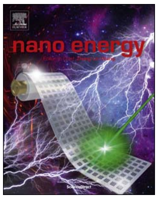
Nano Energy 28 (2016) 12–18

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen



Interface coupling in graphene/fluorographene heterostructure for high-performance graphene/silicon solar cells

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A R T I C L E I N F O

Article history:
Received 29 July 2016
Accepted 10 August 2016
Available online 11 August 2016

Keywords:
Graphene/silicon solar cells
Fluorographene
Doping
Interface

ABSTRACT

One-step approach for doping and interface engineering of the Gr/Si solar cells was realized by using the fluorographene(FG) as an insulator interlayer. Metal/insulator/semiconductor (MIS) like solar cells with a structure of Gr/FG/Si were composed. The F atoms of FG serve as electron acceptors and yield p-type doping, which is beneficial for improving the Schottky barrier. The carrier recombination of the solar cell can be effectively suppressed by the employment of the FG interlayer and the PCE of the solar cell increased from 3.17% to 7.52%. More interestingly, the performance of Gr/FG/Si solar cell can be further enhanced by applying a temporary voltage bias, which was likely associated with rotation of the C–F bonds or/and enhancement of the Gr/FG coupling in electrical field. A PCE up to 13.38% was achieved by combining the AR technology and chemical doping from the top-side of the Gr.

1. Introduction

Graphene (Gr), with novel properties like high-transparency and high-conductivity, [1,2] has attracted intensive interests in the fabrication of low-cost high-performance photovoltaic devices, including graphene/silicon (Gr/Si) solar cells [3]. In the past few years, much effort has been made on developing Gr/Si solar cells, [4–6] among which chemical doping technique is essential for obtaining large Schottky barrier height and high efficiency [7,8]. However, as the dopants are highly oxidative, the chemical doped Gr/Si solar cells usually suffer from fast degradation [9,10]. Another promising strategy is developing the chemical-doping-free Gr/Si solar cells which could be stable for months [9]. Unfortunately, the efficiency of such the solar cells is still low, which is mainly hampered by high resistance of the Gr films and low Schottky barrier of Gr/Si heterojunction [11,12]. Standing on this viewpoint, it is necessary to develop a facile and stable Gr doping technique for practical applications of Gr/Si solar cells.

Other than chemical doping, Gr doping can be achieved by using alternative technologies, including photo-induced doping by PbS quantum dots (PbS QDs) [13] and electrical-field doping by using a liquid gate circuit [14,15]. The former approach is not suitable for solar cells, since PbS QDs would cause much loss in incident light. And the liquid gated devices will suffer from the volatility of the incorporated liquid media, which cannot be used for practice [16]. Meanwhile, doping effect caused by strong interaction has been reported in various Gr-based heterostructures like MoO_3/Gr, [17] and MoF_6/Gr [18]. As no chemical reaction occurs, this technology provides a potential solution for stable Gr doping. Keeping this in mind, we herein explore interaction in graphene/fluorographene (Gr/FG) heterostructure aiming to develop the performance of Gr/Si solar cells.

Fluorographene (FG) is a new kind of Gr derivative with dipoles formed by the C–F bonds on the graphitic basal plane, which has been reported as one of the thinnest insulators [19]. It can be fabricated by exposing Gr to fluoride gases, and the electrical properties can be modulated by its C/F ratio [19,20]. Multiple computational researches have predicted the interaction between FG and other two-dimensional materials like graphene and MoS_2 [21–23]. For instance, the F atoms of FG serve as electron acceptors, which could generate charge transfer from the coupled 2D materials to the FG, and hence yield p-type doping [21]. Lin et al. have compared the optical properties of Gr on hexagonal boron nitride (*h*-BN) and on FG using density functional theory (DFT) [23]. The FG is superior in decoupling Gr from substates, which has been recently proved by Ho et al. [24] These unique properties make FG attractive for idealization of Gr/Si solar cells.

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http://dx.doi.org/10.1016/j.nanoen.2016.08.031
2211-2855/

In this study, an underside p-type Gr doping has been obtained in Gr/FG heterostructures, which is beneficial for improving the Schottky barrier of Gr/Si solar cells. Consequently, we propose a one-step approach for doping and interface engineering of Gr/Si solar cells by using the FG as an insulator interlayer, composing metal/insulator/semiconductor (MIS) like solar cells with a structure of Gr/FG/Si. The carrier recombination of the solar cells can be effectively suppressed by the employment of the FG interlayer, and the power conversion efficiency (PCE) of the solar cell increases from 3.17% to 7.52%. More interestingly, we find that the performance of Gr/FG/Si solar cells can be further enhanced by applying a temporary voltage bias, which is likely associated with rotation of the C–F bonds or/and enhancement of Gr/FG coupling in electrical field [21,22]. A PCE up to 13.38% has been achieved by combining the frequently-used TiO_2 antireflection coating [4] with HNO_3 chemical doping from the top-side of Gr. Such a high performance is comparable with the current records of Gr/Si solar cells [12]. These findings have shed new light on practical applications of Gr/Si solar cells.

2. Materials and methods

2.1. FG preparation, transfer and characterization

The monolayer Gr was grown by a copper-catalyzed low pressure chemical vapor deposition (LPCVD) method at 1000 °C using CH_4 (20 sccm) as the carbon source and H_2 (40 sccm) as the reduction gas. The fluorination of graphene was prepared in an inductively coupled plasma (ICP) system at room temperature using SF_6. The graphene samples were immersed in SF_6 plasma at 10 mTorr with power of 50 W and gas feed rate of 100 sccm for 10 min to obtain the single-side fluorinated graphene (FG).

Both the FG and Gr were transferred by the PMMA assisted wet transfer process. PMMA was spin-coated onto the surface of the Gr at 6000 rpm for 60 s, and curing at 90 °C for 5 min. Then, the Gr on the backside of the Cu foil was removed by an UV-ozone cleaning process for 10 min, the Cu foil was etched away using ammonium persulfate (1 M) aqueous solution. The film was rinsed in DI water several times followed by transferred onto the target substrate (Si or SiO_2), the PMMA was removed by successively soaking the samples in acetone, isopropanol and DI water for 5 min. Raman spectroscopy (SENTERRA Raman microscope, Bruker), X-ray Photoelectron Spectroscopy (XPS) were carried out to estimate the bonding states of carbon atoms in graphene after fluorination.

2.2. Device fabrication and characterization

To fabricate back-gated Gr/FG field-effect transistors, the FG layer and Gr layer were transferred to SiO_2 (100 nm)/n-Si (<0.01 Ωcm) substrates consecutively. Patterned Au electrodes (100 nm) were deposited by using thermal evaporation onto the Gr with a mask, which functions as the drain and source electrodes of FETs. The back contacts were formed by scratching InGa eutectic alloys. Transfer characteristics of the FETs were measured by a Keithley 2400 source meter in dark.

N-type <100> Czochralski Si wafers (300 μm thick) with resistivity of 1–10 Ω cm were used as substrates to fabricate the Gr/FG/Si solar cells. The Si wafers were cleaned by an ultrasonic cleaner in DI water followed by dipping in diluted HF (1:50, v-v) for several minutes to remove the native oxide. The resultant wafers are left in ambient for 1–2 h to newly form a thin native oxide. FG films was transferred onto the wafers and annealed in N_2 with a temperature of 150 °C for 30 min. Then, the sample was immersed in acetone for about 5 min to remove the PMMA coated on the FG. Monolayer Gr films (smaller than the FG) was then transferred right onto the FG. The front contact was formed by coating Ag paste along the edge of the Gr and the backside contact was formed by scratching InGa eutectic alloys on the rear surface of Si. The device active area was determined using black tapes about 0.09 cm^2. The Ag paste and the outside area were completely covered. Conventional Gr/Si solar cells were fabricated in the same way without introducing the FG at the Gr/Si interface. The TiO_2 antireflective coating (AR) was prepared according to the literature [4]. The chemical doping was performed by exposing the device to HNO_3 fumes for ~1 min. Since The Ag electrodes gradually turn yellow during prolonged HNO_3 doping process, the doping process should be carefully controlled to avoid severe oxidation of the Ag electrodes.

The photovoltaic performance of the solar cells were measured by using a Keithley 2400 source meter and calibrated by a standard Si solar cell (94,022 A, Newport®, AM1.5 G, 100 mW/cm^2). Microwave photo-induced conductance decay (MW-PCD) was used to obtain the distribution of effective carrier lifetime on samples. Capacity-voltage (*C-V*) measurements were performed by using a Keithley 4200-SCS semiconductor device parameter analyzer. The external quantum efficiency (EQE) spectra of solar cells were measured by an EQE measurement system (QEX10, PV measurement, Inc.) in the range of 350–1100 nm.

3. Results and discussion

Fig. 1(a) presents typical X-ray photoemission spectroscopy (XPS) spectra of our FGs. The C-1 s peak at 284.1 eV and the F-1 s peak (inset) at 689.1 eV demonstrate the formation of the C–F bonding states. The spectrum of the C-1 s core levels can be deconvoluted into three peaks, which denotes to C–C (284.1 eV), C–CF (285.6 eV) and C═O (287.9 eV) bonding states [19,20]. The C–F bonds fraction can be estimated from the XPS spectra and the resultant stoichiometric composition of the FG is $C_{4.42}F_1$. Such fluoridation is less intensive than those previously reported [24]. However, we found that a stronger fluoridation makes the FG more fragile, which will easily be damaged during the transfer process. Fig. 1(b) shows the Raman spectra of Gr and FG activated by 532 nm He-Ne laser. The characteristic G (~1588 cm^{-1}) and 2D (~2681 cm^{-1}) bands are observed in the spectrum of Gr (in black). The intensity ratio of 2D versus G peak is larger than 2, illuminating that the Gr is monolayer. The D band (~1350 cm^{-1}) is negligible, which indicates that our Gr is of high quality. The fluoridation process has been reported to introduce defects in Gr [24]. As a result, the Raman spectrum of FG (in red) emerged three peaks at ~1623 cm^{-1} (D′ peak), ~2450 cm^{-1} (D+D′ peak) and 2946 cm^{-1} (D+D″ peak) which are all associated with defect-related intra-valley scattering [25]. Meanwhile, the intensity of D band gets largely enhanced and that of 2D band gets decreased. These features are analogous to the formation of fluorine terminated carbon (sp^3) in FG [26,27].

Fig. 2(a) presents the schematic device structure of a Gr/FG/Si solar cell, in which there exists a FG interlayer in-between Gr and Si. Fig. 2(b) compares the current density-voltage (*J-V*) characteristics of Gr/Si solar cells with and without the FG interlayer under sunlight illumination. The open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}) and fill factor (*FF*) of the conventional Gr/Si solar cell are 350 mV, 25.3 mA/cm^2 and 35.7%, respectively, yielding a PCE of 3.17%. By contrast, the introduction of the FG layer in the solar cell results in the profound enhancement of photovoltaic performances. The values of V_{OC}, J_{SC} and *FF* are increased to 440 mV, 27.1 mA/cm^2 and 63.0%, respectively. As a result, the PCE of the Gr/FG/Si solar cell gets improved to 7.52%, which is twice higher than the Gr/Si device. Such a value is much higher than those of the best pristine Gr/Si solar cells in range of