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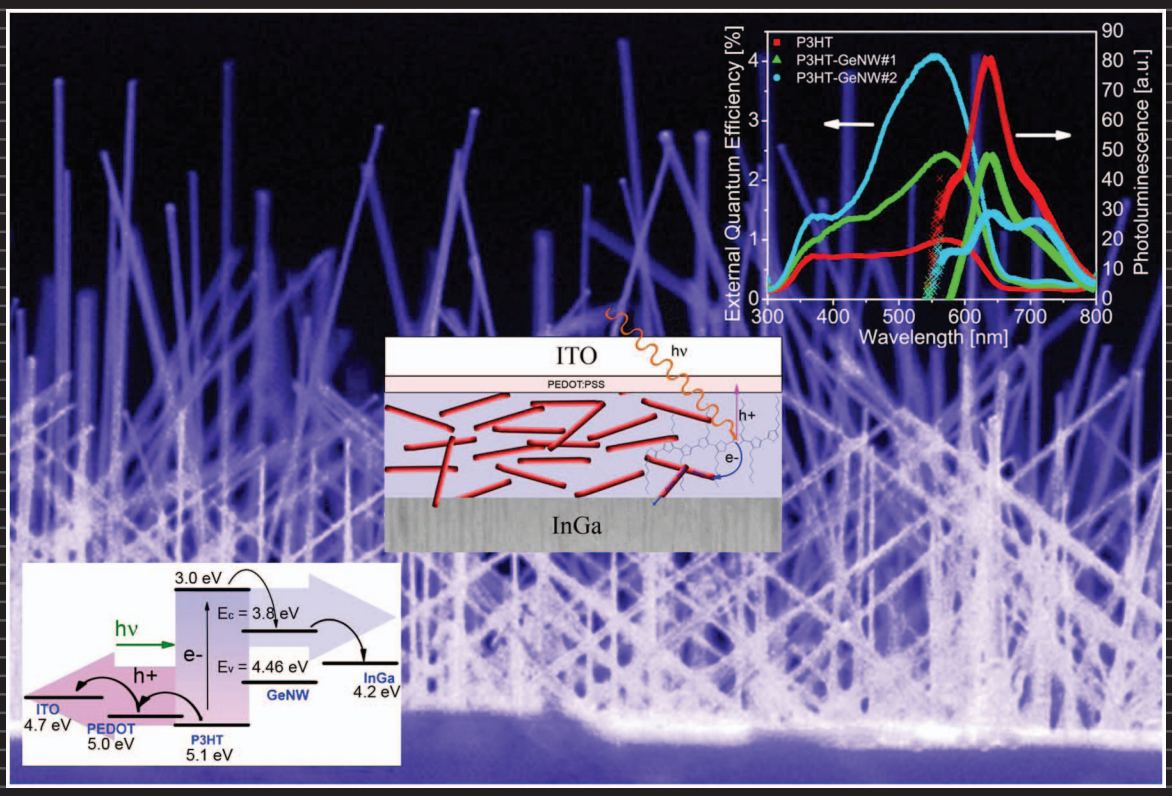

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Photoinduced charge transfer between poly(3-hexylthiophene) and germanium nanowires

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Germanium nanowires (GeNWs) were used to enhance the properties of organic photovoltaic devices. GeNWs were grown to a length of 1–5 μm on SiO_2 by the vapor-liquid-solid method catalyzed by 20 nm Au seeds. Once grown, the GeNWs were dispersed in solution with poly(3-hexylthiophene) and spin cast into films. The photoluminescence and external quantum efficiency of the films indicated a significant increase in exciton dissociation and photocurrent generation. The results imply that the GeNWs may act as an electron acceptor for bulk heterojunction hybrid-inorganic/organic photovoltaic devices. The impacts of GeNW on device characteristics are discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2801554]

Although silicon solar cells dominate the current market, much research and significant progress has been made in a range of other photovoltaic materials and device structures. One approach seeks to develop the highest possible efficiency multijunction devices (likely at a high cost). To date the most efficient device of this type is a multijunction inorganic cell developed by Spectrolab with an efficiency of 40.7%.[1] At the other end of the spectrum are large area low cost (relatively low efficiency) organic-based photovoltaics that can be processed into flexible thin films on an industrial scale. A subset of this category is semiconducting polymer-based solar cells, where one of the most investigated is poly(3-hexylthiophene) (P3HT). The combination of P3HT and 1-(3-methoxycarbonyl) propyl-1phenyl-(6,6)-C_{61} (PCBM, a functionalized fullerene) in a bulk heterojunction configuration affords a power conversion efficiency of approximately 5%.[1]

The organic bulk heterojunction of P3HT:PCBM facilitates the separation and diffusion of charge carriers to their respective electrodes. A photon is absorbed by the P3HT creating an exciton that diffuses to the interface between the two bulk components and dissociates. PCBM with a higher electron affinity is the electron acceptor while the hole remains within the P3HT.

An alternative to PCBM and other fullerene derivatives are inorganic semiconducting nanowires. Nanowires are structures with widths on the order of 5–100 nm and lengths that can that can readily and controllably be grown to lengths of tens of microns. ZnO,[2,3] CdSe,[4] Si,[5] and TiO_2 (Ref. 6) nanowires have been utilized within the polymer active layer of organic photovoltaic devices and other more complex NW structures have been proposed based on first principles calculations.[7] In this role, one of the key benefits of nanowires over fullerenes is their one-dimensional nature which can provide a rapid transport path for charge carriers. As we go to press, a very interesting paper has appeared in print by Lieber and colleagues using an all inorganic core-shell Si nanowires as a solar PV structure.[8]

The use of germanium in photovoltaics is already well known as it is an important component of multijunction concentrator solar cells.[9–12] Initially, Ge was used to replace GaAs as the substrate for solar cells on satellites.[13] Currently, Ge is commonly employed within the base junction or subcell as an active layer to harvest low energy photons. With a bandgap of 0.66 eV, Ge is active within the infrared portion of the solar spectrum. In a GaInP/GaAs/Ge triple junction, the germanium is responsible for ~10% or more of the solar cell's efficiency[14] and is capable of generating more short circuit current (J_{sc}) than the other two subcells combined.[15]

In this letter, we discuss the integration of germanium nanowires (GeNWs) into a P3HT-based solar cell. The schematic structure and energy diagram for this system are shown in Figs. 1(a) and 1(b), respectively.

The GeNWs were first grown to a length of 1–5 μm on SiO_2 using the vapor-liquid-solid[16,15–19] method from 20 nm Au seeds (Ted Pella). Next, the wires were dispersed in chlo-

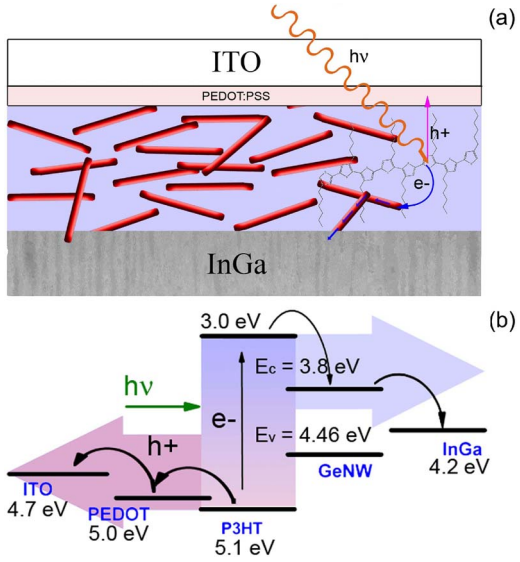

FIG. 1. (Color online) (a) Simplified device structure and (b) energy band diagram for P3HT-GeNW bulk heterojunction solar cell.

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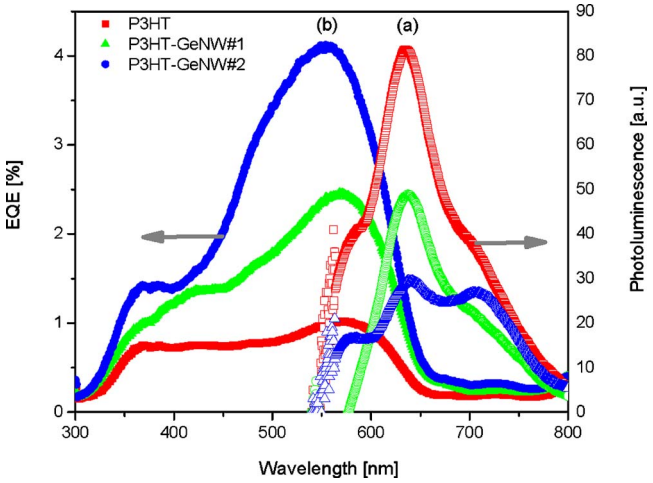

FIG. 2. (Color online) Room temperature (a) photoluminescence from 500 nm excitation and (b) external quantum efficiency of photon-to-electron conversion of pure P3HT and P3HT+GeNW films spin coated on ITO.

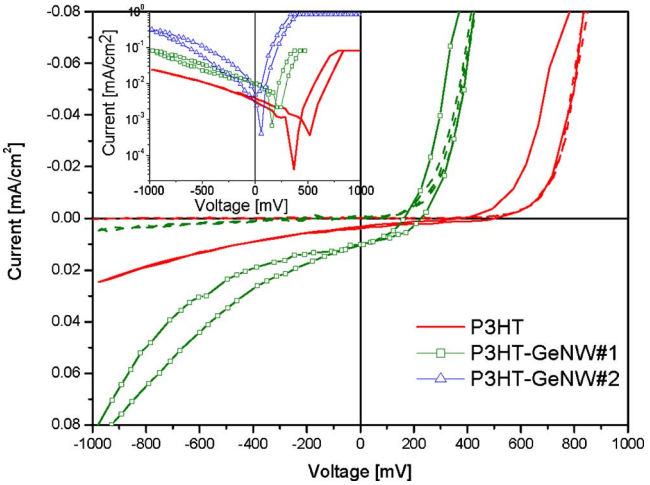

FIG. 3. (Color online) *I-V* curves in the dark (dashed) and under 100 mW/cm^2 (solid) halogen light for pure P3HT and P3HT+GeNW 1 film formed by spin coating on ITO. In the inset is shown a semilog *I-V* plot under illumination for P3HT, P3HT+GeNW 1, and P3HT+GeNW 2.

roform by sonication and mixed with 0.5 ml of a P3HT solution (10 mg/ml in chloroform) by 50 μl increments. The solutions were spin coated (50 μl at ~1500 rpm) on indium tin oxide (ITO)/glass (Delta Technologies, 15 Ω sq^{-1}) precoated with ~50 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS). Samples P3HT-GeNW 1 and 2 contain 50 and 200 μl of GeNW solution, respectively. Absorption spectra in the 250–950 nm range (not shown) had a maximum at 520 nm, attributed to P3HT.[20] In our P3HT-GeNW composites, no absorption related to GeNW was observed, owing to its low bandgap. The only visible change was a slight redshift of the P3HT absorption shoulder. This is usually attributed to π-π stacking in closely packed crystalline P3HT domains.[21] Thus, one interpretation of the change in absorption is that mixing with Ge nanowires induces enhanced crystallinity in the P3HT. Photoluminescence of the samples was measured at room temperature with monochromatic 500 nm excitation and an Ocean Optics S2000 diode array detector.

Although Ge displays photoluminescence at low temperature, it is strongly attenuated at room temperature.[22] Thus, the photoluminescence observed in our room temperature studies is most likely due to P3HT, in agreement with other studies.[23] A significant quenching of the photoluminescent yield is observed in samples containing GeNWs [Fig. 2(a)]. It was observed that the quenching increased when the P3HT/GeNW solution was sonicated prior to spin coating. This observation is consistent with a better dispersion of the GeNW in the P3HT. The dispersion may be improved by shortening of the GeNWs through prolonged sonication. The photoluminescence quenching indicates that excitons generated in the P3HT upon illumination at 500 nm do not recombine radiatively in the presence of GeNWs. Instead, a fraction of the excitons is dissociated at the P3HT-GeNW interface, enhancing the fraction of free electrons and holes capable of generating a photocurrent.

Next, the external quantum efficiency (EQE) of photocurrent generation was measured in the 300–800 nm range with a monochromator, chopper, and detected via a lock-in amplifier [Fig. 2(b)]. Electrical contacts were made to the top of the P3HT-GeNW films with a GaIn eutectic. This eutectic, with a work function of 4.2 eV, is well suited for extracting electrons from GeNWs, as illustrated on the band diagram [Fig. 1(b)]. The device area was constant, and imposed by the size of the illumination spot (~1 mm). An EQE of 1.4% was measured in pristine P3HT, while 2.2 and 4% were measured at 550 nm in samples P3HT-GeNW 1 and 2, respectively. This is consistent with the light quenching data, indicating that percolation pathways for holes and electrons to the electrodes are created within the bulk heterojunction. Although these numbers are not good from an absolute perspective (these are very simple nonoptimized devices), they do show that there are some promises for improvement in device properties when GeNWs are included. Our data are consistent with a model in which the electron transport is enhanced by the presence of the GeNWs, without significant trapping of the holes in the Ge or interface.

Finally, *I-V* curves were recorded under illumination of a halogen light source, of intensity equivalent to 100 mW/cm^2 of AM 1.5G simulated sunlight. In the presence of GeNWs, the forward current was significantly increased, but the devices still had a good diode characteristic in the dark, with little reverse current down to −1 V. This is consistent with the observation that as-prepared the GeNWs are intrinsically *p*-type semiconductors, by enhancing the overall conductivity of the system. A reduction in open-circuit voltage and an increase in short-circuit photocurrent are observed when GeNWs are mixed with P3HT (Fig. 3). It must be noted that no passivation treatment was performed on the GeNWs in this set of experiments. Based on the work of others, the nanowires should be covered with a native GeO_x layer under our experimental conditions, i.e., exposed to ambient environment after growth. Wang *et al.* have shown by x-ray photoemission spectroscopy[24] that such an oxide layer results in band bending of the Ge that increases the work function in *p*-doped GeNW, which would logically result in a reduction of open-circuit voltage. Indeed, the open-circuit voltage in bulk heterojunction solar cells can be approximated as highest occupied molecular orbital $(HOMO)_d$-lowest unoccupied molecular orbital $(LUMO)_a - 2(0.2)$ V to account for losses at electrodes.[25] If we take the HOMO level of P3HT as 5.1 eV and the E_c of the GeNW as 3.8 eV, then the theoretical open circuit voltage should be $5.1-3.8-0.4=0.9$ V. Another sign of the presence of GeO_2 is the hysteresis. This indicates charging and discharging of defects in the dielec-

tric. Similar hysteresis has been observed in field effect transistors built with Ge nanowires[26] and was attributed to water adsorption at the surface of oxidized Ge. The hysteresis could be suppressed with passivation of the nanowires by reaction with various species, including thiols.[27]

In conclusion, we have shown that photoinduced charge transfer in P3HT-GeNW bulk heterojunctions can be observed. The photoinduced charge transfer is evidenced by the inverse correlation between the photoluminescence quenching and the external photocurrent quantum efficiency. This resulted in quadrupling of the EQE of P3HT (under our conditions). However, the *p*-type conductivity and native oxide layer of GeNW resulted in a low open-circuit voltage and photocurrent. The reduction of the open-circuit voltage is consistent with band bending of the nanowires caused by the GeO_2 surface oxide. Contact optimization, *n* doping, and surface treatments of the GeNWs, as well as other material and structural optimization, are expected to improve these results, and are currently underway.

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