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Fluoropolymer-assisted graphene electrode for organic light-emitting diodes

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ARTICLE INFO

ABSTRACT

Organic light-emitting diodes (OLEDs) were fabricated on a graphene electrode, with synthesized graphene being transferred and simultaneously doped with supporting polymers. Poly[methyl methacrylate] (PMMA) and fluoropolymer (CYTOP) layers were used as the supporting polymers. The sheet resistance of CYTOP-assisted graphene (CYTOP-G) with 4 layers of graphene is 200 Ω/sq., which is lower than that of PMMA-assisted graphene (PMMA-G, 330 Ω/sq.) The transmittance value of PMMA-G and CYTOP-G with 4 graphene layers is higher than 85%. CYTOP-G is shown to exhibit a higher tolerance to UV–O_3 treatment and thermal annealing than PMMA-G. Work function of CYTOP-G is 4.7 eV, which is higher than that of PMMA-G (4.3 eV). X-ray photoemission and Raman spectroscopy data indicate that CYTOP-G has numerous C-F bonds on the surface exhibiting p-type semiconductor properties, owing to the high electronegativity of fluorine. The turn-on voltage of an OLED based on CYTOP-G with 4 graphene layers is 4.2 V, which is lower than that of indium tin oxide (ITO)-based one (4.5 eV). Furthermore, the luminance ratio of graphene-based OLEDs to ITO-based OLEDs was calculated to be 104% for CYTOP-G, and 97% for PMMA-G. According to the ultraviolet photoemission spectra, the hole injection barrier in CYTOP-G is lower by about 0.5 eV than the hole injection barrier in PMMA-G. These results are very encouraging to the prospect of replacing ITO electrodes with graphene ones in OLED applications.

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1. Introduction

Graphene has received tremendous attention in the field of electronics owing to its excellent mechanical, thermal, optical, and electrical properties [1–7]. Ever since graphene was separated from graphite by the mechanical exfoliation method, there have been many reports on the synthesis of uniform and large-scale graphene sheets [8–12]. Among these methods, chemical vapor deposition (CVD) is one of the more promising ones for synthesizing graphene with a large area, low sheet resistance (<100 Ω/ sq.), and high transparency (>90%), as well as with a high yield rate [13–16]. One of the potential applications for CVD graphene is as a transparent electrode for the replacement of indium tin oxide (ITO). MoO_3-modified and tetracyanoquinodimethane-treated graphene electrodes are already used in organic photovoltaic (OPV) cells, exhibiting device efficiencies as high as 2.5% and 2.58%, respectively [17,18]. In addition, OPV cells with nitric-acid- or thionyl-chloride-treated graphene electrodes demonstrate a high efficiency of 2.4–2.75% [19]. However, these values are still lower than the efficiency of OPV cells based on ITO.

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With organic light-emitting diodes (OLEDs), theoretical calculation has shown that graphene-based OLEDs are competitive with ITO-based ones. Experimentally, thermally reduced graphene oxide (rGO), O_2-plasma-treated CVD graphene sheet, and n-doped rGO sheet have all been tested as electrodes in OLEDs, and have demonstrated comparable device performance with ITO-based electrodes [20–22]. However, it seems that only devices with surface-treated and doped graphene electrodes exhibit device efficiency comparable to that shown by ITO-based ones [23–25]. Therefore, a doping process for graphene electrodes is necessary for their successful application.

According to these results, there are three major problems facing the replacement of ITO with graphene film. Firstly, graphene has a lower work-function value ($\sim$4.2 eV) than ITO ($\sim$4.7 eV) [26]. This induces an energy level difference between graphene layers and other buffer/active layers, thus increasing the charge injection barrier height. Secondly, the sheet resistance of graphene is still higher than that of ITO, degrading the device performance. Finally, the electrical properties of transferred graphene are different from sample to sample, as the properties of graphene sheets are dependent on the fabrication and transfer methods used [27–30]. In order to overcome these problems, graphene doping chemistry incorporating surface functionalization methods has gained much attention [31–39].

The halogenation of graphene is reported to be an efficient way to decrease the sheet resistance, and to increase the work function of graphene. Halogen atoms (X = F, Cl, Br) have a higher electronegativity than carbon atoms in graphene, which enables effective doping through surface charge localization. Further, carbon atoms can easily react with halogen atoms so that high external energy is not needed in the doping process. Therefore, F_2/Cl_2 plasma or F_2 gas exposure at high temperature can be used to attach F or Cl atoms onto a graphene surface [40,41]. XeF_2 decomposition at room temperature, and photochemical decomposition of Cl_2, were also demonstrated for the halogenation of a graphene surface [42–45]. However, ion bombardment induced by the plasma treatment can result in atomic defects and damage. High temperature annealing with X_2 gas also caused distortion of the graphene networks, and so plasma treatment and high temperature annealing were not recommended [44]. Furthermore, the decomposition of halogenated chemicals can cause environmental issues.

CYTOP is one of a variety of amorphous fluoropolymers possessing high optical transparency, as well as excellent chemical, thermal, electrical, and surface properties. Moreover, it has good solubility in certain fluorinated solvents owing to its amorphous nature. It has been reported that CYTOP allows the possibility to transfer and dope graphene simultaneously [46,47], with CYTOP also containing an abundance of fluorine atoms. Therefore, it is expected that the use of CYTOP-assisted graphene as a transparent electrode of OLED could improve the device properties, as a CYTOP layer in the graphene transfer process could achieve a doped-state for graphene without atomic defects or damage.

In this article, CYTOP-assisted graphene is suggested as an alternative anode for OLEDs. A CYTOP layer was used as a supporting and doping layer in graphene transfer, with poly[methyl methacrylate] (PMMA) also used as a supporting layer for reference. The change of sheet resistance and transmittance with the number of graphene layers, UV–O_3 treatment time, and annealing temperature was investigated. Synchrotron radiation photoemission spectroscopy (SRPES) was used to investigate the effect of the supporting layer on the atomic composition of graphene. To clarify the degree of doping in each sample, the position and intensity of the G band in Raman spectroscopy was investigated. After the fabrication of OLEDs, device performance was compared between CYTOP-based and PMMA-based electrodes. From these results, the advantage of fluorinated graphene sheets as an anode of OLEDs is discussed using the schematic band diagrams.

2. Experimental methods

2.1. Fluorinated graphene film preparation

The graphene samples were grown on 25-μm-thick copper foil in a quartz tube furnace, using a chemical vapor deposition method involving methane (CH_4) and hydrogen (H_2) gas. Under vacuum conditions of 90 mTorr, the furnace was heated without gas flow for 30 min. Before the growth of graphene, copper foil was preheated at 950 °C for 30 min. In order to obtain a large single-crystal copper surface, H_2 gas was supplied to the furnace under 150 mTorr at a rate of 33 cm^3/min (sccm). After the preheating step, a gas mixture of CH_4:H_2 = 200 sccm:33 sccm was supplied under ambient conditions for 10 min to synthesize the graphene. After 10 min of growth, the furnace was cooled to room temperature at a rate of 10–15 °C/min, under 33 sccm of H_2 flow. PMMA was then spin-coated onto the graphene-coated copper foil, and the PMMA-coated foil was heated on a hot plate heated to 180 °C for 1 min, after which O_2 plasma was used to etch the graphene on the other side of the copper foil. In the case of fluoropolymer, CYTOP (supplied by 3 M), was spin-coated onto the graphene-grown copper foil. The CYTOP-coated foil was heated on a hot plate to 160 °C for at least 20 min to ensure bonding between CYTOP and carbon atoms. After curing of the fluoropolymer, the other side of the graphene-grown copper foil was also removed by O_2 plasma etching method. The sample was then immersed in a ferric chloride (1 M $FeCl_3$) bath at room temperature for 12–18 h to etch away the copper foil. After, the remaining PMMA-G and CYTOP-G was carefully dipped into a DI water bath about 7–9 times to remove any residual etchant. The PMMA-G and CYTOP-G sheets were then transferred onto an arbitrary substrate. PMMA was removed by an acetone bath at 50 °C for 30 min after the PMMA/graphene layer had completely adhered to the target substrate. CYTOP was removed by a PF-5056 (performance fluid, supplied by 3 M) bath at room temperature for 5 min after the transfer procedures.