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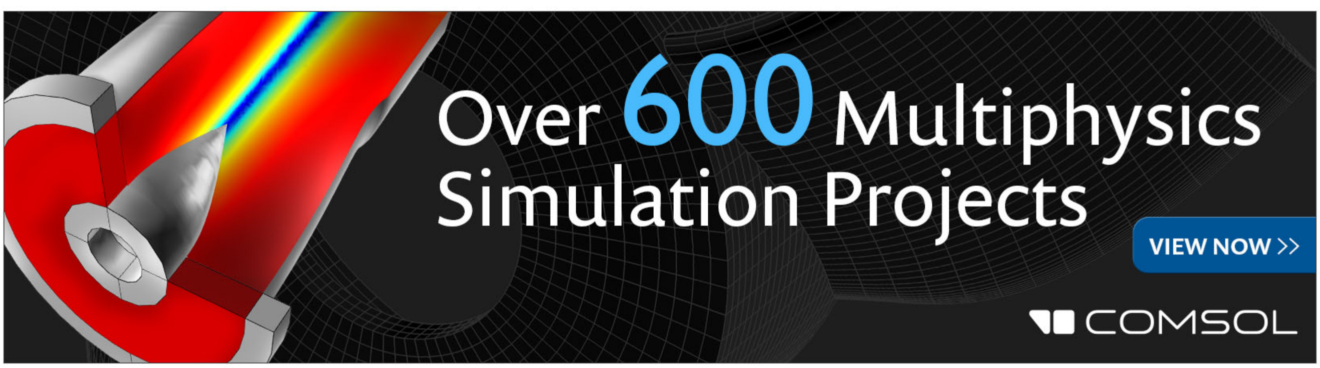

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Photoresponsive properties of ultrathin silicon nanowires

Duy P. Tran,[1] Thomas J. Macdonald,[1] Bernhard Wolfrum,[2] Regina Stockmann,[2] Thomas Nann,[1] Andreas Offenhäusser,[2,a)] and Benjamin Thierry[1,a)]
[1]*Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, MM Bldg., Mawson Lakes Blvd., Mawson Lakes, South Australia 5095, Australia*
[2]*Peter Grünberg Institute, Forschungszentrum Jülich GmbH, 2.4v Bldg., Wilhelm-Johnen St., Jülich 52428, Germany*

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Functional silicon nanowires (SiNWs) are promising building blocks in the design of highly sensitive photodetectors and bio-chemical sensors. We systematically investigate the photoresponse properties of ultrathin SiNWs (20 nm) fabricated using a size-reduction method based on e-beam lithography and tetramethylammonium hydroxide wet-etching. The high-quality SiNWs were able to detect light from the UV to the visible range with excellent sensitivity (~1 pW/array), good time response, and high photoresponsivity ($R \sim 2.5 \times 10^4$ A/W). Improvement of the ultrathin SiNWs' photoresponse has been observed in comparison to 40 nm counter-part nanowires. These properties are attributable to the predominance surface-effect due to the high surface-to-volume ratio of ultrathin SiNWs. Long-term measurements at different temperatures in both the forward and reverse bias directions demonstrated the stability and reliability of the fabricated device. By sensitizing the fabricated SiNW arrays with cadmium telluride quantum dots (QDs), hybrid QD SiNW devices displayed an improvement in photocurrent response under UV light, while preserving their performance in the visible light range. The fast, stable, and high photoresponse of these hybrid nanostructures is promising towards the development of optoelectronic and photovoltaic devices.
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Silicon nanowires (SiNWs) have emerged as versatile class of functional nanomaterials and their utility have been already well demonstrated in a range of technological applications.[1–4] This is mainly due to their high performance when operated as field-effect transistors (FET)[5,6] as well as due to their excellent photoresponsivity.[4] SiNWs are currently being integrated in hybrid nanoscale devices for applications in biosensing,[3] optoelectronics,[7,8] and photovoltaics.[9,10] Contrary to conventional silicon photodetectors, which have photodetection capabilities limited to the visible and near infrared spectrum, photodetectors based on SiNW structures are able to detect ultraviolet light with high sensitivity.[11] This makes SiNWs promising building blocks for high performance photodetectors and full-spectrum photovoltaic devices. Importantly, the maturity of the Si semiconductor industry facilitates large-scale top-down fabrication of SiNWs in comparison to other nanoscale structures made from different materials (i.e., GaN/GaAs nanowires,[12,13] In_2Se_3 nanowires,[14] ZnO nanowires,[15] and CdS/CdSe nanorods[16,17]).

Recently, quantum size effects have been investigated in various semiconductor nanostructures. It was observed that photoresponse properties (i.e., photosensitive, photoresponse speed, and internal gain) improve when the dimensions of the nanostructures are reduced.[16–18] Therefore, it is interesting to study the photoresponse performance of ultrathin SiNWs (sub-25 nm cross-section) as their excellent electrical performances have been reported recently.[19,20] However, since large scale top-down patterning of high quality ultrathin SiNW device is still a challenge,[21] the photoresponse of ultrathin SiNW has not yet been fully investigated. In this study, we characterize the photoresponsive properties of ultrathin SiNWs, fabricated using a top-down size-reduction process. The ultrathin SiNWs were able to detect light from the UV to the visible range with excellent sensitivity (calculated limit of detection ~1.02 pW/array), fast responsivity, and high photoresponsivity ($R \sim 2.5 \times 10^4$ A/W). It is also found that the ultrathin 20 nm SiNWs are higher photosensitivity and faster response than 40 nm SiNWs fabricated using the same process. Furthermore, by sensitizing the SiNWs with cadmium telluride (CdTe) quantum dots (QDs), a modest improvement in the photocurrent response was measured for the hybrid SiNW-QD device in comparison with the non-sensitized SiNW under UV light illumination while preserving performance in the visible light part of the spectrum. The fast, stable, and high photoresponse of the hybrid nanostructures is promising towards the development of high-performance optoelectronic and photovoltaic devices.

The ultrathin SiNWs have been fabricated at the wafer-scale and packaged in a chip unit (length 17 mm, width 8 mm) consisting of 4 independent nanowire arrays (8 nanowires/array) and connected to separate Al (300 nm) source/drain (S/D) contacts as shown in Figs. 1(a) and 1(b). In our design, each fabricated ultrathin SiNW was highly ordered with characteristic dimensions of 10 μm in length, 150 nm in width, and 2 μm wire-to-wire distance [Fig. 1(b)]. A simplified schematic cross-section of the device configuration is presented in the supplementary material.[22] Using an optimized tetramethylammonium hydroxide (TMAH) wet-etching process reported previously,[21] we were able to locally thin down the middle section of the nanowire without detrimental impact on the electrical contacts of the device.

a)Electronic addresses: a.offenhaeusser@fz-juelich.de and benjamin.thierry@unisa.edu.au

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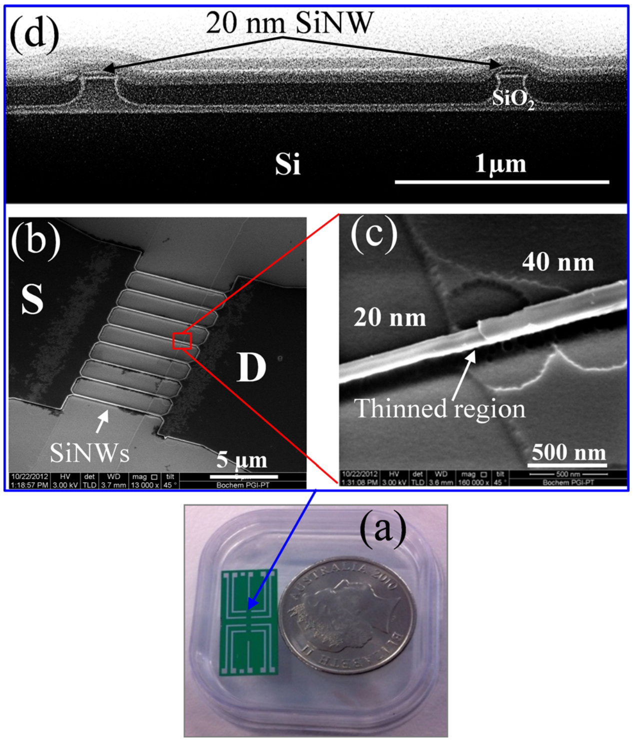

FIG. 1. (a) SiNWs on-a-chip unit. (b) SEM images of a locally confined ultrathin SiNW array fabricated on a silicon on-insulator wafer (SOI) with S/D contact regions. (c) High magnification SEM of a single ultrathin SiNW with 20 nm thinned down region. (d) FIB cross-sectional images at the thinned regions of the 20 nm SiNWs.

As seen in the SEM images presented in Figs. 1(c) and 1(d), the local thickness in the center region of the nanowires was thinned down to ~20 nm, while the remaining parts of the nanowire were kept at 40 nm to enable efficient electrical contacts with the metal feed lines.

The electrical properties of the ultrathin SiNWs with 20 nm thicknesses were characterized at room temperature using a custom-built 16-channel low-noise amplifier system equipped with a dark chamber modified from a previous study.[23] First, the opto-electrical response of the device was measured using monochromatic red light irradiation (peak wavelength at ~680 nm) generated by a light-emitting diode (LED) light source. When increasing the light intensities from 0 to 12.5 mW cm^{-2}, the device clearly showed an increased photocurrent response in both the forward (V_{DS} = 0–3.0 V) and reverse bias (V_{DS} = 0 to −3.0 V) directions with respect to the dark condition [Fig. 2(a)]. In comparison with recent studies characterizing the photosensitivity of SiNWs[11,24,25] as well as with measurements conducted here with the nanowires of higher thicknesses (see supplementary material[22]), ultrathin SiNWs were found to have a quasi-symmetrical photocurrent response for both bias directions. This observation is common for metal-semiconductor-metal (MSM) devices[26] and consistent with a recent report on Ge nanowires.[18] In the fabricated ultrathin nanowires, the observed near symmetrical photocurrents can be attributed to efficient Ohmic electrical contacts. However, a slight deviation from the symmetric behavior in both forward bias and reverse bias voltages can be explained by the intrinsic asymmetry of the thinning structures originating from the fabrication process.

Figure 2(b) shows the dependence of photocurrent (Iphoto) with light intensities. At various forward bias voltages, the photocurrent showed sub-linear increases with the light intensities, indicating the involvement of carrier trapping either in the nanowires or at the interface of Si/SiO_2.[28] This effect reduces the overall photoresponsivity of the ultrathin SiNW as seen in Fig. 2(c). This observation is consistent with a recent report on MoS_2 photodetector[29,30] and can be understood by the saturation of carrier trap states. In semiconductor photosensing, the photosensitive nature of silicon photodetectors relies on the photogeneration and instant separation of electron-hole pairs under electrical fields.[11,31] When light reaches SiNWs, the photon energy is absorbed and generates electron-hole pairs in the nanowires, which are separated immediately by the electric field.[4,9] The generated electrons combine with carrier trap, while the photogenerated

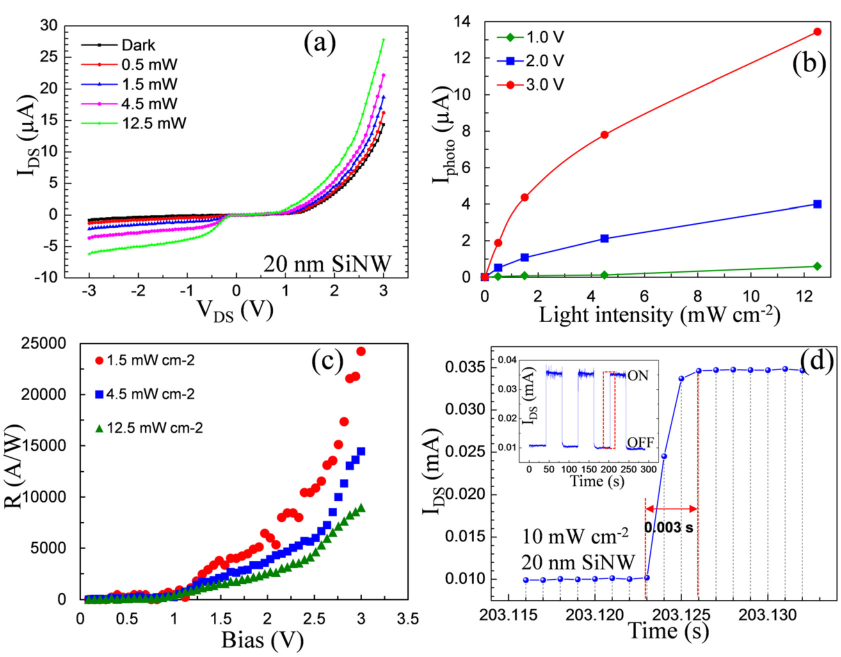

FIG. 2. (a) Photoresponses of as-fabricated ultrathin SiNWs measured under monochromatic red light. (b) Photocurrent (Iphoto) as a function of light intensity at various forward bias voltages from 1.0 V to 3.0 V. (c) Bias voltage-dependent photoresponsivity of fabricated device in different light irradiation. (d) Photocurrent time-response curves of SiNWs under 10 mW cm^{-2} of light intensity and in the dark with a bias voltage of 3.2 V. A magnified section of the time response curve is presented in the inset plot (red square) where the response is limited to the KHz range as seen by Samanta *et al.*[27]

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holes remain in the nanowires and contribute to the increase of the output current. At low light intensities, increasing the incident illumination power will produce more electron-hole pairs which lead to a linear increasing of the photocurrent. However, at higher light intensities, the density of available trap states is reduced, leading to saturation of the photoresponse.[29] This effect can be expected to be accentuated in the case of ultrathin nanostructures as a result of their high surface to volume ratios. From these measurements, a photoresponsivity at 1.5 mW cm^{-2} of light irradiation and 3.0 V biased voltage has been calculated to be $R \sim 2.5 \times 10^4$ A/W, which is several orders of magnitude higher than the current benchmarks of conventional silicon PIN photodiodes (0.7 A/W) and avalanche photodiode (140 A/W). These results are in agreement with a recent report from Das *et al.*[28] In this study, a photoresponse of $R \sim 2.56 \times 10^4$ A/W at 0.1 V bias was reported. This value is consistent to that presented here at 3.0 V of applied bias, which was utilized to provide sufficient axial field for collecting the carriers through the low implantation (B, $1 \times 10^{15}\,cm^{-3}$), ultrathin and long nanowire structures (10 μm, 20 nm thicknesses). It is worth to note that the electrode spacing in Das study[28] is an order of magnitude lower than the present study (1.2 μm vs. 10 μm), while the background doping of the nanowire is 20 times higher. Additionally, a longer wavelength was used (~900 nm vs. ~680 nm). These parameters can be expected to contribute to the high photoresponse of the device. Finally, it is calculated from Figure 2(d) that the time-response of the ultrathin SiNWs is ~3 ms, which equivalent to kHz range. This is expected for MSM nanowire device due to the lead capacitance.[27]

Next, the minimum detectable light intensity has also been determined and found to be approximately 0.85 mW cm^{-2}, equivalent to ~6% increasing of the drain current under illumination (Iill) vs. dark current ((Iill − Idark)/Idark; %) [Fig. 3(a)]. The minimum limit of detection is defined here as the illumination intensity required to reach a signal three times higher than the noise ($S/N \geq 3.0$). In comparison with PIN photodiode with much larger sensing areas (~1 cm^2), the limit of light intensity detection in the ultrathin SiNWs is much lower as the sensing areas of the nanowire array is as small as ~12 μm^2. This yields a calculated value of ~1.02 pW limit of detection on the nanowire arrays, assuming that light scattering and reflection is not significant. On the other hand, similar experiment carried out with 40 nm SiNW revealed a limit of light detection is ~235% higher than that of the thinned down nanowires [Fig. 3(b)]. In addition, the response time of the 40 nm SiNW arrays is two orders of magnitudes slower than that observed for the 20 nm SiNWs. These results confirm the excellent photoresponse properties of ultrathin SiNWs. The high photoresponse properties of ultrathin SiNWs could be attributed to a number of physical properties. In nanowire MSM device, a large photoresponse can be achieved for devices with S/D distances closer than the recombination length[32] or through the store potential between the metal contacts where carriers can be collected through an axial field.[32,33] When comparing the different response of the 40 nm and 20 nm devices, these factors can be assumed to have a minor influence, as these devices share the same nanowire lengths (10 μm), widths (150 nm) and S/D contact areas. The large photoresponse of the ultrathin SiNWs can also be attributed to their large surface-to-volume ratios in comparison to the bulkier device. It can be hypothesized that trapped charges at the surface create an additional electrostatic field which drives the holes carriers close to the nanowires similar to the "field effect" and therefore that the higher surface-to-volume ratio of the ultrathin nanostructures have dominant influence through this surface effect. The obtained results are consistent with a previous report on the size effect of Ge nanowire photodetectors.[18]

Next, the temperature photocurrent dependence and stability of the SiNWs have been studied as presented in Figs. 3(c) and 3(d), respectively. As seen in Fig. 3(c), no detectable photocurrent signal degradation was observed at 5 mW cm^{-2} of light intensity for temperatures ranging from

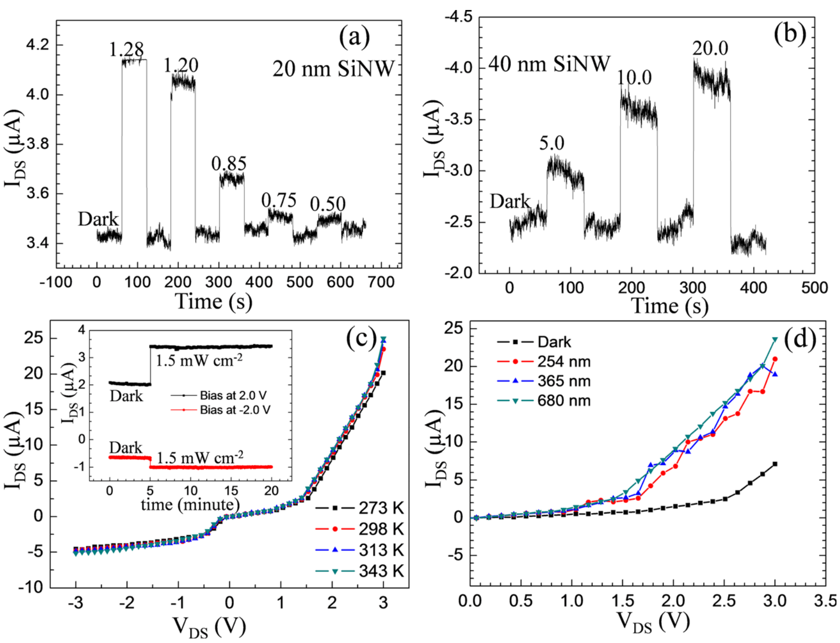

FIG. 3. (a) Dynamic current-time curves with periodical on/off illuminations; light intensities are at 1.28, 1.2, 0.85, 0.75, and 0.5 mW cm^{-2}, measured at 2.14 V. LOD is at ~0.85 mW cm^{-2}. (b) The photoresponse of the control 40 nm SiNWs is shown (dark 5.0, 10.0, and 20.0 mW cm^{-2}). The response time is at 0.5 s, measured at −3.0 V and LOD is at ~2 mW cm^{-2}. (c) Photocurrent dependence of the SiNWs for different temperatures at 5mW cm^{-2} and 680 nm illumination. Inset shows the photocurrent response of the SiNWs over 15 min of 1.5 mW cm^{-2} red light illumination at 2.0 V and −2.0 V biased voltages. (d) I-V characteristic of the SiNWs under different monochromatic light wavelengths (1.5 mW cm^{-2}).

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273 to 343 K. Poor thermal stability is a common limitation of nanoscale photodetectors;[34,35] however, the fabricated devices maintained their high performance even well above room temperature. The stability of the SiNWs was also demonstrated through long-term measurements of the photocurrent response. As shown in the inset plot of Fig. 3(c), the SiNWs were stable in both forward and reversed bias voltages for at least 15 min of continuous measurements under 1.5 mW cm^{-2} of light illumination. Altogether, these results demonstrate the excellent electrical stability and reliability of the nanofabrication technology used here. Finally, the optical response of the SiNWs was characterized at different monochromatic light wavelengths ranging from the UV to the visible range (254–680 nm). As expected, the photocurrents increased with the different light wavelengths in agreement with the previous reports of the photoresponsivity of SiNWs[11] [Figure 3(d)].

To further explore the properties of the ultrathin SiNWs and broaden their functionality, a hybrid QD device was studied. A previous study reported the evidence of photocurrent in SiNWs induced by nonradiative resonant energy transfer from QDs in close contact to the nanostructures.[9,36,37] To study the effect of QDs on the photoresponsivity of the ultrathin SiNWs, a thin coating of aqueous QDs with an emission peak at 550 nm (supplementary material[22]) was formed on the SiNWs, following the procedure described by Lu *et al.*[9] The photoresponse of the hybrid SiNW-QD device was then investigated at various wavelengths. As shown in Fig. 4, UV light illumination of the SiNW-QD hybrid device resulted in increased photocurrent in comparison to the SiNWs without QDs sensitization. The increase in photocurrent response was approximately $59 \pm 10\%$ in the linear regions of the photocurrent plot (i.e., photocurrent regions at $V_{DS} > 2.5$ V) when compared with the control bare SiNWs measured at a wavelength of 365 nm. On the other hand, no difference was observed between the sensitized and non-sensitized SiNWs under visible light (680 nm). The observed increase in photocurrent for the SiNW-QD hybrid device near the absorption peak of the QDs is consistent with the previous observation of energy transfer between the QD and SiNWs. Interestingly, the

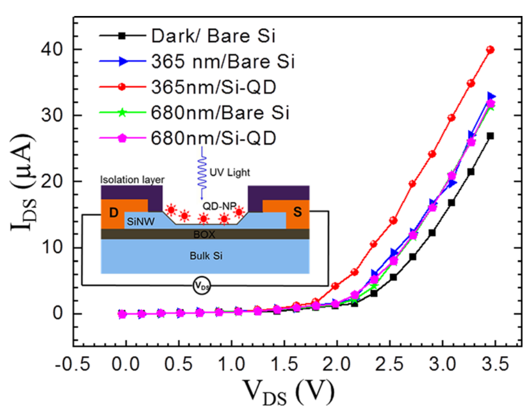

FIG. 4. I_{DS}-V_{DS} measurement of bare ultrathin SiNWs and CdTe QD sensitized SiNWs under UV (365 nm wavelength) light irradiation and response of control device, measured in red light (680 nm wavelength). Inset shows the schematic for cross-sectional device geometry of SiNW QD hybrid. Light intensities are at 5 mW cm^{-2}.

presence of the QDs does not compromise the performance in the visible range. Initial measurement of QD sensitized ultrathin SiNWs in solar full-spectrum (wavelength: 300–1400 nm; 100 mW cm^{-2}) showed a modest increased photocurrent when compared to the untreated SiNW devices (supplementary material[22]). However, the photocurrent change was not significant, which might be due to the relatively low ratio of UV light in the solar full-spectrum (ca. 10%). Further developing the concept of hybrid QD sensitized ultrathin SiNWs could open applications in optoelectronic switches, photodetectors, and hybrid photovoltaic devices.

In summary, the photoresponsive properties of ultrathin SiNWs have been studied. Owing to the high-quality of the ultrathin SiNW devices fabricated using an advanced top-down process, high stability, reliability, and excellent photoresponse properties were achieved from the UV to the visible range. The photoresponse properties of the ultrathin SiNWs and their behavior can be explained by the predominance of the surface effect on ultrathin SiNWs in comparison to bulkier counter-parts. In addition, by sensitizing the SiNWs with CdTe QDs, an improvement in the photocurrent response under UV illumination of 59% was obtained, while preserving their performance in the visible light. This innovative approach is promising for the development of hybrid photoresponsive nanostructures in the areas of photovoltaics and optoelectronics.

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