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Well-aligned single-crystalline silicon nanowire hybrid solar cells on glass

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ABSTRACT

Hybrid solar cells are fabricated on the glass substrate using well-aligned single-crystalline Si nanowires (SiNWs) and poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM). Their key benefits are discussed. The well-aligned SiNWs are fabricated from Si wafer and transferred onto the glass substrate with the P3HT:PCBM. Such SiNWs provide uninterrupted conduction paths for electron transport, enhance the optical absorption to serve as an interesting candidate of the absorber, and increase the surface area for exciton dissociation. Our investigations show that SiNWs are promising for hybrid organic photovoltaic cells with improved performance by increasing the short-circuit current density from 7.17 to 11.61 mA/cm^2.

1. Introduction

Organic solar cells have attracted considerable attention in recent years because they have many advantages, such as low cost, processing with low temperature, flexible, large area production, and so on [1–3]. To increase the power conversion efficiency of organic solar cells, the most common strategy is the so-called bulk heterojunction, in which donors such as poly(3-hexylthiophene) (P3HT) and acceptors like [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) are blended to form one mixed layer [4–7]. The bulk heterojunction devices were characterized by an interpenetrating network of donor and acceptor materials, providing a large interface area where photo-induced excitons could efficiently dissociate into separated electrons and holes. However, the interpenetrating network cannot be easily formed in the blended mixture. In addition, the organic materials are not good in carrier transport. Thus, the power conversion efficiency is still limited by the low dissociation probability of excitons and the inefficient hopping carrier transport [8,9].

The semiconductor nanostructures are hence proposed to combine with the organic materials to provide not only a large interface area between organic and inorganic components for exciton dissociation but also fast electron transport in semiconductors. Therefore, many research groups combined organic materials with semiconductor nanostructures to overcome the drawbacks of the organic solar cells. Many inorganic nanowires had been experimented for this purpose, including CdTe, CdS, CdSe, ZnO, and TiO_2 nanowires [10–12]. However, CdTe, CdS, and CdSe materials are harmful to the environment, while ZnO and TiO_2 have a band gap higher than 3 eV and so cannot effectively absorb the solar spectrum. To overcome this, Si nanowires (SiNWs) are suitable for this application because they are environmental friendly and have high absorption coefficient in the infrared region.

SiNW arrays can be fabricated by various techniques such as chemical vapor decomposition (CVD), dry etching, laser ablation, and vapor–liquid–solid (VLS) [13–16]. Unfortunately, these techniques are expensive and require complex equipment and high synthesis temperatures. The wet etching method has recently been developed to prepare aligned SiNW arrays with a high-quality single-crystal phase [17,18]. It has attracted great attention for its low cost, low synthesis temperatures, and simple fabrication. Unfortunately, the SiNWs by wet etching are fabricated from the silicon substrates, so it is difficult to combine with organic materials for solar cells. Here we further develop a technique to transfer silicon nanowires onto other substrates such as glass, plastic materials, and flexible materials. Our approach enables the combination of highly crystalline SiNWs and organic materials to form solar cells on glass or plastics. In this work, we demonstrate the fabrication of SiNW/P3HT:PCBM hybrid solar cells using the above transfer technique.

2. Experiment

The synthesis of SiNWs was carried out with the following procedures [19]. The original n-type CZ-silicon (1 0 0) wafer with a resistivity of 4–7 Ω cm was sequentially cleaned with acetone, ethanol, de-ionized water, and buffered oxide etching fluid. The

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cleaned silicon wafer was then immersed into an aqueous HF solution, containing silver nitrate, for 30 min at room temperature. After the etching process, the silicon wafer was rinsed with de-ionized water and blown dry in air. The tree-like silver pattern wrapping the silicon was detached by HNO_3 solution. Then, the silicon dioxide was removed using buffered oxide etch. Finally, the silicon wafer was rinsed with de-ionized water and blown dry in air.

A schematic of the hybrid solar cells using P3HT:PCBM and SiNWs is shown in Fig. 1(a). The hybrid solar cell devices were prepared with the following procedures. An indium tin oxide (ITO)-coated glass, with a surface resistance of $\sim 7\,\Omega\,\text{square}^{-1}$, was first cleaned by ultrasonic agitation in acetone, isopropanol, and de-ionized water, then dried in an oven at 90 °C for 10 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was deposited by spin coating at 4000 r.p.m. and baked at 80 °C for 10 min in order to modify the ITO surface. To make P3HT:PCBM (1:1 by weight) solution, P3HT was dissolved in 1,2-dichlorobenzene (DCB) to make a 20 mg/ml solution, followed by blending with PCBM in 50 wt%. The P3HT:PCBM 1:1 weight-ratio solution was stirred for at least 24 h at 40 °C in a glove box. The active layer was obtained by spin-coating the blend at 600 r.p.m. for 60 s onto the PEDOT:PSS. The P3HT:PCBM film was dried for 20 min in a glove box. Then, the cells were held on a hot plate at 160 °C for 10 min under N_2 atmosphere.

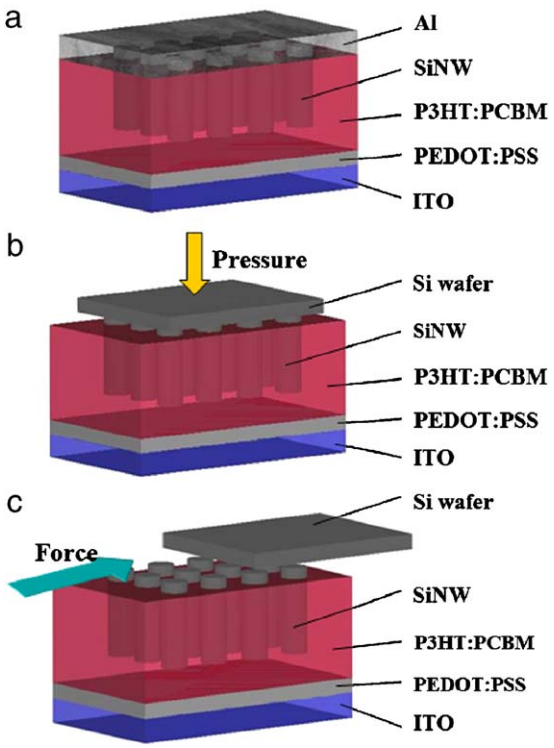

Fig. 1. (a) A schematic of the hybrid solar cell using SiNWs and P3HT:PCBM blend; (b) the setup for transferring the SiNWs onto the P3HT:PCBM blend; and (c) a schematic of the home-made machine with lateral force used to separate the silicon wafer from the P3HT:PCBM blend.

Next, we transferred SiNWs to the P3HT:PCBM film onto the ITO glass. First, P3HT:PCBM film was held on a hot plate at 160 °C for 5 min under N_2 atmosphere. Then, the vertically aligned SiNW arrays were pressed into the P3HT:PCBM film on a hot plate at 160 °C for 10 min under N_2 atmosphere. Fig. 1(b) shows the setup for transferring the SiNWs onto the P3HT:PCBM film. After SiNWs were pressed into the P3HT:PCBM film, the device was cooled to room temperature. Next, a home-made machine with lateral force was used to separate the silicon wafer from the P3HT:PCBM film (Fig. 1(c)), and the SiNWs were inserted into the P3HT:PCBM film. Next, the samples were quickly placed in a vacuum chamber. A 500 nm film of aluminum (Al) was evaporated onto the devices through a shadow mask to form the top contact. The active layer of the cell, as defined by the shadow mask, was 0.15 cm^2. After removing the shadow mask, our hybrid solar cells incorporated with SiNWs were completed. For comparison, another device without the SiNWs was also fabricated with the same steps except for the transfer of SiNWs.

3. Results and discussion

The morphologies of SiNWs were examined by scanning electron microscopy (SEM). Fig. 2(a) shows the SEM image of the top of the SiNW arrays before being transferred onto the P3HT:PCBM blend. The density of the SiNWs is about 2×10^7 mm^{-2}. The inset shows the cross-sectional SEM image of the vertically aligned SiNW arrays. The length of the SiNW is about 1.28 μm.

The SEM picture of the SiNWs transferred onto the P3HT:PCBM film is shown in Fig. 2(b) using the above transfer method. The pressure was set at 55 kg/cm^2. The orientation of SiNWs outside the P3HT:PCBM film was slightly tilted toward the same direction. This tilted angle is between 0° and 45°.

The absorption spectra of the P3HT:PCBM film and the SiNWs/P3HT:PCBM film were characterized in the 350–1100 nm range by UV–vis absorption spectroscopy. Fig. 3 shows the measured absorption spectra. The P3HT:PCBM film of 500 nm thickness shows the peak of optical density of 1.385 at 506 nm. The maximum absorption of the solar spectrum occurs from 350 to 620 nm. However, the P3HT:PCBM film exhibits little absorption beyond 650 nm. The SiNWs/P3HT:PCBM film has improved light harvesting from 650 to 1100 nm (Fig. 3) because the cutoff

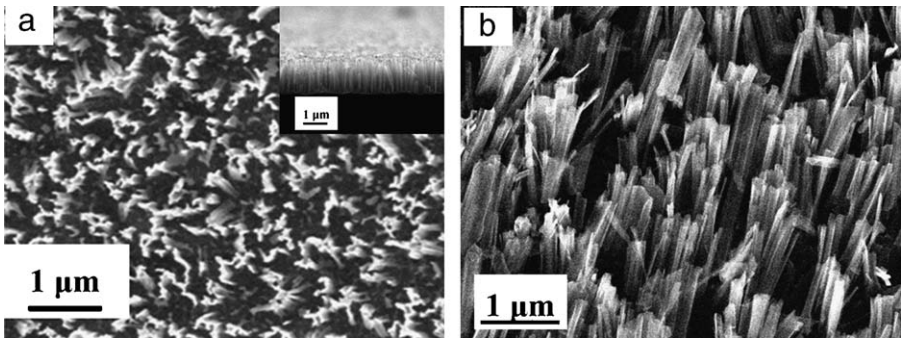

Fig. 2. SEM images of (a) the SiNWs on the silicon wafer (top view), the inset is cross-sectional view and (b) the SiNWs later transferred on the P3HT:PCBM blend (top view).

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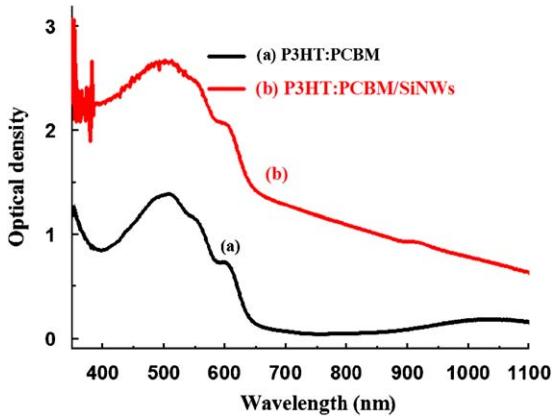

Fig. 3. UV–visible absorption of P3HT:PCBM blend on the ITO glass (a) with SiNWs and (b) without SiNWs.

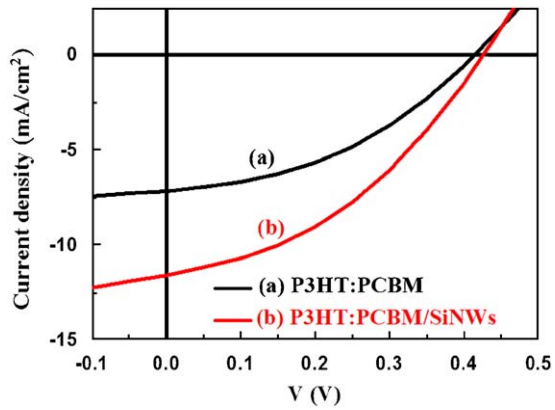

Fig. 4. The current density–voltage characteristics for the solar cells with and without the SiNWs under simulated AM1.5 illumination.

wavelength of Si is about 1100 nm. The absorption of SiNWs increases as the wavelength decreases. Compared with ZnO nanorod arrays in conjunction with the P3HT:PCBM blend of hybrid solar cell, the combination of SiNWs and P3HT:PCBM blend has the advantage of compensating the absorption of P3HT:PCBM blend with improved light harvesting in the near-infrared and visible region. In contrast, the band gap of ZnO is higher than 3 eV, so it cannot effectively absorb the solar spectrum in the near-infrared and visible regions. In addition, the SiNWs have another advantage that the single-crystal Si provides higher mobility than the single-crystal ZnO [20,21].

The current density–voltage (J–V) characteristics for the solar cells with and without the SiNWs under simulated AM1.5 illumination were measured and are shown in Fig. 4. With the SiNWs, the device has improved performance with a short circuit current density (J_{sc}) of 11.61 mA/cm^2, an open circuit voltage (V_{oc}) of 425 mV, a fill factor (FF) of 0.39, and a conversion efficiency (η) of 1.93%. Without the SiNWs, the device exhibits a J_{sc} of 7.17 mA/cm^2, V_{oc} of 414 mV, FF of 0.407, and η of 1.21%. With the SiNWs, the J_{sc} increases from 7.17 to 11.61 mA/cm^2. The increase of J_{sc} can be contributed to the following reasons. First, the SiNWs provide fast and direct pathways to increase the charge carrier collection and transport. This also leads to the reduction in the series resistance from 18.09 to 10.59 Ω cm^2. Second, the high-density SiNWs increases the interface areas of Si-P3HT, improving the dissociation of excitons. Third, the SiNWs can compensate the absorption of the P3HT:PCBM blend with improved light harvesting in the near-infrared region. In addition, because both devices were stored in air at room temperature without encapsulation, degradation from oxygen and water occurs in both devices [22–28]. However, we observed that there is no difference in the degree of degradation between devices with and without the SiNWs. In other words, the insertion of the SiNWs does not cause damage to the organic layer. Our results indicate that the combination of the SiNWs and P3HT:PCBM blend is an attractive route to obtain high J_{sc} and efficiency by improving the optical absorption in the near-infrared and visible regions, dissociation of excitons, and the electron transport.

4. Conclusions

In conclusion, we have demonstrated the fabrication of the SiNW/P3HT:PCBM blend hybrid solar cells using the SiNW transfer technique. Our investigations show that after introducing the SiNWs, the J_{sc} increases from 7.17 to 11.61 mA/cm^2 and η increases from 1.21% to 1.91%. The results clearly indicate that combination of the SiNWs and P3HT:PCBM blend is an attractive route to obtain high J_{sc} and efficiencies by improving the optical absorption, dissociation of excitons, and the electron transport. Silicon wafer is commercially available and cheap. Compared to hybrid solar cells reported previously [10–12,29], Si nanowires can be fabricated at low temperature from solution processing without any vacuum equipment or high-temperature processing. In addition, this transfer method for Si nanowires is simple and fast. It is not a laborious way. This method is suitable for plastic solar cells because it can be processed fast, is cheap and simple.

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References

[1] B.C. Thompson, J.M.J. Fréchet, Organic photovoltaics–polymer–fullerene composite solar cells, Angewandte Chemie—International Edition 47 (2008) 58–77.
[2] S. Günes, H. Neugebauer, N.S. Sariciftci, Conjugated polymer-based organic solar cells, Chemical Reviews 107 (2007) 1324–1338.
[3] E. Bundgaard, F.C. Krebs, Low band gap polymers for organic photovoltaics, Solar Energy Materials and Solar Cells 91 (2007) 954–985.
[4] H. Spanggaard, F.C. Krebs, A brief history of the development of organic and polymeric photovoltaics, Solar Energy Materials and Solar Cells 83 (2004) 125–146.
[5] K.M. Coakley, Y.X. Liu, C. Goh, M.D. McGehee, Ordered organic–inorganic bulk heterojunction photovoltaic cells, MRS Bulletin 30 (2005) 37–40.
[6] S.A. Gevorgyan, F.C. Krebs, Bulk heterojunctions based on native polythiophene, Chemistry of Materials 20 (2008) 4386–4390.
[7] X.N. Yang, J. Loos, S.C. Veenstra, W.J.H. Verhees, M.M. Wienk, J.M. Kroon, M.A.J. Michels, R.A.J. Janssen, Nanoscale morphology of high-performance polymer solar cells, Nano Letters 5 (2005) 579–583.
[8] P.E. Shaw, A. Ruseckas, I.D.W. Samuel, Exciton diffusion measurements in poly(3-hexylthiophene), Advanced Materials 20 (2008) 3516–3520.
[9] H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.J.H. Spiering, R.A.J. Janssen, E.W. Meijer, P. Herwig, D.M.d. Leeuw, Two-dimensional charge transport in self-organized, high-mobility conjugated polymers, Nature 401 (1999) 685–688.
[10] W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, Hybrid nanorod–polymer solar cells, Science 295 (2002) 2425–2427.
[11] Y. Kang, D. Kim, Well-aligned CdS nanorod/conjugated polymer solar cells, Solar Energy Materials and Solar Cells 90 (2006) 166–174.
[12] S. Günes, N.S. Sariciftci, Hybrid solar cells, Inorganica Chimica Acta 361 (2008) 581–588.
[13] H.J. Fan, P. Werner, M. Zacharias, Semiconductor nanowires: from self organization to patterned growth, Small (2006) 700–717.

[14] E.Z. Liang, C.J. Huang, C.F. Lin, Use of SiO_2 nanoparticles as etch mask to generate Si nanorods by reactive ion etch, Journal of Vacuum Science and Technology B 24 (2006) 599–603.
[15] A.M. Morales, C.M. Lieber, A laser ablation method for the synthesis of crystalline semiconductor nanowires, Science 279 (1998) 208–211.
[16] B.M. Kayes, M.A. Filler, M.C. Putnam, M.D. Kelzenberg, N.S. Lewis, H.A. Atwater, Growth of vertically aligned Si wire arrays over large areas ($>1\,cm^2$) with Au and Cu catalysts, Applied Physics Letter 91 (2007) 103110.
[17] K.Q. Peng, Y.J. Yan, S.P. Gao, J. Zhu, Synthesis of large-area silicon nanowire arrays via self-assembling nanoelectrochemistry, Advanced Materials 14 (2002) 1164–1167.
[18] K. Peng, Y. Yan, S. Gao, J. Zhu, Dendrite-assisted growth of silicon nanowires in electroless metal deposition, Advanced Functional Materials 13 (2003) 127–132.
[19] T. Qiu, X.L. Wu, Y.F. Mei, G.J. Wan, P.K. Chu, G.G. Siu, From Si nanotubes to nanowires: synthesis, characterization, and self-assembly, Journal of Crystal Growth 277 (2005) 143–148.
[20] S.S. Li, W.R. Thurber, The dopant density and temperature dependence of electron mobility and resistivity in n-type silicon, Solid-State Electronics 20 (1977) 609–616.
[21] A.H. Jayatissa, Preparation of gallium-doped ZnO films by oxidized ZnS films, Semiconductor Science and Technology 18 (2003) 27–30.
[22] J.A. Hauch, P. Schilinsky, S.A. Choulis, R. Childers, M. Biele, C.J. Brabec, Flexible organic P3HT:PCBM bulk-heterojunction modules with more than 1 year outdoor lifetime, Solar Energy Materials and Solar Cells 92 (2008) 727–731.
[23] M. Jorgensen, K. Norrman, F.C. Krebs, Stability/degradation of polymer solar cells, Solar Energy Materials and Solar Cells 92 (2008) 686–714.
[24] E.A. Katz, S. Gevorgyan, M.S. Orynbayev, F.C. Krebs, Out-door testing and long-term stability of plastic solar cells, The European Physical Journal Applied Physics 36 (2006) 307–311.
[25] F.C. Krebs, Air stable polymer photovoltaics based on a process free from vacuum steps and fullerenes, Solar Energy Materials and Solar Cells 92 (2008) 715–726.
[26] F.C. Krebs, Degradation and stability of polymer and organic solar cells, Solar Energy Materials and Solar Cells 92 (2008) 685.
[27] F.C. Krebs, K. Norrman, Analysis of the failure mechanism for a stable organic photovoltaic during 10,000 h of testing, Progress in Photovoltaics: Research and Applications 15 (2007) 697–712.
[28] F.C. Krebs, H. Spanggaard, Significant improvement of polymer solar cell stability, Chemistry of Materials 17 (2005) 5235–5237.
[29] A.D. Pasquier, D.D.T. Mastrogiovanni, L.A. Klein, T. Wang, E. Garfunkel, Photoinduced charge transfer between poly(3-hexylthiophene) and germanium nanowires, Applied Physics Letters 91 (2007) 183501.

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