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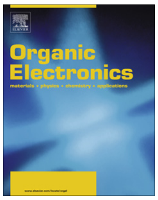

Orientation effect on GaAs/ultrathin polymer/PEDOT:PSS hybrid solar cell

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ABSTRACT

The surface orientation of inorganic semiconductors affects the density of surface states, energy levels, and other intrinsic properties of the semiconductor, all of which would have an impact on the performance of related polymer/inorganic hybrid solar cells. With a set of conjugated polymers having different energy levels and band gaps (P3HT, PNDT-DTffBT, and PBnDT-DTffBT), we show that the photovoltaic behavior of GaAs/ultrathin polymer layer/PEDOT:PSS planar solar cells is noticeably affected by the surface orientation of n-GaAs, (111)B or (100). In all of these hybrid solar cells, a Schottky barrier is formed between the GaAs and the anode, with these ultrathin polymer layers serving as the electron blocking layer (EBL) and the hole transport layer (HTL). The lower density of surface states of GaAs(111)B helps reduce the surface recombination and results in a higher short circuit current for (111)B based hybrid solar cells than for (100) based ones. However, the higher valence band maximum (VBM) of (111)B compared to that of (100) could lead to increased recombination from blocked hole transport, if the highest occupied molecular orbital (HOMO) level of the HTL polymer is lower than the VBM of GaAs. Considering all these effects, P3HT stands out as the best polymer to pair with GaAs in the studied set, with an efficiency of 4.2% achieved for the device based on P3HT/GaAs(111)B.

1. Introduction

Gallium arsenide (GaAs), a III–V semiconductor, has been actively explored as a desirable candidate to construct high-efficiency inorganic solar cells. However, the steep price associated with inorganic GaAs cells also precludes their large-scale adoption as an energy generation alternative. With the hope of lowering the cost and achieving higher efficiencies, GaAs based organic/inorganic hybrid solar cells (which are promising due to the material's attractive features including a direct band gap, high absorption coefficient, and excellent charge carrier mobilities [1,2]), have been attempted, although only in sporadic but notable reports [3–5]. While significant progress has been made in boosting the efficiency via nanostructures, (e.g., over 9% has been achieved with vertically aligned GaAs nanowires blended with poly(3-hexylthiophene), i.e., P3HT) [6], efficiencies are still lower than those of hybrid solar cells based on Si (13.8% has recently been achieved) [7]. Indeed, the operating mechanisms for these hybrid cells are still under active investigation. For example, a recent study indicated that GaAs nanowires coated with semiconducting polymers form a type II heterojunction if appropriate alignment between the band of GaAs and that of the polymers is established [8]. On the other hand, we recently demonstrated that a planar heterojunction of polymer/n-GaAs(100) operates via the Schottky barrier formed between the n-GaAs and its corresponding anode, instead of the previously assumed type II heterojunction [9]. Additionally, we showed that the surface passivation of GaAs(100) in our planar junctions of polymer/

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n-GaAs(1 0 0) can noticeably improve the device performance. However, such surface passivation has an almost negligible effect on the efficiency of the planar junction of GaAs(1 1 1)B, as we disclosed in another report [10], presumably because GaAs(1 1 1)B has fewer surface states than GaAs(1 0 0). Interestingly, a much higher efficiency was obtained from the planar junction of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (i.e., PEDOT:PSS)/GaAs(1 1 1)B (with or without surface passivation) than that of the PEDOT:PSS/GaAs(1 0 0) (surface passivated) [10]. Soci and co-workers also found that GaAs(1 1 1)B tends to promote increased hole transfer from its valence band states to the highest occupied molecular orbital (HOMO) of the polymer (P3HT) compared to GaAs(1 1 0) surfaces [11]. Together, these recent results clearly indicate that the efficiency of GaAs/polymer hybrid solar cells would highly depend on the GaAs surface orientation, an interesting discovery that warrants further investigation. In this article, we intend to complement our previous study on polymer/GaAs(1 0 0) by focusing on the planar junction of polymer/GaAs(1 1 1)B. For fair comparison, an identical set of polymers were chosen, including P3HT, poly(benzodithiophene–dithienyldifluorobenzothiadiazole) (i.e., PBnDT-DTffBT) [12], and poly(naphthalenedithiophene–dithienyldifluorobenzothiadiazole) (i.e., PNDT-DTffBT) [13].

2. Experimental details

The original device configuration in our previous report [9], PEDOT:PSS/polymer/n-GaAs, was also maintained. All devices were fabricated following a similar fabrication procedure [9], briefly described as follows. Si-doped n-type GaAs(1 1 1)B wafer with a carrier concentration of $1–5 \times 10^{18}\ \mathrm{cm}^{-3}$ (Semiconductor Wafer Inc.) and an annealed AuGe/Ni/Au back ohmic contact were cleaned by dipping in acetone and isopropanol sequentially for 5 min each. The cleaned GaAs wafer was then immersed in aqueous HCl (10% v/v) solution for 30 s to remove the native oxide. Subsequently, the GaAs wafer was passivated by immersing in a 30 mM ethanolic solution of 1-octanethiol for 5 h and then further passivated by soaking in a 22 wt% aqueous ammonium sulfide solution for 15 min. Next, a hot polymer solution in o-dichlorobenzene was spin coated on top of the passivated GaAs wafer at 1700 RPM for 1 min to deposit a thin polymer film on GaAs. Such a GaAs/polymer heterojunction was kept in a sealed petri dish for overnight to slowly dry up the solvent. The thickness of this active polymer layer is about 10 nm, measured by a profilometer (Alpha-Step D-100 Stylus Profiler, KLA-Tencor) and confirmed by ellipsometry (J.A. Woollam VASE). In the meantime, a 5% DMSO-doped PEDOT:PSS (Clevios™ PH500) was further mixed with Zonyl FSO-100 surfactant (Sigma–Aldrich, 5 mg Zonyl FSO-100 in 1 ml doped PEDOT:PSS) for better adhesion to the polymer layer. The PEDOT:PSS was then spin coated onto the GaAs/polymer junction at 2500 RPM for 1 min. Separately, the 5% DMSO doped PEDOT:PSS was also spin coated on top of a pre-cleaned ITO glass at 1200 RPM for 10 s. With the PEDOT:PSS layer on ITO glass being still wet, the previously fabricated PEDOT:PSS/polymer/GaAs substrate was put face down on top of this PEDOT:PSS coated ITO substrate to complete the device fabrication with PEDOT:PSS serving as the "adhesion" layer. The entire device (ITO/PEDOT:PSS/polymer/GaAs/cathode) was then dried in a vacuum oven at room temperature for 3 h, followed by thermal annealing inside of the glove box at 110 °C for 30 min. The photovoltaic performance characterization of finished devices was conducted under one sun condition (AM1.5, 100 mW/cm^2, calibrated by a NREL certified standard silicon cell) at room temperature in a nitrogen purged glove box. The active area was determined by directly measuring a photograph of the entire device. The incident photon-to-current conversion efficiency (IPCE) measurement was carried out under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with an Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode. The samples of GaAs(1 1 1)B and (1 0 0) for ultraviolet photoelectron spectroscopy (UPS) were prepared in the same way as the GaAs substrate used in the hybrid solar cells, i.e., removing the native oxide and performing the two-step passivation.

3. Results and discussion

It has been found that surface passivation can largely reduce the density of surface states and lower surface non-radiative recombination [14]. The lower density of surface states would also reduce the Fermi level pining effect, to enhance the built-in electrical field in the solar cell, leading to higher open circuit voltage [9]. Although the previous theoretical study showed that for a GaAs(1 1 1)B surface, the passivation would not significantly improve the power conversion efficiency [10], we still performed the two-step passivation for a better comparison. Our previous results showed that thermal annealing improves the morphology of the ultrathin polymer layers in the GaAs(1 0 0)/polymer hybrid devices, achieving enhanced charge transport. Therefore, thermal annealing was also performed for the devices based on GaAs(1 1 1)B. Because of the significantly higher carrier mobility of GaAs than those of our polymers, the smaller mobility difference between GaAs at different crystalline orientations should not lead to a significant difference in performance, and was therefore ignored. We compared the device performance of the solar cells with an approximately 10 nm layer of polymer on both GaAs(1 1 1)B and (1 0 0) surfaces.

Fig. 1 presents the *J*–*V* curves of solar cells of ITO/PEDOT:PSS/polymer/GaAs(1 1 1)B under illumination and in the dark. The corresponding curves under illumination for solar cells based on GaAs(1 0 0) surface are also shown in Fig. 1 for comparison (re-plotted from Ref. [9]). The details of the performance of all devices are also listed in Table 1.

Interestingly, different polymer/GaAs devices respond differently as the GaAs surface orientation is switched from (1 0 0) to (1 1 1)B. For example, the short circuit current (J_{sc}) of cells based on P3HT or PNDT-DTffBT/GaAs(1 1 1)B is significantly higher than the J_{sc} of corresponding cells on GaAs(1 0 0), thereby resulting in higher efficiencies for cells