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Electrostatically Doped Silicon Nanowire Arrays for Multispectral Photodetectors

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ABSTRACT

Nanowires have promising applications as photodetectors with superior ability to tune absorption with morphology. Despite their high optical absorption, the quantum efficiencies of these nanowire photodetectors remain low due to difficulties in fabricating a shallow junction using traditional doping methods. As an alternative, we report non-conventional radial heterojunction photodiodes obtained by conformal coating of indium oxide layer on silicon nanowire arrays. The indium oxide layer has a high work function which induces a strong inversion in the silicon nanowire and creates a virtual $p$-$n$ junction. The resulting nanowire photodetectors show efficient carrier separation and collection leading to an improvement of quantum efficiency up to 0.2. In addition, by controlling the nanowire radii, the spectral response of the In$_2$O$_3$/Si nanowire photodetectors are tuned over several visible light wavelengths, creating a multispectral detector. Our approach is promising for the development of highly-efficient wavelength selective photodetectors.

KEYWORDS

nanowire photodetectors, silicon nanowire, radial junction, dopant-free, electrostatic doping, multispectral, photosensors
The electrical and optical properties of silicon nanowires (NWs) attracted applications in nanoelectronics, photodetectors, and solar cells. The electrical properties of the NWs stem from carrier transport in quasi 1-D systems of high surface to volume ratio. The interplay between the material’s refractive index and the subwavelength dimensions gives NWs a superior ability to tune their spectral response. However, even after decades of intensive research in active nanowire devices which take part in the carrier generation as a photodetectors, real-world applications are still absent. This is mainly due to the lack of means to control the doping and recombination in NW arrays. The traditional doping processes like ion implantation induce lattice defects and thermal diffusion doping cannot create sharp interfaces. Thus such methods cannot be used to achieve high quality shallow p-n junctions on the NWs. In addition, a high doping significantly increases the Auger recombination and reduces the carrier mobility. Therefore, it is important to find a different approach for creating junctions in the NW. Our approach is to engineer the interfacial junction by electrostatically doping the NW surface by coating with a specific work function material. Electrostatic doping, also known as gate-induced doping without the thermal diffusion, is an emerging concept and has been recently used for increasing the efficiency of bulk devices such as solar cells. The difference in the work functions of NW and the coated material induces an interfacial potential which creates a depletion, accumulation, or inversion near the interface. When such a coated material is used as an electric contact, it selectively allows one carrier transport and thus the name "carrier selective contact (CSC)".

For photodetection applications, the CSC material must not negatively affect the light detection of the SiNW array. Several materials and deposition techniques have been used to create CSC’s. Examples include transition metal oxides, transparent conducting oxides, and carbon-based conductors. Such materials have a higher work function than n-type Si,
creating hole collection contacts. Similarly, low work function metals\textsuperscript{22,23} and alkaline metal compounds\textsuperscript{13,24–26} are required for electron collection. Although some metal oxides such as ZnO and TiO\textsubscript{2} can be deposited onto 3-dimensional surface by chemical vapor methods, the physical vapor deposition or spin-coating technique used to form most of CSC materials do not coat conformally on the high aspect ratio NWs. Thus, we elected to use In\textsubscript{2}O\textsubscript{3}, which satisfies our optical and electrical requirements and can be coated by an atomic layer deposition (ALD) process as the CSC material. The ALD process is crucial as it creates thin conformal coating of uniform thickness on the high aspect ratio SiNWs. In\textsubscript{2}O\textsubscript{3} is a good candidate for CSC material with \textit{n}-type Si as it has a high work function, high conductivity and is transparent in visible region. With this configuration of ALD-deposited In\textsubscript{2}O\textsubscript{3} layer on \textit{n}-Si NW arrays, we created efficient radial heterojunction NW photodetectors which can be more efficient than axial ones due to the shorter photocarrier travel length.\textsuperscript{8} Here, we present radial heterojunction photodiodes using an In\textsubscript{2}O\textsubscript{3} layer that induces a junction on the NWs.

The fabricated In\textsubscript{2}O\textsubscript{3}/SiNW devices show an enhanced quantum efficiency (QE) of about 0.2, which is higher than those of previously reported SiNW-based multispectral photodiodes (Table S1). In addition, by controlling the geometrical radius of the NW, the optical response of the In\textsubscript{2}O\textsubscript{3}/SiNW can be tuned to absorb a particular wavelength. This spectral filtering effect produced distinct QE spectra for NW arrays having different diameters. Later, we used this feature to achieve single and dual monochromatic wavelength identifications over a wide range of wavelengths. Thus, we show that efficient SiNW array photodiodes can be achieved by an electrostatic doping. This configuration of materials and geometry can be used to create a solid-state multispectral detector that provides higher efficiency wavelength identification over a conventional complementary metal–oxide–semiconductor (CMOS) sensor.
RESULTS AND DISCUSSION

Structure and Junction Designs of Si-In\textsubscript{2}O\textsubscript{3} Core-Shell Nanowire Photodiodes

The concept of electrostatically doping a semiconductor is closely related to creating a Schottky barrier. The presence of the Schottky barrier is a consequence to having two materials, of different work functions, in contact. The traditional Schottky barrier occurs when a metal is placed in contact with a semiconductor.\textsuperscript{27} Similarly, a Schottky barrier formed when In\textsubscript{2}O\textsubscript{3} is deposited on the \textit{n}-Si NWs can be treated using the classical Schottky-Mott rule\textsuperscript{10}. The large difference in the work functions of \textit{n}-Si and In\textsubscript{2}O\textsubscript{3} induces a charge carrier inversion near the interface. This creates a virtual \textit{p}-doping in the nanowires through inversion which mimics a \textit{p-n} junction inside the \textit{n}-Si. Detailed explanation of the Schottky junction is provided in Supporting Information Note A. For photodetector applications, photocarriers are absorbed by the \textit{n}-Si and separated by the built-in electric field in the inversion layer. With this understanding, we designed dopant-free SiNW-based photodetectors.

The fabricated detectors are schematically illustrated in Figure 1a. We started with an \textit{n}-type silicon wafer of a resistivity of 1 to 10 ohm-cm (dopant concentration of $4.5 \times 10^{14} - 5 \times 10^{15}/\text{cm}^3$), and fabricated the SiNWs using electron beam lithography and inductively coupled reactive ion etching;\textsuperscript{28} an example is shown in Figure 1b. The SiNWs were HF treated to form H-terminated silicon. Then a thin In\textsubscript{2}O\textsubscript{3} layer was created using the ALD process which created a conformal coating on the SiNWs, Figure 1c. We investigated the quality of the interface between the In\textsubscript{2}O\textsubscript{3} coating and the surface of the single crystalline SiNW, using a focused-ion-beam sectioning and examined the cross-section using transmission electron microscopy (TEM). We found that the In\textsubscript{2}O\textsubscript{3}/SiNW core-shell nanowire has $\sim$ 40 nm thick conformal In\textsubscript{2}O\textsubscript{3} shell wrapping the Si core. The TEM image of the cross-section of a single In\textsubscript{2}O\textsubscript{3}/SiNW shows a polycrystalline
In\textsubscript{2}O\textsubscript{3} shell with a grain size of 32±6 nm (Figure 1d). In addition, we found that the interface between the polycrystalline In\textsubscript{2}O\textsubscript{3} shell and the single crystalline Si core consists of an amorphous layer due to the lattice mismatch between the silicon and In\textsubscript{2}O\textsubscript{3} (Supporting Information Figure S1). We used atom-probe tomography (APT) to examine this amorphous layer. APT provides spatial elemental reconstruction at an atomic scale due to the direct detection of the atoms through time-of-flight mass spectroscopy.\textsuperscript{29} For the APT investigation, a commercial sharp Si nanotip structure was used and was coated with In\textsubscript{2}O\textsubscript{3} layer using the same ALD process that formed the CSC on the NWs. The SEM images, presented in the Supporting Information Figure S2, established that the tomographic reconstruction, as shown in Figure 1e, is accurate in morphology and scale. The mass spectrum of the material at the interface, presented in Supporting Information Figure S3, shows elemental peaks of indium oxide, silicon, and silicon oxide. The silicon oxide peaks are above the level of the background counts, and the 2D concentration profile shows the existence of silicon oxide, SiO\textsubscript{x} at the interface between In\textsubscript{2}O\textsubscript{3} layer and silicon (Figure 1f). This layer must have formed during the initial steps of the ALD process\textsuperscript{30} as water is used in the ALD precursor for growing the In\textsubscript{2}O\textsubscript{3} layer. The H-terminated silicon is exposed to the water precursor and reacts with oxygen to form an ultra-thin SiO\textsubscript{x} layer. The chemical compositions of In\textsubscript{2}O\textsubscript{3}/Si junction were further characterized by X-Ray Photoelectron Spectroscopy (XPS). Supporting Information Figure S4 shows the depth profile of a planar In\textsubscript{2}O\textsubscript{3}/Si substrate. The binding energy of O 1s (~532.8 eV) is slightly higher than that for indium oxide (~530.4 eV). This O 1s peak could indicate the formation of Si-O bonds at the interface between the In\textsubscript{2}O\textsubscript{3} and silicon layers.\textsuperscript{31} The APT and TEM analysis support the formation of a SiO\textsubscript{x} layer of thickness of about 2 nm.

The electrical properties of the In\textsubscript{2}O\textsubscript{3} layer were studied using Hall measurements and XPS. The as-deposited, the In\textsubscript{2}O\textsubscript{3} layer shows relatively low resistivity of 2 m\Omega·cm with a carrier density
of $5 \times 10^{19}$/cm$^3$ and a mobility of 30 cm$^2$/V-sec$^2$. As shown in Figure 2a, the In$_2$O$_3$ layer achieves a higher work function of $5.50 \pm 0.15$ eV compared to $4.44 \pm 0.01$ eV for a moderately-doped $n$-Si of dopant concentration of $\sim 10^{15}$ atom/cm$^3$. A schematic for the resulting band-diagram for In$_2$O$_3$/SiO$_x$/Si junction is shown in Figure 2b. The conductor/insulator/semiconductor structure has been intensively studied in solar cell structures, where the interfacial defect sites at the conductor/semiconductor interface could be effectively passivated by an insulator layer. The presence of the 2nm SiO$_x$ layer requires the carriers to tunnel through this layer as they traverse the In$_2$O$_3$/n-Si interface. We measured the current-voltage (I–V) characteristics of the devices under dark and illuminated conditions with light intensity of 100 mW/cm$^2$ (Figure 2c). The I–V curves indicate a diode behavior with an on–off ratio of about 91 under the bias of ±0.5 V. The dark current density of the In$_2$O$_3$/SiNWs device is about $63 \mu$A/cm$^2$ at a bias of $-0.5$ V and a photocurrent to dark current ratio of about 670 was measured at zero bias.

**Optical and Electrical Responses of In$_2$O$_3$/Si Nanowires**

The spectral response of the In$_2$O$_3$/SiNW devices was obtained from experiments and compared with finite difference time domain (FDTD) simulations. Details on the simulation methodology can be obtained from the methods section. The experimental absorption spectra of the In$_2$O$_3$/SiNWs arrays are shown as Figure 3a. Although the trend of spectral red-shift with increasing NW radius is consistent with the predictions of the optical FDTD simulations (Supporting Information Figure S7), some important differences are observed. The absorption behavior is further discussed in Supporting Information Note B. The strong spectral dips in experiment (Figure 3a) for the In$_2$O$_3$/SiNWs of Si radius from 60 nm to 75 nm are not seen in the simulations (Supporting Information Figure S7). To understand this difference, we studied the
morphology of the etched structures. Even minor changes in morphology are known to significantly affect the optical absorption of NWs.\textsuperscript{35-38} Thus we performed SEM on NW after forcing In\textsubscript{2}O\textsubscript{3}/SiNWs to lay horizontally on the substrate for a thorough inspection of morphology. Detailed SEM images of such In\textsubscript{2}O\textsubscript{3} coated SiNWs are provided in the Supporting Information Figure S9. From the SEM images we find that the RIE process we used for etching the SiNWs, created an undercut such that the diameter under the tip is slightly smaller than the base diameter, leading to necking. Based on these SEM observations, we modified the simulated geometry and simulated tapered In\textsubscript{2}O\textsubscript{3}/SiNWs, using tip, center, and base diameters as measured from the SEM images. Figure 3b shows the simulated absorption spectra using the tapered In\textsubscript{2}O\textsubscript{3}/SiNWs and we find that the inclusion of tapering in the simulations resulted in absorption spectra that match the experimental results. Generally, the tapered NWs absorbed a broad spectrum compared to the sharp absorption peak of untapered NWs.\textsuperscript{35} In addition, the neck region of our tapered In\textsubscript{2}O\textsubscript{3}/SiNW has less Si and thus a reduced effective index. Consequently, the higher index NW tip over the necking region acts as Mie resonator and generates resonant reflection.\textsuperscript{39} This leads to the strong dips in the absorption spectra in the NWs with large radii.

In Figure 4a, we present simulated spectral absorption efficiency considering absorption only in carrier separation region i.e. Si region. A more detailed breakdown of absorption in Si and In\textsubscript{2}O\textsubscript{3} is presented in Supporting Information Figure S10. The external quantum efficiency (EQE) was calculated using the measured responsivity (see Supporting Information Figure S11). The experimental EQE spectra of In\textsubscript{2}O\textsubscript{3}/SiNW devices presented in Figure 4b, show similar red shifts with increasing NW diameter as shown in the simulations of Figure 4a. The positions of the dips of the calculated absorption efficiencies are in general agreement with those of the experimental EQEs. It is important to note that by direct comparison of absorption to EQE, one implicitly
assumes that the internal quantum efficiency (IQE) = 1. Thus we are assuming that all carriers
generated by the absorbed light are collected without any recombination. However, for actual
devices this is not achievable, mostly due to the fact that transport and collection of photocarriers
are strongly affected by the presence of trap states in the bulk, surfaces and interfaces. Particularly,
the high density of surface/interface states in NWs leads to rapid recombination of the minority
carriers. In Figure 4a, the absorption at the wavelength of 400 nm is ~0.6. In contrast, the
experimental EQE is 0.02 at the wavelength of 400 nm (Figure 4b). The simulated absorption and
experimental EQE spectra show differences as a result of electrical losses. For example, for a Si
NW of a radius of 50 nm, charge carrier lifetime is about 8.33 ps,\(^{40}\) which is several orders of
magnitude lower than the 1 ms lifetime in bulk Si.\(^{41}\) To take the recombination induced lifetime
reduction into account, we included an effective minority carrier lifetime in the electrical
stimulations. Further details on the electrical modeling are provided in the Supporting Information
Note C. The recombination induced shorter lifetime should result in a lower EQE. For the
simulation, we chose a wide range of effective minority carrier lifetimes (\(\tau_{\text{eff}}\)) between 0.05 ns and
5 ns. The outcomes of the simulations are given in Figure 5a for an In\(_2\)O\(_3\)/SiNW device with a
SiNW of radius of 65 nm. At short wavelengths, less than the position of the absorption dip, the
EQE degradation is significant with reducing lifetimes. The EQE increases non-linearly with
increasing lifetime and edges towards saturation at higher lifetimes (see Supporting Information
Figure S12). The results indicate that the charge transport in NW is less affected above certain
large lifetime and thus EQE becomes less sensitive to the presence of defect states. In Figure 5b,
we show EQE vs wavelength with a comparison of simulated EQE data with experimental results.
We find reasonable agreement (see Figure 4b, 5b) for effective minority carrier life time of \(\tau_{\text{eff}} = \)
0.25 ns. Thus we estimate lifetimes of about 0.25 ns for the studied NW which fall in the ballpark range found in literature\textsuperscript{40} of 40 nm to 100 nm radius NWs.

The above-mentioned observations can be correlated with the location of generated photocarriers along the length of the nanowire at different wavelengths. To elucidate these observations, we simulated the axial band diagram of In\textsubscript{2}O\textsubscript{3}/SiNW device (see Figure 5c and 5d). We note that two physical phenomena are taking place here: (1) As anticipated, a strong inversion layer is formed on the surface of the Si NW due to the high work function In\textsubscript{2}O\textsubscript{3} layer. Thus the surface of the Si NW becomes \( p^+ \)-Si, resulting in generating a radial \( p^-p^+ \) junction. (2) The inversion layer, formed at the interface between In\textsubscript{2}O\textsubscript{3} and Si substrate, generates a \( p^-n \) junction with the background \( n \)-type doping in the substrate. Thus, the In\textsubscript{2}O\textsubscript{3}/SiNW device has a radial \( p^-p^+ \) junction on the SiNW and an axial \( p^-n \) junction under the SiNW (Figure 5e and 5f). Holes should then be collected through the \( p^+ \)-shell of SiNW, and the electrons should diffuse in the \( p^- \) core along the length of the SiNW to the substrate. Here we have assumed that the presence of the SiO\textsubscript{x} will only attenuate the number of the diffusing carriers. The observed severe EQE degradation at the short wavelength can then be explained by the high recombination probability that the minority carriers would face when traversing the length of the NW to reach the \( n \)-type substrate. To get an idea of the mean free path of the carrier, we calculate the diffusion length using \( L=(\tau\times C)^{1/2} \), where \( \tau \) is the minority carrier lifetime and \( C=36 \text{ cm}^2/\text{s} \) is the diffusion coefficient for electrons.\textsuperscript{42} In the simulations with a long \( \tau_{\text{eff}} \) of 5 ns, the diffusion length is 4.24 \( \mu \text{m} \), whereas for short \( \tau_{\text{eff}} \) of 0.05 ns, the diffusion length is only 0.42 \( \mu \text{m} \). The data of Figure 5b gives an estimate for \( \tau_{\text{eff}} \) to be of the order of 0.25 ns, or a diffusion length in the range of 0.95 \( \mu \text{m} \). For long wavelength light (500–600 nm), which is absorbed deeper along the NW, the generated carriers have to traverse a shorter distance to be collected in the substrate and thus is weakly
affected by change in lifetime. However, for shorter wavelengths (400–500 nm), where photocarriers are generated near the tip of the nanowire, the photocarriers generated at the tip of the nanowire would recombine before reaching the In$_2$O$_3$/Si substrate interface limited by the carrier diffusion length. In this case, the spectral carrier collection efficiency becomes wavelength dependent: for short wavelength, light is mainly absorbed in the tip of the nanowire while for long wavelength, light is absorbed in the middle of the NW (Figure 6), resulting in sharper degradation of EQE at 400 nm vs 550 nm.

**Single and Dual Monochromatic Wavelength Identifications**

The Si NW array photodetectors show radius-dependent tunable spectral response in the visible spectrum as shown in Figure 4b. We tested the capability of the current six NWs system for identification of wavelengths for single monochromatic illumination and two concurrent monochromatic illumination, and examined how to use each photodetector array as a discrete wavelength channel. In general the identification accuracy of any detection system depends on both orthogonality of its spectral channels and the number of these channels. In a NW system, a larger number of channels is possible. In fact, nine color filters were constructed from NWs of nine different radii. By proper choices of the values of the radii and array dimensions, it is possible to have non-overlapping spectral absorption. Since our goal here was to highlight efficient detection in our NW/metal-oxide heterostructures, no effort was directed towards morphology optimizations to achieve non-overlapping spectral channels. Consequently, our 6 channels active NW detectors suffer from a significant spectral overlap (see Figure 4b). In visible imaging, a commercial color CMOS sensor has 3 separate red, green and blue channels and thus can also be used for such spectral identification. The three channels created using dye filters and the channels
have much smaller overlap with each other (see Supporting Information Figure S13 for RGB response curves) compared to our detectors. Thus we tested these two systems and we examined the outcomes of having overlaps among the 6 channels.

At first, we tested the wavelength identification for a single monochromatic illumination. To identify a wavelength, the relationships between the spectral responses in all wavelengths should be understood. This is difficult due to the overlapping channels in our detectors. It can be approached by feature identification process through regression and more accurately by machine learning (ML) techniques.\textsuperscript{43,44} Thus, we applied a ML algorithm that can learn from a training dataset of individual channel response for different illumination wavelengths. This learning then allows the algorithm to make more accurate predictions of the wavelength of the monochromatic illumination. The details of the algorithm and the model are provided in the Supporting Information Note D. In short, the algorithm performs supervised learning on a known dataset of photo-response spectra and tries to match the response with a known wavelength. Our figure of merit is the prediction error which represents the percentage of the difference between the expected and predicted values as a fraction of the expected one. Figure 7a shows the prediction error of wavelength measurement as a function of the wavelength for the six In\textsubscript{2}O\textsubscript{3}/SiNW device and for the CMOS sensor with the RGB filters. For the sensor with color dye filters, the error increases when two of RGB color matching functions have strong overlap in the 450 to 500 nm and 575 to 625 nm spectral region. By contrast, the In\textsubscript{2}O\textsubscript{3}/SiNW devices show accurate predictions of wavelength over a broadband of 420-690 nm, with an error of less than 5%. These results show that although In\textsubscript{2}O\textsubscript{3}/SiNW device has channels with much larger spectral overlap, compared to commercial CMOS sensor, a higher number of channels is more important for wavelength identification. With an increase in the number of distinct radius NW channels, identification should
be more accurate. For commercial CMOS sensors, multiple color channels would require synthesis of different dyes for multispectral applications which are much harder to achieve than tunable structural color exhibited by NW arrays.

We further assessed both systems on their theoretical ability to identify or discriminate two distinct wavelengths in concurrent illumination. Details of the test conditions for dual monochromatic wavelength identification are provided in Supporting Information Note E. We used a bivariate Pearson correlation to test whether there is a statistically significant linear relationship between the actual wavelength of the incident light and the predicted one, and to determine the strength of the association. A correlation coefficient close to 1 indicates a high strength of the relationship between two different elements, or that the device cannot distinguish the two different elements. In this calculation for each wavelength pair, we count the number of misidentifications with other wavelength pairs for which the correlation coefficient is larger than 0.97. Thus we achieve a confusion count for each wavelength pair against all wavelengths in a confusion matrix form. Figure 7b and 7c show the confusion matrix plots of the confusion number for each wavelength pair. We find that the conventional CMOS sensor shows a higher confusion matrix value compared to the SiNW spectral detectors. This result for the CMOS sensor is similar to single wavelength detection and shows high confusion for overlap regions in color matching functions (480 nm to 570 nm). In contrast, the Si NW photodetectors can easily identify the UV and visible light between each of the six radii arrays. This is also observed in the longer wavelength region of the visible spectra where the In$_2$O$_3$/Si NW devices show an improved accuracy of the wavelength measurement in the long wavelength region from 600 to 700 nm compared to the conventional RGB sensor.
Although we only used a 6 channel In$_2$O$_3$/SiNW detector, an extension to higher numbers for a multispectral imaging can be readily realized by using a larger number of radii for identification in more bands. This is a significant advantage over CMOS color sensors where adding additional color filter is difficult as it requires formulation of specific dyes, having accurate absorption wavelengths for each channel filter. This fabrication complexity quickly increases due to the extra alignment steps with each additional spectral channel dye filter. Further, the multispectral detection capability can be improved by design optimizations that minimize spectral overlap between the NW arrays. These improvements can be done by achieving a higher EQEs with better NW surface passivation, morphology, doping and contact optimizations.

CONCLUSIONS

In summary, we demonstrated heterojunction photodetectors in vertical SiNWs by using an In$_2$O$_3$ shell layer that induced electrostatic doping. The ALD process created a highly conformed coating of the In$_2$O$_3$ layer with a high work function. This layer induced a virtual $p$-doping in the NWs through inversion. The virtual $p$-$n$ junction allowed efficient carrier separation and the EQEs in the In$_2$O$_3$ shell coated SiNW array photodetectors were significantly improved by a factor of 4 compared to earlier work on conventionally doped Si NW array photodetectors. In addition, we showed that the In$_2$O$_3$/SiNW core-shell photodetector can be tuned to respond to particular wavelengths by controlling the radius of the SiNW. A photodetection system that allows spectral selection can be used to construct multispectral sensors or for wavelength identification. This solid-state system, when fully optimized, will have significant advantages over the current systems that employ diffraction elements, by being rugged, small, portable, and energy-efficient.
With this capability, the tunable spectral response of the In$_2$O$_3$/SiNW core-shell photodetectors were tested and demonstrated a more accurate wavelength detection than a conventional CMOS sensor with color dye filters. They have high potential for creating small multispectral sensors with low energy consumption needed for mobile applications. Our architecture for creating dopant-free heterojunctions can be extended and utilized for fabricating a multitude of other nanoscale active devices, in which traditional doping methods are suboptimum.
EXPERIMENTAL SECTION

Sample Fabrication. A SiNW array on an n-type Si (100) substrate (phosphorus-doped with sheet resistance of 1-10 $\Omega$ cm) is prepared using e-beam lithography followed by reactive ion etching (RIE) process. The substrate is first cleaned in acetone and isopropyl alcohol (IPA). To coat thin e-beam resist layer, pristine e-beam resist solution (ZEP520A, ZEON CORPORATION) is diluted in the solvent anisole (99.7%, Sigma Aldrich) with a 1:2 volume ratio. We coat the diluted e-beam resist solution on the substrate at the speed of 3500 rpm for 45 s and then anneal the substrate at 180 °C for 3 min. E-beam lithography (ELS-125, Elionix) is performed at dose of 450 $\mu$C/cm$^2$ with a beam current of 1 nA to produce disk patterns in six different devices. Typically, each array comprises an area of 500 $\mu$m × 500 $\mu$m. The disks radii range from 50 to 75 nm, in steps of 5 nm. The exposed e-beam resist is developed in anhydrous o-Xylene (97%, Sigma Aldrich) for 45 s and then rinsed in IPA for 30 s. Thin Al$_2$O$_3$ film with thickness of 60 nm is deposited by e-beam evaporating system, and the lift-off process is performed in resist etchant (Removal PG, MicroChem) for 180 min. The Al$_2$O$_3$ disks pattern is used as the etching mask of Si using the DRIE. The vertical SiNW arrays are fabricated in the DRIE with a source power of 2500 W, a stage power of 60 W, and a chamber pressure of 8 mTorr using SF$_6$ gas of 165 sccm and C$_4$F$_8$ gas of 105 sccm at 10 °C. The length of etched SiNW arrays is ~2.3 $\mu$m. After plasma etching, any polymeric coating is removed using a mixture of sulfuric acid and hydrogen peroxide ($H_2SO_4:HO_2 = 2:1$) followed by O$_2$ plasma cleaning (150 W, 300 s). In order to preserve the integrity of the SiNWs during the water drying, the as-cleaned SiNWs are dried using CO$_2$ critical point dryer (Auto Samdri 815 Series A, Tousimis). Prior to loading the samples in the homemade ALD chamber, Al$_2$O$_3$ remaining on the SiNW tips and the native silicon oxide, that is normally formed on the Si substrate, are removed by the diluted HF solution (1% in deionized water). A 40-
nm-thick In$_2$O$_3$ layer is then conformally deposited at 200 °C to fabricate the In$_2$O$_3$/SiNW junction.$^{32}$ To create the top metal electrode with optical window, the In$_2$O$_3$/SiNWs are covered with optical photoresist (Shipley 1822, MicroChem) and then exposed to UV light with 150 mJ/cm$^2$ using an optical aligner (MJB4, Karl Suss). The exposed photoresist is then developed using MF-319, MicroChem, by immersion for 3 min. For the top electrode, 250-nm-thick Al film is deposited onto the In$_2$O$_3$ layer using the thermal evaporator. As the bottom electrode, we deposit a well-known electron selective contact (0.5-nm-thick LiF film) by the thermal evaporator between the Si and Al electrode. The photoresist is stripped by dipping in a lift-off solvent (PG removal, Microchem). After the lift-off process, the In$_2$O$_3$/SiNWs are dried using CO$_2$ critical point dryer. The process schematic is presented in Supporting Information Figure S14.

**Electrical Characterization.** Measurements of the electrical performance was done from the current–voltage (I–V) sweeps. The samples were mounted on a Cu pad of a printed circuit board (PCB) using highly conductive silver paste. The top electrode is connected to an Al pad on the PCB using Au bonding wires. I–V sweeps are performed using a source meter (Keithley 2400) in a dark set-up and also under illumination.

**Optical Characterization.** We measured the optical properties of In$_2$O$_3$/SiNW devices using our homemade setup.$^{45}$ Light from a Xe lamp (66004, Oriel) with a total power of 75 W was focused onto the input slit of a monochromator (CM110, Spectral Products). The incident light with a narrow bandwidth can be tuned from 400 to 800 nm by rotating the grating of the monochromator. A pinhole with a diameter of about 500 μm is placed at the output slit of the monochromator. The light passing through this pinhole is chopped using an optical chopper system (SR540, Stanford Research Systems) at 100 Hz. Then, the light was focused onto the sample with
a microscope objective lens (M Plan Apo, 10x, NA=0.28, Mitutoyo), forming a focused spot with a diameter of about 80 μm. A half angle of the incident light is ± 16.5 degrees. We mounted the sample on a translation stage to position the focused light beam on the center of the nanowire device. PCB mounted sample is then connected to a lock-in amplifier (SR830, Stanford Research Systems) to measure the photocurrent as a function of wavelength. The incident light intensity was measured using calibrated Thorlabs Si photodetector (SM05PD1A-CAL-SP).

**Optical and Electrical Simulations.** To understand light wave propagations in the In$_2$O$_3$/SiNWs, we performed three-dimensional simulations using the finite difference in the time domain. Using commercial software package (FDTD Solution from Lumerical Inc.) we obtained the optical characteristics. The refractive index of In$_2$O$_3$, used in the simulation, was obtained experimentally by using ellipsometry (WVASE32, J.A. Woollam). Light was injected by a plane wave at normal incidence to illuminate the structure. The x- and y-boundaries of the simulation domain were set with periodic boundary condition. We used a perfectly matched layer at the z-boundaries of the domain, and performed the simulation on one unit cell of 400 nm × 400 nm. We also analyze the simulated profile of various modes in nanowire using a commercial software package (Mode solution from Lumerical Inc.). We also performed the electrical modeling of In$_2$O$_3$/SiNW devices using a commercial device simulation package (Device solution from Lumerical Inc.). EQE then calculated with the optical generation rate obtained from the FDTD modeling at each wavelength.
ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Schottky junction of In$_2$O$_3$/n-Si contact; High-magnification TEM images of plan view cross-section with In$_2$O$_3$/SiNW; SEM images of a fabricated In$_2$O$_3$/Si nanotip; APT mass spectrum of a In$_2$O$_3$/Si nanotip; XPS depth profiles of planar In$_2$O$_3$/Si substrate; Optical simulation of vertical SiNWs with and without In$_2$O$_3$ coating layer; Simulated absorption spectra for different radius SiNWs from 40 to 90 nm; Simulated absorption spectra of Si nanowires for different incident angles; Comparisons of Simulated absorption spectra for SiNWs and In$_2$O$_3$/SiNWs (pitch 400 nm) with different Si radii from 50 to 75 nm; Experimental refractive index and extinction coefficient of an In$_2$O$_3$ layer; SEM images of fabricated In$_2$O$_3$/SiNWs for different Si radii from 50 to 75 nm; Modeling of electrical simulation; Absorption spectra of the In$_2$O$_3$, Si, and total system for In$_2$O$_3$/SiNWs with Si core radius of 55, 65, and 75 nm; Experimentally measured responsivities of of In$_2$O$_3$/SiNWs devices; Calculated EQE vs effective lifetime of In$_2$O$_3$/Si nanowires device (Si core radius of 65 nm) at the wavelength of 500 nm; Algorithm of wavelength measurement test (Python 3.0); EQE vs wavelength for a conventional CMOS sensor; Calculation of dual monochromatic wavelength identification test; Summary of previously reported SiNW-based photodiodes; Length and diameter at tip, necking region, and bottom for each of the NW radii.

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Author Contributions

†H.D.U. and A.S. contributed equally to this work. H.D.U., A.S., and F.H. conceived and designed the research. H.D.U., A.S., and A.J. performed the experiments and analyzed the data. H.D.U. and A.S. performed the optical and electrical simulations. H.D.U., A.S., R.G.G., and F.H. wrote the manuscript.

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Figure 1. Core-shell structures of In$_2$O$_3$/SiNW. (a) Device schematic of In$_2$O$_3$/SiNW photodetector. (b) SEM image of SiNW array without In$_2$O$_3$ layer. (c) SEM image of In$_2$O$_3$-coated SiNW array. (d) TEM image of plan view cross-section with In$_2$O$_3$/SiNW. (e) Atom-probe tomographic reconstruction of In$_2$O$_3$-coated Si tip. (f) Representations of In$_2$O$_3$, Si and SiO$_x$ at the interface between In$_2$O$_3$-shell and Si-core.
Figure 2. Inversion layer of In$_2$O$_3$/SiNW photodiode. (a) Kinetic energy cut-off of XPS measured on In$_2$O$_3$-coated substrate. (b) Energy band diagram of In$_2$O$_3$/Si junction. (c) Current-voltage ($I$-$V$) curves of In$_2$O$_3$/SiNW devices under dark and illuminated conditions. Inset of panel c presents log$I$-$V$ curves under dark and illuminated conditions.
Figure 3. Optical responses of In$_2$O$_3$/SiNWs. (a) Experimental and (b) simulated absorption spectra of In$_2$O$_3$/SiNWs for different Si radii.
Figure 4. Electrical responses of In$_2$O$_3$/SiNW photodiodes. (a) Simulated Si absorption efficiency of In$_2$O$_3$/Si nanowires with a range of Si core radius. (b) Experimentally measured EQE vs of In$_2$O$_3$/Si nanowires device with a range of Si core radius.
Figure 5. Effective minority carrier lifetime and junction structures. (a) Simulated EQE vs wavelength for $\text{In}_2\text{O}_3$/Si nanowires device (Si core radius of 65 nm) with several effective minority carrier lifetimes. (b) Simulated EQE vs wavelength of $\text{In}_2\text{O}_3$/Si nanowires device, with an assumed effective minority carrier lifetime of $\tau_{\text{eff}} = 0.25$ ns. (c) Schematic of $\text{In}_2\text{O}_3$/SiNW for the electrical simulations of energy band diagram. Red line indicates the simulation monitor along the NW. (d) Energy band diagram of $\text{In}_2\text{O}_3$/SiNW which shows a radial $p$–$p'$ junction in SiNW and a $p$–$n$ junction between SiNW and Si substrate. Schematics of junction structures (e) without and (f) with $\text{In}_2\text{O}_3$ layer onto SiNW.
Figure 6. Light absorption of In$_2$O$_3$/SiNW depending on the wavelength. Electric field distributions ($|E|^2$) of In$_2$O$_3$/SiNW at the wavelengths of (a) 400 and (b) 550 nm. The white solid line indicates the interface between In$_2$O$_3$ and Si.
Figure 7. Single and dual monochromatic wavelength identifications. (a) Single wavelength measurements for conventional camera and In$_2$O$_3$/SiNW photodetectors. Double wavelength measurements for (b) conventional CMOS sensor and (c) In$_2$O$_3$/SiNW photodetectors.
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