Solar Cell Based on Hybrid Structural SiNW/ Poly(3,4 ethylenedioxythiophene): Poly(styrenesulfonate)/ Graphene

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Solar energy is considered as a potential alternative energy source. The solar cell is classified into three main types: i) solar cells based on bulk silicon materials (monocrystalline, polycrystalline), ii) thin-film solar cells (CIGS, CdTe, DSSC, etc.), and iii) solar cells based on nanostructures and nanomaterials. Nowadays, commercial solar cells are usually made by bulk silicon material, which requires not only high fabrication costs but also limited performance. In this study, the fabrication of high-performance solar cells based on hybrid structure of silicon nanowires/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)/graphene (SiNW/PEDOT:PSS/Gr) is focused upon. SiNWs with different lengths of 125, 400, 800 nm, and 2 µm are fabricated by a metal-assisted chemical etching method, and their influence on the performance of the hybrid solar cells is studied and investigated. The experimental results indicate that the suitable SiNW length for the fabrication of the hybrid solar cells is about 400 nm and the best power conversion efficiency obtained is about 9.05%, which is about 2.1 times higher than that of the planar Si solar cell.

1. Introduction

The solar cells based on nanostructured materials have been received much attention from scientists in improving the power conversion efficiency.[1,2] Improving light trapping and photocarrier collection is one of the most promising methods to enhance the power conversion efficiency (PCE) of the solar cells. Among all the structures, silicon nanowires (SiNWs) structure not only exhibits an excellent absorption capacity but also provides a large surface area in comparison to bulk Si or thin-film Si.[3–6] Therefore, using the SiNW structure for the fabrication of solar cells have been considering as a potential technique to improve the conversion efficiency and reduce cost production in comparison with solar cell based on thin film and bulk Si structures.[3] Garnett and Yang have studied solar cells using SiNW to increase the area of the p–n junction layer based on the core–shell structure. The photoelectric conversion efficiency obtained was 0.5%.[7] Ko et al. develop a solar cell based on SiNW asymmetric structure. The results show that the reflectivity of solar cells is very low (around 4–5%) and the photoelectric conversion efficiency is ≈8%.[8] However, this type of solar cells is expensive because the manufacturing process requires expensive equipment and complex processes, such as high temperature and high vacuum conditions. Therefore, a new type of solar cell has been studied which is based on hybrid structures combining SiNWs and organic materials.[9–13] This type of solar cell has low cost,
lightweight and high flexibility. Among all the organic materials, poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) is widely used in the fabrication of solar cells based on SiNW/organic structure. Recently, several studies have been carried out to improve the working stability of solar cell with temperature, humidity, and reduce the degradation of organic materials as well as increase the uniformity of a conductive polymer layer on the Si substrate by employing carbon nanotubes, fullerenes, graphene oxide as additive materials. Graphene has excellent properties such as low impedance, high transmittance, good mechanical properties, high thermal stability, and chemical stability. In addition, graphene is easy to functionalized with various functional groups, which can combine easily with organic and/or inorganic materials. Moreover, graphene could be fabricated with low-cost production and large scale. Therefore, graphene can be used as a transparent electrode, electron transport layer, hole transport layer, or electron/hole separation layer combined with conductive polymers in fabricating the solar cells based on organic/inorganic hybrid structure. In this study, SiNWs fabricated with different lengths of 125, 400, 800 nm, and 2 µm by metal-assisted chemical etching method were used for hybrid solar cell fabrication. The influence of SiNW length on the optical properties and PCE of the solar cells was investigated and presented.

2. Results and Discussion

Figure 1 shows the scanning electron microscopic (SEM) images of SiNW structures with different etching times. The

Figure 2. Reflectance spectra of planar Si and SiNWs coated PEDOT:PSS/Gr.
obtained results show that the increase of the etching time will lead to an increase the length of SiNWs. The SiNWs formed vertically to the silicon substrates with high density and diameter in the range of 100–200 nm. The etching rate of SiNW structure was determined to be 133 nm min\(^{-1}\). The obtained results show that SiNW length can be controlled by changing the etching time. It is interesting to note that the etching time seems not much influence to the size and shape of the SiNWs. Besides, no trapezoid shape and smaller size of SiNWs were observed. This demonstrated that the sidewall etching can be neglected in the formation of SiNWs. This is consistent with the other work reported recently.\(^{[10]}\) However, the congregation of the tips of the SiNWs has observed with the samples etched longer than 6 min (Figure 1). In other words, the aggregation of tips will happen if the length of SiNWs is long enough. The formation of the tip aggregation may have restricted the etching agent, thus decreased the etching rate over a long time. Besides, this cluster may prevent the penetration of PEDOT:PSS/Gr solution into the SiNW structure during the hybrid solar cell fabrication process. The influence of the SiNW length on the optical properties and the performance of the hybrid solar cells based on SiNW/PEDOT:PSS/Gr will be discussed in the following parts.

Figure 2 shows the effect of SiNW length on the reflectance spectra of SiNW/PEDOT:PSS/Gr in the range of 300/1100 nm. As can be seen, the sharp transition around 1000–1150 nm is attributed to the band edge of Si.\(^{[10]}\) The results show that the reflectance of SiNW is lower than planar Si (38%) and the longer SiNW structure the lower reflectance. The reflectance of SiNW is much improved compared to that of planar Si cell. Considering the cell using 400 nm SiNWs, the \(\eta\) of 9.05% is nearly 2.1 times higher than that of planar Si cell (4.38%). The \(J_{sc}\), \(V_{oc}\), and FF of the cell also increased respectively to 43%, 29%, and 21% for the cell using 400 nm SiNWs. The enhancement in PCE of cells based SiNWs could be due to the subwavelength light trapping and the light scattering interactions among the densely packed SiNWs.\(^{[32]}\) In conclusion, the SiNW structure having low reflection, strong broadband light absorption is a promising structure to improve the power conversion efficiency of the hybrid solar cells.

The solar cell parameters such as \(V_{oc}\), \(J_{sc}\), \(R_s\), \(R_{sh}\), FF, and \(\eta\) are summarized in Table 1. Figure 3 shows the \(J–V\) characteristic of the hybrid solar cells based on SiNW/PEDOT:PSS/Gr structures and solar cell parameters normalized with respect to a planar Si of hybrid solar cells based SiNWs. The cell using planar Si showed an \(\eta\) of 4.38% with a \(J_{sc}\) of 18.51 mA cm\(^{-2}\), a \(V_{oc}\) of 0.41 V, and an FF of 58%. When using SiNW as a substrate, the \(\eta\) increased to 8.39%, 9.05%, 7.33, and 5.32% corresponding to SiNW length of 125, 400, 800, and 2 \(\mu\)m, respectively. It is interesting to note that the \(\eta\) of the cells based SiNWs is much improved compared to that of planar Si cell. Considering the cell using 400 nm SiNWs, the \(\eta\) of 9.05% is nearly 2.1 times higher than that of planar Si cell (4.38%). The \(J_{sc}\), \(V_{oc}\), and FF of the cell also increased respectively to 43%, 29%, and 21% for the cell using 400 nm SiNWs. The enhancement in PCE of cells based SiNWs could be due to the low reflectance, the effective carrier transportation among SiNWs and the good carrier collection at the electrodes.\(^{[33]}\) The decrease in the reflectance is attributed to the morphology of SiNW and the presence of graphene in PEDOT:PSS solution as discussed in the previous reports.\(^{[32,33]}\) Besides, the interaction between the graphene and PEDOT:PSS not only provided additional charge transport pathways in the hole transport layer but also suppressed the electron recombination at the junction

Table 1. Chemical composition and photovoltaic properties of the prepared hybrid solar cells: short circuit current density \(J_{sc}\), open circuit voltage \(V_{oc}\), series resistance \(R_s\), shunt resistance \(R_{sh}\), Fill factor (FF), and efficiency \(\eta\).

| No. | Structure | SiNW length [nm] | \(J_{sc}\) [mA cm\(^{-2}\)] | \(V_{oc}\) [V] | \(R_s\) [\(\Omega\) cm\(^{-2}\)] | \(R_{sh}\) [\(\Omega\) cm\(^{-2}\)] | FF [%] | \(\eta\) [%] |
|-----|-----------|-----------------|-----------------|--------|---------|---------|-------|------|
| 1   | Planar Si/PEDOT:PSS+Gr | 0                | 18.51           | 0.41   | 6.79    | 127.5   | 58    | 4.38 |
| 2   | SiNWs/PEDOT:PSS+Gr | 125              | 25.93           | 0.51   | 4.76    | 397.5   | 66    | 8.59 |
| 3   | SiNWs/PEDOT:PSS+Gr | 400              | 26.64           | 0.53   | 2.74    | 536.2   | 64    | 9.05 |
| 4   | SiNWs/PEDOT:PSS+Gr | 800              | 22.42           | 0.46   | 2.63    | 185.2   | 70    | 7.33 |
| 5   | SiNWs/PEDOT:PSS+Gr | 2000             | 17.95           | 0.45   | 15.39   | 142.5   | 41    | 5.32 |

Figure 3. a) \(J–V\) characteristic of solar cells using different SiNW length under 100 mW cm\(^{-2}\) illumination with an AM 1.5 G solar simulator and b) solar cell parameters normalized with respect to a planar Si of hybrid solar cells based SiNWs.

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interface and thus enhancing the carrier collection efficiency of the PEDOT:PSS hole transporting layer.\[32\] The PCE of the solar cells increased with the SiNW length less than 400 nm then decreased with longer SiNWs. Solar cells based on 400 nm SiNW/PEDOT:PSS/Gr have the highest PCE of 9.05% and $J_{sc} \approx 26.64$ mA cm$^{-2}$, $V_{oc} \approx 0.53$ V, FF $\approx 64\%$. The 400 nm SiNW solar cells having highest $R_s$ value of 626.1 2 cm$^{-2}$ in comparison to other types of solar cells to be considered as one of the key factors lead to increasing of $V_{oc}$ of the cell.\[34\] In addition, the increase of $V_{oc}$ could also result from the increase of the lifetime of minority carriers.\[34\] Solar cells based on short SiNWs can reduce the recombination of carriers because of the short charge transport distance from p–n junction to the electrodes and thus the lifetime of minority carrier increases. The PCE of solar cells decreases with the SiNWs longer than 800 nm. This is attributed to the aggregation of SiNW tips as discussed in the previous section. This prevented the penetration of PEDOT:PSS/Gr into SiNW structure to form a large p–n junction area. Besides, the recombination in the solar cell increases when the length of SiNW increased. This is possible due to the increasing charge transport distance. Table 2 presents the reported performance parameters of hybrid Si/PEDOT:PSS solar cells. Comparing to other reports, the obtained results are in line with earlier reports,\[21,51,54\] in which using carbon nanomaterials as an additive component for PEDOT:PSS. Gogolin et al.\[45\] reported a very high PCE (16.2% HV) for a hybrid solar cell, but note that the structure was used a well-passivating electron selective a-Si:H(i/n) layer stack at the front of our solar cells. Similarly, Fang et al.\[46\] reported PCE up to 12.54% as using modified Si wafer with an ideal concentration for the fabrication of the hybrid solar cells.

3. Experimental Section

Materials: N-type silicon wafer having a thickness of 525 µm and resistivity from 1 to 10 Ω was purchased from SEHOUNG Wafertech.

| No. | Structure            | Substrate | Contacts | $V_{oc}$ [mV] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | η [%] | Ref.        |
|-----|----------------------|-----------|----------|---------------|-------------------------|--------|-------|-------------|
| 1   | SiNW/PEDOT:PSS       | c-Si      | ITO      | 530           | 29.3                    | 67     | 10.62 | [35]        |
| 2   | SiNW/PEDOT:PSS:AgNW  | n-Si (100)| Ti-Ag/ITO| 574           | 35.55                   | 71.37  | 14.56 | [36]        |
| 3   | SiNW/PEDOT:PSS       | p-Si (100)| Ni-Ag/ITO| 530           | 29.5                    | 61.2   | 9.65  | [37]        |
| 4   | SiNW/PEDOT:PSS       | n-Si (100)| Ni-Ag/ITO| 500           | 29.8                    | 58     | 8.7   | [38]        |
| 5   | SiNW/PEDOT:PSS: nc-Si QDs | n-Si (100)| Ti-Ag/Ag | 595           | 37.83                   | 60.9   | 13.73 | [39]        |
| 6   | SiNW/PEDOT:PSS       | n-Si (100)| ITO      | 470           | 19.28                   | 61     | 5.09  | [40]        |
| 7   | SiNW/PEDOT:PSS       | n-Si (100)| Ni-Ag/Ag | 540           | 18.54                   | 65.5   | 6.62  | [41]        |
| 8   | SiNW/PEDOT:PSS       | n-Si (100)| Au mesh  | 539           | 36.03                   | 67.8   | 13.2  | [42]        |
| 9   | SiNW/PEDOT:PSS       | n-Si (100)| Al/Cu    | 440           | 29.8                    | 51     | 7.3   | [43]        |
| 10  | SiNW/PEDOT:PSS       | n-Si (100)| Al/Ag    | 420           | 24.5                    | 41.22  | 4.0   | [44]        |
| 11  | SiNW/PEDOT:PSS       | n-Si (100)| Al/IITO  | 460           | 21.6                    | 64     | 6.35  | [45]        |
| 12  | PEDOT:PSS/Si/a-Si:H   | p-Si      | Al/IITO  | 679           | 32                      | 74.3   | 16.2  | [46]        |
| 13  | PC61BM/Si/PEDOT:PSS  | n-Si      | Al/Ag    | 620           | 32.12                   | 62.56  | 12.54 | [47]        |
| 14  | SiNW/PEDOT:PSS       | n-Si      | Al/Ag    | 430           | 9.38                    | 45     | 1.82  | [48]        |
| 15  | a-Si:C/a-Si:H/n-Si/a-Si:H/PEDOT:PSS | n-Si    | Ti/Al/Ag | 600           | 30.97                   | 59.4   | 11.04 | [49]        |
| 16  | SiNW/PEDOT:PSS       | n-Si (100)| Al/Cu    | 460           | 26.66                   | 54     | 6.87  | [50]        |
| 17  | Si/PEDOT:PSS         | n-Si (100)| Al/Ag    | 481           | 37.8                    | 45.4   | 8.25  | [51]        |
| 18  | SiNW/PEDOT:PSS       | n-Si (100)| Al/Ag    | 530           | 26.3                    | 64.2   | 9.0   | [52]        |
| 19  | Si/PEDOT:PSS         | n-Si (100)| Al/Ag    | 510           | 28                      | 54     | 7.8   | [53]        |
| 20  | n-Si/p-Si/PEDOT:PSS  | n-Si (100)| Al/Ag    | 266           | 26.9                    | 36     | 2.57  | [54]        |
| 21  | n+c-Si/PEDOT:PSS:CNT | c-Si      | Al/Ag    | 576           | 25.6                    | 62.6   | 9.24  | [55]        |
| 22  | Si/PEDOT:PSS         | n-Si (100)| Ag/Ag    | 598           | 15.7                    | 58     | 5.1   | [56]        |
| 23  | (n)a-Si:H/(i)a-Si:H/PEDOT:PSS | a-Si     | Ag/ITO  | 860           | 19.8                    | 34     | 5.78  | [57]        |
| 24  | SiNWs/CuSCN/PEDOT:PSS| n-Si (100)| Al/Ag    | 610           | 29.2                    | 68     | 12.19 | [58]        |
| 25  | SiNW/PEDOT:PSS:GO    | n-Si (100)| Ti-Ag/ITO| 518           | 31                      | 59.6   | 9.57  | [23]        |
| 26  | SiNW/PEDOT:PSS:Gr    | n-Si (100)| Al/Ag    | 530           | 26.64                   | 64     | 9.05  | This work   |
Company, Korea. Acetone, isopropanol, hydrofluorocarbon (HF) acid, H₂SO₄ (98%), HNO₃ (68%), H₂O₂, KOH, AgNO₃, were purchased from Shantou Xilong Chemical Company, China.

**Fabrication of Silicon Nanowires:** Clean n-type Si was cut into pieces of 1.5 x 1.5 cm in size. These pieces Si substrates were dipped in HF solution (2%) for 2 min to remove the SiO₂ layer on top of the Si surface. The SiNW structure was formed using a one-step chemical wet etching process. The clean Si substrates were immersed in etching solution which was a mixture of HF (4.6 M) and AgNO₃ (0.02 M) for different times of 1, 3, 6, ..., 60 min. After finishing the etching process, the Si substrates were immersed in deionized (DI) water to remove all residual Ag that was formed during the etching process, which was followed by washing with DI and dried under N₂ gas flow.

**Fabrication of Solar Cells:** Firstly, graphene was functionalized using a mixture of acid H₂SO₄:HNO₃ (3:1) at 70 °C for 5 h to attach the carboxylic (COOH) functional group on the surface. The functionalized Gr was dispersed into deionized water with a concentration of 1 mg mL⁻¹ by ultrasonic for 45 min at room temperature. Then the functionalized Gr solution was dispersed into PEDOT:PSS with a concentration of 0.5% in weight by ultrasonic for 6 h to obtain a homogenous PEDOT:PSS/Gr solution. Secondly, the PEDOT:PSS/Gr solution was coated on the surface of SiNWs by a spin coating method, following these spin steps: 2000 rpm during 10 s then 6000 rpm during 60 s. After that, the n-SiNW/Gr solution was coated on the ultrasonic for 45 min at room temperature. Then the functionalized Gr residue acid, followed by HNO₃/H₂O (1/1) solution in order to remove all residual Ag that was formed during the etching process, which was followed by washing with DI and dried under N₂ gas flow.

**Characterization:** The surface morphology of the samples was studied by field emission scanning electron microscope (FESEM, Hitachi 54800). UV–vis spectroscopy was used to measure the optical reflectance spectra of samples by using a Jacob V-570 UV/vis/NIR spectrophotometer. The UV–vis–NIR spectroscopy was used to measure the optical reflectance spectra of samples by using a Jacob V-570 UV/vis/NIR spectrophotometer. The J–V characteristic of solar cells was measured by Keithley 2400 under an illumination condition of AM 1.5 G with a density of 100 mW cm⁻².

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

conversion efficiencies, hybrid solar cells, PEDOT:PSS, silicon nanowires

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