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Adding colors to polydimethylsiloxane by embedding vertical silicon nanowires

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We demonstrate that embedding silicon nanowires into polydimethylsiloxane (PDMS) presents a means for adding color, i.e., provides filtering at visible and near-infrared wavelengths. Silicon nanowires are etched from a silicon wafer and transferred to a PDMS film. Each measured transmission spectrum exhibits a dip at a wavelength determined by the nanowire radius. This is in agreement with electromagnetic simulations, which also help elucidate the roles of scattering and absorption in the observed results. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4766944]

Due to a range of exciting possibilities, numerous investigations have been made of silicon nanowires.[1–3] It is, therefore, surprising how little attention has been generally paid to their optical properties, particularly to the dramatic effects that arise from resonance and waveguiding phenomena. Some of the exceptions are as follows. Cao *et al*. demonstrated that enhanced scattering results from resonances in horizontal nanowires, as observed by dark-field scattering spectroscopy.[4] We recently showed that vertical silicon nanowires take a surprising variety of colors, spanning the visible spectrum.[5] The effect arose from the guided mode properties of the individual nanowires, not from scattering or diffractive effects of the array. They could be readily observed in bright-field microscopy, or even with the naked eye. In that work, however, the nanowires were on a silicon substrate. Many applications, for example, color filters, would be enabled by having the nanowires on a substrate that is transparent at visible and near-infrared wavelengths. This is the subject of the present paper.

Polydimethylsiloxane (PDMS) is chosen as the substrate into which the silicon nanowires are transferred for several reasons. PDMS is a soft elastomer and can undergo large deformation, making it suitable for potential applications that achieve tunability via stretching. PDMS is optically transparent at visible and near-infrared wavelengths and is biocompatible.[6,7] Importantly, PDMS is widely used for microfluidic chips. Recently, there has been growing interest in the incorporation of optical elements into microfluidic chips,[8–11] due to the possibility for optical sensing in a very small platform.[12] Color filters are important optical components in optical sensing, and there have been several efforts at realizing these in PDMS. Dye-doped PDMS has been used as a long pass filter for fluorescent detection in a microfluidic channel.[13] Structural color has been realized in PDMS by self-assembled colloidal photonic crystals.[14,15] The realization of multiple filter functions on a single substrate with dye-doped PDMS is challenging, however, due to the need for multiple fabrication steps and multiple dyes with appropriate properties. This task is similarly challenging with colloidal photonic crystals, as these achieve filtering via periodic effects, meaning that they cannot be scaled to arbitrarily small footprints.

Here, we demonstrate that embedding vertical silicon nanowires in PDMS presents a means for adding color with several favorable attributes. Multiple colors can be implemented in a single substrate, all using the same material (silicon), by appropriate choice of nanowire radius, which is readily achieved in the lithography step. As the color effect arises at the level of the single nanowire, the patterning of color with high resolution is possible. Incorporation of vertical silicon nanowires into PDMS devices also opens up other interesting possibilities for optical sensing in microfluidic chips, e.g., silicon nanopillar-based field-enhanced surface spectroscopy.[16] The process by which the etched nanowires are transferred from the silicon substrate to the PDMS is of key importance. Several previous works have demonstrated the transfer of vertical silicon micro- and nanowires to PDMS. Vertical silicon wire arrays were transferred into PDMS using razor blade cutting,[17] but these were grown microwires rather than etched nanowires. In another method, the occurrence of horizontal cracks in silicon nanowires was used advantageously in the transfer process, enabling them to be broken from the substrate more easily.[18] This method is limited, however, to silicon nanowires made by metal-assisted etching. Shear forces have been used for transferring nano-and microwires.[19] The method intentionally leaves a gap between the silicon substrate and the medium to which the wires are transferred to facilitate the nanowires being broken from the substrate by shear force. However, controlling the gap is not easy, and the method was demonstrated for relatively large and long structures. In summary, the techniques mentioned above are not feasible for relatively small nanowires suitable for color filtering that are produced by top-down anisotropic dry etching, which have diameters of $\sim$100 nm, are 1–2 μm tall. Here, we report a simple technique for transferring etched vertical nanowires into the PDMS. We demonstrate that multiple colors can be added to a sheet of PDMS using embedded arrays of silicon nanowires.

The fabrication method for the PDMS-embedded vertical silicon nanowire array is shown as Fig. 1(a). First, we fabricate silicon nanowires by dry etching.[5] Polymethylmethacrylate

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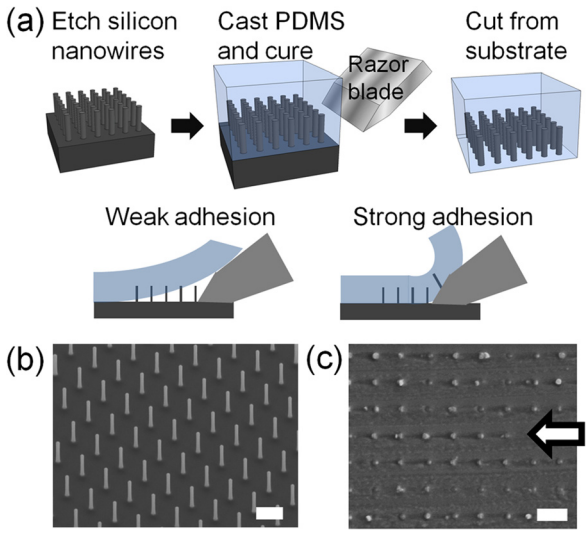

FIG. 1. (a) Method for transferring vertical silicon nanowires into PDMS. Bottom pictures show the difference between weak adhesion and strong adhesion cases. (b) SEM images of vertical silicon nanowire array (30° tilted view). Radii of nanowires are 65 nm and heights are 1.5 μm. (c) SEM images of bottom surface of PDMS embedded vertical silicon nanowires. Arrow indicates direction of razor blade insertion. Scale bars are 1 μm.

(PMMA) resist is spin coated onto the silicon wafer. Electron-beam lithography (Elionix ELS-7000), aluminum evaporation, and lift-off are used to produce an etch mask that comprises aluminum disks. The wafer is then dry etched using inductively coupled plasma reactive ion etching (ICP-RIE, STS technologies) with 60/160 sccm of SF_6/C_4F_8 gases for the etching and surface passivation. The etching speed was 60 nm per min. The fabricated nanowires are 1.5 μm tall, including the aluminum disks (0.04 μm thick) on top, and are on a square array with a pitch of 1 μm. A scanning electron microscopy (SEM) image of fabricated nanowires with radii of 65 nm is shown as Fig. 1(b). We next spin coat PDMS at 1000 rpm for 60 s onto the wafer. A mixture with the PDMS base and curing agent in a ratio of 5:1 is used. The film is cured at 230 °C on a hotplate for 1 h. The PDMS film thickness is about 50 μm. The cured PDMS film is removed by scraping it from the substrate with a razor blade, using the method of Ref. 17. In that work,[17] however, the wires were much larger (~100 μm tall and ~1.5–~2 μm diameter), and made by vapor-liquid-solid (VLS) growth. We initially applied the method of Ref. 17 to our etched vertical nanowires, but the yield was small. Because their adhesion to the PDMS was low, the nanowires readily escaped from the PDMS during the razor blade scraping step (Fig. 1(a)). It is for this reason that we cure the PDMS at 230 °C, which is higher than the standard PDMS curing temperature, as this increases the adhesion between the PDMS and silicon. This results in the nanowires remaining within the PDMS film during the razor blade scraping process (Fig. 1(a)), and excellent yield.

An SEM image of bottom surface of the PDMS film, the side into which the nanowires are embedded, is shown as Fig. 1(c). It can be seen that the surface of PDMS film is not very smooth. This is because small residues of broken nanowires are left on the substrate, preventing the PDMS from being cut cleanly. The razor blade also can be damaged during the process, which also affects the roughness. The root mean square (RMS) surface roughness is about 35 nm, as measured by atomic force microscopy (AFM). That the surface is not smooth could induce light scattering, although we did not observe any detrimental effects from this in our work. We note however the surface could be smoothened by the spin coating of an additional PDMS layer if scattering were to prove problematic. The PDMS film shrinks after the fabrication process due to its large coefficient of thermal expansion (CTE) of ~310 ppm/°C. We cure the PDMS at 230 °C, but use it at room temperature (20 °C). We, therefore, expect that, at room temperature, the nanowire pitch will be 0.935 μm rather than 1 μm. This is reasonably consistent with the measured nanowire pitch of 0.947 μm.

An optical microscope image of four vertical silicon nanowire arrays on a silicon substrate before transfer is shown as Fig. 2(a). The nanowire radii (R) range from 50 nm

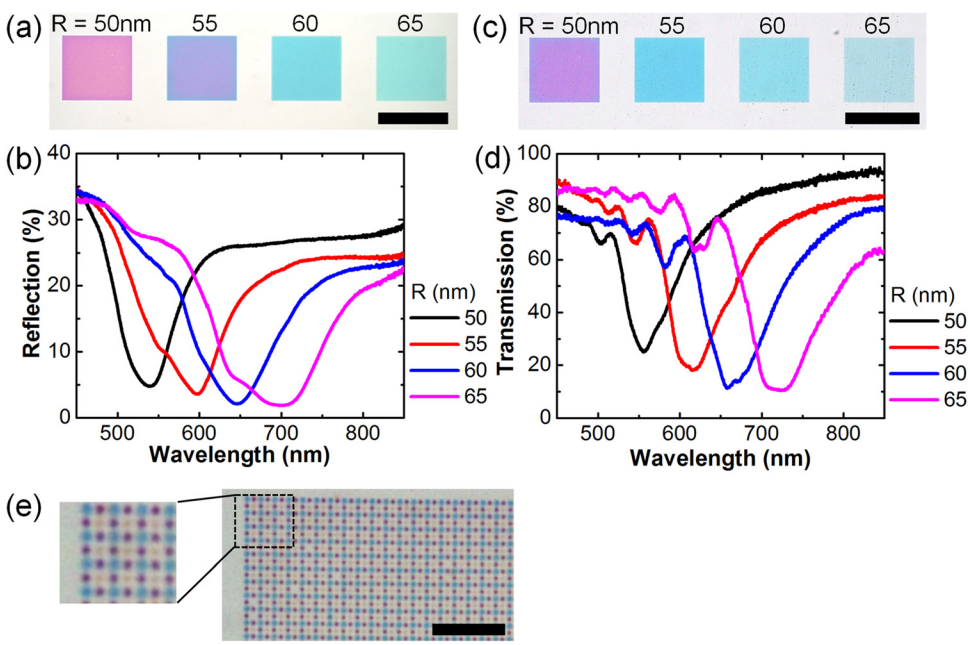

FIG. 2. (a) Optical microscope images of etched vertical silicon nanowire arrays on silicon substrate in reflection mode. Scale bar is 100 μm. (b) Measured reflection spectra of nanowire arrays on silicon substrate. (c) Optical microscope image of PDMS embedded vertical silicon nanowire arrays in transmission mode. Scale bar is 100 μm. (d) Measured transmission spectra of PDMS embedded nanowire arrays. (e) Bright-field optical microscope image of PDMS embedded nanowire arrays with different radii. Nanowires with design value radii of 50 nm, 60 nm, and 70 nm appear yellow, purple, and blue, respectively. Scale bar is 10 μm.

to 65 nm in steps of 5 nm. It should be noted that these, and all other radii quoted in this paper, are the design values in the electron beam lithography step. The nanowires are 1.5 μm tall and have 1 μm pitch. Each array has an extent of 100 μm by 100 μm and contains 10 000 nanowires. The difference in color between the arrays is clearly seen. We use a microscope fitted with a spectrometer (Horiba Jobin-Yvon LabRAM) to measure the reflection spectrum of each array. Unpolarized white light is incident upon the sample through the objective lens (10×, NA = 0.25), with the reflected light collected by the same lens. Reflection spectra are normalized by the reflection measured from a silver mirror. As shown in Fig. 2(b), each reflection spectrum shows a dip, whose position red shifts with increasing nanowire radius. This is due to wavelength selective coupling and spatial distribution of the nanowire's waveguide mode.[5] At short wavelengths, the mode is tightly confined to the nanowire core. The unfocused illumination does not excite it efficiently because of poor spatial overlap. At long wavelengths, the mode is expelled from the core, and is excited efficiently. The absorption within the core is small, however, due to the mode being delocalized from the nanowire. At intermediate wavelengths, both coupling and absorption are high, leading to a reflection dip. It is expected that the dip position shifts to the longer wavelength when the radius of nanowire increases because of the scale-invariance of Maxwell's equations.

A transmission mode microscope image of the vertical silicon nanowire arrays after transfer to the PDMS is shown as Fig. 2(c). It can be seen that the goal of adding color to PDMS is achieved. Interestingly, it is evident that embedding the nanowires into PDMS modifies that color that they appear. The nanowires with radii of 50 nm, for example, appear magenta when on the silicon substrate, but purple when embedded in PDMS. A homebuilt set-up is used to measure transmission spectra of the arrays. Collimated unpolarized white light is incident upon the sample, with the transmitted light collected with a microscope objective lens (50×, NA = 0.55) and into a spectrometer. The transmission spectra are normalized by spectra measured through a PDMS region not containing nanowires. The results are shown as Fig. 2(d). Transmission dips are slightly red shifted compared to the reflection dips. The average value of the dip shift is 15 nm. The dip shift arises because of the increase in the refractive index of the embedding medium from n = 1 (air) to n = 1.43 (PDMS). This effect is also seen in extinction spectra of spheres when the index of the surrounding medium increases, as predicted by Mie scattering theory.[21] We also simulate the implications of the change in nanowire pitch that results from the PDMS shrinkage. The transmission dip position is found to be almost unmodified, and the transmission at the dip is reduced by 5% when pitch is decreased from 1 μm to 0.947 μm. We conclude that the change in pitch is, therefore, unimportant in the observed red-shift.

Our method permits the high resolution patterning of multiple colors in PDMS. Each nanowire independently shows a color that is controlled by its radius. Fig. 2(e) is analogous to a Bayer pattern, but with yellow, purple, and blue colors rather than red, green, and blue. The nanowires are 1.98 μm tall and have a pitch of 0.95 μm pitch (in PDMS). The magnified-view inset of Fig. 2(e) shows that individual nanowires exhibit color. An individual nanowire can, therefore, be thought of as the analog of a single ink dot in printing. The color of the nanowires in Fig. 2(e) can be seen to differ from nanowires of the same radius in Fig. 2(c). This is because even though the lithography design value for nanowire radius is the same, the etching step differs. In addition, the nanowires of Fig. 2(e) are longer than those of Fig. 2(c) (1.98 μm rather than 1.5 μm).

To quantify the roles of absorption and scattering, we simulate a single nanowire in PDMS with the finite-difference time-domain (FDTD) method. The silicon nanowire is taken as having a radius of 50 nm, a length of 1.46 μm, and the aluminum etch mask (0.04 μm thick) is included. The refractive index of background medium (PDMS) is taken to be 1.43.[20] Perfectly matched layers are used on all boundaries, and the total-field scattered-field (TFSF) configuration is employed. The scattering, absorption, and extinction cross sections are calculated (Fig. 3(a)). It can be seen that scattering contributes to the extinction cross section more than absorption. The dip in the transmission spectrum occurs around the extinction maximum. The simulation (Fig. 3(a)) suggests that the majority of each transmission dip originates from scattering rather than absorption.

We next simulate arrays of nanowires, choosing the parameters to match those of the experiments. Periodic boundary conditions are applied in the x- and y-directions, where the z-direction is along the nanowire axis. The unit cell size

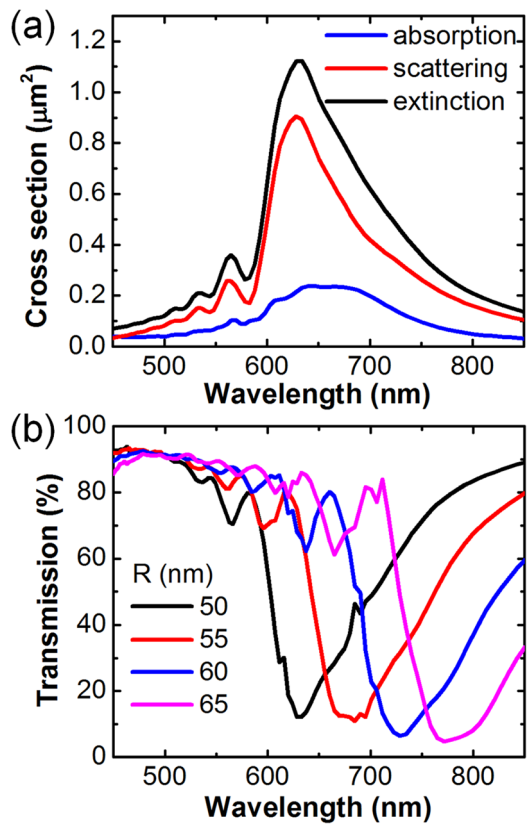

FIG. 3. FDTD simulation results. (a) Extinction cross-section of single vertical silicon nanowire with 50 nm radius. (b) Simulated transmission spectra of vertical silicon nanowire arrays (947 nm period) with radii from 50 nm to 65 nm. Simulation models the transmitted light being collected by an objective lens with NA = 0.55.

is 947 nm × 947 nm. The nanowire radii range from 50 nm to 65 nm in steps of 5 nm. The nanowires are again taken as being 1.46 μm long, with an additional 0.04 μm thick aluminum cap. The field monitor plane is located at 0.5 μm beyond the tops of the nanowires. To find the transmission, we take the integral of the outgoing power through the monitor plane and normalize it by the source power. We need to account, however, for the numerical aperture of the objective lens used in the experiments (NA = 0.55). To consider this, we calculate the far-field projection of the monitor plane, assuming that these far-fields are in air (n = 1.0). This allows us to find the fraction of power within the collection angle of the objective lens. This is accounted for in the results of Fig. 3(b). It can be seen that the transmission dip for the array of nanowires with radii of 50 nm occurs at the same position as the extinction peak for the single nanowire. We conclude that, like the single nanowire extinction, the transmission dip for the nanowire array is mostly due to scattering, rather than due to absorption.

It can be seen that the experiments (Fig. 2(d)) and simulations (Fig. 3(b)) are in reasonable agreement, apart from the simulations being red-shifted from the experiments in terms of dip position. We believe that this is due to the fact that simulated structures are perfect cylinders, and do not account for the tapered sidewalls present in the real structures that result from undercutting in the etching step. Nanowires with radii of 40 nm and below collapse during the etching process due to this undercut. In addition, the top radius of etched nanowire tends to be slightly smaller than the actual mask size. In Ref. 22, for example, ~5 nm notches were observed for nanowires with diameters of 100 nm. For this reason, the simulations are red-shifted with respect to the experimental results.

In summary, we described a method for transferring etched vertical silicon nanowire arrays into PDMS. We demonstrate that this presents a means for adding color to PDMS. We anticipate that this approach could find applications not only for color filtering but potentially for nanowire-based sensing in lab-on-a-chip devices.

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