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Effects of nanowire texturing on the performance of Si/organic hybrid solar cells fabricated with a 2.2 μm thin-film Si absorber

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Hybrid solar cells are fabricated by spin coating poly(3,4-ethylene-dioxythiophene):polystyrenesulfonate (PEDOT:PSS) on planar Si and Si-nanowires (SiNWs) arrays prepared by electroless chemical etching. With only a 2.2 μm thick Si absorber thin film, the short-circuit current density and power conversion efficiency (PCE) of SiNWs/PEDOT cell increase from 12.5 to 13.6 mA/cm^2 and from 5.4% to 5.6%, respectively, as compared to planar Si/PEDOT cell. A maximum external quantum efficiency of 56.6% is obtained for the SiNWs/PEDOT cell. The promising PCE obtained demonstrates the potential of realizing Si/PEDOT and SiNWs/PEDOT hybrid cells using low-cost Si thin films instead of bulk Si substrate. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692590>]

In the past few years, there has been significant interest in the design of solar cells using Si nanostructures such as Si nanowires (SiNWs),^{1–5} ascribed to their excellent light harvesting capability.^{6–9} Lieber and co-workers have demonstrated single SiNW p-i-n solar cells grown by the vapor-liquid-solid (VLS) technique and electron-beam lithography with moderate power conversion efficiency (PCE) up to 3.4%.^{1,10} Apart from this, other solar cells based on similar VLS-grown SiNWs arrays were reported with relatively low PCE of less than 2.3%, attributed to the poor quality of the radial p-n junction and gold catalyst residue impurity.^{4,11,12} Recently, Si micro- or nanowires solar cells fabricated with precisely controlled Si micro- or nanowires arrays achieved through deep reactive ion etching have exhibited more promising PCE of 4%–9%, with short circuit current density (J_{sc}) higher than that of their planar counterparts.^{7,13–15} However, their fabrication processes that involve photolithography, thermal diffusion, or silica bead assembly technique are not cost-effective, and the latter also poses scalability issue. Arising from these issues, hybrid cells based on planar Si or SiNWs prepared by electroless chemical etching and organic semiconductors have emerged as a potential cost-competitive PV structure.^{16–22} The electroless chemical etching technique is simple, fast, and scalable to wafer size as compared to the VLS and RIE techniques in the fabrication of SiNWs, while the organic semiconductors are compatible with low temperature and solution based fabrication processes. A promising PCE of up to 10% for such Si/organic hybrid solar cells has been previously demonstrated.^{18,19,21,22} Nevertheless, it should be highlighted that the outstanding performance is contributed substantially by the photocurrent generated in the costly bulk Si wafer. For low cost application, alternative approaches that bypass bulk Si wafer, such as having the SiNWs fabricated on thin film Si should be

considered. In this work, we fabricate SiNWs/poly (3,4-ethylene-dioxythiophene):polystyrenesulfonate (PEDOT:PSS) hybrid heterojunction solar cells using only a thin layer of 2.2 μm epitaxial Si absorber layer deposited on a heavily doped Si substrate. Electroless chemical etching of SiNWs and spin coating technique are utilized in our process. SiNWs arrays with different wire lengths were prepared and for each wire length, four hybrid cells were fabricated and characterized. Another four planar Si/PEDOT hybrid cells were also fabricated for comparison. An average PCE of 5.0% and a maximum PCE of 5.4% have been obtained for the planar Si cells, whereas an average PCE of 5.3% and a maximum PCE of 5.6% have been demonstrated for the SiNWs cells with a NW length of 0.3 μm . Given that the effective Si absorbing thickness is only 2.2 μm , the result demonstrates that it is possible to achieve high efficiency and low cost Si/organic hybrid cells using thin film Si.

The fabrication process of the hybrid solar cell is shown in Fig. 1. Initially, n^{++} Si (100) substrate with an arsenic

FIG. 1. (Color online) Schematic diagrams of the fabrication process of SiNWs/PEDOT hybrid solar cell.

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doping concentration of $\sim 1 \times 10^{20} \text{ cm}^{-3}$ was heated in-situ in ultra pure H_2 at 1100°C in a rapid thermal chemical vapor deposition (RTCVD) reactor to remove the native surface oxide. A $2.2 \mu\text{m}$ thick single crystalline epitaxial Si layer with a phosphorus doping concentration of $1.5 \times 10^{16} \text{ cm}^{-3}$ was then grown on top of the n^{++} Si substrate at 1000°C using dichlorosilane (DCS) precursor and phosphine (PH_3) dopant gas. The thickness, doping, and crystallization of the epitaxial layer are confirmed by the cross-sectional SEM image, dynamic secondary ion mass spectrometry (DSIMS) profile, and x-ray diffraction (XRD) spectra shown in Figs. 2(a)–2(c), respectively. The interface between the epitaxial Si and the n^{++} Si substrate can be identified in the SEM micrograph due to the different charging effects arising from the large difference in their doping concentrations. Following the epitaxial growth, SiNWs arrays were fabricated on the epitaxial Si layer through electroless chemical etching in a solution consisted of 4.6 M hydrofluoric (HF) acid and 0.02 M silver nitrate (AgNO_3).³ The etch time was varied to fabricate SiNWs arrays with different lengths of 0.3, 1.0, and $1.5 \mu\text{m}$. Conductive PEDOT:PSS (PH500) mixed with 5 wt. % dimethyl sulfoxide (DMSO) was then spin coated on top

FIG. 2. (Color online) (a) Cross-sectional view SEM image of the $2.2 \mu\text{m}$ epitaxial Si thin film grown on top of n^{++} Si substrate, (b) DSIMS profile of the epitaxial Si thin film and (c) XRD spectra of the epitaxial Si thin film and bulk single crystalline Si wafer.

of the SiNWs arrays to form the core-sheath heterojunction. Finally, a layer of silver grid and aluminum were evaporated on the PEDOT layer and the backside of Si substrate, respectively, to complete the cells each with a device size of 0.95 cm^2 . For comparison, planar Si hybrid cells were also fabricated using the same procedure. The doping concentration of $\sim 1 \times 10^{20} \text{ cm}^{-3}$ of the n^{++} Si substrate corresponds to a minority-carrier diffusion length of less than $0.3 \mu\text{m}$.²³ Hence the Si substrate functions as a conducting channel rather than a photocurrent contributor, and this allows us to mimic a Si thin film with an effective absorbing thickness of $\sim 2.2 \mu\text{m}$. Therefore, this study serves as a proof-of concept to demonstrate the feasibility of SiNWs/PEDOT hybrid cells fabricated using Si thin film technology.

Figure 3(a) shows the cross-sectional view SEM image of a planar Si spin coated with a compact PEDOT film of $\sim 125 \text{ nm}$ thick. Figures 3(b)–3(d) show SiNWs arrays with different lengths (L) of 0.3, 1, and $1.5 \mu\text{m}$, respectively, spin-coated with a PEDOT layer. It can be seen that the SiNWs prepared by electroless chemical etching are vertically aligned and closely packed, except for the sample with longer SiNWs of $1.5 \mu\text{m}$. It is also seen that due to its long polymer chain, PEDOT does not penetrate well to the bottom of the SiNWs to fill all the gaps.¹⁹ Thus there is incomplete coverage of the sidewalls of the SiNWs. For shorter L of $0.3 \mu\text{m}$, PEDOT forms a continuous canopy of $\sim 125 \text{ nm}$ thick above the SiNWs arrays [Fig. 3(b)]. As L increases to $1.5 \mu\text{m}$, there is enhanced aggregation at the top of the SiNWs forming larger SiNWs bundles [Fig. 3(d)], ascribed to the action of the Van Der Waals force and attractive capillary force during the drying process of the vertically aligned NW arrays.²⁴ This leads to larger gaps formed among the adjacent SiNWs bundles and thus a non-uniform surface contour of the coated PEDOT layer.

Figures 4(a) and 4(b) show the current density-voltage (J - V) characteristics of the planar Si cell and SiNWs cells with different L under 100 mW/cm^2 illumination (AM 1.5G) and dark condition. The photovoltaic data of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and PCE are summarized in Table I. It is seen that the planar Si cell ($L=0$) exhibits a respectable PCE of 5.4%. The PCE rises to a maximum value of 5.6% at $L=0.3 \mu\text{m}$

FIG. 3. Cross-sectional view SEM images of the (a) planar Si coated with a compact PEDOT layer and (b), (c), (d) SiNWs with wire length of 0.35, 1, and $1.5 \mu\text{m}$ after they were coated with a PEDOT layer.

FIG. 4. (Color online) The current density-voltage (J - V) characteristics of the planar Si cell and SiNWs cells with different wire lengths (a) under AM 1.5G 100 mW/cm^2 illumination and (b) under dark condition.

and drops to 3.4% as L is further increased to 1.5 μm . The maximum PCE obtained here is lower than the 9% which we have previously reported for a similar cell fabricated on Si wafer with a 400 μm thick absorber substrate.¹⁹ Nevertheless, the PCE of 5.6% obtained is quite promising given that the cell has only a 2.2 μm thick Si absorber layer.

As seen from Table I, V_{oc} drops sharply from 0.605 to 0.461 V as L increases from 0 to 1.5 μm , which is attributed to a lower shunt resistance (R_{sh}) of the devices with longer SiNWs. Figs. 3(c) and 3(d) reveal that longer SiNWs lead to a non-uniform surface morphology of the coated PEDOT layer. It is possible that the protrusion of the SiNWs tips is very close or even in direct contact with the top silver electrode. This will lead to local shunting across the cells and an early turn-on of the diode in the dark condition as shown in Fig. 4(b), resulting in lower V_{oc} . Similar results of a reduction in V_{oc} arising from lower R_{sh} for SiNW and ZnO nanowires based solar cells have also been reported previously.^{2,25} The hybrid cells with $L=0$ and 0.3 μm exhibit an extremely high FF of more than 70%, which is the highest ever reported for Si/organic based hybrid cells. The FF is higher than what we have obtained previously,¹⁹ mainly attributed to the highly doped Si substrate used for the cells in this work resulting in better ohmic contact and lower series resistance. The FF decreases to 57.4% for longer L , ascribed to the drop in V_{oc} and R_{sh} as discussed above. The rough surface of the PEDOT layer associated with longer L will also lead to a higher series resistance and reduce the FF .

Figure 5 shows the external quantum efficiency (EQE) spectra of the planar Si cells and SiNWs cells with different L . The SiNWs cell with $L=0.3 \mu\text{m}$ exhibits the highest EQE with a maximum value of 56.6% at 515 nm. As L increases to 1.5 μm , the EQE of the cells decreases monotonically, despite an enhanced light trapping by longer SiNWs. This trend is consistent with the variation in J_{sc} as shown in Table I. The drop in EQE at the shorter wavelength for the cells with longer SiNWs is attributed to a higher recombination rate for the photo-excited minority carriers along the SiNWs.¹⁹ It is

also seen that the EQE is very low at the near infrared region (NIR) from 700 to 1100 nm for all the samples compared to similar samples fabricated with a thick Si absorber substrate.¹⁹ This is expected as long wavelength light that is absorbed in the heavily doped substrate beyond the 2.2 μm Si epitaxial layer does not contribute to photocurrent, due to the short minority-carrier diffusion length and high recombination rate.

The excellent FF as high as 71.9% and the simple fabrication steps of our cells show the viability of using thin film Si for Si/PEDOT hybrid solar cells. It has been shown that epitaxial crystalline Si thin film up to 20 μm can be grown on several low cost substrates such as ceramic, upgraded metallurgical grade (UMG) Si or Si ribbons,^{26,27} whereas polycrystalline Si thin layer can be deposited on a textured glass substrate.^{28,29} Such Si thin films can be potentially used for the fabrication of Si/PEDOT hybrid solar cells to bypass the use of costly bulk Si wafer. The PCE of our hybrid cells so far is limited by their relatively lower J_{sc} of $\sim 13 \text{ mA}/\text{cm}^2$, attributed to insufficient light capturing of long wavelength photons by the 2.2 μm thin layer as well as minimum light reflection between the epitaxial Si thin layer and the underneath Si substrate. However, the J_{sc} is expected to improve if several approaches are utilized, such as growing a thicker epitaxial Si layer, applying good surface passivation on the SiNWs, and transferring the device to a substrate with a textured surface or a back reflector to increase the light trapping in the thin active device layer. Consequently, the Si/PEDOT hybrid cells would deliver a high efficiency to render them suitable for practical application.

In conclusion, we have demonstrated an efficient hybrid solar cell based on SiNWs and PEDOT using only a 2.2 μm

TABLE I. The current density-voltage (J - V) characteristics of the planar Si cell and SiNWs cells with different wire lengths.

SiNWs length (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0 (planar)	12.5	0.605	71.1	5.4
0.3	13.6	0.570	71.9	5.6
1	13.3	0.485	64.1	4.1
1.5	11.3	0.461	57.4	3.0

FIG. 5. (Color online) The EQE spectra of the planar Si cell and SiNWs cells with different wire lengths.

Si absorber layer. We obtained a promising PCE of 5.4% and 5.6% for the planar cell and the 0.3 μm SiNWs cell, respectively. The 0.3 μm SiNWs cell demonstrates an enhanced J_{sc} of 13.6 mA/cm² and EQE of 56.6% as compared to the planar cell. Cells with longer SiNWs lead to poor performance because of lower shunt resistance and higher recombination rate. More importantly, this proof-of concept study suggests a promising route to realizing cheap and efficient Si/organic based hybrid cells fabricated with low cost Si thin film.

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