Topological Control of Porous Silicon Photonic Crystals by Microcontact Printing

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Free-standing, uniformly wrinkled multilayered photonic crystals are prepared in porous Si by conformal electrochemical etch of a highly doped p** type Si wafer that is pre-shaped with periodic grooves. The grooves are prepared by first microcontact printing a parallel line of oligomeric polydimethylsiloxane and then electrochemically etching the patterned wafer. The etch proceeds anisotropically, with the resist-covered regions etching more slowly than the resist-free regions. The grooved substrate is then etched using a sinusoidal current density waveform, generating a porosity-modulated photonic crystal (rugate filter) that is conformal with the grooves. This porous multilayer is then removed, resulting in a freestanding nanostructure with a corrugated topological modulation in the x–y plane and a rugated porosity modulation in the z-direction. In addition to the resonant photonic reflectance signature from the porosity-modulated rugate filter (along the z direction), the structures display optical diffraction in transmission from the x–y plane due to the spatially modulated grooves. The silicon wafer that remains after removal of the porous multilayer still contains a rippled surface, allowing the process to be repeated without additional microcontact printing. Six generations of freestanding, three-dimensional diffraction gratings are produced from a single wafer and only one initial patterning step.

1. Introduction

The word ‘rugate’ comes from the Latin word for ‘wrinkle’. The term is commonly used in optics to describe a multilayer optical filter in which the refractive index varies smoothly between two values. In physiology the term is used to describe a fold in a tissue or membrane. In this work we prepared a structure that adheres to both definitions—containing a physical undulation in one direction and a refractive index undulation in another. Porous Si, prepared by electrochemical etch of single-crystal silicon substrates, demonstrates nanometer-level control of the structure in one dimension—the direction of propagation of the electrochemical etching process. The etch proceeds typically in the <100> crystallographic direction of the wafer, and the pore size and the porosity of the material can be modulated during the etch by modulation of the etching current. One-dimensional multilayered nanostructures such as Bragg stacks, rugate filters, and microcavities can be generated in several minutes on wafers received directly from the manufacturer, without the need for a pre-patterning or masking step.[1–3] Two- or three-dimensional patterns can also be generated in porous Si layers, although to generate these more complicated structures, some type of physical or shadow mask must be used.[4] Two-dimensional patterns can be imposed before, during, or after the electrochemical preparation of porous Si. For example, pre-patterning a crystalline silicon substrate with an HF-resistant mask (e.g. a polymeric photoresist,[5] silicon nitride,[6] porous aluminum oxide[7]), or with impurity dopants by ion implantation[8–12] leads to spatially selective etching. In addition, a pattern can be introduced during the etch by illumination of the silicon wafer with a white light source[13–16] or with interfering laser beams,[17] which results in a two-dimensional pattern by modifying the etch rate in the illuminated region(s). Finally, a pattern can be generated on an already-formed porous Si layer by selective removal of porous Si using several post-processing procedures.[18–22] From a standpoint of ease of use and speed, a particularly interesting post-processing step is dry-removal soft lithography.[23,24]

Dry-removal soft lithography (DRSL) is a variant of microcontact printing, which is a versatile tool to create patterns on a variety of surfaces.[25] The DRSL procedure is applied after the porous Si etch, and it involves placing a morphologically patterned stamp consisting of polydimethylsiloxane (PDMS) in contact with the porous Si film. The raised features on the PDMS fixture selectively adhere to the corresponding regions on the porous Si film. Gentle peeling then removes only the adhered porous Si domains from the Si substrate. In this work...
we use a PDMS stamp similar to the DRSL method, except that the stamp is used in a fashion more analogous to conventional microcontact printing: a pattern of oligomeric dimethylsiloxane is transferred to a roughened Si surface prior to the etch. The dimethylsiloxane residue acts as a chemical resist, and subsequent etch of the Si substrate yields a layer of porous Si possessing the \( x-y \) pattern of the master. Due to inhibition of etching in the masked region, the procedure gives rise to a thicker porous layer in the unmasked areas than in the masked areas. After removal of this sacrificial porous Si layer, a crystalline Si wafer remains that is no longer flat, but possesses hills and valleys corresponding to the positive and negative relief pattern of the PDMS master. The morphologically patterned Si wafer can then be etched with a time-modulated current waveform, yielding a multilayered photonic crystal (rugate filter) in the \( z \) direction that is conformal with the Si wafer surface topology in the \( x-y \) plane. Two main advantages of this technique over the previously described methods are (1) microcontact printing is a simpler, less time-consuming process; and (2) multiple copies of the complex porous nanostructure can be prepared from the same wafer after a single stamping event.

2. Results and Discussion

2.1. Fabrication of Corrugated Rugates

The ‘corrugated rugate’ filter of this work is a porous Si photonic nanostructure that contains both physical and refractive index modulations. The samples were prepared as outlined in Figure 1. A crystalline Si wafer was first electrochemically roughened by application of a brief current pulse (3 s, 442 mA cm\(^{-2}\)) in an ethanolic HF electrolyte. This procedure generates a thin (600 ± 20 nm) layer of porous Si that contains a high density of surface hydrides. We postulate that these hydride species undergo a catalyzed hydrosilylation reaction when in contact with the residual unreacted olefinic silicones and catalyst remaining in the polydimethylsiloxane (PDMS) stamp. The reaction was accelerated by heating the sample at 150 °C on a hotplate for 3 h, and a small weight was placed on top to improve contact between the stamp and the Si surface (Figure 1, Step 1). After removal of the PDMS stamp, optical (Supporting Figure S1) and scanning electron microscope (SEM, Figure 2A) images of the Si samples revealed lines of residue partially infiltrated and grafted to the roughened Si surface (Figure 1, Step 2). The transferred residue pattern matched the line pattern on the original PDMS stamp. The attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectrum of the residue (Supporting Figure S2) displayed peaks characteristic of pristine PDMS.\(^{[26]}\)

Once patterned with PDMS, the Si sample was subjected to an electrochemical etch at a current density of 88 mA cm\(^{-2}\) for 2 min (Figure 1, Step 3). This produced a densely spaced array of pores of approximately 30 nm in diameter that propagated primarily in the \(<100>\) direction, perpendicular to the polished (100) original surface of the Si wafer (Figure 2B). The regions of the Si wafer that were masked with PDMS were observed to etch more slowly, with a final thickness of 5.1 ± 0.1 µm, compared to 6.4 ± 0.1 µm for the regions that were not masked. A relatively smooth transition between the hills and valleys of the Si substrate, with a peak-to-valley separation of 1.3 ± 0.1 µm, were
substrate using an electropolishing etch similar to that used in step 4 of Figure 1. The freestanding porous film retained the corrugated physical pattern, as verified through optical microscopy and the observation of strongly diffracted light when illuminated with a laser beam. The Si substrate remaining after removal of the porous Si film could be used to make additional patterned films. With the etching parameters chosen for this study, up to six generations of “corrugated rugates” could be prepared from the same wafer from a single etching event. Each time the patterned bulk Si wafer was re-etched, the patterned features became less pronounced in the cross-sectional SEM images (Supporting Figure S4). However, a shorter etch duration yielding a thinner porous film would increase the number of generations possible.

2.2. Optical Properties

All generations of freestanding “corrugated rugates” possessed diffractive optical properties. The diffraction pattern and its diffractive efficiency derives, in principle, from two phase gratings, i.e. a bulk refractive index grating and a surface relief grating, due to refractive index modulation in the bulk of the material and amplitude modulation at the surface of the material, respectively. For a given incidence angle and wavelength $\lambda$, the former features only one diffraction angle, while the latter features multiple diffraction angles. The relative contributions of the two gratings to the resulting diffraction pattern depend on the morphological and optical parameters of the two gratings, discussed below.\[28\]

The diffractive optical properties and the fidelity of each generation of “corrugated rugate” were quantified by imaging the diffraction pattern in the far field (transmission mode) using diode lasers (635 nm, 641 nm, and 650 nm wavelength, 2 mW power, 2 mm$^2$ spot size), as indicated in Figure 3. Figure 3 shows the diffraction pattern of the corrugated rugate illuminated at 641 nm at normal incidence. Within the experimental error, the position of the diffracted peaks follows the Fraunhofer equation (Equation 1), indicating that the contribution to light diffraction due to the grating formed by surface topology significantly dominates over the contribution due to the grating formed by variations in the bulk refractive index in these structures:

$$d \sin \theta_m = m\lambda$$  \hspace{1cm} (1)$$

where $d$ is the spacing between the raised features in the porous Si diffraction grating (8 µm), $\theta_m$ is the angle between the diffracted beam and the transmitted beam, $m$ is the diffraction order, and $\lambda$ is the wavelength of the incident laser. The

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Figure 2. Representative cross-sectional SEM images showing the various stages used to prepare a “corrugated rugate” structure in which corrugated physical undulations propagate in the $x$-direction and a sinusoidal porosity modulation (optical rugate filter) propagates in the $z$-direction of a silicon wafer. (A) Si surface containing a 600 ± 20 nm thick porous layer that has been patterned via thermal microcontact printing with a PDMS stamp. (B) Porous layer resulting from electrochemical etch of the PDMS-patterned Si wafer from (A). Si regions masked with PDMS etch more slowly, yielding a porous layer with thickness varying between 5.1 ± 0.1 µm at the thinnest and 6.4 ± 0.1 µm at the thickest. (C) Bulk Si substrate after the porous layer from (B) has been removed by electropolishing. (D) Final “corrugated rugate” structure in which a porous multilayer has been electrochemically etched into the spatially modulated sample from (C). The sample shown possesses 40 layers; the typical samples used in this study were prepared with 100 layers, with an average porosity of 68 ± 1%. 

observed in the SEM image (Figure 2B). The porous Si layer was then removed by electropolishing (application of anodic current pulse in an anodic solution containing 3.3% HF), leaving behind the patterned bulk Si substrate that retained the corrugated profile of hills and valleys (Figure 2C). Subsequent etching of the undulated Si substrate using a sinusoidal current density waveform generated a conformal rugate filter\[27\] with an average porosity (by gravimetric measurement\[19\]) of 68 ± 1%. The porosity bands generated by the sinusoidal etch clearly conformed to the undulations on the bulk silicon substrate (Figure 2D). Other spatially modulated patterns could be produced using different PDMS masks. For example, circular structures were patterned using a PDMS master consisting of cylindrical holes that were 22 µm in diameter and 40 µm tall, with 42 µm pitch (Supporting Figure S3).

To produce replicates of freestanding “corrugated rugates,” the patterned rugate filter was removed from the bulk Si
first generation film, though the intensity of higher order diffracted light decreased as the generation number of the porous Si sample increased and only six orders of diffraction were observable from the fifth generation film (Figure 3). The relative intensity of the diffraction spots did not monotonically decay with increasing orders for the first 3 generations of the corrugated rugate samples. This is in conflict with the expectations for a standard, mechanically grooved grating; on the other hand, a monotonic decay in intensity with diffracted order was observable for the latter rugate generations.

Figure 4A presents a comparison of the intensity of the diffracted spots observed from a free-standing, corrugated porous Si rugate filter measured with two different laser diodes, operating at 635 and 650 nm. For this sample, the intensity of the diffraction spots was relatively weak for the 1st and 2nd orders relative to the zeroth and 3rd orders.

The sinusoidal current density waveform applied to the Si anode during the electrochemical etch produced a multilayered porous Si film containing a pseudo-sinusoidal porosity gradient\[27,29\] that approximates an optical rugate filter. The resulting "corrugated rugate" displays a peak in the reflectance spectrum whose wavelength corresponds to the stop band of the periodic structure, $\lambda_{sb}$ (Figure 5). There was some variability in the value of $\lambda_{sb}$ (Supporting Table S1) measured on different generations of films, which is attributed to process variability in the sample preparation.

### 2.3. Analysis of Diffractive Optical Properties

The diffraction features of "corrugated rugates" versus generation number can be explained in terms of variation of the corrugation amplitude $w$ of the surface of the porous Si sample as the generation number increases, consistent with the SEM measurements (Supporting Figure S4). In surface relief gratings, as coherent light passes through the wrinkled surface, a local phase shift is imparted with a magnitude dependent on the corrugation amplitude of the surface. The diffraction intensity pattern from a coherent beam normal to a non-absorbing surface grating with sinusoidal topography can be calculated using the Fraunhofer approximation\[28,30,31\] (see Supporting Information, Discussion), which shows that small corrugation amplitudes produce gratings featuring a monotonic decrease of the diffraction light intensity at higher diffraction order, whereas higher corrugation amplitudes displace the diffracted intensity to higher orders.

The Fraunhofer approximation is followed closely only for low values of $w$ and for the case of a single sinusoidally-corrugated surface. The "corrugated rugates" of the present work feature two in-phase sinusoidal surfaces (one at the front and one at back of the sample) and the corrugation amplitude ranges from tens of nanometers up to several hundred nanometers, depending on the generation number of the sample. In this case, numerical simulations based on the Fourier Modal Method (FMM) can be expected to be more accurate with respect to the Fraunhofer approximation.\[12] FMM calculations were performed to investigate the diffraction behavior of the "corrugated rugates" of this work as a function of $w$ and the average refractive index of the porous layer and its contents,

measured and calculated angles of the diffracted peaks are listed in Supporting Table S1.

The measured position of each of the diffraction spots was in good agreement with the calculated values for all the rugate generations, with a maximum percentage error of about 5%. Nine orders of diffraction were observed from the
The angular dependence of the diffracted intensity from the samples in reflection mode, as opposed to the transmission configuration of Figure 4. Measured at an incident angle of 10.5°, the reflected diffraction pattern is consistent with that expected for a surface grating. The zero-order peak was observed at a reflection angle similar to the incident angle, and the intensity of the subsequent diffraction orders decreased symmetrically. Four orders of diffraction were observed in reflectance mode in the best case.

For comparison purposes, samples were prepared following the same procedure used to produce physical grooves in the x–y plane, but with a uniform porous layer (in the z direction), rather than the periodic porosity gradient of a rugate structure. This uniform porous layer was prepared using the average of the upper and lower current limits used to prepare the rugate structures. Diffraction spots measured from these samples displayed a more monotonic decrease in intensity with increasing order for all the etched generations, as expected for a simple physical grating (Supporting Figure S6). Thus the sinusoidal etch used to generate the “corrugated rugate” samples appears to affect either the corrugation amplitude or the average refractive index value of the grating somewhat. For instance, a smaller value of either corrugation amplitude or average refractive index will result in a reduced phase shift (see Equation S2 in Supporting Information, Discussion) and, in turn, a more monotonic diffraction pattern. This interpretation was confirmed by FMM simulations.

Resonant grating effects can occur when the wavelength of the probe laser is strongly absorbed by the grating. For example, Hupp and Bailey observed resonant enhancement of laser light scattered from a 2D grating composed of a vapochromic inorganic dye. In that work, samples were exposed to chemical vapors to shift the dye absorption such that it coincided with the wavelength of the probe laser. Resonant enhancement of up to 3.5 orders of magnitude was observed in the diffraction pattern.
In that case, the dye molecule was an isotropic absorber of light. The samples in the present work are reflective photonic crystals, with minimal absorbance at the red wavelengths used in the diffraction experiments, and no significant resonant enhancement effects were observed.

3. Conclusion

In this work, a simple means to generate a micron-scale surface topology on a crystalline silicon wafer using microcontact printing and electrochemical etching was demonstrated. The electrochemical etch that produces porous Si conforms to the surface of the silicon wafer, such that a porous layer etched into such a pre-patterned wafer will maintain a uniform thickness despite micrometer-scale variations in surface topology on the original silicon wafer. This allows the generation of some interesting 3D structures. We demonstrated the utility of this approach by generating a complicated optical nanostructure: a porous Si photonic crystal that contained a sinusoidal porosity gradient (optical grating filter structure) in the z direction and a diffraction grating based on physical corrugation in the x–y plane. The porous layers were found to be conformal with the corrugated Si surface, thus generating the buckled multilayers. The multilayers were removed from the substrate to produce corrugated free-standing porous Si multilayer films. The patterned Si substrate retained its wavy surface morphology, and the transmitted laser beam produced up to 9 orders of diffraction from this microstructure. The Si substrate could be etched up to six consecutive times from the original microcontact printing step to produce additional free-standing corrugated porous Si films. A noticeable loss in physical corrugation occurred with each successive generation.

4. Experimental Section

Materials: Polished, p++ type silicon wafers (boron doped, 0.0005–0.0012 Ω cm resistivity, polished on the (100) face) were purchased from Siltronix, Inc. Polydimethylsiloxane (PDMS) stamps were prepared with Sylgard 184 elastomer (Dow Corning). Aqueous hydrofluoric acid (HF, 49%) and all solvents were purchased from Fisher and used as received.

Preparation of Porous Si Photonic Crystal Diffraction Gratings: A thin layer (600 nm) of highly porous Si was etched into a wafer of Si of area 1.2 cm² by application of an anodic pulse of current density 442 mA cm⁻² for 3 s in 3:1 v/v 49% aqueous hydrofluoric acid: ethanol. The wafer was removed from the etch bath, rinsed with ethanol, dried under a stream of dry N₂ and immediately placed in contact with a PDMS stamp. A 100 g (238 g/cm³) weight was placed on top of the stamp to apply even pressure, and the entire assembly was heated at 150 °C for 3 h. The PDMS stamp contained a diffraction grating pattern that was molded from a master (mechanically ruled) grating consisting of 4.8 µm wide lines spaced 3.2 µm apart and 6 µm deep. Next, the pattern was etched into the Si wafer by application of an anodic current density of 88 mA cm⁻² for 2 min in a 3:1 v/v 49% aqueous HF:ethanol electrolyte solution. The porous layer was removed using an electropolishing reaction, in which a current density of 4.2 mA cm⁻² was applied for 10 min in a 3.3% aqueous HF (49%) in ethanol electrolyte. A grating filter was etched into the resulting patterned Si wafer by application of a sinusoidal current density-time waveform varying between 11.5 and 34.6 mA cm⁻², with a period 12.7 s and 100 repetitions, using a 3:1 v/v 49% aqueous HF:ethanol electrolyte solution. The porous layer was removed using the previously mentioned electropolishing step, and it was immediately placed in contact with a glass slide followed by heating in an oven at 70 °C for 1 h. Circles were patterned in Si using the same method, but employing a PDMS stamp pattern consisting of circular holes that were 22 µm in diameter and 40 µm deep, with 42 µm spacing between the hole edges.

Infrared Spectroscopy: Fourier transform infrared (FTIR) spectra of porous Si samples and of the silicone resist layer deposited on porous Si by microcontact printing were obtained with a diamond crystal attenuated total reflectance (Smart iTR) attachment to a Thermo Scientific Nicolet 6700 FTIR spectrometer, using a resolution of 4 cm⁻¹ and an average of 128 scans.

Scanning Electron Microscopy: Grating patterns and porous layer thickness were examined using a Philips XL30 environmental SEM operating in secondary electron mode. Accelerating voltages of 10 and 20 keV were used.

Light Diffraction Imaging: Diffacted light was imaged using a Canon EOS Digital Rebel XTi camera, using an F/4 aperture setting and a 1/13 s exposure time. Diode laser sources (OZ Optics), operating at wavelengths of 635, 641, or 650 nm, ~2 mW output, and with a 2 mm² spot size were used to illuminate the samples. Intensity of diffracted light was measured in a Fraunhofer arrangement, with the sample mounted on a single axis goniometer and the intensity of diffracted spots detected as the photocurrent from a photodetector. The linearity of the detector was verified for the range of photocurrent values measured using a series of neutral density filters.

Simulation of Diffraction Properties: The diffraction properties of the nanostructures were modeled using LightTrans Virtual Lab software. Average refractive index of the samples was calculated by application of the Bruggeman effective medium model using porosity values determined gravimetrically.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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