Preparation and Characterization of Flexible Optical Composite Films Based on Bragg-Structured Interferometer

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Abstract

Three types of functionalized flexible optical composite films based on Bragg structure porous silicon interferometer have been successfully fabricated by casting a toluene solution of polystyrene onto the free-standing porous silicon. The optical properties of composite films are measured. Surface functionalization of porous silicon is determined by FT-IR measurement. Reflectance and transparency properties of composite films are measured for the possible application of tunable optical filter and indicate that the transmission peak occurred at the identical location where the reflection peak appeared.

Key words: Composite, Transparency, Reflection, Surface Functionalization

1. Introduction

The development of nanometer scale technology is of great interest, because conventional lithographic method is too complex to fabricate. Since the discovery of porous silicon (PSi)[1], it has been intensively investigated for a variety of applications such as chemical and biological sensors, medical diagnostics, and drug delivery[2-14]. The morphology and optical properties depend on surface orientation, doping level and type, temperature, the current density, and the composition of the etching solution[15-23]. Recently, optical devices based on multi-structured PSi have been brought to the attention of the scientists. Multilayer PSi such as distributed Bragg reflector (DBR) PSi or rugate PSi exhibit unique optical properties providing a reflection band at specific wavelength in the optical reflectivity spectrum.

DBR PSi as multi-layered PSi has been developed and typically prepared by an applying a square current waveform to the etch cell. DBR PSi resulted in two discrete indices and displayed photonic structure of Bragg filters. Chemical modification of PSi multilayer exhibited the modification of its physical, chemical, and electronic properties. However, PSi has a limitation for an application of optical devices, because PSi can be easily air-oxidized at ambient temperature[24]. Air-oxidation of PSi causes a change of optical properties. To overcome this issue, stable composite film of PSi might be an alternative way to retain optical properties of PSi. In the present work, we have developed three types of composite films having different surface functionalities of PSi. The fabrication, optical characterization, and surface functionalization of optical active composite films are reported.

2. Experimental Section

2.1. Preparation of DBR PSi

DBR PSi samples were prepared by an electrochemical etch of heavily doped p++-type silicon wafer (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 aqueous 48% hydrofluoric acid (ACS reagent, Aldrich Chemicals) and absolute ethanol (ACS reagent, Aldrich Chemicals). Galvanostatic etch was carried out in a Teflon cell applying 20 cycles of a two-electrode configuration and performed in a dark room. DBR PSi was prepared by using a periodic pseudo-square wave current between 5 mA·cm² for 90 s and 50 mA·cm² for 3 s. All samples were then rinsed several times with ethanol and dried under argon atmosphere prior to use. The resulting DBR
PSi were removed from the silicon substrate by applying electropolishing current at 460 mA cm$^{-2}$ for 100 s in a solution of 48% aqueous HF and ethanol (3:1 by volume) and 29 mA cm$^{-2}$ for 200 s in a solution of 48% aqueous HF and ethanol (1:15 by volume) to obtain a free-standing DBR PSi film.

2.2. Surface Modification of Porous Silicon
Three types of DBR PSi were prepared in this study. (1) Fresh H-terminated DBR PSi, (2) Dodecyl-derivatized DBR PSi; freshly etched DBR PSi chip was placed in 250 mL of schlenk flask under argon atmosphere. After 20 mL of 1-dodecene was added, the reaction mixture was refluxed for 4 h. Dodecyl-derivatized DBR PSi chip was washed several times with ethanol and dried under argon gas prior to use. (3) Oxidized DBR PSi; DBR PSi was thermally oxidized by using a furnaces. The sample was heated at 300°C for 5 min in ambient air condition and then allowed to cool to room temperature.

2.3. Thermal Oxidation of Free-Standing DBR PSi Film
Surface of DBR PSi film was predominant hydride-terminated after the etching procedure. This surface was sensitive to oxidation and hydrolysis upon exposure to aqueous solution. Thermally oxidized DBR PSi samples were obtained by heat treatment in a furnace (Thermolyne F6270-26 furnace equipped with controller) using the following parameters: initial ramp rate, 5°C/min to 300°C; hold time, 3 h; and passive cooling to ambient temperature.

2.4. Preparation of DBR PSi/Polystyrene Composite Film
In a typical preparation, 4 g of polystyrene (Aldrich, Mw = 280,000) are dissolved in 20 mL of toluene (Fisher Scientific). The toluene solution has been cast on the top surface of individual DBR PSi films. The resulting composite films have been annealed at 95°C for 20 min.

2.4. Instruments and Data Acquisitions
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 DBR smart particles was observed with cold field emission scanning electron microscope (FE-SEM, S-4800, Hitachi). Interferometric reflectance spectra were recorded by using an Ocean Optics S2000 spectrometer fitted with a bifurcated fiber optic probe. Spectra were recorded with a CCD detector in the wavelength range 400–1200 nm. The illumination of the surface as well as the measurement of the reflected light was performed along an axis coincident with the surface normal.

3. Results and Discussion
DBR PSi displays a high reflectivity band with a Bragg wavelength $\lambda_{\text{Bragg}}$ depending on the thickness of the porous layers ($d_1$, $d_2$) and the corresponding refractive indices of their porous layer ($n_1$, $n_2$). The $m^{th}$ order of the Bragg reflection is given by:

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

High reflective DBR PSi in a specific narrow spectral region can be prepared by applying a square current waveform. The reflectivity can be controlled to appear anywhere in the visible to near-infrared spectral range, depending on the programmed etch waveform. The electrochemical etch process generates an optical uniform-layer of PSi whose thickness and porosity can be controlled by the current density, the duration of the etch cycle, and the composition of the etchant solution. Fig. 1 showed the Schematic diagram for the preparation of DBR PSi. Fig. 2 illustrates the schematic diagram to obtain DBR interference reflection resonance.

Fig. 1. Schematic diagram of the etch cell with the counter electrode (cathode) arranged symmetrically, used to generate the DBR PSi.
Fig. 3 shows a reflectance spectrum of freshly prepared DBR PSi under the illumination with a tungsten-halogen lamp. The interference spectrum is sensitive to the refractive index of the porous silicon matrix.

Fig. 4 and 5 show the surface and cross-section FE-SEM images of DBR PSi. The surface image of DBR PSi indicated that the pore size of particle retained a good porosity without destruction of porous structure. The prepared DBR PSi had cylindrical macropores with the average pore size of 50 nm with 4 micron meter depth.

Fig. 6 illustrates an influence on the position of reflection peaks of DBR PSi by surface chemistry modifications. The oxidation of freshly prepared DBR PSi causes the reflection peak shifted to the shorter wavelength due to the decrease of its refractive index. However, the surface alkylation of DBR PSi causes the reflection peak shifted to the longer wavelength due to the increase of its refractive index.

Due to the dopant content of DBR PSi, FT-IR spectra to characterize the surface functionalization of porous layer were measured with p-type porous silicon using transmission-mode. Fig. 7 shows the transmission-mode FT-IR spectra for the fresh PSi and oxidized PSi. Fresh PSi exhibits the stretching and bending vibrational frequencies of Si–H species were observed at $\nu$(Si–H) = 2090, $\nu$(Si–H$_2$) = 2115, $\nu$(Si–H$_3$) = 2140, and $\delta$(Si–H) = 908 cm$^{-1}$, respectively. Thermal oxidation of PSi exhibits a characteristic large and broad Si–O–Si vibrational frequency at 1100 cm$^{-1}$. In addition, PSi exhibited new vibrational frequencies for the (OSi–H) and (OSi–H) vibrational modes at 2277 and 883 cm$^{-1}$, respectively. Thermal oxidation of PSi displayed a decrease of the
Si–H vibrational band intensity and an increase of the OSi–H vibrational band. Fig. 8 shows the diffuse reflectance FT-IR spectra for the fresh DBR PSI and oxidized DBR PSI. Both fresh and oxidized DBR PSI exhibits the identical stretching and bending vibrational frequencies compared to that of p-type porous silicon.

Fig. 9 shows the transmission-mode FT-IR spectra for the dodecyl derivatized p-type PSI. The dodecyl derivatized PSI exhibits new stretching vibrational frequencies of C–H species were observed at \(\nu(C-H) = 2850\), \(\nu(C-H_2) = 2920\), and \(\nu(C-H_3) = 2970\) cm\(^{-1}\). Alkyl derivatization of PSI resulted in a decrease of Si–H vibration peak intensity without forming a Si–O–Si and OSi–H vibrational frequencies. Fig. 10 shows the diffuse reflectance FT-IR spectra for the dodecyl derivatized DBR PSI whose C–H vibration frequencies were conformed at the identical position with that of p-type porous silicon.

After an electropolishing of DBR PSI samples to obtain free-standing DBR PSI, the dissolved polystyrene in toluene solution has been cast on the top surface.
of individual DBR PSi films. The resulting composite films have been annealed to fill the pore with polystyrene completely.

Fig. 11 shows the reflection and transmission spectra of DBR PSi/polystyrene composite film. Transmission peak occurred at the identical location where the reflection peak appeared. These composite films are flexible and stable in aqueous solutions for several days without any degradation and could be useful for a possible application such as deformable and tunable optical filters.

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4. Conclusions

Three types of functionalized flexible optical composite films based on Bragg structure porous silicon interferometer have been successfully generated and its optical properties have been characterized. Surface characterization of DBR PSi has been determined by FT-IR measurement. Reflectance and transparence properties of composite films are measured for the possible application of tunable optical filter.

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References


