Research Highlights

Harnessing the Nano-optics of Silicon Nanowires for Multispectral Imaging

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Abstract—Given the considerable interest that has existed for silicon nanowires lately, it is surprising how little attention has been generally paid to the dramatic influence that wave-guiding and resonance phenomena can have upon their optical properties. This paper reviews recent work at Harvard University on the optical properties of silicon nanowires. We show that they can take a striking variety of colors, and that this enables color and multispectral imaging.

Index Terms—Image sensors, infrared imaging, multispectral imaging, nanowires, nanofabrication.

I. Introduction

Silicon nanowires have been investigated intensively over the past decade, due to the interesting possibilities they present for electronics. It is therefore striking that, until recently, little work had been generally done on their optical properties. This is partly a consequence of the fact that the dominant method by which they are produced—the vapor-liquid-solid (VLS) technique [1]—does not usually produce orderly arrays of nanowires. In the VLS method, metal clusters heated in presence of vapor-phase silicon (Si), resulting in liquid metal/Si droplets. The Si reactant feeds into the liquid droplets, supersaturates them, nucleating solid silicon. The solid–liquid interfaces act as sinks for continued Si incorporation into the lattice and growth of the Si nanowires. A photograph of Amit Solanki (Postdoctoral Fellow, Harvard) and Peter Duane (Harvard and Zena Technologies) loading a silicon substrate into a furnace for nanowire growth is shown as Fig. 1. In Fig. 2, a scanning electron micrograph (SEM) of Si nanowires grown in the author’s laboratory at Harvard is shown. The nanowires are typical of the VLS method, exhibiting a variety of diameters, positions, and orientations. This occurs unless steps are taken to confine the metal clusters, e.g. with oxide buffer layer (e.g. [2]). In this Research Highlight we review our recent work on the realization of highly ordered arrays of vertical silicon nanowires using etching [3], rather than the VLS method. We furthermore demonstrate a method for embedding the nanowires into polydimethylsiloxane (PDMS) [4], the transparent polymer used for contact lenses and microfluidic chips. Lastly, we show that this facilitates the exciting prospect of color and multispectral imaging [5].

II. Multicolored Silicon Nanowires

Rather than the “bottom up” VLS method, we used “top-down” nanofabrication to realize nanowires with precise control over their location, radius and length. The starting substrate was a

Figure 1. Peter Duane (left) and Amit Solanki (right) load substrate into furnace in author’s laboratory for silicon nanowire growth at Harvard University.

Figure 2. SEM of Si nanowires grown by VLS method in author’s laboratory at Harvard. Growth parameters: T = 485 °C, P = 100 Torr, deposition time = 10 min, gas flows: 5% SiH4 in H2 at 100 sccm and Ar at 100 sccm. Starting substrate: Si wafer with Au layer (nominal thickness 5 nm).
silicon wafer. We then performed electron beam lithography, aluminum evaporation, and the lift-off process. This resulted in an array of aluminum disks (Fig. 3(a)) that then served as the mask for the subsequent inductively-coupled plasma reactive ion (ICP-RIE) etching step, in which the nanowires were formed. The last step (not shown in Fig. 3(a)) involved removal of the aluminum disks from the sample using aluminum etchant. All nanofabrication work was performed in the cleanroom facility of the Center for Nanoscale Systems at Harvard University. Photographs of Hyunsung Park, a PhD candidate at Harvard University, performing electron-beam lithography and ICP-RIE are shown as Fig. 3(b) and 3(c), respectively. SEMs of fabricated structures are shown as Fig. 3(d). The nanowires have radii of \( \sim 45 \text{ nm} \), are \( \sim 1 \mu \text{m} \) long, and are in a square array with a pitch of \( 1 \mu \text{m} \). The overall array extent is \( 100 \mu \text{m} \times 100 \mu \text{m} \). It can be seen that the etching methods results in excellent control over the geometrical parameters of the nanowires.

Optical microscopy (Fig. 4(a)) revealed that the Si nanowires displayed a remarkable variety of colors. Each colored square of Fig. 4(a) comprised a \( 100 \mu \text{m} \times 100 \mu \text{m} \) region containing Si nanowires on a \( 1 \mu \text{m} \) pitch. It can be seen that there was a striking color change as the nanowire radius increased from \( 45 \text{ nm} \) to \( 70 \text{ nm} \). This was also evident in the pattern shown as Fig. 4(b), in which the letters comprised nanowires with different radii. A zoom-in of the letter “A” is shown as Fig. 4(b), with the blue dots comprising individual Si nanowires.

To understand the mechanism by which the Si nanowires obtain their color, we conducted reflection measurements using an optical microscope fitted with a halogen white light source and a spectrometer (Horiba Jobin Yvon LabRam). The reflection spectra were measured on arrays of nanowires with radii ranging from \( 45 \text{ nm} \) to \( 70 \text{ nm} \). The reflection spectra measured from the nanowires were normalized to those obtained from a silver mirror. It can be seen that each spectrum showed a dip whose position shifted to longer wavelengths as radius of the nanowire increased (Fig. 5).

As the nanowires are fabricated in arrays, one might think that their multicolored nature originates from “grating” or diffractive effects of the array. This is not the case, however. We confirmed this by measuring arrays with the same nanowire radius but larger pitch (1.5 and \( 2 \mu \text{m} \)). We found that the position of the spectral dip shifted by less than 1%. The magnitude of extinction was reduced, but this was to be expected because there were fewer nanowires per unit area. We also repeated the
we plot the major transverse component of the HE\textsubscript{1,1} mode at the bottom interface between air and Si. In Figs. 6(b)–(d), along the length of the nanowire, and reflected or transmitted wire mode can be scattered at the top of the nanowire, absorbed along the length of the nanowire, and reflected or transmitted at the bottom interface between air and Si. The light that does interact with the nanowire mode is reflected or transmitted at the bottom interface between air and Si. The light that does interact with the nanowire mode can be scattered at the top of the nanowire, absorbed along the length of the nanowire, and reflected or transmitted at the bottom interface between air and Si. In Figs. 6(b)–(d), we plot the major transverse component of the HE\textsubscript{1,1} mode at three representative wavelengths for a nanowire with radius 45 nm. At short wavelengths, the mode is tightly confined to the nanowire (Fig. 6(b)) and therefore not efficiently excited by unfocused light normally incident from free space due to poor spatial overlap. As a consequence, the reflection at the bottom interface is similar to that at a flat air-Si interface (without nanowires). At long wavelengths (Fig. 6(d)), the mode is mostly expelled from the nanowire. It can therefore be efficiently excited, even with unfocused illumination. The mode is so delocalized, however, that its effective index approaches that of air. Absorption is low and the reflection at the bottom interface is again similar to that at a flat air-Si interface (without nanowires). On the other hand, at some intermediate wavelength, the mode can be efficiently excited from free space while being localized in the nanowire. This can be seen in the plot of Fig. 6(c). The light can be absorbed by the nanowire or alternatively efficiently coupled to the substrate. In both cases, the reflection at the bottom interface is reduced, leading to the reflection dips seen in Fig. 5. As the nanowire radius is increased, the wavelength at which this trade-off between delocalization and confinement occurs red-shifts. As we will see in the next section, this presents a means for defining a filter array, in which the filtering function varies as a function of position. One key advantage is that a single lithography defines the radii of all nanowires, and therefore their optical responses.

![Figure 5. Measured reflection spectra of nanowire arrays.](image)

## III. Multispectral Imaging with Silicon Nanowires

Having demonstrated the multicolored nature of vertical silicon nanowires, it occurred to us that the phenomenon could be used advantageously for the realization of filter arrays for imaging applications. In the work of Figs. 3–6, however, the nanowires were on silicon substrates. For transmission-mode filters at visible and near-infrared wavelengths, however, one would need them to be substrates transparent in those spectral bands. This is what we set out to do next.

We chose to use polydimethylsiloxane (PDMS) as the substrate into which to transfer our nanowires. The choice was made primarily because PDMS is transparent at visible and near-infrared wavelengths. Furthermore, PDMS is used extensively for the realization of microfluidic chips, and there has been some interest in developing integrated color filters for fluorescent detection. PDMS is also a soft elastomer and can be deformed substantially. By demonstrating the embedding of nanowires in PDMS, therefore, we reasoned that we might also open up the possibility of future optical elements whose response could be tuned by stretching. The fabrication method we devised is shown as Fig. 7, and described below.

The first part of the fabrication method (Fig. 7) involved etching Si nanowires, using the process described in the previous section. We next spin coated PDMS onto the wafer. A rotation speed of 1000 rpm and a time of 60 s were used. The mixture that was applied contained the PDMS base and curing agent in a 5:1 ratio. We cured the film at 230 °C on a hotplate for 1 h. As we explain further below, this is a comparatively high temperature. The resultant PDMS thickness was about 50 \( \mu \)m. We next removed the cured PDMS film by scraping it from the Si substrate with a razor blade using a modified version of the method of Ref [6]. In Ref [6], the wires were made by the VLS method and they were much larger (\( \sim 1.5–2 \) \( \mu \)m diameter, and \( \sim 100 \) \( \mu \)m tall). We initially applied the method of Ref [6], but the yield was poor, with the nanowires escaping from the PDMS during the razor blade step. We found that increasing the curing temperature to 230 °C improved the results considerably. We believe that this is due to the adhesion between the PDMS and silicon being increased, meaning that the nanowires remain within the PDMS film during the scraping step.

An optical microscope image of four arrays of vertical silicon nanowires on a silicon substrate is shown as Fig. 8(a). As before, the colors of the nanowires can be seen to be strongly dependent on their radii. It should be mentioned that the radii noted in Fig. 8(a), as well as all other radii quoted in this paper, are the design values employed in the electron-beam lithography step. In Fig. 8(b), we show a transmission mode optical microscope image of the nanowire arrays after transfer to the PDMS. The transfer process has excellent yield and the nanowires can be seen to add color to the PDMS. It is evident, however, embedding the nanowires in the PDMS modifies the color.
that they appear. The nanowires with radii of 50 nm, for example, appeared magenta when on the Si substrate, but purple when transferred to the PDMS. This red-shift is a result of the refractive index of the medium surrounding the nanowires being increased from \( n = 1 \) (air) to \( n = 1.5 \) (PDMS). We also note that the pitch of the nanowires was a little smaller (0.947 \( \mu \)m rather than 1 \( \mu \)m) after transfer to the PDMS. This is due to the fact that we cured the PDMS at 230 °C, but used it at room temperature (20 °C). The PDMS therefore shrank after fabrication, due to the fact that it has a large coefficient of thermal expansion (\(~310 \text{ ppm/}°\text{C}\)). We did however also simulate the effect of the reduced pitch upon the transmission spectrum. We found that the wavelength of the transmission dip was almost unmodified. This led us to conclude that the reduction in pitch was not the origin of the red-shift we observed.

The results of Fig. 8 confirmed to us the feasibility of filter arrays based on silicon nanowires. We next sought to demonstrate their use in multispectral imaging. We were motivated for several reasons. In multispectral imaging, the spectrum is divided into several bands. This permits objects and materials to be identified by their reflection or absorption spectra. Many applications have been demonstrated, including remote sensing, vegetation mapping, food-quality control, face recognition and non-invasive biological imaging. To obtain images in multispectral bands, systems employing multiple cameras, motorized filter wheels, line-scanning or tunable filters are used. These add cost, weight and size, however, and relatively few commercial multispectral imaging systems exist. We reasoned that our approach could enable compact systems for multispectral imaging, with the nanowires embedded in PDMS acting as a filter array. Multiple filter functions, spanning visible to the near-infrared (NIR), could be simultaneously defined in the e-beam lithography step. We describe the results we obtained below.

We fabricated our multispectral filter using the method illustrated schematically as Fig. 7. The filter was then stuck on a monochrome charge-coupled device (CCD) image sensor (Fig. 9, left). The cover glass had been removed from the image sensor. The filter was mounted directly on the microlens array of the image sensor, and we found that adhesive was not necessary. A transmission-mode optical microscope of the filter before mounting is shown on the right side of Fig. 9. The filter comprised 20 \( \times \) 20 unit cells, each occupying an extent of \(~75 \times 75 \mu\)m. Each unit cell contained eight different filters, with an additional transparent region in its center. The transparent region contained no nanowires, and is denoted “0” in Fig. 9. Each filter comprised 24 \( \times \) 24 nanowires in a square array on a 1 \( \mu \)m pitch. The nanowires had heights of 1.67 \( \mu \)m. The filters denoted “1” to “8” in Fig. 9 contained nanowires with radii ranging from 45 nm to 80 nm in 5 nm steps.

In Fig. 10, the multispectral imaging system concept is shown. The approach is analogous to the Bayer filter pattern approach used in color image sensors, in which arrays of dye-based red/green/blue filters are used. Here, however, our array contains eight filter functions that span visible to NIR wavelengths, rather than the three filter functions used in color imaging. A single exposure can therefore capture an image for each spectral channel (Fig. 10).
To use our filter array for multispectral imaging, we performed the following characterization measurements. We determined the spectral response of our multispectral imaging system by illuminating it with light from a monochromator from 400 nm to 1000 nm in steps of 10 nm, and capturing an image from the CCD at each wavelength. From each image, the value of the pixels associated with each filter was recorded. We intentionally chose the size of each filter (24 × 24 nanowires) to correspond to 4 × 4 pixels of the image sensor.

We found the transmission spectra \( T(\lambda) \) of our filter channels by normalizing the measured pixel values of the filter channels by those measured from the clear reference area containing no nanowires ("0" of Fig. 9). The results are plotted in Fig. 11(a) along with the image sensor’s relative response [7]. We then found the relative response of each filter channel by multiplying the image sensor’s response (black dashed line of Fig. 11(a)) by \( 1 - T(\lambda) \). In this way, the transmission dips are converted to response peaks. We show the results as Fig. 11(b). We next illustrated that our approach permitted the realization of a variety of filter functions. To show this, we assumed the objective is for the system to have the spectral response shown as Fig. 11(c). Channels VIS1-3 were assigned to have the ideal response of the CIE (1964) 10-deg color matching functions [8]. Channels NIR1-5 were assigned to have Gaussian shapes with center wavelengths matching those of Channels 4–8, respectively. The full-widths-at-half-maximum (FWHMs) were all chosen to be 100 nm. Next, we used the least squares method to find the linear combination of Channels 1–8 (Fig. 11(b)) to achieve a response most similar to the model (Fig. 11(c)). This yielded the actual response as shown in Fig. 11(d). Differences can be seen between the actual and model responses, but are much smaller than the un-optimized result (Fig. 11(b)).

We next set about demonstrating color imaging with our system. We did not use any filters (e.g. IR blocking filters) in addition to our multispectral filter array. We took nine images of each scene, with mechanical scanning of the image sensor in a 3 × 3 array. We did this in order to increase the resolution and reduce the pixel calculation error due to geometric position mismatch between the color filter channels (Channel 0 and Channels 1–8). To generate color images, we combined Channels VIS1-3 to obtain standard red/green/blue (sRGB) images. We then applied color correction, using results we obtained by imaging a Macbeth color checker card. Gamma correction was applied next. An image of resistors produced in this way is shown as Fig. 12(a). The color codes can be seen to be very

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Figure 8. (a) Optical microscope image (reflection mode) of etched vertical Si nanowires on silicon substrate (\( R \): nanowire radius). Nanowires are 1.5 \( \mu \)m tall, and in a square array with pitch 1 \( \mu \)m. (b) Transmission-mode optical microscope image of Si nanowires after transfer to PDMS film.

Figure 9. (LEFT) photograph of multispectral filter (PDMS film with embedded Si nanowires) mounted on ¼ inch monochrome charge-coupled device (CCD) image sensor. RIGHT: Transmission-mode optical microscope image of PDMS-embedded arrays of vertical silicon nanowires.

Figure 10. Concept schematic of multispectral imaging system. PDMS film with embedded Si nanowires is mounted on monochrome image sensor.
vivid. In Fig. 12(b), an image of the Macbeth ColorChecker card is shown. The results were seen to be quite similar to those produced by a conventional color camera.

Our next goal was to demonstrate multispectral imaging by making use of the five NIR channels of our filter array. In particular, we sought to demonstrate that our device could distinguish vegetation from other materials by constructing a normalized difference vegetation index (NDVI) image. NDVI images represent the normalized ratio between NIR and visible channels, with
\[
\text{NDVI} = \frac{(\text{NIR} - \text{VIS})}{(\text{NIR} + \text{VIS})}
\]. They are used for mapping vegetation. Vegetation has high NIR reflectance and low visible reflectance, giving it a high NDVI value. To demonstrate our system’s capabilities, we imaged a scene containing a plant, single leaf and a Macbeth ColorChecker card. As before, we used Channels VIS1-3 to produce a color image. This is shown as Fig. 12(c), and was seen to be quite similar to that produced with a conventional color camera. We furthermore produced an NDVI image by taking Channel VIS3 as the visible channel and Channel NIR3 as the NIR channel. The results are shown as Fig. 12(d), and demonstrate the capability of our system to distinguish vegetation. The plant, single leaf and green color checker card square can be seen to have very similar (dark green) colors in Fig. 12(c). In the NDVI image of Fig. 12(d), however, the single leaf and the leaves of the plant can be seen to produce high NDVI values while the green color checker card square does not. We also note that the violet color patch also produced a high NDVI value, but that this was to be expected due to its material properties.

To further demonstrate the capabilities of our multispectral system, we next performed an experiment where we imaged through an object that was opaque at visible wavelengths. The object we chose was a glass plate painted with a black permanent marker. Like many dyes, the marker ink transmitted infrared wavelengths. We arranged a scene in which a cross-shaped object was located in front of the painted black screen, while a donut-shaped object was located behind it. White-light and IR light emitting diodes (LEDs) were used to illuminate the scene, which was imaged with our CCD camera.
fitted with our multispectral filter. We show the results we obtained as Fig. 13. It can be seen that, in the visible-wavelength image, the object in front of the screen is visible. For the NIR image (NIR5 channel), however, both front and back objects can be seen.

IV. Conclusions and Future Prospects

We have shown that a filter based on vertical silicon nanowires enables multispectral imaging from visible to NIR wavelengths. Our multispectral filter harnesses the phenomenon that vertical silicon nanowires can show a variety of colors, in contrast to the gray color that silicon appears in bulk form. This phenomenon is ascribed to wavelength-selective coupling to the guided nanowire mode. We note that the method we introduce is very practical from a manufacturing standpoint because all filter functions are defined at the same time in a single lithography step. A fully-functional device results from an additional two steps (etching and embedding in PDMS) that are relatively simple. The filter device we introduce could enable multispectral imaging systems that have smaller footprints and are of lower cost than current approaches. In addition, as we discuss briefly below, this work opens up the exciting future prospect of image sensors based on nanowires.

In conventional image sensors (Fig. 14(a)), color separations are performed using absorptive dye color filters, with the final image found via demosaicing. Primary color RGB filters transmit red, green and blue light. This limits efficiency, however, because much of the spectrum is blocked, i.e. red and blue for a green filter. Here, we suggest a novel means for simultaneously achieving high efficiency and high color accuracy (Fig. 14(b)).

We suggest pixels consisting of Si nanowires (incorporating
photodetectors) formed above planar photodetectors. Part of the spectrum would be absorbed by the Si nanowire, and converted to photocurrent, in a manner akin to an RGB filter image sensor. The remaining part of the spectrum will be absorbed by the planar photodetector, and again converted to photocurrent. By appropriate choice of nanowire radius, pixels with different spectral responses would be obtained. In this way, high efficiency color separations could be possible.

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