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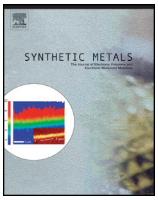

Organic solar cells with surface-treated graphene thin film as interfacial layer

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ABSTRACT

The effects of surface-treated graphene thin films on the performance of organic solar cells (OSCs) were systematically investigated for different surface treatments. Four different surface treatments were introduced for controlling the graphene work function and conductivity: annealing in argon ambient, dipping in acetone, ultraviolet irradiation, and nitrogen plasma treatment. The treated graphene films were utilized as interfacial layers between indium tin oxide electrodes and molybdenum oxide-based hole extraction layers in OSCs. The best performance was observed for the device that incorporated acetone-treated graphene, and was attributed to the increased short-circuit current due to the improved shunt and series resistance.

1. Introduction

Owing to their outstanding charge transport, optical transparency, and mechanical flexibility properties, graphene [1] and graphene oxide (GO) [2–4] have been considered by many researchers as transparent electrodes [5], active layers, interfacial layers [6,7] and electron acceptors in a number of optoelectronic devices such as organic solar cells (OSCs) and organic light-emitting diodes (OLEDs) [8]. Graphene was originally obtained from natural graphite by mechanical exfoliation, using a technique known as the Scotch tape method [1]. Currently, rather than using liquid-phase exfoliation, graphite intercalation and direct synthesis of graphene using a carbon feedstock by chemical vapor deposition (CVD) are much preferable owing to the scalability of these methods for applications in large-size electronics and owing to the advantages of uniform grain boundaries, resulting in the minimization of flake-to-flake contact resistance [1,9]. Considering transparent electrodes such as anode [10] and cathode [11,12], although indium tin oxide (ITO) is critical for transparent electrodes in OSCs and OLEDs and has excellent characteristics, it is a rare earth metal and the cost associated with using it is high. Regarding the OSCs interfacial layers, most of the previous studies have focused on the alternative role of a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole extraction layer (HEL) because its acidity etches/corrodes ITO and its aqueous hygroscopic property allows the moisture to penetrate into the active layer, resulting in poor device stability. In terms of carrier transport properties, owing to the sp^2–sp^3 hybridized two-dimensional (2D) one atomic layer thickness of the basal plane, a significant lateral carrier transport is explained by hopping between the sp^2 localized states and by vertical carrier transport occurring at laterally isolated sp^2 clusters in the sandwich structure of graphene electrode/active layer/metal electrode [13].

Various techniques of chemical doping [14] by charge transfer have been employed, such as attaching a functional group to the graphene/GO edge, modifying the work function to be used in an anode and a cathode, and considering the sp^2–sp^3 hybridized 2D basal planes. NH_2-terminated self-assembled monolayer (SAM) and CH_3-terminated SAM induced strong n-doped and p-doped graphenes, respectively, resulting in considerable changes in the work function of graphene electrodes [15]. The work function of GO was tuned with $—OSO_3H$ groups attached to the carbon basal plane surrounded with edge-functionalized —COOH groups [16]. Graphene was also doped by nitric acid (HNO_3) and thionyl

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chloride ($SOCl_2$) with simple dipping for 2 h, inducing decreased sheet resistance [17]. Physical doping such as nitrogen (N_2) plasma [18,19] was also introduced to control the work function of graphene, which was attributed to charge transfer between graphene and SAM material.

In the present study, graphene was used as an interfacial layer between an ITO electrode and molybdenum oxide (MoO_3) [20] as a HEL in OSCs, because hydrophobic graphene was not matched with hydrophilic PEDOT:PSS during the spin-casting process. The work function and the conductivity of graphene were controlled by different physical surface treatments, such as thermal annealing in the presence of argon (Ar) ambient, dipping in acetone, ultraviolet (UV) irradiation, and N_2 plasma treatment. The best performance was obtained for the device that used graphene that has been treated by immersion into acetone. For this case, the obtained short-circuit current density (J_{sc}) was 9.40 mA/cm^2, the fill factor (FF) was 62.20, the open-circuit voltage (V_{oc}) was 0.58 V, and the power conversion efficiency (PCE) was 3.40%.

2. Experimental

The ITO-coated glass substrate was cleaned using a substrate-cleaning detergent by ultrasonication, deionized (DI) water, acetone, and isopropyl alcohol, and finally treated in a UV-ozone chamber for 10 min. Graphene was prepared in a previously described fabrication process [18,19,21]. First, copper (Cu) foil (Sigma–Aldrich, 25 μm thick) was positioned in the CVD chamber with gaseous H_2 flowing at 100 sccm and the temperature rising from room temperature (RT) to 1020 °C; this stage lasted for 1.5 h. Next, gaseous CH_4 was added into the CVD chamber at 20 sccm, and the samples were maintained for additional 30 min. Then, the H_2 flow was maintained and the CH_4 flow was stopped, and the temperature in the CVD chamber was reduced at a rate of 150 °C min^{-1}. The poly(methyl methacrylate) (PMMA) was coated on graphene with the Cu foil, and was then dipped in the Cu etchant (Transene CE-100) for etching the Cu. After rinsing in DI water twice, the graphene/PMMA was transferred onto an ITO glass and was dried at RT for 6 h. To remove the PMMA, samples were dipped in acetone or moved to the annealing chamber. During annealing, the temperature was kept at 400 °C for 20 min and Ar gas was flowed into the chamber at 20 sccm with pressure maintained at $\sim 7 \times 10^{-2}$ Torr. The entire process was repeated three times, yielding tri-layer graphenes.

Physical surface treatments were introduced after preparing the graphene on the ITO glass, and the samples were transferred to thermal evaporator and 10 nm thick MoO_3 films were deposited onto graphene samples at 2×10^{-6} Torr. Then, in a nitrogen-filled glove box, a solution of poly(3-hexylthiophene) (P3HT) (20 mg mL^{-1}) and [6,6]-phenyl-C_{61}-butyric-acid-methyl-ester ($PC_{61}BM$) (20 mg mL^{-1}), dissolved in 1,2-dichlorobenzene (DCB), was spin-coated on top of the MoO_3 layer. The thickness of the active layer was about 250 nm. The thin film thicknesses were measured using a KLA-Tencor Alpha-Step IQ surface profilometer with an accuracy of ±1 nm. The active solutions used in the device fabrication were filtered using a 0.20 μm PTFE syringe filter. The device fabrication was completed by thermal evaporation of 1 nm LiF and 120 nm Al as the cathode under vacuum at a base pressure of 2×10^{-6} Torr. The device area, defined through a shadow mask, was 0.38 cm^2.

Current density–voltage (J–V) characteristics of the OSCs were measured under simulated AM 1.5 G illumination with an irradiance of 100 mW cm^{-2} (Oriels Sol AAA^{TM} Class models 94043A). The irradiance of the sunlight-simulating illumination was calibrated using a standard Si photodiode detector fitted with a KG5 filter. The J–V curves were measured automatically using a Keithley 2400 SourceMeter source measurement unit. Series resistance (R_s) and shunt resistance (R_{sh}) were obtained from the slopes of the dark current curves. The IPCE measurement system (Oriel IQE-200) consisted of a 250 W quartz-tungsten-halogen (QTH) lamp as the light source, a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector.

3. Results and discussion

Fig. 1(a) shows the schematics of graphene fabrication processes for various physical surface treatments. After the

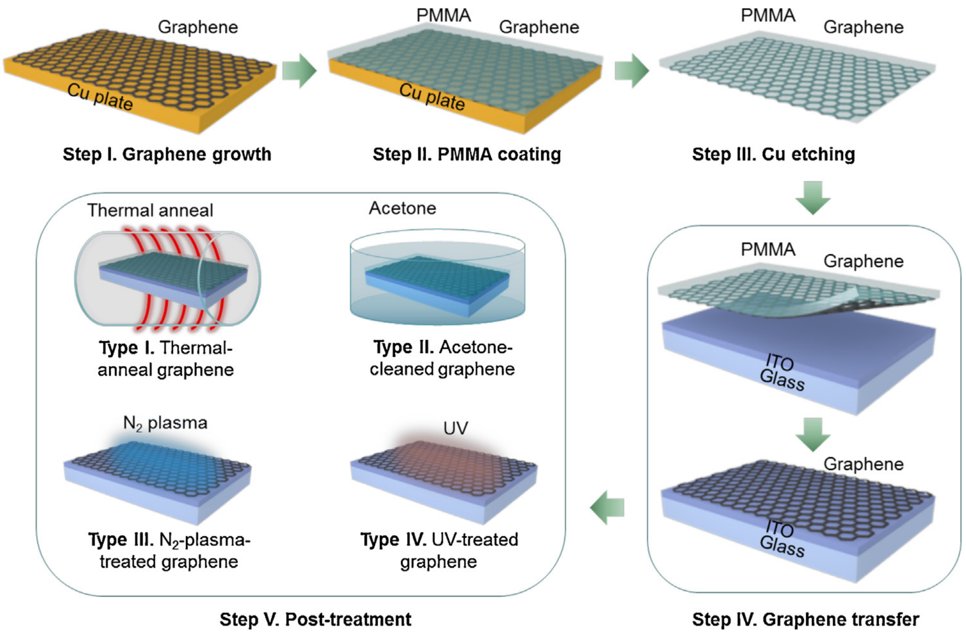

Fig. 1. Schematic of the synthesis and transfer process of graphene films using various physical surface treatments. After being transferred to the ITO glass, type I is thermally annealed at 400 °C for 20 min with Ar flowing at 20 sccm into a vacuum chamber; type II is surface-treated by immersion into an acetone bath for 2 h; type III is N_2 plasma-treated at 30 W with N_2 flowing at 70 sccm for 60 s after the immersion into an acetone bath for 2 h; type IV is UV-irradiated for 10 min after the immersion into an acetone bath for 2 h.