Bulk Heterojunction Organic-Inorganic Photovoltaic Cell Based on Doped Silicon Nanowires

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ABSTRACT

Heterojunction photovoltaic devices were fabricated using single crystal silicon nanowires and the organic semiconductor regioregular poly-(3-hexyl thiophene) (RR-P3HT). N-type nanowires were first grown on an n+ silicon substrate by the vapor-liquid-solid (VLS) method. Devices were then fabricated by filling the gap between the nanowires and a transparent PEDOT:PSS-coated ITO electrode with RR-P3HT evaporated from chlorobenzene. Device performance indicates that both silicon and P3HT act as absorbers for photovoltaic response. Initial results show both open circuit voltage and short circuit current are both lower than expected, most likely duedue to the methods of photovoltaic cell construction.

1 INTRODUCTION

Polymeric organic semiconductors have been used to fabricate photovoltaic materials for more than a decade with steady improvement in both materials and device architectures [1]. Some of the advantages of these materials are ease of fabrication and high optical absorption by thin films. However, charge carrier mobilities are typically orders of magnitude lower than commonly used inorganic semiconductors. In addition, excitons in organic semiconductors have a much high binding energy than crystalline inorganic semiconductors, and thus relatively large electric fields are required for dissociation into charge carriers after photoexcitation. The fields necessary for exciton dissociation (and hence charge carrier formation) exist only at heterointerfaces, and thus organic layers must be kept relatively thin to produce efficient devices.

In order to exploit some of the advantages of organic semiconductors while minimizing the impact of their major disadvantage, poor charge transport, photovoltaic devices have been fabricated using bulk heterojunctions of organic polymers. In this configuration there are interpenetrating networks of materials, minimizing the distance that excitons must travel before dissociating at a heterointerface. A particularly successful version of this type of device uses (6,6)-phenyl C61 butyric acid methyl ester (PCBM) as the donor, resulting in efficiencies exceeding 3% [2]. A natural extension of this idea is the use of inorganic semiconductors as one of the materials. Effective photovoltaic devices have been fabricated using inorganic nanoparticles [3]. The problem that occurs with this type of architecture is that one of the conduction paths requires percolation of charges to reach the contact electrode. In this work we propose the use of doped single crystal nanowires as the inorganic material in an organic-inorganic bulk heterojunction photovoltaic cell. The n-type silicon nanowires are grown on a highly doped n-type silicon substrate, resulting in a continuous conducting pathway for charge carriers in the inorganic phase.

2 NANOWIRE FABRICATION

Silicon nanowires were fabricated via VLS growth mechanism on n-type silicon (111) wafers. The wafers were coated with a thin Au film (~ 3 nm) by sputtering or evaporation, then placed in tube furnace on a Mo block for nanowire growth. Nanowires were grown at 420-450° C using 10% disilane in Ar at a pressure of 2 Torr. Full details of the growth have been previously published [4]. N-type doping of the nanowires was achieved by incorporating 100 ppm phosphine into the gas flow used during growth, producing a doping level of approximately 3 x 10^{16} [5].

Growth of nanowires via the VLS process occurs at reaction sites comprised of small Au islands. To determine the size and density of Au islands produced on the substrates used in these experiments, an Au film was deposited on a Si wafer, the wafer was heated to the growth temperature used for nanowire growth in the tube furnace, then cooled and examined using atomic force microscopy (AFM). Figure 1 shows an AFM scan taken with a Digital Instruments microscope of an Au film after annealing at 420° C. Au nanoparticle diameters were 46 +/- 17 nm, and particle density on the surface was 3.7 x 10^{10} particles/cm^2. Silicon nanowire diameters are typically several nm larger than the size of the Au nanoparticles used to nucleate and control the growth in the VLS process [6]. The length of the nanowires used in these experiments was 5-10 µm, produced during a 15 min. growth period in the furnace. The length varies between individual wires, with some dependence on wire diameter.

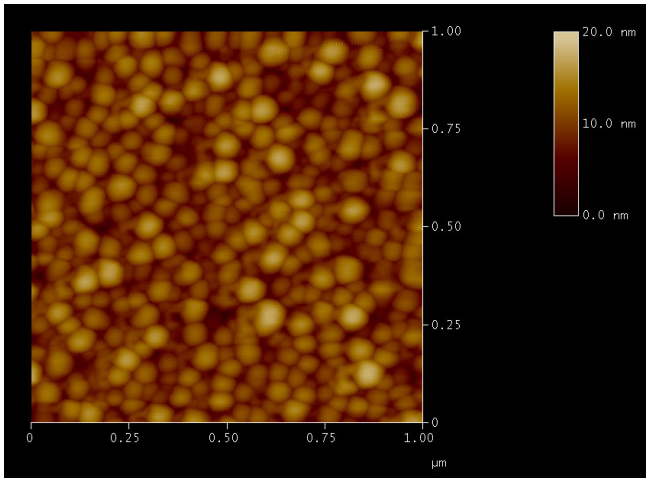

Figure 1. AFM image (tapping mode) of Au nanoparticles on a silicon surface following anneal at 420° C.

The silicon nanowires used in these experiments were single crystalline material with a principle growth axis along the (111) direction, as shown in the HRTEM image in figure 2. The wire tips are typically terminated with Au, and the edges of the wires have an amorphous SiO_2 layer approximately 4 nm thick. To provide better junctions between the n-type nanowires and the p-type organic semiconductor used to create the p-n heterojunction, the oxide was etched in buffered HF immediately prior to placing the nanowire samples in a nitrogen glove box for device fabrication.

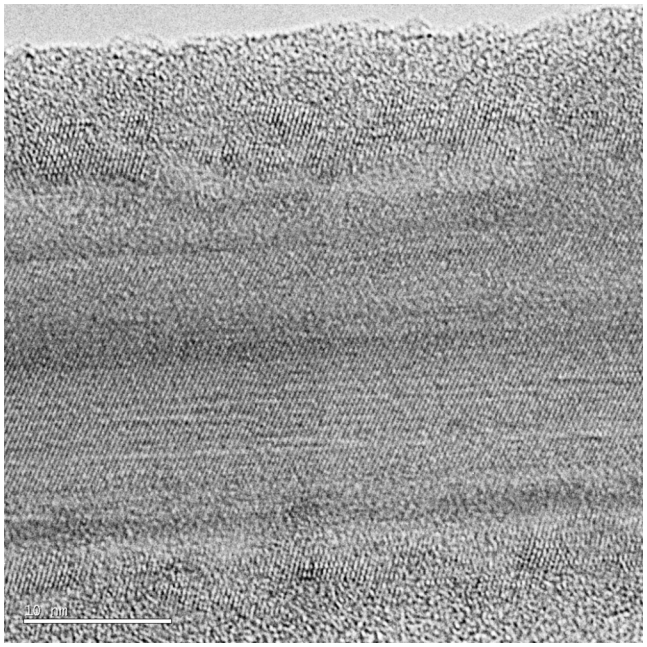

Figure 2. HRTEM image of silicon nanowire showing crystalline core and 3-4 nm amorphous oxide at the edges of the wire.

Quantum effects are important in small silicon nanowires, increasing the bandgap and causing the lowest energy transition to be direct. However, both theory and experiment have shown that these effects are only important for wire diameters below approximately 8 nm [7,8]. Thus the wires used in these experiments, with an average diameter of nearly 50 nm, behave essentially like bulk silicon as far as electronic transitions are concerned. However, the area of the heterojunction is considerably larger than would be the case for planar devices without nanowires. For the wire parameters discussed above, the area increase is approximately 2 x 10^4 greater than for a planar device. The random orientation of wires has the additional benefit of trapping more light than would a planar or textured surface.

3 ORGANIC-INORGANIC DEVICES

For this work we chose to use regioregular poly(3-hexylthiophene) as the p-type organic semiconductor at the heterointerface due to its high carrier mobility and low bandgap (2.0 eV) compared to other polymeric semiconductors. The interface between silicon and organic semiconductors has been investigated by a number of groups [9-11]. The heterojunction between n-Si and RR-P3HT was found to be a nearly ideal diode with a rectification ratio of greater than 10^3 [10]. Due to the fact that the nanowires used in this study were grown on an opaque n-Si wafer, the contact to the P3HT was made using a transparent ITO conductor on glass. Poly-[3,4-(ethylenedioxy)-thiophene]: poly-(styrene sulfonate) (PEDOT:PSS) has been widely used as a hole transport layer [1], and was used in our devices between the P3HT and ITO electrode.

The structure of the devices fabricated for this study is shown in figure 3. Briefly, nanowires were first grown on an n-type silicon substrate, and transferred to a nitrogen glove box following a brief (10 sec.) HF etch to remove surface oxide. PEDOT:PSS (Bayer Baytron P) was spin coated onto glass with a thin transparent electrode of sputtered ITO and also transferred to the glove box. Several drops of a solution of P3HT in chlorobenzene (5 g/l, deoxygenated by nitrogen bubbling) were applied to the surface of the PEDOT-PSS film, and the n-Si nanowire sample was placed face-down on top of the transparent electrode. The P3HT film was allowed to evaporate slowly over several days, then the sandwich was annealed for 1 hr. at 100° C to allow the P3HT film to form an oriented layer [12]. The device was then sealed with epoxy and removed from the glovebox for testing. Contact to the n side of the cell was made by scratching the back surface of the n-Si wafer to remove oxide and applying a Ga contact; contact to the p side was made by soldering a wire to the ITO using In-alloy solder.

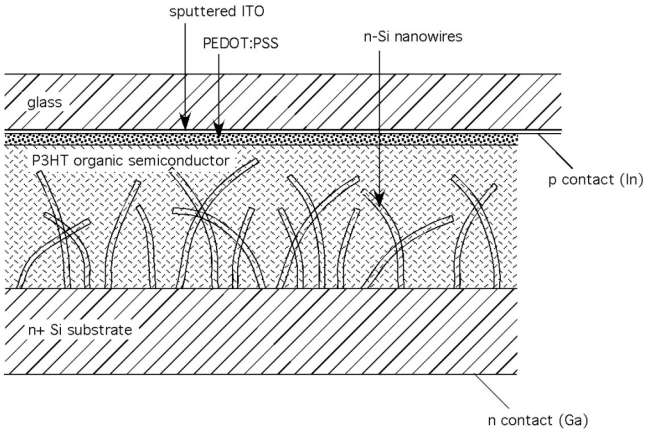

Figure 3. Diagram of the silicon nanowire PV cell structure (not to scale).

Energy levels relative to the vacuum level are shown in figure 4 for the components of the photovoltaic cell (without any adjustments for dipole formation or band bending due to Fermi levels). The HOMO of P3HT is positioned to inject holes into PEDOT-PSS and hence into the ITO electrode, and should accept holes generated by light absorption in the silicon nanowires. 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 Ga electrode.

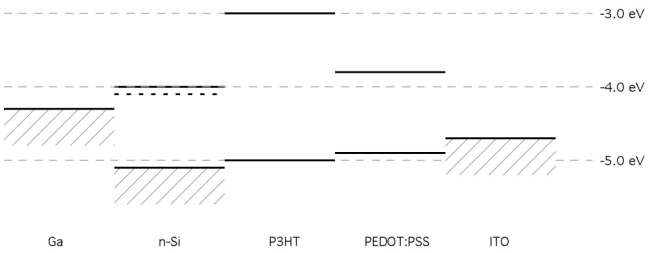

Figure 4. Energy levels of components of the cell.

Diode characteristics were observed for the assembled devices (figure 5). However, a relatively high leakage current was observed in the reverse direction. A likely suspect for this is nanowire penetration of the P3HT and possibly PEDOT:PSS layers during drying of the P3HT layer due to hydrostatic forces. Another possibility for high currents through the device is degradation of the P3HT polymer through exposure to oxygen. Although materials were handled in a nitrogen glove box and encapsulated prior to testing, this failure mechanism is well known for P3HT devices [13]. There may also be carrier recombination at the heterointerface, although P3HT heterojunction devices have been fabricated with very high internal quantum efficiency and low recombination [14].

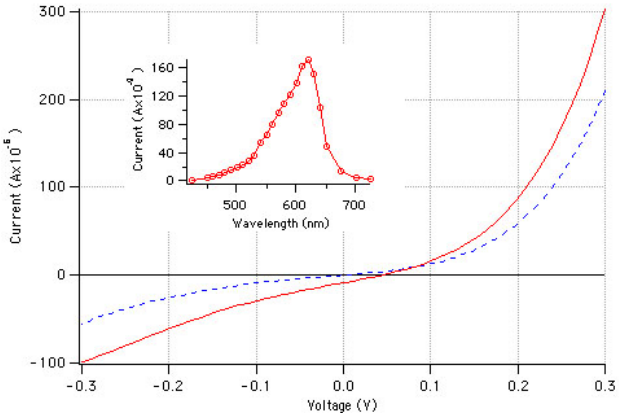

Figure 5. IV curve for silicon nanowire PV cell under 100 mW/cm^2 illumination (solid line) and dark (dashed line). Inset shows photoresponse as a function of wavelength.

The peak in photoresponse of the cell is at 600 nm (figure 5 inset). Since the absorption peak of P3HT is between 500 and 550 nm (2.0 eV bandgap), a substantial fraction of the photovoltaic response must be due to absorption in the silicon nanowires.

Open circuit voltage for the initial set of devices (0.05 V) are lower than expected, due most likely to a low shunt resistance in the cells. High dark currents in the devices indicate that conduction barriers are not present. Oxidation of the Si nanowire surface would limit currents to lower values than those observed.

Low short circuit photocurrents in the devices fabricated (J_{sc} = 5 x 10^{-6} A/cm^2 at 100 mW/cm^2 illumination) are likely due to the assembly method chosen, which requires a thicker layer of P3HT than would be optimal. Carrier mobilities are rather low in P3HT, and holes generated in the silicon nanowires must be transported across the P3HT film to the ITO electrode. For light absorbed in the P3HT layer, excitons are generated which must diffuse to a heterojunction for dissociation and collection. Hence the layer thickness should be kept very thin (~10 nm) to permit eciton diffusion and carrier collection. We are exploring alternate geometries such as a thin film coating of P3HT over the nanowires and a thicker PEDOT:PSS layer for charge transport to improve device efficiency.

4 CONCLUSIONS

Photovoltaic cells using heterojunctions of n-type silicon nanowires and P3HT organic semiconductor have been assembled and tested. The cells show evidence of carrier generation in both the silicon and polymer sides of the heterojunction. The first cells constructed have low V_{oc} and I_{sc}, but the geometry shows promise for both high light absorption and efficient carrier transport to electrodes. Efforts are underway to modify materials parameters

(nanowire doping, polymer thickness, and charge transport layer composition) to improve device characteristics.

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