

Macroscale Transformation Optics Enabled by Photoelectrochemical Etching

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Transformation optics<sup>[1,2]</sup> provides a powerful tool for controlling electromagnetic fields and designing novel optical devices based on the form invariance of Maxwell's equations under coordinate transformations.<sup>[3]</sup> As a result, we can understand the way light behaves in an artificially distorted space by applying a mathematical transformation that equates this distorted space to undistorted space with spatially varying optical properties, illustrated in Figure 1. Figure 1a shows light propagation through untransformed space, and Figure 1b shows the effect of the transformation on the behavior of light and the refractive index of the material. This allows the design of many novel and potentially useful devices including perfect lenses<sup>[4]</sup> and invisibility cloaks.<sup>[5,6]</sup> In practice, devices designed by this method often require material optical properties that cannot be achieved at visible or near-IR light wavelengths. The conformal transformation technique,<sup>[7-9]</sup> can relax this requirement to isotropic dielectrics with gradient refractive indices. However, there are few effective methods for achieving large arbitrary refractive index gradients at large scales, so the limitation for building transformation optical devices is still in fabrication. Nanofabrication techniques such as electron beam lithography or focused ion beam milling have been demonstrated to achieve large control of refractive indices for a carpet cloak,<sup>[10–14]</sup> a multifunctional optical Janus device,<sup>[15]</sup> and a Luneburg lens,<sup>[16,17]</sup> but those devices are limited to small sizes on the order of hundreds of micrometers and are very expensive and time consuming to produce. These fabrication techniques are

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intrinsically unscalable to volume production or macroscale devices. Here we present a photoelectrochemical (PEC) silicon etching technique that provides a simple and effective way to fully control the macroscale profiles of refractive indices by structuring the porous silicon on the nanoscale. We demonstrate continuous index variation from n = 1.1 to 2, a range sufficient for many transformation optical devices.

For large scale optical devices, standard fabrication techniques do not allow engineered refractive index profiles to be patterned into optical media with the precision and range required for transformation optics. Doped glasses, the current industry standard engineered materials for gradient index optics, are limited to relatively modest gradients and variations as well as restricted geometries.<sup>[18,19]</sup> The reported maximum index variation is 0.27, and is more commonly 0.1 or less.<sup>[20,21]</sup> Recent work shows that similar flexibility and large scale patterning can be achieved using photopolymers. However, it is limited to a refractive index variation of less than 0.003,<sup>[22]</sup> which is three orders of magnitude smaller than we demonstrate. Similar capabilities have also been demonstrated using interference lithography<sup>[23]</sup> and direct laser writing,<sup>[24]</sup> but these are also limited to smaller refractive index variations and are not as easily scalable.

Porous silicon produced by electrochemical etching<sup>[25,26]</sup> can have a large variation of refractive index achieved by forming an effective medium<sup>[27]</sup> with a network of nanoscale pores. The density of the pores and thus the effective refractive index can be controlled by changing etching conditions. A Bragg mirror and other 1D multilayer optical devices with index variations in perpendicular direction (z direction) have been demonstrated in porous silicon by periodically adjusting the etching current with time.<sup>[28-30]</sup> In these devices the etch conditions vary during the etching process, and as a result, the refractive index in the z-direction can be controlled. This technique is effective as an alternative to optical thin film deposition, but in order to extend this technique to 2D devices it is necessary to impose lateral (x-y plane) gradients. This has been demonstrated by using electrodes designed to shape the electric field in the electrochemical cell during etching.<sup>[31]</sup> However, the refractive index profile is determined by the designed electrode, which limits the flexibility of the technique, as each different design will require a new, precisely machined electrode. This technique has only been used for simple, symmetric index patterns. For more complicated devices, electrode design would be difficult.

Our PEC etching is a flexible and powerful method for fabrication of porous silicon that uses light projected onto the surface of the silicon rather than modulation of current density during the etching to spatially control the material

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**Figure 1.** A simple 1D transformation, which gives the optical properties required for light in real space to behave as designed in transformed space. a) Light propagation through untransformed space. b) Light propagation through transformed space.

properties.<sup>[32,33]</sup> This process depends directly on the charge carrier concentration in the material. The light absorbed at the surface of the silicon locally modulates the carrier density distribution in the silicon, which affects the pore formation rate and thus the effective refractive index.

This PEC silicon etching process is sensitive to the illumination as well as to the dopant type and concentration. The chemical reaction requires the presence of holes, so n-type silicon does not etch in the dark, requiring illumination to generate the necessary holes. The required illumination and sensitivity to illumination intensity permits optical control of etching in n-type porous silicon. However, n-type porous silicon tends to have high scattering, non-uniform pore size, and strong photoluminescence, making it a poor material for optical devices. P-type silicon, because of the abundance of holes, etches well in



the dark and is typically much more sensitive to current density during the etch process than to illumination. The resulting structure has more uniform pores and is more optically transparent than n-type porous silicon, making it suitable for 1D optical devices,<sup>[34,35]</sup> with etch depths on the scale of the wafer thickness. However, optical patterning has not previously been demonstrated in p-type silicon, making the fabrication of two or 3D devices difficult.

This work is, to our knowledge, the first time light has been used to control porosity in p-type silicon. As a demonstration we fabricated in-plane gradient index devices using

our PEC etching method. **Figure 2** illustrates the chemistry of the PEC method and electron images of the resulting structures. In Figure 2a, the applied current in the electrochemical cell causes holes to drift toward the surface of the silicon, while electrons drift in the opposite direction. When two holes react with a surface silicon atom, the atom becomes oxidized, and can be dissolved by hydrofluoric acid (HF). As pores form, it becomes unlikely for holes to diffuse all the way to the silicon surface, so etching only happens at the interface between the porous and bulk silicon. When light is absorbed by the silicon, an exciton, an electron–hole pair, forms near the surface. For low intensity illumination, the number of charge carriers generated by light absorption is not large enough to significantly affect the electrochemical reaction. However, when the light intensity becomes strong enough, the charge carrier density due to



**Figure 2.** PEC etching for p-type porous silicon showing optical control of refractive index. a) Electrochemical dissolution of silicon in HF and the effect of optical excitation. b) Schematic of etching setup including a DMD light projector for photopatterning during etching. Scanning electron images of c) top view of the fabricated porous silicon waveguide and d) cross section of waveguide with gradient and low index layers visible. The Cal script logo in (b) is a federally registered trademark and may not be used without permission of The Regents of the University of California.

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photoexcitation can approach or exceed the carrier density due to the doping. This can change the effect of the doping, which is one of the most important parameters affecting porous silicon formation. This results in p-doped silicon behaving as though it were less heavily doped as illumination increases, which inhibits etching. The balance of charge carriers controls pore formation, resulting in lower porosity and therefore higher refractive index in more strongly illuminated areas. Using a low etching current and high illumination intensity, we increase the influence of illumination on the etching process, allowing us to spatially control the porosity using light. The opposite effect is seen in n-type silicon, where absorbed light provides the necessary holes and enables etching.

This process allows us to pattern the porosity of the p-type silicon by projecting an image on the surface of the silicon using a digital micromirror device (DMD) during the etching process (see Figure 2b). Any grayscale image can thus be projected onto the chip during etching, meaning there is no symmetry requirement. Any arbitrary pattern can be etched. This new technique unlocks extreme flexibility in gradient index pattern control for making transformation optical devices.

A silicon chip approximately 2.5 cm<sup>2</sup> was placed in a custombuilt Teflon electrochemical cell in contact with an aluminum bottom electrode (see Figure 2b). The cell was then filled with 6.5 mL of electrolyte, prepared with 1 part 49% HF solution to 3 parts ethanol by volume. The top electrode, a ring of platinum wire, was placed in the cell so it was just covered by the electrolyte. An illumination pattern was then projected onto the chip using a DMD projector and three lenses to focus and resize the image to 2 cm<sup>2</sup>. The optical power density of the projected light ranged from 50 to 5500 W m<sup>-2</sup>. A constant current of 10 mA was applied for 4 min, resulting in a constant etching rate of approximately 0.35 µm min-1. The effect of illumination and etch depth on etch rate was minimal. The pores are approximately cylindrical, and the pore diameters range from approximately 10 to 30 nm. The pore length is equivalent to the etching depth. Figure 2c shows the scanning electron image of top view of the fabricated porous silicon. To access a lower index range, some porous silicon samples were then placed in a rapid thermal annealer under 15 µmol s<sup>-1</sup> oxygen gas at 300 °C for 5 min and then at 800 °C for 8 min to form porous silicon oxide.

After etching, the patterned porous film could be removed from the bulk silicon and transferred to another substrate. This was achieved by electropolishing, a process similar to the electrochemical etching used to form porous silicon. For electropolishing to occur, the concentration of HF in the electrolyte was reduced, allowing the interface between the porous silicon and bulk silicon to be fully electrochemically oxidized before it was dissolved by the HF. To release the porous film, first a porous film was etched by the previously described method. The electrolyte solution was then removed, and the film was mechanically scored around its edge to aid in the release from the substrate. A new electrolyte solution of 1 part 49% HF and 20 parts ethanol was added, and the sample was returned to the electrochemical cell and etched in the dark potentiostatically at 30 V for 1 min. The electrolyte was then removed and the sample was flooded with ethanol. The sample floated on the ethanol, allowing it to be mechanically transferred onto any other material. After transfer, the sample was then dried in

## a

Electrochemical Etching

Mechanical Scoring

### Electropolishing

### Transfer of Porous Film



**Figure 3.** Release and substrate transfer for porous silicon films. a) Substrate transfer is achieved by electrochemically etching to form porous silicon, scoring the edge of the porous layer to aid in release, electropolishing with low HF concentration and high bias to separate the porous layer from the substrate, and floating the released layer on ethanol to a new substrate. b) Released samples on various substrates. Bottom image shows patterned lines with varying refractive index after transfer to a transparent substrate.

hexane to improve adhesion and minimize damage to the film. The silicon substrate from which the film was transferred could then be reused. **Figure 3** shows this process and samples transferred onto various surfaces, including curved surfaces.

In order to make a waveguide, with light travelling in a high index medium between two lower index materials, an additional etching step was required. Porous silicon has a lower index than bulk silicon, meaning that a layer of porous silicon on top of bulk silicon will not confine light. The material underneath the gradient index material must have a lower index. In this etching process, the etching occurs from the interface between

silicon and electrolyte. Unlike in typical thin film deposition in which subsequent layers deposit on top of previous ones, the first etched layer is on top and subsequent etching proceeds downward as etching always occurs at the interface between the porous and bulk silicon without affecting previously etched porous silicon. This occurs because once the material is etched and becomes porous, it will no longer react due to the increased electrical resistance of the porous layer, which inhibits the electrochemical etching process. The top to bottom nature of this etching process allows us to form an isolation layer by performing a second electrochemical etch before removing the wafer from the electrochemical cell. For this step, the current was increased to 50 mA and a cover was placed on the cell to keep it in the dark. The sample was etched for an additional 4 min. The higher current resulted in a layer of porous silicon with a larger average pore size and thus a lower effective refractive index below the device layer. The isolation layer below and air above form a complete waveguide. Figure 2d shows the layers of the waveguide in cross section. The top layer contains the gradient index device, which is 1.4 µm thick. The next layer is the low index isolation layer with a refractive index of 1.2, which is 3.0 µm thick. Below the isolation layer is the bulk silicon substrate, approximately 500 µm thick.

The refractive index of the resulting film was characterized by Fourier transform IR (FTIR) reflectance interferometry. We demonstrate the ability to spatially vary the effective refractive index of porous silicon between 1.4 and 2.0, shown in Figure 4, at near-infrared wavelengths by projecting a spatially varied light intensity pattern onto the surface of the silicon in the electrochemical cell. Increasing illumination intensity inhibits pore formation, resulting in a less porous material and a higher effective refractive index. The device can then be thermally oxidized, converting the structure to SiO<sub>2</sub>, reducing the index and allowing the device design to extend to visible wavelengths of light. After oxidation, the refractive index ranges between about 1.1 and 1.4. Figure 4a shows the refractive index of porous silicon and porous silicon oxide as a function of illumination intensity. The intensity values correspond to position in Figure 4b, on which a linear gradient was etched in order to measure the refractive index for different illumination intensities. Index measurements were performed in a wavelength range from 1.2 to 2.3 µm. The index variation due to material dispersion across this range is about 0.04, small enough to allow broadband devices to be designed in the near-IR. The graph in Figure 4 shows the average index across this wavelength range. This range of achievable refractive index variation is sufficient for many transformation optical devices. For example, for the Luneberg lens, the required relative refractive index range is from 1 to 1.41. The required refractive index for carpet cloaks depends on the design, but a larger refractive index gradient allows a larger feature to be cloaked in a smaller total cloak area.

As an example, we used this PEC etching technique to demonstrate a gradient index parabolic lens (see **Figure 5**) with the refractive index  $n = n_0(1 - k r^2/2)$ , where  $n_0$  is the base index at the center of the lens and k the gradient constant. In order to couple light into and out of the waveguide, electron beam lithography followed by dry etching with carbon tetrafluoride (CF<sub>4</sub>) gas was used to fabricate gratings directly in the porous





**Figure 4.** The effective refractive index of porous silicon. A smooth gradient in refractive index can be achieved over an index range of 1.4 to 2.0 for porous silicon and 1.1 to 1.4 for porous silicon oxide. a) Refractive index distribution as a function of light intensity projected during etching. Lower curve shows refractive index of the same material after oxidation by rapid thermal annealing. The insets are scanning electron images of the porous silicon at illumination intensity 200, 2500, and 4000 W m<sup>-2</sup>, respectively. b) Porous silicon sample with a smooth gradient for index measurement.

silicon (see Figure 5b). The gratings consist of ten periods of 1 µm each with a depth of approximately 500 nm, and were optimized for a light wavelength of 1.5 µm. To observe light propagation through the waveguide, a supercontinuum light (Fianium, Southampton, UK) was focused on the input grating to couple broadband IR light into the device, and the device was imaged with an infrared charge-coupled device (CCD) as shown in Figure 5a. The sample was translated using a micrometer stage to move the laser spot along the grating. We observed light scattered from within the waveguide as well as light coupling out from the gratings to determine the propagation path of light in the device. Light propagation through the devices was simulated using a custom ray tracing program written in Mathematica, shown in Figure 5c. The simulation, matching a well-known result in gradient index optics, shows that light inside the parabolic gradient index waveguide follows a sinusoidal pattern. Figure 5 shows a device designed to contain one half period of the sinusoidal oscillation. A half period lens images an object from its front surface to its back surface with a magnification of -1, meaning that a focused spot on the left side of the lens above the lens's axis is imaged to a point of identical size on the right side mirrored about the axis, so the spot appears below the axis as illustrated in Figure 5d-f. From the period of the sinusoidal pattern,  $\Lambda = 12.3$  mm, we can calculate the gradient constant  $k = (2\pi/\Lambda)^2 = 0.26$ . This agrees with



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**Figure 5.** The fabricated gradient index parabolic lens showing light bending inside the device due to the index gradient. a) 4f system for imaging propagation of light through porous silicon gradient index lens samples. b) Schematic of gradient index lens sample showing light bending as it passes through the device, entering at the back plane of the lens and imaging to a point at the imaging plane mirrored about the axis. c) Simulated ray trace of light (solid line) traveling through a parabolic lens at three locations. The refractive index at the center is 1.80 and decreases gradually to 1.45 at the edge. d–f) The images taken using the 4*f* system show the propagation of light through the parabolic lens with the spot at the output mirrored about the axis of the lens. Experimental results given by the white traces closely match the theoretical ray trace results (solid lines).

the theoretical value of k based on the design of the lens, which is 0.27. We also designed and fabricated waveguides of one quarter period and one eighth period with the same refractive index gradient. The focal lengths of all of these devices match closely with the predictions based on ray tracing.

We have demonstrated that photoelectrochemical etching has the potential to become a next generation fabrication technique for transformation optical devices. Its versatility, low cost, and high throughput will enable a new generation of optical elements that can take full advantage of the principle of transformation optics. There are still many areas for further improvement of this technique. The scattering of the device layer should be reduced as much as possible by optimizing wafer doping and etching conditions. Additionally, it is possible to extract more index variation than seen in the devices presented in this paper through higher dynamic range light sources. Most interestingly, it is possible to extend this technique for 3D fabrication by varying the illumination and current over time, which can create truly arbitrary refractive index gradients in three dimensions. Combining 3D etching with control of the substrate geometry by polishing the material after etching or patterning the substrate before etching to achieve the curved surfaces can further improve the flexibility to fabricate unique devices. This technique could be used to enhance optical interconnects, small cameras, satellite imaging systems, or any application where space, weight, and image quality are at a premium.

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