Nano Energy (2015) **13**, 509–517

Available online at www.sciencedirect.com

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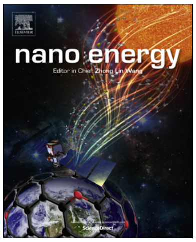

RAPID COMMUNICATION

Tunable graphene/indium phosphide heterostructure solar cells

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Received 4 January 2015; received in revised form 5 March 2015; accepted 12 March 2015
Available online 23 March 2015

KEYWORDS
Graphene;
Indium phosphide;
Schottky junction;
Solar cells

Abstract
Graphene based van der Waals heterostructure has attracted wide attention recently, especially for graphene/semiconductor Schottky junction. Herein, through delicately designing and engineering the van der Waals heterostructure between graphene and indium phosphide (InP), which has a suitable bandgap of 1.34 eV for solar energy conversion, we have achieved graphene/p-InP solar cells with power conversion efficiency (PCE) of 3.3% under AM 1.5G illumination. The chemical doping or electrical field modulation has been used to tune the Fermi level of graphene, which leads to a PCE of 5.6% for the device under gating effect. Furthermore, the interface recombination rate could be reduced while graphene is doped or gated, as evidenced by transient photoluminescence measurements. Considering the stability of cell performance under illumination and the high resistance to space irradiation damage of InP, graphene/InP heterojunction may be promising for special applications such as space solar cells.

Introduction

Graphene is the first discovered two-dimensional atomic crystal with honeycomb lattice structure, which combines many supreme parameters: high electron mobility of $\sim 1\times10^5\ \mathrm{cm^2/V/S}$ [1], intrinsic mechanical strength of 130 GPa [2] and optical transmittance of 97.7% with wide spectrum range [3], holding great

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http://dx.doi.org/10.1016/j.nanoen.2015.03.023
2211-2855/

potentials to revolutionize electronic and optoelectronic applications. Moreover, the Fermi level of graphene is highly tunable [4-6]. Recently, other two-dimensional atomic crystals have attracted worldwide attention, such as hexagonal boron nitride [7-9], transition metal dichalcogenides [10,11]. In parallel with the efforts on graphene-like materials for potential components in electronic [12,13] and optoelectronic [14,15] devices, the heterostructures based on stacking of different two-dimensional crystals have gained close attention [16,17]. The atomically thin van der Waals heterojunction can behave as a diode and exhibit a photovoltaic effect [18,19], however, the power conversion efficiency (PCE) of corresponding photovoltaic device is relatively low (~0.2%, [18]) attributed to the low light absorbance, limiting its solar energy conversion applications.

The heterostructures based on graphene and bulk semiconductor Schottky junction offer a new platform for solar cell applications [20-22]. Since Si is the dominated material in the current photovoltaic applications, much attention has been paid on the graphene/Si Schottky junction solar cells [23-25]. Compared with the widely used Si, indium phosphide (InP) has a direct bandgap of 1.34 eV, which locates at the optimum energy range for solar energy conversion [26]. InP is a promising material for high conversion efficiency solar cells, including InP-based homojunction [27] and heterojunction [28] solar cells. In addition, InP solar cell exhibits higher resistance to space radiation damage than Si and GaAs solar cells [29], thus InP based solar cells may be promising for space applications. Regardless of its high importance, graphene/InP Schottky junction solar cells have not been investigated. On the other hand, the low density of states near the Dirac point of the electronic band of graphene promises its Fermi level highly tunable, where doping technique such as extrinsic dopant decoration or gating effect can play significant role which has not been thorough explored yet. Herein, we point out that graphene/InP Schottky junction could be a candidate for solar cells, as PCE of 5.6% has been achieved by gate doping of graphene layer, although not fully optimized. Moreover, thin film InP could be a substrate for graphene based flexible solar cells.

Experimental

Single layer graphene was grown on copper substrate by low pressure chemical vapor deposition (CVD) method in a quartz tube furnace [30]. The growth was carried out at 1000 °C for 30 min using CH_4 and H_2 with a flux ratio of 3:1. After growth, the furnace was cooled to room temperature with a cooling rate of ~30 °C/min. The p-type (100) InP wafer with a hole concentration of $2\times10^{18}\,\text{cm}^{-3}$ was used as the substrate. After chemically cleaned in acetone and isopropanol, the native oxide of InP wafer was deliberately removed by dipping into $HCl:H_2O$ (1:3) solution for 3 min. 60 nm SiN_x was deposited on the single-face polished InP substrate by plasma-enhanced CVD equipment. The enclosed region (10.0 mm^2) on the SiN_x film defines the active area using photolithography mask method. Graphene was transferred onto the InP substrate by the PMMA supporting technique [31]. 60 nm Au was thermally evaporated on the rear surface of the InP wafer to form low resistance contact. Ag paste was coated on the graphene surface, followed by an annealing of 120 °C for 10 min. A reduced viologen (1,1′dibenzyl-4,4′-bipyridinium dichloride) solution of 10 mM in toluene was spin—coated on graphene for n-type doping [32]. In addition, gate structure was introduced into the graphene/p-InP solar cells. As for the graphene/InP Schottky junction, an extra insulation layer (Al_2O_3, 40 nm) by atomic layer deposition system was used as the gate dielectric layer on the active region of the solar cells. Another layer of graphene transferring onto the Al_2O_3 dielectric surface with Ag contact was used as the gate electrode.

The graphene used in this study was characterized by optical microscope (ZEISS, AX10) and Raman spectroscopy (Renishaw, InVia-Reflex) with the excitation wavelength of 532 nm. Transient photoluminescence (PL) measurements were used to evaluate the charge recombination and separation behaviors at graphene/InP interface. The excitation light source (PicoHarp 300 system) was a 450 nm pulsed laser with 1 MHz repetition rate and 50 ps pulse duration with power of 10 μW. The diameter of the excitation laser spot was 10 μm. The PL signal was collected by a multimode optical fiber and recorded by a Horiba Jobin Yvon iHR550 spectrometer. All spectra were collected until the peak value reaching 3000 counts. The current-voltage data of the solar cells were recorded using Keithley 4200 and Agilent B1500A system, together with a solar simulator (NBeT, solar-500) under AM 1.5G condition at an illumination intensity of 100 mW/cm^2, calibrated by a standard Si solar cell. External quantum efficiencies (EQE) of the graphene/InP solar cells were measured with PV Measurements QEX7 system.

Results and discussion

The schematic structure of the graphene/InP solar cell and a typical digital photograph of solar cell are illustrated in Fig. 1a and b, respectively. The solar cell is based on the graphene/p-InP van der Waals heterostructure. A Schottky junction is formed induced by the work function difference between graphene and InP substrate, which collects electrons and holes while light illuminates the junction, respectively. The area of active region is 10.0 mm^2 as measured by optical microscope. Fig. 1c shows the Raman spectrum of CVD-grown graphene transferred on Si/SiO_2 substrate. Typical features of single layer graphene can be observed, with an intensity ratio of G peak and 2D peak $I_{2D}/I_G=3.1$. It is noteworthy that the D peak of as-grown graphene is very weak, indicating high quality of the graphene. Fig. 1d shows the current density (J) versus voltage (V) curves of graphene/p-InP solar cell in the dark and under 1 sun AM 1.5G illumination condition. The dark J-V curve exhibits rectifying characteristics, indicating that a good graphene/InP Schottky junction is formed. Under illumination, the short-circuit current density (J_{SC}) of the graphene/InP solar cell with as-grown graphene becomes 20.6 mA/cm^2, and the open-circuit voltage (V_{OC}) and PCE achieve 0.49 V and 3.3%, respectively. Similar J-V curves of graphene/p-InP solar cells under AM 1.5G illumination condition can be seen in Supplementary Fig. S1.

Fig. 2a shows the J-V curves of graphene/p-InP solar cells with as-grown and doped graphene under AM 1.5G illumination condition. The corresponding optical micrographs of graphene before and after doping can be found in Supplementary Fig. S2. With doping, J_{SC} increases from 20.6 mA/cm^2 to 22.6 mA/cm^2, and V_{OC} is enhanced from 0.49 V to 0.55 V, together with the fill factor (FF) increasing from 0.33 to 0.37, leading to PCE improved from 3.3%