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Double-shot inkjet printing for high-conductivity polymer electrode

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ABSTRACT

This paper presents a printing method to form a high-conductivity patterned poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film. A modified PEDOT:PSS ink containing a secondary dopant (dimethyl sulfoxide) and fluorosurfactant (Zonyl FS-300) was inkjet-printed to form a uniform conducting layer, and the dimethyl sulfoxide, conductivity enhancer, was over-printed onto it to further enhance its conductivity. We achieved high-conductivity greater than 1000 S cm^{-1} by only using inkjet-printing technique. The mechanism of conductivity enhancement was investigated with X-ray photoelectron spectroscopy and atomic force microscopy analyses. The printing process for high-conductivity PEDOT:PSS was applied to pattern a transparent anode for the fabrication of an organic light emitting diode.

1. Introduction

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been considered as one of the promising soft electrode materials for emerging flexible and printed electronic devices such as organic light emitting diodes (OLEDs) [1,2], organic solar cells [3,4] and organic electronic circuits [5–8]. Although a pristine PEDOT:PSS film shows very low conductivity below 1 S cm^{-1}, with the addition of a secondary dopant such as dimethyl sulfoxide (DMSO) and ethylene glycol (EG) the conductivity can be improved by 2–3 orders of magnitude, typically 600–700 S cm^{-1} for spin-coated films [9–11]. But, this value does not meet the requirement for the electronic applications, and several post-treatment methods have been devised in order to further increase its conductivity to over 1000 S cm^{-1}. Chou et al. dropped a small amount of DMSO directly onto a spin-coated PEDOT:PSS film to increase its conductivity up to ~1000 S cm^{-1} [12]. More recently, Alemu et al. combined both methods (dropping & dipping of Methanol) and had the conductivity of a spin-coated PEDOT:PSS film enhanced to over 1300 S cm^{-1} [13]. Higher conductivity of ~1400 S cm^{-1} was achieved by dipping spin-coated samples into an EG bath for 30 min [14]. Although these post-treatments are simple and can be easily used in laboratories, they may not be applicable to roll-to-roll manufacturing of patterned flexible and transparent electrodes with high-conductivity.

This paper presents a printing method to form a high-conductivity patterned PEDOT:PSS film. We used inkjet printing technology with high positional accuracy, high speed and roll-to-roll processability. The optimized printing condition was examined to form a uniform and smooth PEDOT:PSS film, and the film was then post-processed with the same inkjet nozzle to achieve higher conductivity. We discuss the effect of printing a secondary dopant on the film with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Finally, the suggested printing method was applied to fabricate an OLEDs.

2. Experimental details

Conducting PEDOT:PSS dissolved in water was used in this work (Clevios PH 1000, Heraeus). The solid content of the PH 1000 solution was 1–1.3% and had a PEDOT to PSS ratio of 1:2.5 by weight. 5 wt% of DMSO (Sigma-Aldrich) was added into the PEDOT:PSS to enhance conductivity. The surface tension of the solution was modified by adding fluorosurfactant (Zonyl FS-300, Sigma-Aldrich). The equilibrium surface tension was measured at 23 °C with a bubble tensiometer (SITA pro line t15) and was significantly reduced from 72 m Nm^{-1} to 21 mN m^{-1}. The rheological property of the modified-PEDOT:PSS solution (m-PEDOT:PSS) can be found elsewhere [15].

The modified PEDOT:PSS ink, m-PEDOT:PSS, was deposited to form a conductive film onto a glass substrate (Eagle XG, Corning) using a high-resolution inkjet-printing system (Jetlab II, MicroFab) with a piezoelectric printhead (MJ-A, 40 μm nozzle, MicroFab). The ink was filtered with a 0.45 μm membrane filter before jetting. A square shaped unipolar control waveform with rise and fall times of 5 μs and a dwell time of 25 μs was sent to the printhead to eject a fine drop at the speed of ~5 ms^{-1} and at the frequency of 500 Hz. The temperature of the printing substrate was maintained at 40 °C. The ejected conducting ink formed a single main drop within 230 μs and no satellite drops were generated under the jetting condition. After being annealed at 120 °C, the conductivity of the printed film was further enhanced by overprinting DMSO along its surface with the same nozzle. The

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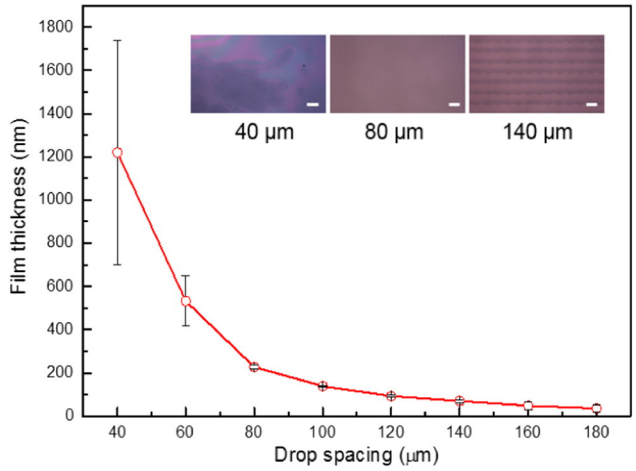

Fig. 1. Variation in film thickness against drop spacing for printed PEDOT:PSS.

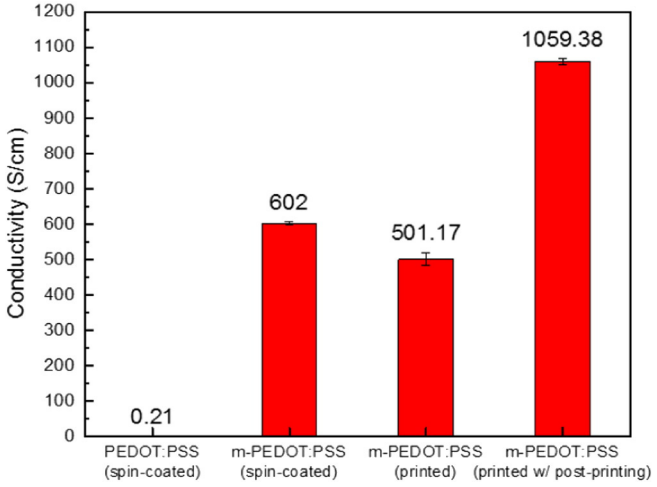

Fig. 2. Comparison of conductivities of various PEDOT:PSS films formed by different processes.

conductivity of the printed electrode was precisely measured with a four point probe resistivity meter (Loresta-AX, Mitsubishi Chemical). The mechanism of increase in conductivity was investigated by AFM (VEECO Dimension 3100 + Nanoscope V) and high-resolution XPS (HR-XPS, AXOS Nova, Kratos Analytical, Ltd) using a monochromatic Al-Kα source (1486.6 eV photon energy). The printed m-PEDOT:PSS conducting electrode was used to fabricate an OLED with a structure of m-PEDOT:PSS/TPD/Alq_3/LiF/Al. On a patterned PEDOT:PSS film with a thickness of ~100 nm by inkjet printing, TPD (40 nm), Alq_3 (40 nm), LiF (1 nm) and Al (100 nm) were deposited using thermal evaporation system. The current density verse voltage (*J*–*V*) and luminance verse voltage (*L*–*V*) characteristics were measured by Keithley 236 and CS-1000 (Konica Minolta Co.) system.

3. Results and discussion

In order to find the optimized printing conditions for uniform and smooth films, the m-PEDOT:PSS ink was printed with varying drop spacing from 40 μm to 180 μm. As seen in Fig. 1, the change in drop spacing had an effect on film morphology. At small drop spacing (40 and 60 μm) a non-uniform film was formed, and at large drop spacing resulted in a wavy film. From this result, the drop spacing of 100 μm was chosen to achieve high uniformity and smoothness of printed conducting films.

Fig. 2 shows the conductivity values of PEDOT:PSS films made by different methods and solutions. The pristine PEDOT:PSS film by spin-coating showed poor conductivity less than 1 S cm^{-1}. Conductivity has greatly increased up to ~600 S cm^{-1} by adding DMSO and Zonyl surfactant into the aqueous solution. We obtained comparable high-conductivity from m-PEDOT:PSS films formed by inkjet-printing as described in the previous section. A post-treatment was carried out on the printed film by inkjet-printing as-received DMSO with the same nozzle. This additional printing process led to a significant increase in conductivity over 1000 S cm^{-1}. It is noteworthy that this high value was achieved simply by inkjet printing process performed in air. This value is comparable to the conductivity obtained from other post-treatments such as dipping or dropping which may not be applicable to roll-to-roll manufacturing.

It was found that the thickness of the printed film was slightly reduced after the post-printing process, and this gives an idea that the enhancement of conductivity by additional printing of highly dipolar DMSO might result from removal of non-conducting PSS molecules from the film surface. In order to investigate the effect of the post-printing on PSS molecules, the amount of PSS removed from the printed PEDOT:PSS film was evaluated with HR-XPS. As seen from Fig. 3, the S(*2p*) peaks observed at the binding energy of 168.7 eV corresponding to the sulfur signal from PSS and 164.2 and 165.3 eV corresponding to the sulfur signal from PEDOT. The calculated surface ratio of PSS to PEDOT for the film with and without post-printing process is 0.33:1 and 0.58:1, respectively, showing that the PSS content was significantly reduced by 43% resulting from the printing of DMSO. We believe that the removal of hydrophilic insulating PSS leads to the thickness reduction of the film and brings about reorientation of the hydrophobic conducting PEDOT polymer chains from a coiled to extended-coil structure, allowing closer inter-chain interaction between the conducting polymers [13].

We also investigated the correlation between conductivity and surface morphology of PEDOT:PSS films with and without DMSO treatment by AFM. As shown in Fig. 4, distinct structural change, weakly separated PEDOT-rich grains (bright) and PSS-rich grains (dark) were observed from a pristine PEDOT:PSS film, while well-separated grains with better connection of PEDOT-rich grains were found from a post-processed m-PEDOT:PSS film. We believe that inter-chain interactions between conducting PEDOT polymers with linear or extended-coil structure make charge hopping easier and thus lead to a significant increase in conductivity.

In order to prove this printing process, we have applied our printed high conductivity films to fabricate OLEDs. Fig. 5(a) shows the

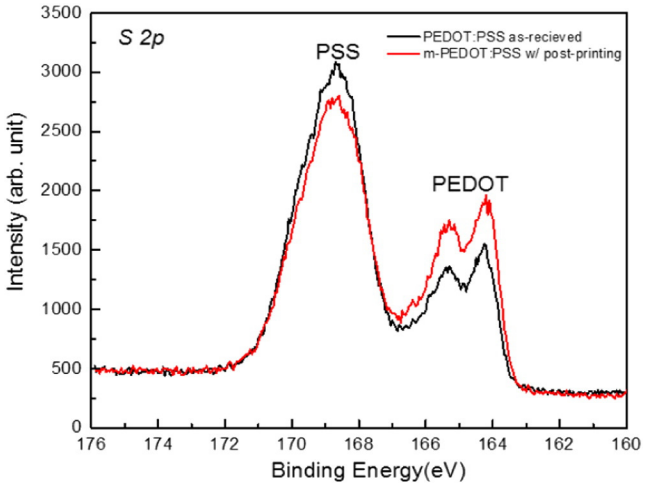

Fig. 3. XPS of pristine PEDOT:PSS and m-PEDOT:PSS with post-processing.