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# Optimization of electrohydrodynamic-printed organic electrodes for bottom-contact organic thin film transistors

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ABSTRACT

In this study, we investigate the optimization of printed (3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) as source/drain electrodes for organic thin film transistors (OTFTs) through electrohydrodynamic (EHD) printing process. The EHD-printed PEDOT:PSS electrodes should fulfill the prerequisites of not only high conductivity but also optimum surface tension for successful jetting. The conductivity of PEDOT:PSS was dramatically enhanced from 0.07 to 352 S/cm by the addition of dimethylsulfoxide (DMSO). To use the DMSO-treated PEDOT:PSS solution in the EHD printing process, its surface tension was optimized by the addition of surfactant (Triton X-100), which was found to enable various jetting modes. In the stable cone-jet mode, the patterning of the modified PEDOT:PSS solution was realized on the surface-functionalized $SiO_2$ substrates; the printed line widths were in the range 384 to 81 μm with a line resistance of $8.3 \times 10^3$ Ω/mm. In addition, pentacene-based OTFTs employing the EHD-printed PEDOT:PSS as source and drain electrodes were found to exhibit electrical performances superior to an equivalent vacuum-deposited Au-based device.



## 1. Introduction

Over the last decade, there has been significant progress in the development of organic thin film transistors (OTFTs) for use in organic and flexible electronics [1]. For example, new organic semiconductor materials such as diketopyrrolopyrrole (DPP) have been prepared with high field-effect mobility values (up to 11 $cm^2/V \cdot s$) that surpass that of amorphous silicon which is currently used as a semiconductor material in displays [2]. In particular, the fabrication of OTFTs with solution processing techniques is advantageous because of their low cost, flexibility, and the possibility of large area deposition under ambient conditions [3]. The solution processing of organic electrodes has been performed in various applications such as flexible displays, radio frequency identification tags, solar cells, and sensor applications [4–8]. Although metal- or oxide-based electrode materials (e.g., gold, aluminum, and indium tin oxide) exhibit good conductivity and alternation of work function for the injection of free carriers from the electrode to the channel, their poor mechanical stability and the inhomogeneity of the organic semiconductor film between the electrode and the channel, especially in bottom-contact OTFT architectures, are critical bottlenecks to the commercialization of OTFTs [9]. Therefore, organic electrode materials providing efficient carrier injection and good conductivity are required. Among the available organic electrode materials, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) exhibits great potential for the various electronic applications because of solution processability, thermal stability and high transparency. However, the conductivity of

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pristine PEDOT:PSS electrode (<1 S/cm) is typically inferior to those of vacuum-deposited metal electrodes, which has prompted diverse attempts to modify PEDOT:PSS so as to enhance its conductivity [10]. Various co-solvents such as dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and ethylene glycol (EG) have been used in such attempts [11–13]. DMSO is an excellent co-solvent to use in electrode fabrication with a view to improving conductivity, and it also promotes smooth surface morphologies which are important in multilayered organic devices [14].

Inkjet printing is considered a low cost and simple fabrication technique for patterning electrodes [15]. However, the unpredictable positions of droplets and drop spreading during the printing process result in poor resolution and low OTFT performance [16]. Electrohydrodynamic (EHD) printing can be used as an alternative because the electric field enables uniform jetting without disruption. In particular, the EHD printing process for fabricating electronics has the important advantages of easy solution processability, high accuracy, non-vacuum system with low cost, and the possibility of large area deposition [17]. However, water-based inks such as PEDOT:PSS are not generally suitable for EHD printing processes because the surface tension of $H_2O$ is too high, which prevents stable jetting formation and thus causes printing problems [18,19]. Hence, further systematic investigation is required for the micro-patterning of PEDOT:PSS as a electrode of organic devices, and its conductivity must be improved.

In the present study, we successfully demonstrated the preparation of PEDOT:PSS electrodes for OTFTs by using the EHD printing process. The addition of DMSO and surfactant (Triton X-100) to the PEDOT:PSS plays a significant role in enhancing its conductivity and adjusting its surface tension as well. The dramatic increase in conductivity of PEDOT:PSS (352 S/cm) was achieved by varying the DMSO ratio. Moreover, the parameters of the EHD printing process including the flow rate, voltage, and printing speed were precisely controlled for various surface tension values of PEDOT:PSS solution to produce the optimum patterning of the PEDOT:PSS electrodes. As a result, bottom-contact OTFTs with EHD-printed PEDOT:PSS electrodes and a device architecture with pentacene and HMDS-treated $SiO_2$ as the semiconductor and dielectric layers, respectively, were fabricated with a field-effect mobility of 0.157 $cm^2/V \cdot s$. This value is approximately 100-fold higher than that of the equivalent bottom-contact pentacene OTFT with Au electrodes. In addition, we examined the work function of PEDOT:PSS and Au electrodes and crystalline morphologies of pentacene films on those electrodes to investigate the charge carrier injection behaviors of the two OTFTs.

## 2. Experimental

### 2.1. Materials

PEDOT:PSS (CLEVIOS™ PH 1000) and DMSO were purchased from Heraeus and Aldrich, respectively. These materials were used without any purification. Four different solutions of PEDOT:PSS were prepared with DMSO in the volume ratios 1:0.04, 1:0.08, 1:0.16, and 1:0.2. Thin films were spin-coated with the solutions on cleaned glass at 2000 rpm for 20 s. Triton X-100 as a surfactant was added to each sample at 0.1 wt% to optimize the surface tension of the PEDOT:PSS ink for the EHD printing [20].

The EHD printing process for patterning electrodes: Fig. 1 shows a schematic diagram of the EHD printing process, in which the glass syringe is filled with each of the modified PEDOT:PSS solution and a metallic nozzle holder is attached to the end of the syringe. Then, the solution is ejected through the nozzle with a diameter of 220 μm at a specific flow rate by using a motorized pump. Further, a voltage generated with a power supply was applied to induce an electric field between the nozzle and the copper substrate as the ground. The printing speed was controlled with an x and y axis stage to increase the line resolution. The whole process was interfaced with a computer and monitored with a CCD camera.

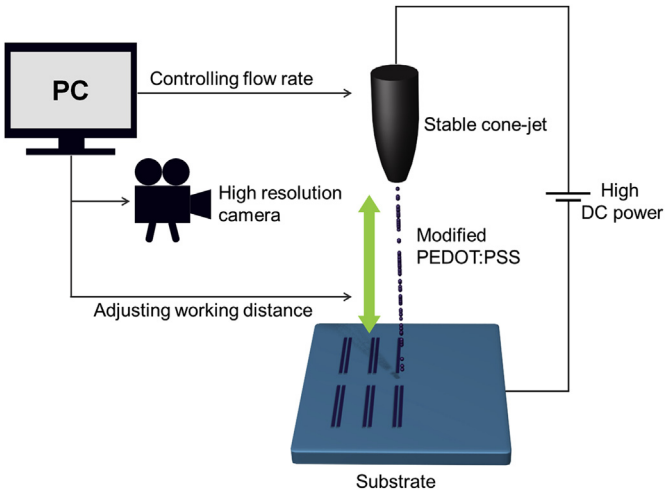


**Fig. 1.** Schematic diagram of EHD printing process for patterning PEDOT:PSS.

### 2.2. Fabrication of OTFTs

Highly doped n-type (100) Si wafers with 300 nm thick thermally grown $SiO_2$ layers were used as gate substrates. Hexamethyldisilazane (HMDS, Aldrich) and dimethyl chlorosilane-terminated polystyrene (PS-b, PS-Si$(CH_3)_2$Cl, $M_W$ = 8000, PDI = 1.06, Polymer Source) were used as surface modification layers without further purification. Surface-modified oxide dielectrics were fabricated by first cleaning the substrates with an organic solvent (acetone), and then exposing the surfaces to UV-ozone. HMDS was used as a master solution without any dilution; PS-b was dissolved in toluene (1.0 wt%). All solutions were spin-coated onto the substrates in ambient air, and the resulting films were annealed at 120 °C for 30 min. The layers were sonicated in a toluene bath for 3 min to remove the ungrafted HMDS and PS-b residues, then annealed at 120 °C for 10 min to remove residual solvent. 50 nm thick pentacene (Aldrich) films were deposited as the active layers *via* organic molecular beam deposition (deposition rate = 0.2 Å/s; vacuum pressure = $10^{-7}$ Torr; substrate temperature = 25 °C).

Characterization: the EHD-printed PEDOT:PSS films were characterized by an atomic force microscope (AFM), optical microscope (OM), and ultraviolet photoemission spectroscopy (UPS). UPS was performed using the 4D beamline in the Pohang Accelerator Laboratory (PAL) in Korea. The work function (Φ) values were obtained using $\Phi = h\upsilon - E_{cutoff} + E_{Fermi}$. The $h\upsilon$ is the incoming photon energy (90 eV), and the −5 V bias was applied to make a clear boundary in the $E_{cutoff}$ region. 2D-grazing incidence X-ray diffraction (2D-GIXD) experiments were performed on pentacene films at the 3 C beamline (wavelength = 1.54 Å) in the PAL.

## 3. Results and discussion

Fig. 2a shows the variation in the conductivity with the DMSO to PEDOT:PSS volume ratio. The conductivity increased with increasing the volume ratio; the maximum conductivity was obtained at the ratio 1:0.2. In general, DMSO, a polar solvent with a high dielectric constant, reduces the electrostatic interaction between PEDOT (positively charged) and PSS (negatively charged)