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1-D Photonic Crystals Based on Bragg Structure for Sensing and Drug Delivery Applications

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Abstract

Free-standing multilayer distributed Bragg reflectors (DBR) porous silicon dielectric mirrors, prepared by electrochemical etching of crystalline silicon using square wave currents are treated with polymethylmethacrylate (PMMA) to produce flexible, stable composite materials in which the porous silicon matrix is covered with caffeine-impregnated PMMA. Optically encoded free-standing DBR PSi dielectric mirrors retain the optical reflectivity. Optical characteristics of free-standing DBR PSi dielectric mirrors are stable and robust for 24 hrs in a pH 12 aqueous buffer solution. The appearance of caffeine and change of DBR peak were simultaneously measured by UV-vis spectrometer and Ocean optics 2000 spectrometer, respectively.

Key words : Distributed Bragg Reflector (DBR), Polymethylmethacrylate (PMMA)

1. Introduction

Synthesis of nanostructured materials[1] has emerged as a useful and versatile technique to provide the use of encoded materials for chemical[2] and biological sensors[3], high throughput screening[4], and controlled release drug delivery[5]. Chemical or biomolecule detection can be based on changes in the spectral interference pattern that results from the reflection of white light at the interfaces above (air or solution) and below (crystalline silicon) the porous silicon layer[6]. The spectral positions of the reflection peak shift as a function of the refractive index of the material filling the pores. Biomolecule penetration into the pores of porous Si layers, driven either by nonspecific adsorption[7-9] or by specific binding (to an antibody, for instance)[10,11] is observed as a shift of the Fabry-Pe´rot fringes to longer wavelengths. This corresponds to an increase in refractive index of the film as protein displaces aqueous solution in the pores. To design an optical interferometric biosensor from porous silicon, the pore size must be adjusted by appropriate choice of electrochemical etching conditions. The pores have to be large enough to allow the biomolecule of interest to enter but small enough to avoid light-scattering effects. These requirements can be met with the well-established methods for porous silicon fabrication involving anodic dissolution of single-crystalline silicon in HF-containing solutions. Depending on several parameters, such as silicon wafer dopant type and resistivity, current density, and electrolyte composition, a wide range of pore sizes and morphologies can be obtained[12,13]. In addition, the pore diameters can be systematically varied in either horizontal or vertical directions (relative to the wafer surface), leading to pore gradient[7] and multilayer[14-16] structures. Unlike the single-layered Fabry-Pe´rot films, biosensors based on porous silicon multilayers have utilized optical transduction methods other than wavelength shifts of the interference pattern. For example, Martin-Palma et al. detected binding of polyclonal mouse antibodies to an amine-modified porous silicon multilayer by observing a reduction in the intensity of reflected light[17]. Additionally, Chan et al. formed porous silicon multilayer structures such as Bragg mirrors and microcavity resonators and used modulation of the photoluminescence spectra from these structures to distinguish between Gram(-) and Gram(+) bacteria[18].

Here, we examine the distributed Bragg reflector DBR porous silicon/PMMA composite materials for the controlled release drug delivery. Free-standing porous silicon multilayer dielectric mirrors, prepared by electrochemical etching of crystalline silicon, are treated

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with polymethylmethacrylate (PMMA) to produce flexible, stable composite materials.

2. Experimental Section

2.1. Preparation of DBR PSi and DBR PSi/PMMA Composite Films

DBR PSi samples are prepared by electrochemical etch of heavily doped p++-type silicon wafers (boron doped, polished on the 1 0 0 face, resistivity of 0.8-1.2 mΩcm, 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). Typical etch parameters for DBR PSi structure involves using a periodic square wave current between 5 $mAcm^{-2}$ for 90 s and 50 $mAcm^{-2}$ for 3 s with 10 repeats.

The thickness of DBR PSi with 10 repeats is about 11 μm. The resulting DBR PSi films have been removed from the silicon substrate by an applying of electropolishing current at 460 $mAcm^{-2}$ for 1 min in a solution of 48% aqueous HF and ethanol (3:1 by volume), and then at 22 $mAcm^{-2}$ for 2 min in a solution of 48% aqueous HF and ethanol (1:30 by volume) to obtain free-standing DBR PSi films. In a typical preparation, 100 mg of PMMA (Aldrich, Mw = 120,000) and 5 mg of caffeine (Aldrich) are dissolved in 20 mL of THF (Fisher Scientific). Three milli litres of mixture solution have been cast onto the surface of free-standing PSi film and dried at room temperature for 30 min. Free-standing porous silicon multilayered dielectric stacks are prepared by periodic anodic etching of boron-doped, p++-type silicon wafers in a solution of 48% aqueous HF and ethanol (3:1 by volume). Typical etch parameters for DBR PSi structure involves square current waveform between 5 and 50 $mAcm^{-2}$ with 10 repeats. The resulting DBR porous silicon film has been removed from the substrate by applying an electropolishing current at 460 mA cm^{-2} for 1 min and 22 $mAcm^{-2}$ for 2 min.

2.1. Instrumentation and Data Acquisition

Optical reflectivity spectra are 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 is positioned at the focal plane of the optical microscope. The quantity of caffeine release from the DBR PSi/PMMA composite is measured at the fixed absorption wavelength of 274 nm on a time scale.

3. Result and Discussion

Biocompatible polymers are of great interest for their use in prosthesis, tissue engineering, and drug delivery system. As a drug delivery system, the status of the biomaterials should be desired to monitor in vivo in some cases. Here, we present that the measurement of the decay in intensity and shift in wavelength of the DBR peak could be used to monitor the release of the drug from the DBR PSi/PMMA composite materials. This freestanding multilayer DBR porous silicon treated with polymethylmethacrylate (PMMA) to produce flexible, stable composite materials in which the porous silicon matrix is covered with caffeine-impregmated PMMA. DBR PSi/caffeine-impregmated PMMA composite materials retain their unique photonic structures shown in Fig. 1.

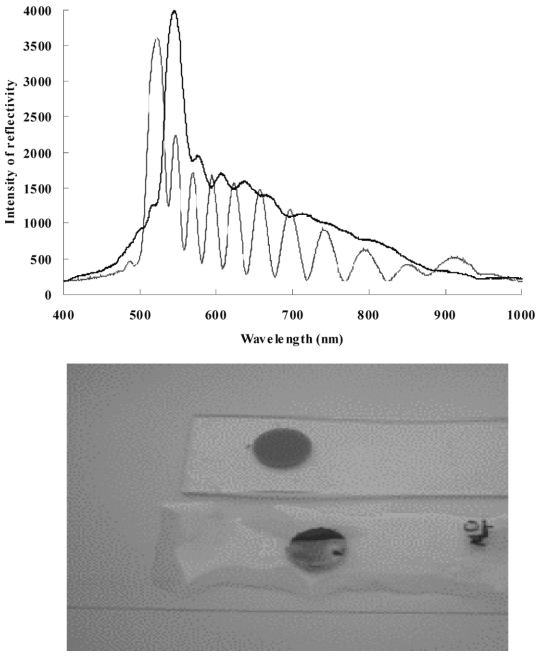

Fig. 1. Reflectivity spectra (left) of DBR PSi (dotted line) and DBR PSi/caffeine-impregmated PMMA composite (solid line) and photograph (right) of DBR PSi film (top) and DBR PSi/caffeineimpregmated PMMA composite (bottom).

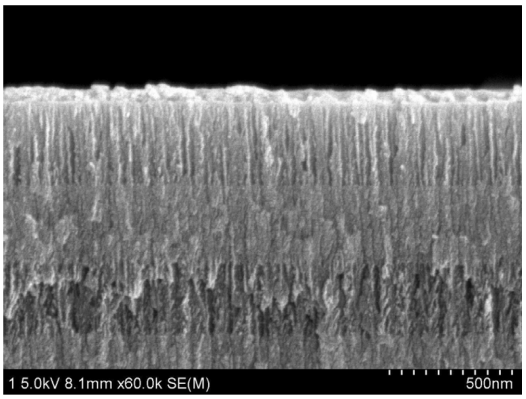

Fig. 2. Cross-sectional SEM image of DBR porous silicon.

Fig. 2 showed the cross-section SEM images of DBR PSi. The cross-sectional image of DBR PSi indicated that the multilayer of DBR PSi exhibits a depth of few microns and the applied square current density during the etching process resulted two distinct porous layers containing different refractive indices. The composite films were highly flexible and showed significantly improved mechanical stability without apparent degradation. Their optical properties were retained upon flexing.

The appearance of caffeine and change of DBR peak were simulataneously measured by UV-vis spectrometer and Ocean Optics 2000 spectrometer, respectively. Reflection peak of DBR PSi/caffeine impregmated PMMA composite was shifted to longer wavelength. This is due to the change of refractive indices of DBR PSi/caffeine impregmated PMMA composite films indicating that the pores of DBR PSi were replaced with caffeine and PMMA instead of air. These composite materials are stable in aqueous buffer solutions without any degradation. Optical characteristics of DBR PSi/caffeine impregmated PMMA composite remains completely for 3 days in pH 7 aqueous buffer solution. The release of caffeine and the shift of reflection peak shown in Fig. 3 were measured by the use of UV-vis spectrometer. The blue shift of reflection peak results in the decrease of refractive index of composite materials during the caffeine release.

The measurement of caffein release from DBR PSi/caffeine impregmated PMMA composite film was investigated for 3 days in pH 7 aqueous buffer solution. (Fig. 4) Absorption measurement for the caffeine release from the composite films was achieved as a function of

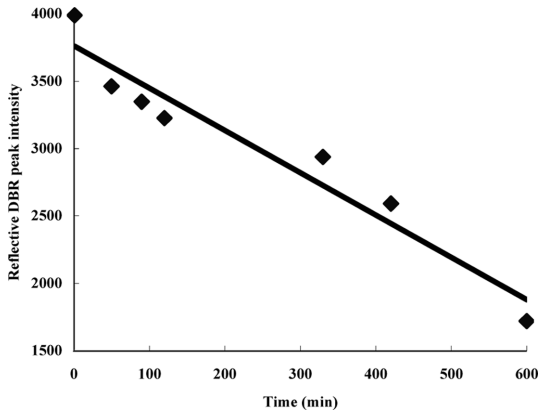

Fig. 3. Decay profile of the reflection peak intensity on a time scale.

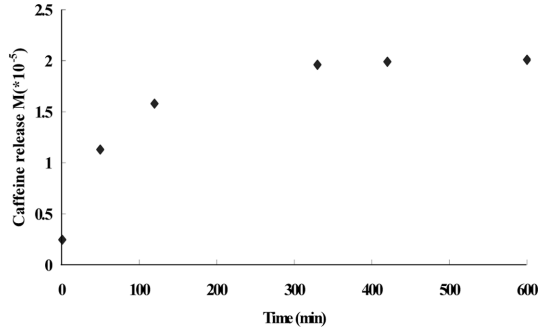

Fig. 4. Appearance of the free caffeine in the solution.

time at fixed wavelength of the absorption maxima of caffeine. The release of caffeine was exponentially increased during first 3 hours.

4. Conclusion

The DBR PSi/PMMA composite films were used for the release of caffeine for drug delivery application. The DBR PSi/PMMA composite films were highly flexible and showed significantly improved mechanical stability of porous silicon. These DBR PSi/PMMA composite films were chemically stable in aqueous HF or alkaline solutions for several days without degradation of their optical reflection characteristics. The measurements of reflectivity and absorption exhibited that the drug was released exponentially from the DBR PSi/PMMA composite films. The DBR PSi/PMMA composite films could be a one of good candidate for the controlled release of drug.

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