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High Efficiency Silicon Nanowire/organic Hybrid Solar Cell with Two-step Surface Treatment

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Abstract

A simple two-step surface treatment process is proposed to boost the efficiency of silicon nanowire/PEDOT:PSS hybrid solar cells. The Si nanowires (SiNWs) are first subject to a low temperature ozone treatment to form surface sacrificial oxide, followed by a HF etching process to partially remove the oxide. TEM investigation demonstrates that clean SiNWs surface is achieved after the treatment, in contrast to untreated SiNWs that have Ag nanoparticles left on the surface from the metal-catalyzed etching process used to form the SiNWs. The cleaner SiNWs surface achieved and the thin layer of residual SiO₂ on the SiNWs have been found to improve the performance of the hybrid solar cell. Overall, the surface recombination of the hybrid SiNW solar cell is greatly suppressed, resulting in a remarkably improved open circuit voltage of 0.58 V. The power conversion efficiency has also increased from about 10% to 12.4%. The two-step surface treatment method is promising in enhancing the photovoltaic performance of the hybrid silicon solar cells, and can also be applied to other silicon nanostructures based solar cells.

1. Introduction

Rapidly increasing energy demand has driven enormous efforts towards exploitation of solar energy. Currently, C-Si solar cell has dominated the commercial solar cell market. Despite the large improvement in the efficiency of Si solar cells in the past decades, the electricity generated is still expensive relative to that using fossil fuel.¹ In the past few years, there is significant interest in incorporating Si nanostructures such as Si nanowires^{2, 3} (SiNWs), nanocones^{4, 5} and nanoholes⁶ into solar cells due to their excellent light absorbing characteristics. However, the fabrication of Si solar cells at nano-scale requires costly yet complicated processes such as high temperature thermal diffusion, sputtering deposition, reactive ion etching and photolithography for forming P-N junctions and electrical contacts.⁷ These requirements inevitably increase the fabrication cost of solar cells.

As a low-cost option, the hybrid organic/inorganic SiNW cells, especially the hybrid SiNW/PEDOT:PSS solar cells, have been actively studied in recent years due to the combined advantages of Si nanostructures and organic materials, which include high power conversion efficiency, low material cost, low temperature and simple solution based process capability.⁸⁻¹¹ Currently, hybrid SiNW/PEDOT:PSS cells are reported to have power conversion efficiencies (PCE) of over 11%, demonstrating promising potential for practical application^{12, 13}. Despite the progress made, there remain some challenges facing the hybrid solar cells. Although the nanostructures can serve to greatly enhance the light harvesting ability of the solar cells, there is accompanying severe surface recombination caused by their large and defective surface. This trade-off has significantly affected the performance of the hybrid solar cell.¹⁴ Specifically, most of the Si nanostructures used in the hybrid cells were fabricated using the solution based metal-catalyzed electroless etching (MCEE) technique. The technique leads to residual impurity and defective surfaces, which act as recombination sites and increase the recombination

rate of photogenerated carriers and consequently deteriorate the performance of the hybrid cells.^{15, 16}

Many efforts have been directed to address this problem. For example, Chen et.al fabricated the inverted pyramid nanostructures to reduce the recombination rate by shrinking the surface area of the nanostructures, but not sacrificing their light absorption.¹⁷ Other measures include attaching some chemical molecules to the surface to change its surface state as well as the energy band alignment, with an aim to suppress the surface recombination.^{14, 18} However, these methods either introduce complicated fabricated processes, or use some unstable organic materials, which hamper their practical use. To date, there still lacks a simple and reliable method to solve this problem. For conventional Si solar cells, a SiO_x layer is commonly used for effective surface passivation due to their excellent stability and the simple fabrication process involved.¹⁹ Though this concept can also be applied to Si nanostructures, however, it is not suitable for the hybrid cell due to the high temperature thermal oxidation process and the very small dimensions of the nanostructures.

In this study, we propose a simple two-step surface treatment method to improve the surface quality of SiNWs in SiNW/PEDOT:PSS hybrid cells. The SiNW surface is first treated with ozone gas at low temperature to form a surface layer of sacrificial oxide. The oxidized surface is then partially etched by dilute HF solution to leave behind a thin residual SiO_x layer. Fig. 1(a)-(f) shows the schematic illustration of the complete fabrication process for SiNW hybrid cells with the surface treatment. This two-step surface treatment process effectively removes Ag nanoparticles and defects on the surface, which are introduced by the metal-catalyzed electroless etching (MCEE) process to form the SiNWs, and results in cleaner SiNWs surface. Besides, the thin residual SiO_x layer on SiNWs passivates the surface and reduces surface recombination rate. The suppressed recombination loss arising from the removal of Ag nanoparticles and passivation of the

surface has resulted in a high open circuit voltage (V_{oc}) of 0.58 V and high power conversion efficiency (PCE) of 12.4% for the hybrid cells under the AM1.5G illumination. These are respectively 13.7% and 29.8% enhanced as compared to similar hybrid cells fabricated without the surface treatment. To the best of our knowledge, the V_{oc} of 0.58 V is the highest ever reported for SiNWs/PEDOT:PSS solar cells.

2. Results and discussion

Figure 2 displays SEM images showing the morphologies of planar Si and SiNWs fabricated using the MCEE technique, and coated with PEDOT:PSS layers on top. Presented in Fig. 2(a) is the SEM picture of a planar Si substrate spin coated with a PEDOT:PSS layer, which forms a thin uniform layer of about 80 nm thick. Fig. 2 (b) shows the cross-sectional SEM image of the SiNWs fabricated by the MCEE technique. The SiNWs are dense and have length of about 500 nm, diameters ranging from 20-100 nm, and gaps in between the SiNWs of less than 50 nm. Fig. 2(c) and (e) present the top view of the PEDOT:PSS layer spin coated on SiNWs without and with surface treatment, respectively, while the corresponding cross-sectional pictures are shown in Fig. 2(d) and (f). Continuous PEDOT:PSS films are formed on the top of the SiNWs array for both samples, though with rougher surfaces as compared to the planar cell shown in Fig. 2(a). Moreover, due to the long molecular chain and the fast drying process, the PEDOT:PSS layer is not fully penetrated into the gaps between the SiNWs, resulting in exposed SiNWs surface between the bulk Si substrate and the PEDOT:PSS film.^{2, 20} These etched surfaces, without the coverage of the polymer, are most likely to lead to recombination of carriers. The PEDOT:PSS layer deposited on SiNWs subjected to surface treatment displays a smoother surface, as shown in the Fig. 2(e) and (f). This may be due to the ozone treatment that has resulted in a more hydrophilic surface, which facilitates the better coverage of the PEDOT:PSS layer on the surface of the SiNWs.²¹

Fig. 3(a) shows typical illuminated current density-voltage (J-V) characteristics of the hybrid solar cells with and without the two-step surface treatment process. The curves were recorded under simulated AM 1.5 G irradiation at 100 mW/cm^2 derived from a solar simulator. For comparison, the J-V characteristic of a planar hybrid cell is also shown. The photovoltaic parameters of the hybrid cells, including short-circuit current density (J_{sc}), V_{oc} , fill factor (FF), and PCE are summarized in **Table 1**, which shows the mean values and the standard deviations obtained by averaging ten hybrid cells per cell structure. Compared to the planar cell, the pristine-SiNW cell exhibits an improved J_{sc} from 26.1 to 30.1 mA/cm^2 . This is mainly ascribed to light trapping by the SiNWs. However, the V_{oc} of the pristine-SiNW cell is dropped to 0.51 V compared to the 0.59 V of the planar cell. This can be attributed to the higher carrier recombination loss associated with the defective surface and increased surface area of the Si nanostructures, which is consistent with our previous reports.^{16, 22, 23} The increased recombination also reduces the FF. As a result, the PCE of the pristine-SiNW cell is even slightly lower than that of the planar cell, despite the improvement in its J_{sc} . In contrast, the SiNW hybrid cell with surface treatment reveals recovered V_{oc} of 0.58 V , which is almost the same as that of the planar cell of 0.59 V , and is improved by 13.7% relative to that of the pristine SiNW cell. Likewise, the FF has recovered to 67.7% which is slightly above that of the planar cell of 66.8%. The improved V_{oc} suggests the recombination loss of the SiNW hybrid cell is suppressed after the surface treatment. With the higher V_{oc} and FF, and slightly improved J_{sc} , the SiNW cell with surface treatment exhibits a high PCE of 12.2%, which is improved by about 29.8% as compared to that of the pristine SiNW cell. It is worth noting that our cells generally show lower J_{sc} as compared to those reported in the literature¹², possibly due to differences in the microstructures and consequently the light trapping ability. This indicates that there is room to further boost the efficiency of the hybrid solar cells by optimizing light absorption in the SiNWs and Si substrate, which can

be achieved through measures such as varying the density and the length of the SiNWs, thickness of the PEDOT:PSS layer as well as the coverage area of the front silver grid electrode.

The improvement in V_{oc} observed for the hybrid cells with surface treatment is corroborated by the reduced reverse saturation current density (J_0) of the dark J - V curve shown in Fig. 3(b). The J_0 of the SiNW cell with surface treatment is one order of magnitude lower than that of the pristine SiNW cell, and comparable to that of the planar cell. The series resistance (R_s) of different cells are extracted from the dark current by the plot of $dV/d(\ln J)$ versus J .²⁴ The average R_s extracted from ten hybrid cells per sample are found to be 3.04 ± 0.56 , 1.22 ± 0.40 and $2.08 \pm 0.68 \Omega \text{ cm}^2$ for the planar, pristine and surface treated SiNW cells respectively. The pristine SiNW cell has a smaller R_s than the planar cell, that is attributed to the nanoscale geometry of the SiNWs and the increased junction area, which facilitate carrier transportation and collection. The R_s of the surface treated SiNW cell increases slightly after the surface treatment, which is attributed to the presence of the thin SiOx layer on the surface of the SiNWs. The diode ideality factors n are also extracted through the fitting of the $\ln(J)$ - V curve under forward bias from 0.1 - 0.4 V.²⁵ The average n deduced for the planar cell, pristine and surface treated SiNW cells are 1.27 ± 0.09 , 2.02 ± 0.45 and 1.59 ± 0.29 respectively. Compared to the planar cell, both the SiNW cells possess larger n , which indicates that the incorporation of SiNWs has a negative effect on the Si/PEDOT:PSS junction characteristics. The defective surface of the SiNWs and the incomplete coverage of the PEDOT:PSS layer on the SiNWs may be the two reasons that account for the degradation of the junction. After the surface treatment, the ideality factor of the surface treated cell has improved, which indicates improved junction properties and lower recombination at the PEDOT:PSS/SiNW interface. This is consistent with the improved V_{oc} , FF and J_{sc} , as presented earlier. The external quantum efficiency (EQE) spectra of the hybrid cells were measured and shown

in Fig. 3(c). The results are in agreement with the variation of J_{sc} shown in Fig. 3(a). The two SiNW samples present larger EQE than that of the planar cell over a wide wavelength range from 370 to 1000 nm, which is ascribed to the anti-reflective property of the SiNWs.²⁶ The EQE of the surface treated cell is slightly higher than that of the pristine SiNW cell, which is attributed to its improved carriers collection efficiency associated with the reduced surface recombination.

We believe the improved J - V characteristic of the treated SiNW cell is attributed to the two-step surface treatment process that leads to a cleaner and better passivated SiNW surface. Transmission electron microscopy (TEM) investigation was carried out to further understand the changes to the SiNWs arising from the surface treatment. Fig. 4(a) and (b) show the bright field TEM images of the SiNWs before and after surface treatment respectively. As seen from Fig. 4 (a), some residual particles are attached on the SiNW surface, especially at the tip of the SiNWs. These nanoparticles are identified to be silver based, as deduced from the electron energy loss spectroscopy (EELS) results (support information, Fig. S1). The residual Ag particles, yielded during the MCEE process, are hard to remove completely even though nitric acid has been used to dissolve them with exposure time of up to 3 or 4 hours. It may be due to the small size of the particles of several nanometers to several tens of nanometers, and that they are imbedded in the SiNWs, or the presence of an impurity layer (e.g. SiOx or silicide) covers the particles and prevents them from coming in contact with the nitric acid. However, after the ozone treatment and etching process, most of the silver nanoparticles are removed from the SiNWs, as shown in Fig. 4(b). High resolution transmission electron microscopy (HRTEM) study further provides insight into how the silver nanoparticles are removed by the two steps surface treatment. Fig. 4(c) presents the HRTEM image of a silver particle on the SiNWs without the surface treatment. Clear parallel fringes of crystal plans indicate the single crystalline nature of the SiNWs. No apparent amorphous SiOx layer is

found between the silver particles and the SiNWs. The HRTEM image shown in Fig. 4(d) indicates that after the ozone treatment, an amorphous SiO_x layer is formed on the side wall of the SiNWs, as deduced from EELS study which reveals the presence of the elements Si and O. This SiO_x layer can be easily dissolved by the following HF etching process, resulting in the concurrent removal of the silver particles. Besides the residual particles on the surface of SiNWs, defects on the surface such as dangling bonds and the metallic impurities (mainly diffusion of Ag in Silicon) produced from the MCEE process will also be removed by the two-step treatment process. This arises because of the oxidation of the defective surface to form sacrificial oxide and subsequently etched by the HF.

The enhanced photovoltaic performance of the treated cells is also contributed by the residual SiO_x layer on the SiNWs surface. The SiO_x layer has been demonstrated to be an effective surface passivation material and has long been used in standard Si solar cell process.¹⁹ Low temperature UV ozone treatment has been used to introduce surface oxide to the SiNW hybrid cell for wetting purpose, rather than for the formation of sacrificial oxide, and worse performance has been reported due to the increased series resistance.²¹ In our experiments, we found that the performance of the hybrid cells is dependent on the thickness of the residual SiO_x layer, which can be adjusted by controlling the etching time in the dilute HF solution. HRTEM was used to identify the SiO_x layer on the SiNW, and the images of the SiNWs at different steps of the surface treatment process are presented in Fig. 5. The pristine SiNWs fabricated by the MCEE technique have a H⁺ terminated surface, which can effectively prevent formation of native oxide on the Si surface. Consequently, the SiNWs without the ozone treatment have only a very thin SiO_x layer on the SiNWs, as seen in Fig. 5(a). After the ozone treatment, a thicker SiO_x layer with a thickness of 4 to 5 nm is formed on the SiNWs as shown in Fig. 5(b). For cells not subjected to the following HF etching process, the thick insulating SiO_x layer

formed blocks carrier transportation, and results in dramatically increased R_s and deteriorated cell performance (support information, Fig. S2). This result is consistent with a previous report on Si/PEDOT:PSS hybrid cell ²¹. Shown in Fig. 5 (c) is the HRTEM image of a SiNW subjected to an HF etching time of 70 s after the ozone treatment, where a thin residual SiOx layer of about 1 to 2 nm is seen passivating the SiNW. At this thickness, the carriers can easily tunnel through the SiOx layer and the transport property is hence not affected. In addition, the formation of the SiOx layer can increase the effective electron affinity at the Si surface, and result in favorable band alignment and an internal electric field that is beneficial for the charge separation.²⁷⁻²⁹ The composition of the Si and O in the SiOx layer, which can be calculated from the EELS spectra, are given in Table S1 (Support Information). The as-grown SiNWs have the smallest atomic ratio of O. After the ozone treatment, the O/Si ratio reaches about 1.58, indicating the growth of the SiOx layer. After the HF etching, the atomic ratio of O decreases to about 34%, indicating a partial removal of the SiOx layer.

It is further noted that when the SiOx layer is fully removed by extended HF etching time of 150s, the V_{oc} obtained is only about 0.54 V (support information, Fig. S2). This suggests that the residual SiOx layer after the surface treatment is important in improving the V_{oc} . We have previously reported improvement in performance of planar Si/PEDOT:PSS hybrid cells, attributed to the presence of native oxide ¹⁵. In this study, we have also investigated hybrid cells based on exposing pristine-SiNWs to air from a day to form native oxide on their surface. The cells exhibit a V_{oc} of about 0.54 V (support information, Fig. S2), which is improved compared to the untreated cells, but however it is not as large as that achieved using the two-step treatment method, as Ag nanoparticles are expected to be presence on the surface of the SiNWs. In addition, as the formation of native oxide is not a well-controlled process that depends on many factors such as the temperature, humidity, and the original state of the surface, it is hence not feasible for practical

applications in comparison to the two-step treatment method. This uncontrollable surface condition of the SiNWs of untreated cells also explains the larger variation in the performance of the cells observed relative to the treated cells, as evident from the larger standard deviations of the photovoltaic parameters seen in Table 1.

The SiO_x layer on the SiNW surface will change its wettability and this can be observed using contact angle measurement. Fig. 6(a)-(c) shows the contact angle measurement results of the SiNW substrate before the ozone treatment, after ozone treatment and after the HF etching. The pictures clearly indicate that the oxygen treatment changes the wettability from hydrophobic (contact angle $\theta = 130.1^\circ$) to hydrophilic ($\theta = 67.3^\circ$). After the HF etching step, the wettability is still hydrophilic ($\theta = 85.8^\circ$) with a slightly increased contact angle, which clearly indicates the presence of the SiO_x layer. As stated previously, the hydrophilic surface is advantageous for the penetration of the PEDOT:PSS aqueous solution to the gaps between the SiNWs, and results in better coverage of the PEDOT:PSS onto the SiNW surface.

3. Experimental Section

A conventional metal-catalyzed electroless etching (MCEE) technique was used to fabricate the SiNWs. The SiNWs were fabricated from a single crystal (100) Si wafer with a phosphorous doping concentration of $\sim 5 \times 10^{15} \text{ cm}^{-3}$. The wafers were ultrasonically cleaned in acetone, IPA and deionized (DI) water for 10 min each. The Si substrates were then dipped into an etching solution that contained 4.6 M HF and 0.02 M AgNO₃ at room temperature to fabricate the SiNWs. The length of the NWs was tuned by controlling the etching time. Typically SiNWs with length of 500 nm are obtained for an etching time of 5 min. The samples were then rinsed in DI water for 5 min and put into

concentrated nitric acid to remove the silver particles on the surface of the SiNWs. Subsequently, the etched samples were rinsed in DI water and dried using nitrogen gas.

The Si substrates were then immersed into a 5% aqueous HF solution for 60s to remove native oxide. After that, Ti/Pd/Ag metal films with thickness of 50/50/1000 nm were deposited on the backside of the Si wafer by electron-beam evaporation to form the back electrode. Subsequently, the SiNWs sample was treated in an ozone environment at 50 °C for 10 min with a flow rate of 80 sccm. After the ozone treatment, the SiNWs were etched again in a 5% HF solution for an etching time of normally 60 s, to reduce the thickness of the surface oxide and obtain a cleaner surface. A thin conductive PEDOT:PSS layer was formed by spin coating the PEDOT:PSS solution (Clevios PH1000) on top of the SiNWs.¹⁶ The PEDOT:PSS layer was then dried at 105 °C for 10 min. Finally, the front silver grids electrode with a thickness of 800 nm was deposited on the PEDOT:PSS layer through a shadow mask by electron-beam evaporation. The fraction of the silver grid shading area is 12%. The hybrid cells have the active area of 0.95 cm².

TEM analysis was carried out by a high resolution equipment (Tecnai X-twin). The samples were directly scratched from the same etched SiNW substrate used for the hybrid cells. The J-V characteristics of the hybrid Si/PEDOT:PSS solar cell were measured using a solar simulator under the AM 1.5 100 mW/cm² illumination.

4. Conclusion

In summary, we have demonstrated a two-step surface treatment process to obtain high efficiency SiNW/PEDOT:PSS hybrid cells. The surface treatment can help remove residual impurities and defects near the SiNWs surface, and effectively passivate the SiNWs to reduce the recombination loss at the surface. The Si/PEDOT:PSS hybrid solar cell with surface treatment shows the highest ever reported V_{oc} of 0.58 V, which is almost the same as that of a planar hybrid cell. As a result, a PCE of 12.4% has been achieved for

the hybrid cell, which is up to 14.1% if the silver grid covered area is not considered. The improved PCE indicates that this simple approach of surface treatment is promising in boosting the efficiency of SiNW/organic hybrid cell and will potentially lead to their practical use.

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Supporting Information

Electronic Supplementary Information (ESI) available from <http://pubs.rsc.org>.

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Figure caption

Fig. 1. Schematic illustration of the fabrication process for the hybrid cell based on SiNWs with two-step surface treatment process. (a) SiNW grown on Si substrate, (b) Ozone treatment to oxidize the surface, (c) HF etching to obtain SiNW with cleaner surface, (d) Deposition of Ti/Pd/Ag back contact, (e) Spin coating of PEDOT:PSS layer on top of the SiNW, (f) Deposition of silver grid as front electrode to form complete hybrid cells.

Fig. 2. (a) Cross-sectional SEM images of (a) PEDOT:PSS layer coated on planar Si substrate, (b) nanowires fabricated using the MCEE technique, (c) top view and (d) cross-section view of PEDOT:PSS layer coated on pristine SiNWs, (e) top view and (f) cross-section view of PEDOT:PSS layer coated on SiNWs with the surface treatment. The scale bar is 500 nm.

Fig. 3. (a) The J - V characteristics of the Si/PEDOT:PSS hybrid cells under AM 1.5 G 100 mW/cm^2 illumination. (b) Dark J - V characteristics of the Si/PEDOT:PSS hybrid cells in semilogarithmic scale. (c) EQE spectrum of the various hybrid cells.

Fig. 4. TEM images of the SiNWs before (a) and after (b) the two-step surface treatment. (c) HRTEM image of a silver particle attached on the SiNW surface before the ozone treatment. (d) Silver particles/Si interface after the ozone treatment.

Fig. 5. HRTEM images of the SiNWs (a) before and (b) after the ozone treatment. (c) SiNWs after surface treatment and subjected to HF etching time of 70s. A residual thin SiO_x layer is seen on the SiNW surface.

Fig. 6. Contact angle of the SiNW substrate (a) before oxygen treatment, (b) after oxygen treatment and (c) after HF etching.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1. Summary of photovoltaic parameters of the hybrid cells based on planar Si, untreated SiNWs and treated SiNWs.

Device	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
planar Si	0.59 ± 0.01	26.1 ± 0.3	66.8 ± 2.1	10.3 ± 0.2
Pristine SiNW	0.51 ± 0.02	30.1 ± 0.8	60.8 ± 3.4	9.4 ± 0.5
SiNW with treatment	0.58 ± 0.01	30.8 ± 0.7	67.7 ± 1.4	12.2 ± 0.2