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Simple brush-painting of Ti-doped In_2O_3 transparent conducting electrodes from nano-particle solution for organic solar cells

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ABSTRACT

In this work, we have demonstrated that simple brush-painted Ti-doped In_2O_3(TIO) films can be used as a cost effective transparent anodes for organic solar cells (OSCs). By the direct brushing of TIO nanoparticles ink and rapid thermal annealing (RTA), we can simply obtain TIO electrodes with a low sheet resistance of 28.25 Ω/□ and a high optical transmittance of 85.48% under atmospheric ambient conditions. In particular, the brush painted TIO films showed a much higher mobility (33.4 cm^2/V s) than that of previously reported solution-process transparent oxide films (1–5 cm^2/V s) due to the effects of the Ti dopant with higher Lewis acid strength (3.06) and the reduced contact resistance of TIO nanoparticles. The OSCs fabricated on the brush-painted TIO films exhibited cell-performance with an open circuit voltage (V_{oc}) of 0.61 V, shot circuit current (J_{sc}) of 7.90 mA/cm^2, fill factor (FF) of 61%, and power conversion efficiency (PCE) of 2.94%. This indicates that brush-painted TIO film is a promising cost-effective transparent electrode for printing-based OSCs with its simple process and high performance.

1. Introduction

Solution-based printing technologies for the fabrication of low-cost organic solar cells (OSCs) have evolved significant attention as a promising cost-efficient coating process [1,2]. Considering the key merits of OSCs, they should be fabricated by at the lowest possible cost, avoiding the high cost of vacuum-based coating process [3–6]. Recently, many studies have reported the possibility of solution-based printable OSCs using inkjet printing, screen printing, spray, gravure printing, and flexography printing [7–11]. Among various printing technologies, brush painting has been considered as a promising ultra-low-cost coating process due to its advantages of being a simple, fast process, and atmospheric process. For these reasons, brush painting has been employed in solution-based OSCs and organic thin film transistors (OTFTs) to reduce the cost of fabrication without the use of vacuum processes [12,13]. Kim et al. reported the possibility of brush painting in the fabrication of low-cost OSCs by the direct brush painting of organic active layers. Due to the shear stress induced ordering of the P3HT:PCBM active layer, the OSC showed a high power conversion efficiency (PCE) of 5.4% comparable to the OSCs fabricated by spin-coating processes [14]. We also suggested that brush-painted Ag nanowires (NWs) network electrodes and PEDOT:PSS/Ag NW/PEDOT:PSS multilayers could be cost-effective transparent anodes for OSCs and reported the potential of the brush painting method [15]. Recently, Qi et al. showed the possibility of brush-painting method by demonstrating all brush-painted top-gate OTFTs with a maximum mobility of 0.14 cm^2/V s [13]. However, previous research on simple brush painting has been mainly dedicated to the coating process for organic semiconductors and metal electrodes. In spite of the importance of printable transparent conducting oxides (TCOs) for all-printable OSCs, detailed investigations on brush-painted TCOs using oxide nanoparticles are still lacking. Until now, several groups have investigated the possibility of creating nanoparticle solution-based TCO electrodes. Cranton et al. reported antimony-doped oxide (ATO) electrodes prepared by ink-jet printing and excimer laser annealing. However, the high sheet resistance (~200 kΩ) of the ink-jet printed ATO electrodes makes them difficult to use in OSCs as an anode layer [16]. Hong et al. also reported that inkjet-printed ITO films using ITO nanoparticles have a high transmittance

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of 90% and a resistance of 1.7×10^5 Ω, which is not acceptable as transparent anode in OSCs due to the high sheet resistance [17]. Recently, we suggested the inkjet-printed ITO electrodes using nano-size particles for printable OSCs [18]. However, the inkjet-printed ITO showed a fairly high sheet resistance of 202.7 Ω/□ due to the very slow carrier mobility of 1.24 cm^2/V s. Considering the conduction mechanism of sintered nanoparticle-based TCOs fabricated by the solution process, higher mobility TCO (HMTCO) film is desirable to decrease sheet resistance below 30 Ω/□. However, there has been no report on the use of brush-painted HMTCO films for cost-effective OSCs.

In this work, we investigated the characteristics of simple brush-painted Ti-doped In_2O_3 (TIO) films using TIO nanoparticle ink for use as printable transparent anodes in cost-efficient OSCs. By the direct brush painting of TIO nanoparticle ink and rapid thermal annealing under oxygen ambient, we obtained brush-painted TIO films with a low sheet resistance of 28.25 Ω/□ and a high optical transmittance of 85.48%, which are applicable as transparent anodes in OSCs. Due to the effective Ti dopant with a high Lewis acid strength value of 3.06 in the In_2O_3 nanoparticles, the brush-painted TIO films showed a much higher mobility than previous solution-process ITO anodes. In addition, the OSCs fabricated on the brush-painted TIO anodes showed a power conversion efficiency of 2.94%, indicating that brush-painted TIO film is a promisingly cost-efficient and ultra-low-cost anode that can replace the conventional sputtered ITO electrode in OSCs.

2. Experimental

Indium trichloride tetrahydrate ($InCl_3 \cdot 4H_2O$, Sigma-Aldrich) and titanium tetrachloride n-hydrate ($TiCl_4 \cdot nH_2O$, Sigma-Aldrich) were used as starting materials. Ammonia solution (28% NH_4OH, Sigma-Aldrich) was used as the mineralizer. $InCl_3 \cdot 4H_2O$ and $TiCl_4 \cdot nH_2O$ were dissolved in de-ionized water, respectively. The $InCl_3 \cdot 4H_2O$ and $TiCl_4 \cdot nH_2O$ solutions were mixed with the weight fraction of In:Ti (97:3). After the solution attained equilibrium, the ammonia solution was added drop by drop into the $InCl_3 \cdot 4H_2O$ and $TiCl_4 \cdot nH_2O$-mixed precursor solution to achieve a final pH of 11 under stirring for 4 h with a water bath and an ultrasonic bath. The synthesis temperature controlled by the water bath was in the range of 40–100 °C. The TIO precursor, 3 wt% Ti-doped In_2O_3, was kept in 40–100 °C water for 4 h, and then was agitated at 3000 rpm for 5 min. The precipitates were washed by centrifugation until there were no chloride ions in solution. The wet precipitates were dried at 80 °C for 10 h to completely remove the water molecules. The TIO particles after drying were thermally decomposed from 400–800 °C with Ar gas in order to form an oxygen vacancy. The TIO precipitator was dissolved under constant stirring at 3000 rpm with ethanol organic solvent. The TIO nanoparticles were dispersed in the ethanol solvent by a 72 h ball-mill process. The total concentration of TIO solution for brush-painting was maintained at a TIO/ethanol ratio of 30/70 weight % with an average particle size of 20–40 nm. The TIO nanoink solution was intended to provide stable brush-painting with good wetting on a glass substrate. The TIO solution was filtered through a 0.45 μm Polytetrafluoroethylene (PTFE) filter in order to get rid of agglomerated TIO particles and other impurities in the solution. The TIO films were coated on the glass substrate by a simple and fast brush-painting technique using a synthetic TIO nanoparticle ink under atmospheric ambient conditions. Fig. 1(a) shows the brush-painting process of the TIO nanoparticle on a glass substrate with a conventional paintbrush made of nylon fibrils. Due to its simplicity and cost effectiveness, brush painting is known as a promising coating process for the fabrication of ultra-low cost OSCs [19,20]. As shown in Fig. 1(b) and (c), a constant lateral brushing of the TIO nanoink-wetted paintbrush on the glass substrate with the temperature controller resulted in uniformly-coated TIO films. Prior to brush-painting, the glass substrates were cleaned by isopropanol, acetone, methanol and boiled isopropanol in an ultrasonic bath. Then, the glass substrates were pretreated with UV/ozone to improve the wettability of the TIO nanoparticle ink. After dipping the paintbrush into the TIO nanoparticle ink, the TIO film was coated on the glass substrate by lateral brush painting at a speed of 2 cm/s with a temperature of 50 °C. In the brush painting process, the control of the brush speed is very important because a fast brushing speed could lead to discontinuous TIO films while a slow brushing speed could lead to a rough surface and non-uniform TIO films. Due to the shear stress of the brush, the TIO nanoparticles were uniformly coated on the glass substrate with a smooth surface morphology. The brush painting is used an effective shear stress ($\tau \approx$ viscosity (υ) $\times$ velocity gradient ($\Delta\upsilon$)) which can be organized and arranged the TIO nanoparticles. There are two boundaries, the TIO solution-glass substrate and the TIO solution-brush, as shown in Fig. 1(b). Therefore, a constant shear stress can be induced uniformly coated the TIO films.

After simple brush-painting of the TIO nanoparticle ink, the brush-painted TIO films were dried on a hot plate at 100 °C for 5 min under ambient conditions to remove the solvent. Fig. 1(c) shows surface and cross-sectional FESEM images of the brush-painted TIO films prepared on the glass substrates. Even though the films were prepared by brush painting under atmospheric ambient conditions, they showed smooth surfaces and uniform thickness, indicating the potential of the simple brush painting method.

After the brush-painting of the TIO nanoparticle ink on the glass substrate, the TIO films were rapidly thermal annealed as a function of RTA temperature (350–500 °C) in oxygen ambient for 5 min to sinter the TIO nanoparticles and activate the TI dopant. The thermal characteristic of the TIO nanoparticles ink was analyzed with a thermal gravity analyzer (TGA: Q-1000, TA instruments) in the temperature range of 25–600 °C, at a heating rate of 10 °C/min in N_2 atmosphere. The particle size and nano-structure of the TIO nanoink and brush-painted film were analyzed by high resolution transmission electron microscope (HRTEM) and Fast Fourier Transform (FFT). The surface morphology of the TIO film was examined by a field emission scanning electron microscope (FESEM: LEO SUPRA 55). The electrical properties of the brush-painted TIO films were examined using Hall measurement (HL5500PC, Accent Optical Technology) at room temperature. The optical transmittance of the brush-painted TIO films was investigated by a UV/visible spectrometer (Agilent 8453) in the wavelength range of 300–1200 nm. The structural properties of the TIO films were investigated by synchrotron X-ray scattering examinations at a beam line 5A of the Pohang Light Source. In order to examine the electronic structure near the conduction band of the amorphous TIO film, near edge X-ray absorption spectroscopy (NEXAS) experiments were performed by using the total electron yield (TEY) mode in the BL-8A1 of Pohang Accelerator Laboratory (PAL) in Korea.

To evaluate the possibility of using the brush-painted TIO films as a transparent electrode for OSCs, we fabricated conventional bulk heterojunction OSCs with optimized TIO and reference ITO films. After cleaning the TIO/glass and ITO/glass, -poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, Baytron P Al 4083) was spin-coated on the TIO and ITO coated glass substrates followed by annealing at 120 °C for 10 min in air. Then, a blend solution containing 20 mg of poly(3-hexylthiophene) (P3HT, Rieke Metal) and 20 mg of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} (PCBM, Nano-C) in 1 ml of 1, 2-dichlorobenzene was spin-coated onto the top of the PEDOT:PSS layers in a nitrogen atmosphere. Subsequently, solvent-annealing treatment was performed by keeping the active films inside a covered glass jar for 120 min, followed by annealing at