Covalent crosslinking of 1-D photonic crystals of microporous Si by hydrosilylation and ring-opening metathesis polymerization

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Free-standing porous Si multilayer dielectric mirrors, prepared by electrochemical etching of crystalline Si, are treated with a ruthenium ring-opening metathesis polymerization (ROMP) catalyst followed by norbornene to produce flexible, stable composite materials in which poly(norbornene) is covalently attached to the porous Si matrix.

Photonic crystals of porous Si are of interest for use in chemical and biological sensors,[1–3] optical switching devices,[4] implantable biomaterials,[5] and in high-throughput screening applications.[6] Use of this material is limited in many cases by its chemical stability,[7] which has driven the development of a variety of modification chemistries for porous Si in the last few years.[8–22] Since porous Si consists of a delicate matrix of nanocrystalline domains, its mechanical stability is also an issue, especially for applications in which the material is thermally cycled or repeatedly flushed with liquids. Recently, Lewis and Grubbs reported a technique in which a ring-opening metathesis polymerization (ROMP) catalyst[23] is employed to graft polymers onto crystalline Si surfaces.[24] In that work, a separate step is necessary to covalently attach the polymer to the Si surface. In this report we apply the methodology of Grubbs and Lewis to multilayered films of porous Si, and find that the catalyzed reaction generates a composite porous Si/polymer material in which the polymer is covalently attached to porous Si *via* Si–C bonds. The chemical and mechanical stability of the chemically crosslinked porous Si matrix are significantly improved relative to porous Si alone.

Freestanding porous silicon multilayered dielectric stacks were prepared by periodic anodic etching of B-doped, p++ type, (100)-oriented silicon wafers with <1.0 mΩ cm resistivity (Siltronix, Inc.) in a solution of 48% aqueous HF and ethanol (3:1 by volume) as previously described.[6,25] Typical etch parameters for a rugate filter structure involved a pseudosinusoidal current waveform oscillating between 80 and 190 mA cm^{-2} with 100 repeats and a periodicity of 2 s. Under these conditions, the maximum size of the pores is about 20 nm in diameter. The resulting porous Si film was removed from the substrate by applying an electropolishing current at 22 mA cm^{-2} for 1 min in a solution of 48% aqueous HF and ethanol (1:14 by volume). The films produced this way are very fragile, and shatter easily when bent.

A polymer composite was prepared in two steps by loading catalyst into the porous Si film and then introducing the monomer solution. The porous Si film was soaked in a 10 mM dichloroethane solution of the ROMP catalyst/precursor (tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine]ruthenium(IV) dichloride, Strem Chemicals, Inc.) at room temperature for 20 min, briefly washed with dichloromethane, dried *in vacuo*, and then placed in a small flask. A 3 M solution of 2-norbornene (TCI America) in dichloroethane was added in such a way that the monomer solution just covered the catalyst-impregnated porous Si film. The flask was heated at *ca.* 100 °C for 30 min. The resulting

composite film was washed with water and dried under a stream of nitrogen.

The Fourier-transform infrared (FTIR) spectrum of the nanocomposite film (Fig. 1) displays absorption bands characteristic of the polymer, with vibrations assigned to C–H and C=C stretching modes at 2780–3090 cm^{-1} and 1550–1810 cm^{-1}, respectively. A mode assigned to CH_2 bending at 1446 cm^{-1} is also observed. The optical reflectance spectrum confirms that the polymer has infiltrated the pores of the porous Si matrix. The spectal feature arising from optical interference in the porous Si multilayer is shifted to longer wavelengths by approximately 90 nm upon introduction of the polymer (Fig. 2). Such a large red shift is characteristic of an increase in the average refractive index of the multilayers,[3] consistent with the
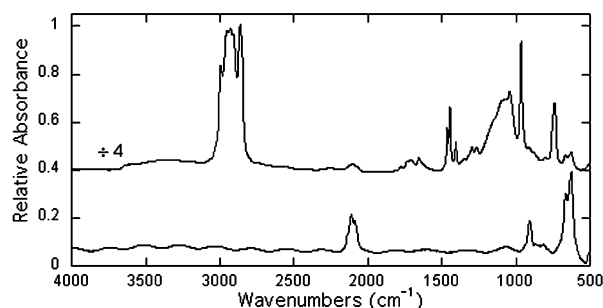

Fig. 1 Transmission-mode FTIR spectra of porous Si film (bottom) and composite porous Si/poly(norbornene) film (top). The top spectrum is scaled as indicated and offset along the *y*-axis for clarity.
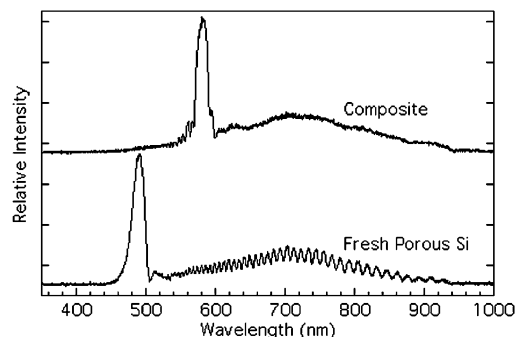

Fig. 2 Reflectivity spectra of a multilayered porous Si rugate filter (bottom) and a porous Si multilayer/poly(norbornene) composite (top). The main peak in each spectrum corresponds to the photonic resonance feature arising from optical interference in the periodic layered structure of each film. The peak maximum shifts from 492 nm (bottom) to 584 nm (top) upon introduction of the polymer into the porous Si film. The reflected light spectra were obtained using an Ocean Optics SD2000 CCD spectrometer using tungsten light illumination. Spectra are offset along the *y*-axis for clarity.

replacement of a significant amount of empty pore volume with polymer.[26]

Composites prepared from freshly etched, hydrogen-terminated porous Si display significantly improved mechanical stability. Free-standing multilayers of porous Si are typically very brittle and will shatter when subjected to minor shear stresses such as occur when handling with tweezers. In contrast, the composites prepared from freshly etched porous Si are highly flexible at room temperature (Fig. 3) or at 77 K, and they display no apparent degradation in their optical reflectivity properties upon repeated flexing (no change is observed in the optical spectrum or in the visual appearance after bending the material shown in Fig. 3 by >90° for >15 cycles).
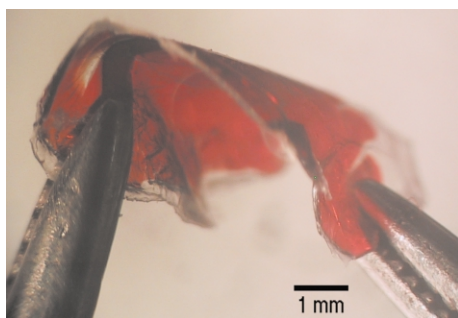

Fig. 3 Flexible 1-D photonic crystal. Photograph of composite porous Si/poly(norbornene) film held between two pairs of tweezers, showing the mechanical stability of the materials.

Polymerization in a freshly etched porous Si template apparently leads to covalent attachment *via* hydrosilylation of the Si–H species present on the porous Si surface. If the porous Si film is thermally oxidized before introduction of catalyst (Fisher Blue M tube furnace: initial ramp rate, 5 °C min⁻¹ to 400 °C; hold time, 0.5 h; passive cooling to ambient temperature), the porous Si/poly(norbornene) composite that results shatter upon application of moderate shear stresses, and readily dissolves when treated with aqueous HF solutions. The polymer is also readily removed from these materials by soaking them in tetrahydrofuran, a solvent for poly(norbornene). In contrast, composites prepared from freshly etched porous Si are stable in aqueous HF or alkaline (3 M KOH) solutions for several days with no apparent degradation and the polymer cannot be removed completely from the pores by soaking in tetrahydrofuran. The infrared spectra of the two different types of composites are similar, except for the much larger Si–O stretching vibration observed at 1000–1200 cm⁻¹ for the oxidized film. Both composites display similar shifts in the rugate peak observed in the optical spectrum, indicating that polymerization occurs to a similar extent in both the oxidized and un-oxidized porous Si matrix.

Preliminary mechanistic investigations suggest that the catalyzed polymerization and the pore crosslinking reactions are unrelated. A simple terminal alkene (1-dodecene) and poly(norbornene) (prepared and purified separately) also undergo thermal hydrosilylation with porous Si in the absence of the ROMP catalyst under the conditions of the experiment (100 °C). An attempted hydrosilylation of 1-dodecene in the presence of the ROMP catalyst at room temperature proceeds to a much smaller extent relative to the thermal reaction in the absence of catalyst. Therefore, the crosslinking reaction between poly(norbornene) and porous Si is believed to proceed mainly through thermal hydrosilylation of unsaturated groups.

The experimental evidence suggests that a significant amount of unsaturated polymer becomes covalently attached when porous Si presenting an Si–H surface is used as the support. The data are consistent with previous reports of catalyzed and uncatalyzed hydrosilylation reactions at hydrogen-terminated porous Si surfaces.[27,28] In the case of oxidized porous Si, there are no Si–H surface groups and thus no covalent bonds can

form, resulting in the observed lower mechanical and chemical stability for this composite. Thus, both the introduction of a soft polymer into the pores and the covalent attachment of this polymer to the supporting porous Si matrix are neccessary to provide a chemically and mechanically robust material.

To our knowledge, this is the first report of ROMP[23] being used for *in situ* polymerization and cross-linking of pores in a porous Si template. To generate a flexible nanocomposite, poly(norbornene) provides an ideal filling material because the polymer itself is soft and flexible. The flexibility and mechanical stability of the porous Si-based nanocomposite can be explained by formation of covalent bonds between surface Si–H groups and the carbon–carbon double bonds of the poly(norbornene) formed during ring-opening metathesis polymerization. This process should provide a convenient method for creating nanocomposites containing functional groups pendant to the polymers.

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