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Improved photovoltaic performance of hybrid solar cells based on silicon nanowire and P3HT

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ABSTRACT

The properties of organic/inorganic poly(3-hexylthiophene) (P3HT): silicon nanowires nanocomposite films and nanocomposite based solar cells as a function of SiNWs concentration and the solvent used for the film fabrication were studied. We demonstrate that the performance of these devices is highly dependent on these parameters. A detailed study of the effects that active layer thickness has on the photovoltaic performances has also been performed for bulk heterojunction hybrid solar cells. Photoluminescence spectroscopy (PL) shows the existence of a critical SiNWs concentration of about 15 wt% for PL quenching corresponding to the most efficient charge pair separation. Photoluminescence responses were correlated with the topography (AFM) of the thin films. The photovoltaic effect of ITO/PEDOT:PSS/SiNWs:P3HT/Al was studied by current–voltage (I–V) measurements under illumination and interpreted on the basis of the charge transfer differences resulting from the morphologies. By optimizing all the physical parameters listed above we fabricated devices with PCE of 0.08%, which is the highest efficiency reported so far for this system.

1. Introduction

The use of silicon nanowires (SiNWs) and conjugated polymers to form organic–inorganic hybrid structures has emerged as a promising technology in the solar cell industry [1–6]. In this approach the nanostructured silicon offers a large surface area and a direct path for charge transport for increased efficiency while the conducting polymer layer offers several advantages such as flexibility, light-weight semi-transparent characteristics and ability to large scale production [7–9].

In this work, we investigate the influence of the SiNWs concentration and the solvent used for the film preparation on the optical properties of P3HT:SiNWs nanocomposite films and the performance of P3HT:SiNWs based solar cells. The effect of the cosolvent on the correlation between the morphology of the active layer and the photovoltaic characteristics of the hybrid solar cells were studied. The films were characterized using photoluminescence (PL) and atomic force microscopy (AFM). The solar cells were characterized by measuring I–V characteristics under AM1.5 solar illumination.

We demonstrate silicon nanowires (SiNWs)/P3HT polymer bulk heterojunction solar cells with a photovoltaic performances, significantly higher than previously reported [10]. Our results reveal that improvement in each parameter determining the performance of the solar cells, i.e. short circuit current density, fill factor and open circuit voltage, are strongly improved by the optimization of the silicon nanowire concentration. We demonstrate that other parameters like the active layer thickness and the solvent used for the film fabrication have strong impact on the efficiency of the device.

The dissociation of the photo-generated charge pairs in P3HT upon incorporation of the SiNWs in the blend has been evaluated by the quenching of the P3HT photoluminescence. The photoluminescence quenching was found to be strongly dependent not only on SiNWs concentration but also on the solvent used for spin-coating.

The relation between the morphology of the composite thin films and the charge transfer between SiNWs and P3HT has been investigated. A direct correlation is observed between the surface roughness and the solar cell performance.

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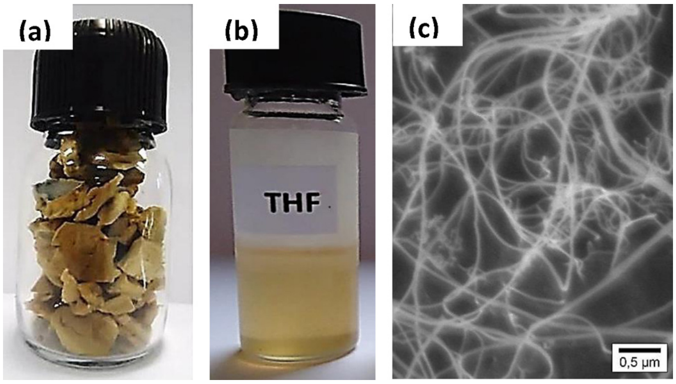

Fig. 1. (a) Images of SiNWs in the form of a foam obtained after optimization of experimental procedure; (b) SiNW solution in THF; and (c) SEM image of the SiNW network.

2. Experiment

2.1. Instrumentation

The photoluminescence spectra have been performed with a "JOBIN YVON-SPEX Spectrum One" CCD detector, cooled at liquid nitrogen temperature. A monochromator was used to select an excitation wavelength corresponding to the maximum of the absorption band of P3HT. The current–voltage characteristics under illumination with a 150 W Xe Oriel solar simulator were obtained with a Keithley 236 source and a PC card for acquisition. Characterizations of the composite morphologies were performed by scanning electron microscopy (SEM JEOL JSM-6320F) at a voltage of 15 kV. The thicknesses of thin films are measured using a mechanical profilometer Veeco Dektak 150.

2.2. Materials

The SiNWs used in this study were prepared as previously reported [11–13]. The as produced SiNWs are obtained as foam (Fig. 1a). This foam is dispersed in THF to produce a SiNWs ink (Fig. 1b) which will be mixed with the polymer at different concentrations. These SiNWs exhibit a diameter less than 40 nm and some 10 nm lengths. The network formed by the entangled nanowires can be observed by scanning electron microscopy (Fig. 1c).

All polymers and solvents were purchased from Sigma–Aldrich and used without further purification. Tetrahydrofuran (THF), which has a relatively high volatility (Teb ≈ 65 °C), was chosen for its good solvent properties for the SiNWs [14]. Orthodichlorobenzene (ODCB) is known as good solvent for the P3HT [15]. The molecular weight of the P3HT used in this study was 54,000–75,000 g mol^{-1}.

2.3. Solar cells fabrication

All the hybrid solar cells in this work were prepared on commercial indium-tin oxide (ITO) coated glass with layer thickness of 130 nm. First ITO substrates were thoroughly cleaned by sonication in acetone and ethanol followed by rinsing with water and sonication in isopropanol and applying ultraviolet-ozone for 10 min. A thin layer of poly(3,4-PEDOT:PSS) (CLEVIOSTM AI 4083) was spin-coated on the cleaned ITO pre-coated glass substrate at a speed of 2500 rpm for 60 s followed by heating on a hot-plate at 120 °C for 20 min.

In this study three different series were prepared. In the first series, the photoactive layer, consisting of a blend of P3HT and SiNWs for different weight ratios of SiNWs ranging from 0 to 30%, was spin coated onto the ITO/PEDOT/PSS layer and was then dried at 140 °C for 10 min. The second series was carried to study the effect of the solvent used for the hybrid films fabrication, then in the last one we performed four solar cells with different thicknesses of the active layer.

For processing the cathode, samples were puted into an Edwards Auto 306 evaporator, in which Al metal electrodes (120 nm) were thermally evaporated at 2×10^{-6} Torr pressure through a shadow mask to produce simultaneously seven diode structures and the device area was 0.25 cm^2. Fig. 2(a) shows a typical device structure of the hybrid photovoltaic cell fabricated in this study.

Energy levels relative to the vacuum level and corresponding to the components of the photovoltaic cells are shown (Fig. 2(b)). The HOMO of P3HT is positioned to inject holes into PEDOT:PSS and hence into the ITO electrode. The LUMO of P3HT is well above the Fermi level of the n-Si nanowires and electron collection should occur efficiently at the silicon interface. Electrons generated in the nanowires will be collected at the Al electrode.

3. Results and discussion

Before the fabrication and characterization of solar cells, the optical properties of the blends based on the SiNWs with different compositions have been studied. We also studied the effect of the solvent used for the film preparation on these properties.

3.1. Effect of the concentration of the SiNWs

As it is known, the degree of PL quenching depends mainly of the available interface area between donor and acceptor moieties for charge pair dissociation. It provides an indication of how well the SiNWs are mixed with the polymer and also depends on the quality of the interface between polymer and SiNWs. Fig. 3 shows the PL spectra of P3HT/SiNWs composite thin films with different concentrations of SiNWs.

From the photoluminescence emission spectra of P3HT and P3HT:SiNWs composites, it was observed that the reduction in PL intensity increases with increasing the SiNWs concentration. An optimum PL quenching is observed for 15 SiNWs wt. %. The PL peak intensity of P3HT decreases by more than 70% in P3HT/SiNWs films as compared to pure P3HT which implies that with increase in SiNWs concentration, there is an increment in the charge transfer from polymer to SiNWs.

It is important to note that the recombination centers could also contribute to photo-generated charge pair dissociation. It is in particular the case of surface defects like silicon dangling bonds. However such effect can be considered as negligible in this study due to the surface passivation of silicon nanowires by a thin oxide layer.

Fig. 3 also shows that the film corresponding to the high SiNWs concentrations (30 wt.%) shows a slight increase in PL intensity in comparison to the film with 15 SiNW wt.%. This increase in emission intensity may be explained by the formation of SiNW aggregates resulting in smaller interfacial area with the polymer. These results can be correlated to the changes in surface roughness observed with AFM in tapping-mode (Fig. 4). The roughness values obtained for various concentrations of SiNWs are summarized in Table 1.

The AFM images clearly show that the layer containing 15 SiNWs wt.% is the more homogeneous with the lowest roughness, while high concentration of SiNWs (30 wt.%) lead to layer containing large agglomerates that can be explained by the tendency of SiNWs to agglomerate in solution as well as during spin-coating to reduce their free energy. These results are in good agreement with the variation of the photoluminescence, which was presented in Fig. 3, where a new increase of the PL intensity appears for SiNW weight fraction larger than 15%.