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Highly conductive flexible transparent electrodes fabricated by combining graphene films and inkjet-printed silver grids

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ABSTRACT

Inkjet-printed Ag grids were combined with graphene films synthesized using a chemical vapor deposition method to form highly flexible transparent electrodes with low resistances. Morphological characteristics, sheet resistances, transmittances, and bending test results are reported. A synergetic effect due to the mechanical pressure from graphene films on Ag grids was discovered and analyzed. Furthermore, polymer solar cells were fabricated with the developed electrodes and 2.9% maximum efficiency was obtained.

1. Introduction

As the prospect of human-friendly flexible electronics becomes imminent, the need for flexible and transparent electrodes for optoelectronic devices such as displays and solar cells is increasing [1–4]. In traditional non-flexible optoelectronic devices, indium–tin oxide (ITO) has been the industrial standard for transparent electrodes. However, its inherent brittle nature limits its usage in flexible devices. To fulfill the growing need for flexible and transparent electrodes, several competing approaches have been developed. The conducting polymer such as PEDOT:PSS is increasing its conductance rapidly by honing the synthesis method and after-production treatment [5,6]. However, its environmental instability is likely to affect its application. Metallic nanowire mesh electrodes are also a popular approach [4,7,8]. However, the difficulty in precisely controlling the distribution of nanowires can be a bottleneck of this approach. Recently, graphene films synthesized by chemical vapor deposition (CVD) have emerged as a promising material [2,3]. However, their synthesis has not yet met the needs of an industrial protocol [9]. Notably, the high resistance values of synthesized graphene films require use of stacked multilayer graphene films fabricated by complicated multiple growth-and-transfer processes for device applications [10,11].

Combining the metal grid structure and graphene is a logical approach to achieve high conductivity in transparent electrodes. In fact, Zhu et al. demonstrated that highly conductive electrodes could be produced using this strategy [12]. However, their approach used a cumbersome lithographic technique and energy-demanding vacuum sputtering processes [13] to prepare the metal grid structure. Therefore, their method is not suitable for mass production. To improve the fabrication procedure for mass production, a printing method can be adopted for the preparation of the metal grid [14]. However, electrodes using a combination of printed metal grids and graphene films have not yet been developed. Recently, the combination of Ag nanowires and graphene also has been investigated for use as transparent electrodes and produced promising results [15–18]. However, the above mentioned difficulty of precisely controlling the distribution of the nanowires may limit the development of these approaches.

In this work, we used the inkjet printing method, which is considered as a next-generation printing method due to its maskless-patterning, low cost, high material usage, simplicity, and rapid process [14], to form an Ag grid. The grid was then

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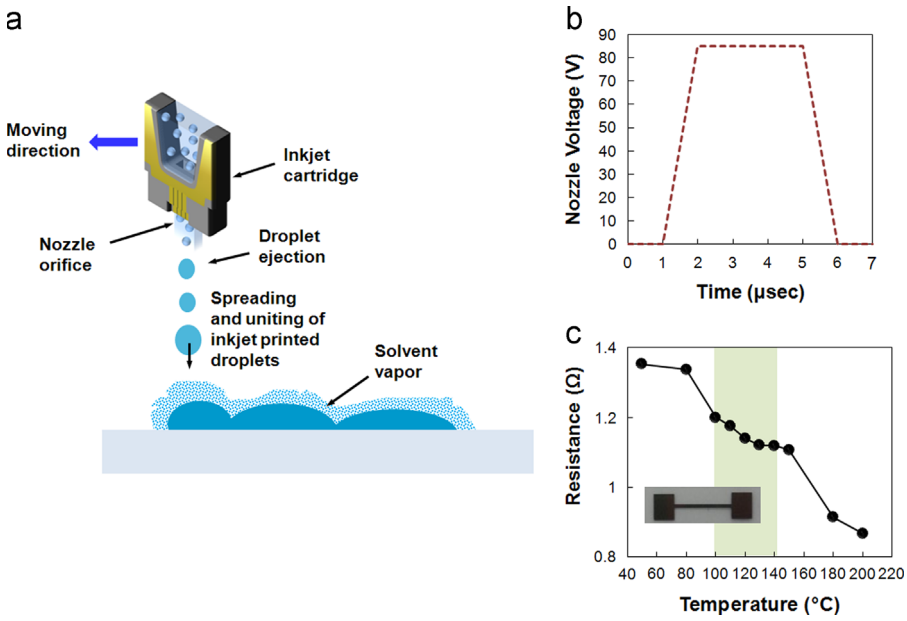

Fig. 1. (a) Schematic of the inkjet printing process for Ag grids. (b) The applied nozzle voltage profile when printing the Ag grid. (c) The after-anneal resistance vs. annealing temperature. The temperature range near the optimum annealing temperature is marked by a green box. A photograph of the test pattern is shown in the inset. The channel in the pattern is 1 cm long, 300 μm wide, and 150 μm thick. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

combined with a graphene film synthesized by the CVD method to produce highly conductive flexible transparent electrodes with a sheet resistance of 12 Ω/sq and 73% transparency at 550 nm. Furthermore, we discovered that such low resistance in the combined electrode was benefited from a synergetic effect of the mechanical pressure on Ag nanoparticles in the grid pattern exerted by the graphene film. Consequently, the resistance was lower than the expected value of the parallel combination of resistances of two individual layers. We also fabricated polymer solar cells (PSCs) with the developed electrodes and obtained the best power conversion efficiency (PCE) of 2.9%, which indicates the possibility of our graphene-grid combined electrode as a transparent electrode.

2. Experimental details

The Ag grid (denoted as GD) was prepared using an Omnijet 100 Premium inkjet printer from UniJet, Co. equipped with a 16-nozzle Semijet Mini Refillable Cartridge 38pico (Fig. 1(a)). Silverjet DGP 40LT-15C ink from Advanced Nano Products, Co. was used. The printing parameters were optimized at a density of 300 DPI, a frequency of 800 Hz, and the meniscus at 10% to obtain a continuous and well-defined Ag-grid pattern. The nozzle voltage input profile in a single cycle is shown in Fig. 1(b). A voltage of 85 V was applied for 4 μs to eject the ink droplet. During printing, the printing stage was heated to 80 °C. After printing, the printed grid was annealed at 120 °C for 15 min. The annealing condition is optimized by studying the after-anneal resistance of a test pattern (shown in the inset of Fig. 1(c)) on poly(ethylene terephthalate) (PET) substrates as the data shown in Fig. 1(c). The annealing temperature was selected below the glass transition temperature of PET, which is 140 °C.

The graphene (denoted as GR) film was synthesized using the CVD method similar to previously reported procedures [19,20]. Briefly, GR films were synthesized on Si/SiO_2 (300 nm)/Ti (20 nm)/Ni (300 nm) in a 10 cm diameter quartz tube chamber with gas flows of 20 sccm methane, 80 sccm hydrogen, and 2000 sccm argon for 2 min at 900 °C and 760 Torr. Following synthesis, the GR films were transferred from the nickel substrate by etching the nickel in an aqueous iron chloride ($FeCl_3$) solution (1 M) and cleaned in DI water for three times. Finally, the GR films were transferred on to PET substrates preformed with GD to obtain the combined film (denoted as GDGR). During transfer, a polymethylmethacrylate (PMMA) coating was applied as a protective layer and was removed using acetone after the transfer. The reference indium-tin oxide (ITO) on the PET film was purchased from Aldrich, Co.

The samples were examined using an optical microscope (Axio Scope, Zeiss, Co.) and a field-emission scanning electron microscope (FESEM, Quanta 200FEG, FEI, Co.) operating at 20 kV. The optical transmittance of the samples was measured using an UV–vis spectrometer (Cary 5000, Varian, Inc.), and the sheet resistance of the samples was measured by a Hall measurement system (Bio-Rad, Inc.). The flexibility of the samples was tested using a bending tester (ZBT-200, Z-Tec, Co.).

Polymer solar cells with conventional structure of [GD or GDGR]/PEDOT:PSS (Clevios P, 100 nm)/P3HT:ICBA (150 nm)/TiO_x (10 nm)/Al (100 nm) were fabricated on PET substrates with an active area of 4.64 mm^2. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spun-cast (2000 rpm, 60 s) in aqueous solution (13 mg/ml) followed by baking at 100 °C for 20 min in air to form a 100-nm-thick layer on the electrodes. The use of thick PEDOT:PSS layer decreased the detrimental effects on the device performance induced by the lumpy Ag-grid pattern and also the PMMA residues on GR films [21]. Then the films were transferred into a glove box to spin-cast the active layer. The used solution was a mixture of poly(3-hexylthiophene) (P3HT) and indene–C_{60} bisadduct (ICBA) (1:1 w/w) in chlorobenzene (20 mg/ml) [22]. Afterwards, the films were dried for 10 min at 80 °C in the glove box. Next, a titanium sub-oxide (TiO_x) solution (1:300 dilution in isopropanol) was spun-cast on top of the active layer [23]. The films were then baked at 80 °C for 10 min. Finally, Al metal was deposited through mask patterns by thermal evaporation under high vacuum completing the device fabrication.

The current density–voltage (*J–V*) characteristics of the devices were measured in the glove box using a Keithley 236 source measurement unit. The solar cell performance was measured under