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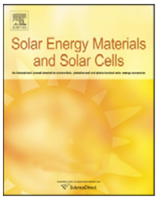

Letter

Multilayer graphene films as transparent electrodes for organic photovoltaic devices

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ABSTRACT

We have fabricated ITO-free organic solar cells (OSCs) based on multilayer graphene (MLG) electrodes. MLG electrodes with high transparency (~84.2%) and low sheet resistance (~374 ± 3 Ω/square) were obtained on glass substrates using chemical vapor deposition and a multi-transfer process. The OSCs fabricated on MLG electrodes had an open circuit voltage of 0.52 V, a short circuit current of 6.90 mA/cm^2, a fill factor of 32.6%, and a power conversion efficiency of 1.17%. The performance of the OSCs fabricated on transparent MLG electrode was not comparable to that of OSCs fabricated on ITO electrodes; cost-effective MLG electrodes are a viable alternative to sputter-grown ITO electrodes for cost-efficient and flexible OSCs.

1. Introduction

Organic solar cells (OSCs) have attracted significant interest in research fields due to their potential to provide low cost processes, large area devices, light weight, and flexibility [1–4]. Among key materials for OSCs, transparent electrodes representing indium tin oxide (ITO) play an important role in the performance of OSCs because the main features of OSCs, such as fill factor and short-circuit current density are critically dependent on the series resistance and optical transmittance of the transparent electrodes. Many useful approaches have been developed to fabricate OSCs based on indium tin oxide (ITO) electrodes, which were prepared using a vacuum based sputtering process [5,6]. However, the scarcity and high cost of indium, which is the main element in the ITO electrode are critical drawbacks of ITO-based OSCs as discussed by Kreb et al. [7–9]. In addition, Kreb et al. recently reported that the energy involved in processing the ITO electrode accounts for 87% in roll-to-roll based OSC fabrication [10]. This high energy consumption of the ITO process is a main bottleneck in the fabrication of cost-efficient OSC module. To overcome the drawbacks of ITO electrodes, indium-free transparent electrodes such as PEDOT:PSS, carbon nanotube (CNT) electrodes, graphene electrodes, and several indium-free oxide electrodes (Ga-ZnO, Al-ZnO, $ZnSnO_3$, $Nb\text{-}TiO_2$) have been widely suggested [11–17]. In particular, transparent graphene electrodes fabricated by various methods have been investigated as a promising alternative to ITO electrodes due to their low resistance, high transparency, superior flexibility, and low cost [18]. Recently, Hong et al. fabricated 30 in. multilayer graphene (MLG) electrodes on a plastic substrate using a roll-to-roll process [19]. They obtained a low sheet resistance of ~30 Ω/square and high transparency of ~90%, which are acceptable for replacing commercial ITO electrodes. Moreover, Loh et al. and Zhou et al. reported that OSCs fabricated on MLG have a power conversion efficiency (PCE) of 1.23% and 1.27% respectively [20,21]. Jo et al. also reported that an inverted OSC with a work-function engineered graphene cathode showed improved efficiency of 1.23% than inverted solar cell with untreated graphene electrode [22]. Despite the low PCE value of OSCs with graphene electrodes, graphene is the most attractive 2-dimensional transparent and flexible electrode for use in cost-efficient OSCs, which could be fabricated using roll-to-roll process. Although researchers have obtained large-scale MLG films on a plastic substrate, there have been fewer attempts to fabricate OSCs based on MLG electrodes. In particular, the detailed research on the multilayer graphene anode prepared by a multi-transfer method to replace a conventional ITO anode in OSCs is still lacking.

In this work, we fabricated OSCs based on MLG electrodes, which were prepared using the CVD method and a multi-transfer process on a glass substrate. The MLG electrode transferred onto a

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glass substrate showed a sheet resistance of 374 ± 3 Ω/square and an optical transparency of 84.2%. The PCE of bulk-heterojunction OSCs prepared on the MLG was 1.17%. These findings indicate that MLG could be alternative transparent electrode in place of ITO electrodes to realize large-area and flexible OSCs with a low-cost fabrication process.

2. Experimental

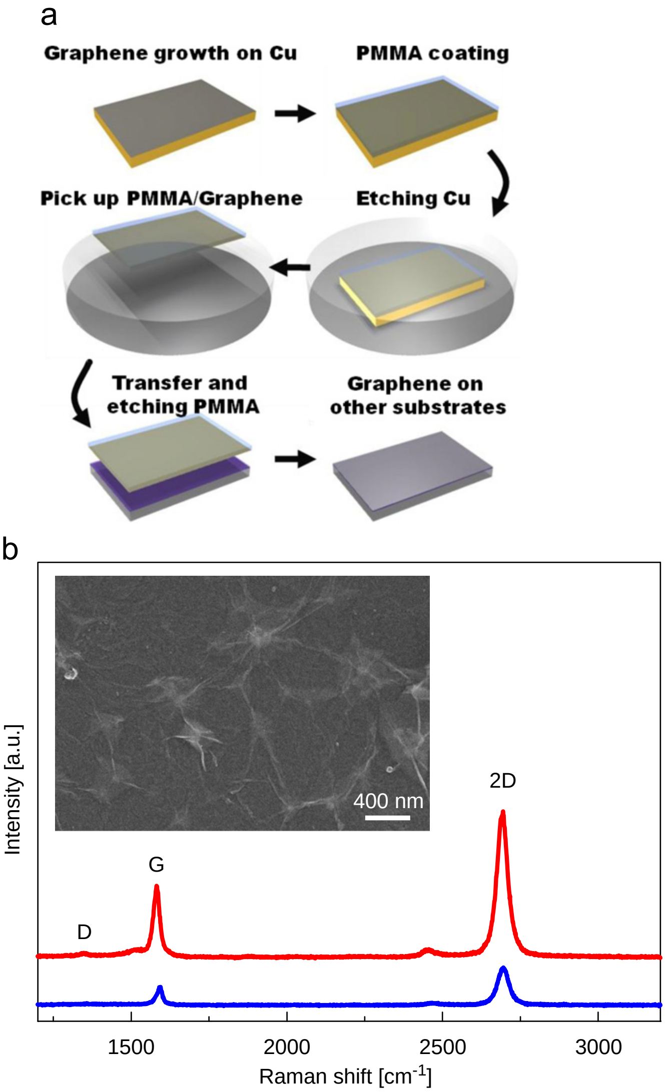

Fig. 1. (a) Schematic illustration of the synthesis and transfer of a thin graphene layer onto glass substrates. A spin-coated PMMA layer was used as a polymer support for the process. (b) Raman spectra of the transferred MLG and a graphene monolayer.

To prepare the MLG electrode on glass for OSCs, a thin layer of graphene was grown on Cu foils using CVD [23]. Cu foils were placed inside of a quartz tube furnace and heated to 1000 °C, with 4 s.c.c.m. of flowing H_2 at 400 mTorr. After annealing the Cu foils for 30 min at 1000 °C, graphene was synthesized with a flowing gas mixture of 20 s.c.c.m. CH_4 and 4 s.c.c.m. H_2 at 900 mTorr for 30 min. Polymethylmethacrylate (PMMA) was used as a supporting layer in the transfer of a thin layer of graphene from the Cu foils to glass substrates. PMMA was spin coated at 1000 rpm on graphene/Cu, and the underlying Cu was etched with an appropriate Cu etchant. The PMMA/graphene layer was rinsed with deionized (DI) water to remove the residual etchant and amorphous carbon on the surface. The PMMA/graphene layer was then gently placed onto the glass substrate. The PMMA/graphene/glass substrate was dipped into acetone for a while to remove the PMMA layer and was subsequently rinsed with isopropyl alcohol (IPA) and DI water. The transfer process was repeated four times to prepare the MLG films on the transparent glass substrate [24]. Fig. 1(a) shows a detailed schematic illustration of the transfer process. The electrical and optical properties of the MLG films were characterized using Hall measurements (HL5500PC, Accent Optical Technology) and a UV/visible spectrometer (UV 540, Unicam), respectively. The surface morphology of the MLG film transferred onto the glass substrate was examined using a field emission scanning electron microscope (FESEM JSM-6500F) at an operating voltage of 15 keV. To evaluate the application of MLG films as anodes in OSCs, we fabricated conventional bulk heterojunction OSCs with poly(3-hexylthiophere) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{61} (PCBM) active materials. After the patterning of the MLG electrodes, a PEDOT:PSS solution (Baytron P VPAI 4083) was spin coated on the a-MLG electrodes. Then, the coated PEDOT:PSS film was dried at 120 °C for 10 min in air using a hot plate. After coating of the PEDOT:PSS film, a blend solution of 25 mg of P3HT (Rieke Metals) and 25 mg of PCBM (Nano-C) in 1 ml of 1,2-dichlorobenzene (DBC) was also spin-coated on top of the PEDOT:PSS layers in an N_2 atmosphere. Subsequently, a solvent-annealing treatment was performed by keeping the active films inside a covered glass jar for 2 h directly after spin coating, followed by additional thermal annealing at 110 °C for 10 min, thus forming the active layer with a thickness of ~230 nm. Finally, circular shape Ca(20 nm)/Al(100 nm) cathode layers were evaporated on the P3HT:PCBM active layer with a metal shadow mask as shown in Fig. 3. Photovoltaic characteristics were measured using a Keithley 1200 instrument under 100 mW cm^{-2} with AM 1.5 G. A reference Si solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc.) was used for calibration for accurate measurement

3. Results and discussion

Raman spectra were measured to evaluate the MLG transferred onto the glass substrate. The bottom spectrum in Fig. 1(b) represents a graphene monolayer, while the upper spectrum corresponds to four layers of graphene on the glass substrate. The Raman spectrum of the MLG, which had four layers of graphene on glass, showed higher intensities and shift positions of the G and 2D bands compared to the spectrum of the graphene monolayer. The inset scanning electron microscopy (SEM) image shows typical features of graphene with wrinkles and flakes.

Fig. 2 shows the optical transmittance of the MLG films transferred onto the glass substrate and a reference ITO electrode; the inset shows the sheet resistance of the MLG film at different positions measured *in-situ*. The MLG film had a high transparency of 84.2% between 400 nm and 600 nm, corresponding to the main absorption region of the organic active layer (P3HT:PCBM) [25]. Note that the transparency of the MLG film was fairly constant regardless of wavelength, unlike the conventional ITO film showing transparency modulation in the blue wavelength region. As shown in the inset pictures, the transparency of the MLG film was better than that of the conventional ITO film. Even though the MLG film consists of four layers of graphene, it had a fairly high sheet resistance of 374 ± 3 Ω/square (inset pictures). At this moment, the sheet resistance of the MLG (4 layers) film is higher than those of previously reported MLG films because we did not do any chemical treatment. In addition, cracks or residual PMMA on the graphene surface during the multi-transfer process increase the sheet resistance of the MLG that is obtained by the transfer process. The inset pictures show the uniformity of the