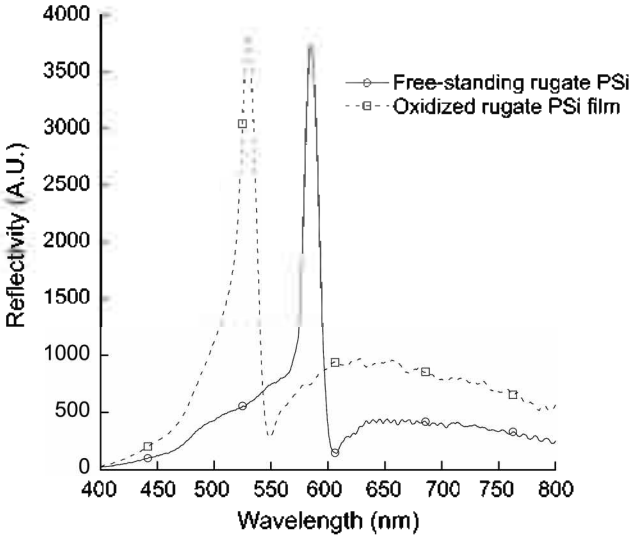

Figure 1. Optical reflectivity spectra of free-standing and oxidized rugate PSi film.

substrate as well as the applied current density, the temperature, and the concentration of the HF etching solution. The pore size of p-type PSi can be increased by increasing the concentration of the dopant and decreasing the aqueous HF concentration. High current densities result in the desired well-defined cylindrical macropores, rather than the random orientation of highly interconnected micropores. The surface and cross-sectional FE-SEM images of rugate PSi shown in Figure 2 illustrate that the thickness of rugate PSi is about 37.5 μm. FE-SEM image of rugate PSi displays a sinusoidally varying porosity gradient in the direction perpendicular to the plane of the filter. FE-SEM image of rugate PSi indicates that the prepared rugate PSi has cylindrical mesopores with the average pore size of 10 nm.

The waveform used in the present work involves a sine component, which is represented by

$$Y = A \cdot \sin(kt) + B$$

where Y represents a temporal sine wave of amplitude A, frequency k, time t, and an applied current density B. The position of reflection band depends on the frequency. In this work, the value of A and B was 11.55 and 23.05 mA, respectively. When the frequency was 0.125 Hz, a sharp reflection line at 585 nm was obtained.

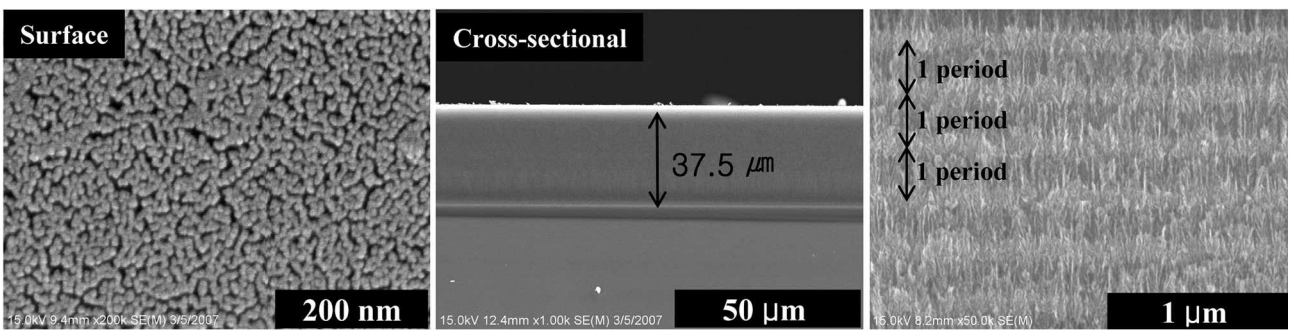

Figure 2. Surface and Cross-section SEM images of rugate PSi.

The resulting rugate PSi films can be lifted off from the silicon substrate to obtain a free-standing rugate PSi films by an applying of lift-off current in a solution of HF and ethanol. The reflectivity of free-standing rugate PSi film occurs at the identical location. Free-standing rugate PSi films are very brittle when these films are subjected to minor shear stresses. Thermal oxidation of these films is carried out in the furnace at 450 °C for 2 h. The reflection spectrum for the oxidized rugate PSi film exhibits its reflectivity at 531 nm, shifted to shorter wavelengths by 54 nm due to the decrease of an average refractive index from silicon to silicon dioxide.

After the thermal oxidation of rugate PSi film, the presence of silicon oxide has been determined by FT-IR measurement as shown in Figure 3. The FT-IR spectrum of fresh rugate PSi film exhibits vibrational bands in the fingerprint region of the spectrum. υ_{Si-H} and δ_{Si-H} vibrations associated with surface Si-H species are also apparent at 2117 and 941 cm^{-1}, respectively. However, the oxidized rugate PSi film exhibits vibrational bands characteristic of υ_{OSi-H}, δ_{OSi-H}, and υ_{Si-O} vibratioal modes are observed at 2270, 881, and 1070 cm^{-1}, respectively.

Polystyrene has been dissolved in toluene and cast on the top surface of oxidized rugate PSi film. After drying out in ambient atmosphere, the resulting composite film has been annealed in an oven at 95 °C to fill the pores with the polymer. The reflection band of oxidized rugate PSi/polystyrene composite film appears at 569 nm, shifted to longer wavelengths by 38 nm upon introduction of the polymer into the pores. Such a large red shift is due to an increase in the average refractive index of the multilayers, indicating the replacement of a significant amount of empty pore volume with the polymers. Since one side of oxidized rugate PSi films are coated with the polymers, the oxidized rugate PSi matrix from the composite films can be easily removed in dilute aqueous HF solution. After removal of oxidized rugate PSi from the composite film, the polymer replica has been successfully obtained and exhibits its reflection band at 534 nm, shifted to shorter wavelengths by 35 nm as shown in Figure 4. This blue shift indicates that the removal of oxidized rugate PSi template by chemical dissolution results the decrease of refractive index.

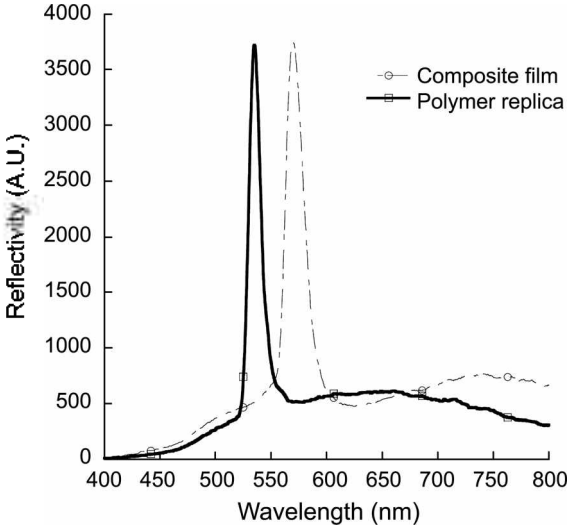

Figure 4. Optical reflectivity spectra of rugate PSi/polymer composite film and polymer replica.

To determine the presence of silicon, XRD measurement for the rugate PSi film and polymer replica film has been investigated. Figure 5 shows the X-ray diffraction pattern of samples prepared. The peak at about 69°, which can be seen in Figure 5 (top), is attributed to the diffraction from the crystalline silicon of the rugate PSi film. However, the X-ray diffraction pattern of the polymer replica in Figure 5 (bottom) indicates that the oxidized rugate PSi template has been completely removed from the composite films and no crystalline silicons are remaining.

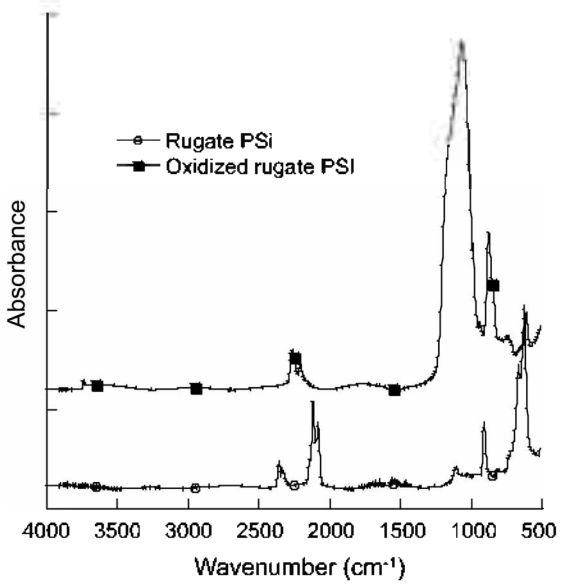

Figure 3. FT-IR spectra of free-standing and oxidized rugate PSi film.

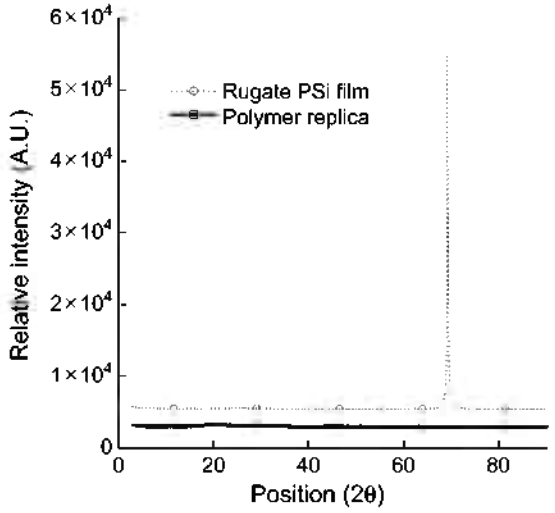

Figure 5. X-ray diffraction patterns of rugate PSi film and photonic polymer replica.

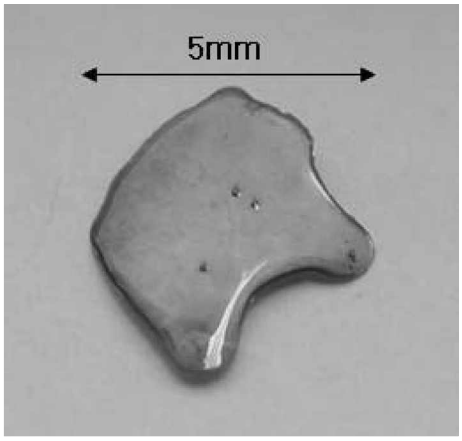

Figure 6. Photograph of polymer replica showing a reflection band at 534 nm.

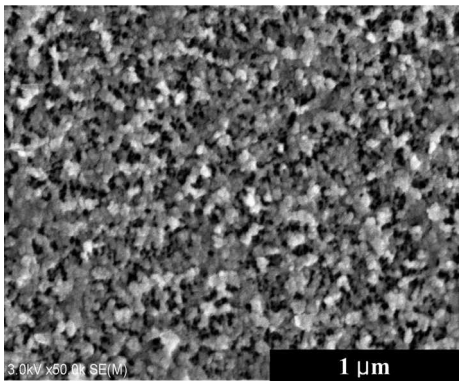

Figure 7. Surface SEM image of polymer replica.

Photograph of rugate-structured polymer replica is shown in Figure 6 and illustrates that its green color results from the reflection of the polymer replica. This polystyrene replica exhibits a sharp reflection peak in the reflectivity spectrum and replicates the photonic feature of rugate PSi master. The polymer replica is also highly flexible and displays significantly improved mechanical stability without apparent degradation. Its optical property is retained upon flexing.

The surface morphology of polymer replica is obtained with cold FE-SEM and shown in Figure 7. FE-SEM image of rugate-structured polymer replica indicates that the surface of polymer film has a negative structure of rugate PSi. Therefore, the polymer castings replicate the photonic feature and the nanostructure of rugate PSi master.

It is interesting to note that the photonic band widths of replicas are about 14 nm which is much narrower than that of rugate PSi master and the polymer replicas reported previously (*ca.* 50 nm).[18] These polymer replicas are stable in aqueous solutions for several days without any degradation and could be useful for a possible applications such as vapor senor, deformable and tunable optical filters, and bioresorbable materials.

Conclusions

The rugate-structured photonic polymer replica showing a reflectivity at 534 nm has been prepared by casting of polymer solution onto an oxidized porous silicon multilayer and then the chemical dissolution of oxidized rugate PSi template from the polystyrene composite film. The photonic polymer replicas are robust and flexible. They exhibit an excellent reflectivity in reflection spectrum. The photonic band gaps of replicas are narrower than that of typical semiconductor quantum dots. X-ray diffraction pattern and SEM images indicate that the polymer replica replicates the photonic feature and the nanostructure of rugate PSi master. The methods have been provided for the construction of photonic structures with polymers.

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