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Ultrasonically sprayed and inkjet printed thin film electrodes for organic solar cells

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ABSTRACT

Thin film pi-conjugated poly(3,4ethylenedioxythiophene): poly(styrenesulphonate) (PEDOT:PSS) as a hole transport layer on indium tin oxide is a key element in some of the most efficient organic photovoltaic and light emitting devices to date. Films are typically deposited by spincoating, which is not readily scalable. In this paper we investigate the critical parameters for both inkjet and ultrasonic spray deposition of PEDOT:PSS thin films on commercial indium tin oxide as a potentially scalable approach to contact formation. Inkjet parameters investigated include drop spacing and substrate temperature. Ultrasonic spray coating parameters investigated include substrate temperature and solution flow rate. We also show that the ink viscosity has a Newtonian character, making it well suited for inkjet printing. Films were characterized via optical profilometry, sheet resistance and atomic force microscopy. Optimized inkjet printed and ultrasonic sprayed PEDOT:PSS films were then compared to spincast layers in a prototypical bulk heterojunction photovoltaic device employing a poly(3-hexylthiophene) and [6,6]-PCBM (6,6-phenylC61-butric acid-methyl ester) blend as the absorber. Practically all three approaches produced devices of comparable efficiency. Efficiencies were 3.6%, 3.5% and 3.3% for spin, spray and inkjet depositions respectively.

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1. Introduction

One of the most attractive routes to clean solar generated electricity is the development of large-scale, efficient, solution processable organic photovoltaic devices (OPV). To realize this goal, requires scalable methods of device processing showing large area deposition with little efficiency loss. Spin coating is currently the laboratory standard for rapid development of small area films from solution. However, there is inherently a large amount of waste in spin casting and it is not compatible with reel-to-reel or large area processing, thus alternatives are needed. In addition, while small devices are reproducible, techniques have not been developed that confirm the scalability of the technology.

Emerging as a next generation deposition technique, inkjet printing has applications ranging from patterning printed circuit boards to flat panel displays and photovoltaics. Piezoelectric drop on demand inkjet is an ideal process for the precise deposition of picoliters of liquid materials. When designing inks for inkjet printing, the composition and character of the solution, deposition accuracy and properties of the resultant film are highly sensitive to nozzle design and the waveform applied to the piezoelectric element. Inks with Newtonian viscosities allow more control of the parameters needed for nozzle design. Polymeric intensive inks require heavy dilution, high solubility, low volatility and acceptable nozzle surface interactions to minimize clogging. These critical parameters must be optimized to allow for proper drop formation, accuracy, and continuous film formation. Once an ink has been developed, inkjet printing enables precise material deposition, rapid prototyping, unlimited layering, and high throughput. Inkjet is broadly used in the fabrication and testing of thin film transistors [1–3], polymer light emitting diodes (LED) and displays [4–6] and for combinatorial bulk heterojunction (BHJ) libraries [7]. Several recent articles provide reviews of current inkjet technology [4,8,9].

In addition to inkjet printing, several spray deposition techniques are also being explored for large area deposition of solution processible materials. Evaporative spray deposition from ultradilute solution (ESDUS) has shown promise [10,11] but requires heating of the solution. Air brush spray methods are inexpensive and allow high throughput however precise deposition control is limited [12,13]. Ultrasonic spray deposition eliminates the heating step used in ESDUS and narrows the drop size dispersion thereby increasing deposition uniformity. Improving upon simple spray techniques [12,14], ultrasonic spray deposition moderates sprayed droplet sizes through precisely controlled ultrasonic drop formation creating a narrow distribution of drop sizes. The drop sizes are comparable or even smaller than inkjet drops. Shown in Fig. 1 the atomized solution is directed onto a substrate by a clean gas stream. Deposited films are optimized by varying solution flow rate, carrier gas flow and substrate temperature. This approach is well suited for large area organic conductor processing and can build upon recent spray

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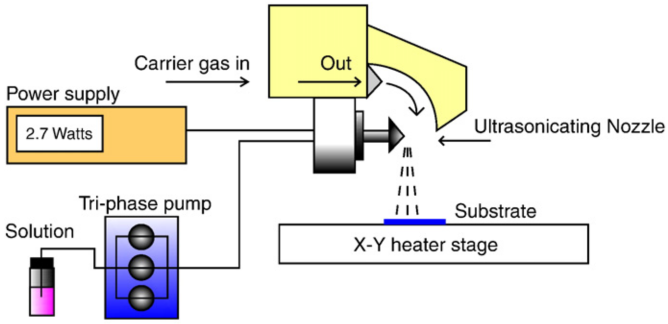

Fig. 1. Schematic of ultrasonic spray deposition system. The ultrasonic nozzle mediates a narrow drop size distribution while the tri-phase pump maintains regular flow.

deposition developments in the fields of organic transistors [14] polymer LEDs [11] organic solar cells [12] and small molecule devices [15]. Ultrasonic spray deposition clogs less readily than inkjet facilitating the use of lower boiling point solvents and higher solution concentrations. It also has upper viscosity limits similar to inkjet on the order of 50×10^{-3} Pa s. Thick films are easily made via layer-by-layer deposition after optimization of solution properties, substrate temperature and desired surface treatment.

The focus of this paper was to look at the parameters necessary to optimize the film quality for both inkjet and ultrasonic deposition methods with the goal to produce smooth, continuous films with electronic properties comparable to spin coated films. We employed commercial Pi-conjugated poly(3,4-ethylenedioxythiophene):poly (styrenesulphonate) (PEDOT:PSS), currently the most widely used conducting polymer in the field of organic electronics. As an intrinsically conducting, electrostatically bound ionic blend it is applicable for thin film applications and large scale processing [16]. It is used as a hole transport layer on transparent conducting oxides serving to control the interfacial properties, both as a transparent conductor and as a planarizing layer. In addition, PEDOT:PSS has been used in a myriad of antistatic applications as well as for chemical fuses [17], thin film transistors, polymer LED displays and organic photovoltaics [6,18]. The electronic benefits offered by the use of PEDOT:PSS include high workfunction, a tunable bandgap, hole transport/ electron blocking properties, and a uniform surface [18]. In polymer photovoltaics, utilizing PEDOT:PSS as the effective electrode increases rectification and device performance [19,20] leading to improved open circuit voltage (V_{oc}) and fill factor (*FF*). Thin films of the electrode material PEDOT:PSS were fabricated in this study via spin coat, inkjet and ultrasonic spray methods. The optimized films were characterized by optical profilometry, resistivity measurements and atomic force microscopy (AFM). The deposited films were then incorporated in OPV devices with bulk heterostructures of poly(3-hexylthiophene) (P3HT) and 6,6-phenylC61-butric acid-methyl ester (PCBM) as the active layer. The device architecture used to test the PEDOT:PSS layers is shown in Fig. 2. Results indicate that once optimized, device performance is nominally equivalent irrelevant of the PEDOT:PSS deposition method.

2. Experimental details

Baytron P VP AI 4083, an aqueous dispersion of PEDOT:PSS, was obtained from HC Starck, P3HT from Reike, PCBM from Solenne-BV, and dichlorobenzene from Aldrich. PEDOT:PSS was prepared by diluting with 75% DI water. The P3HT:PCBM blend solution was prepared using 1:1 mass ratio of polymer to fullerene for a 50 mg/mL total concentration in dichlorobenzene. The blend solution was heated to 60 °C and stirred for several hours. Viscosity measurements were performed on a TA Instruments AR-G2 controlled stress rheometer using a 60 mm diameter 1° cone and 1 mL of solution. A standard flow test was performed (i.e., viscosity is measured over a range of shear rates) on the inks [21].

Patterned indium tin oxide (ITO) coated glass substrates (Colorado Concept Coatings) were prepared by ultrasonic brushing with a liquinox surfactant solution followed by a DI water rinse. The substrates were subsequently cleaned in ultrasonic baths of acetone and isopropanol followed by an oxygen plasma surface treatment.

For the ultrasonically spray coated PEDOT:PSS films we used a Sonotek ultrasonic spray nozzle #8700-120, Omega Engineering mass flow regulator and a Fluid Metering Inc. VMP Tri reversible flow pump. The ultrasonic nozzle drop dispersion characteristic is quoted in the manufacture specifications as 10 µm to 100 µm diameters in size with the median of ejected drops having 18 µm diameters. Sprayed PEDOT: PSS films were optimized for minimized surface roughness while seeking the greatest uniform area. Edge effects presented difficulties for substrates smaller than 1.3 cm^2. The optimum spray parameters for deposition of PEDOT:PSS on ITO were nozzle height of 5 cm, N_2 flow of 8 L/min, solution flow of 2.6 mL/min, substrate temperature of 40 °C, power of 2.4 W and the solution temperature near 22 °C. Average roughness for these parameters measured by optical profilometry was minimized at 4.0 nm.

Inkjet PEDOT:PSS films were fabricated on a Dimatix 2800 drop on demand inkjet printer. Single layer thin films were optimized for minimum surface roughness and maximum continuity by varying individual drop spacing and substrate temperature. Films yielding optimum film quality had the largest drop spacing while maintaining an interconnected continuous network of lines (See Fig. 4). Substrate and ink temperatures were 28 °C while drop spacing was 25 µm for optimum inkjet PEDOT:PSS film quality.

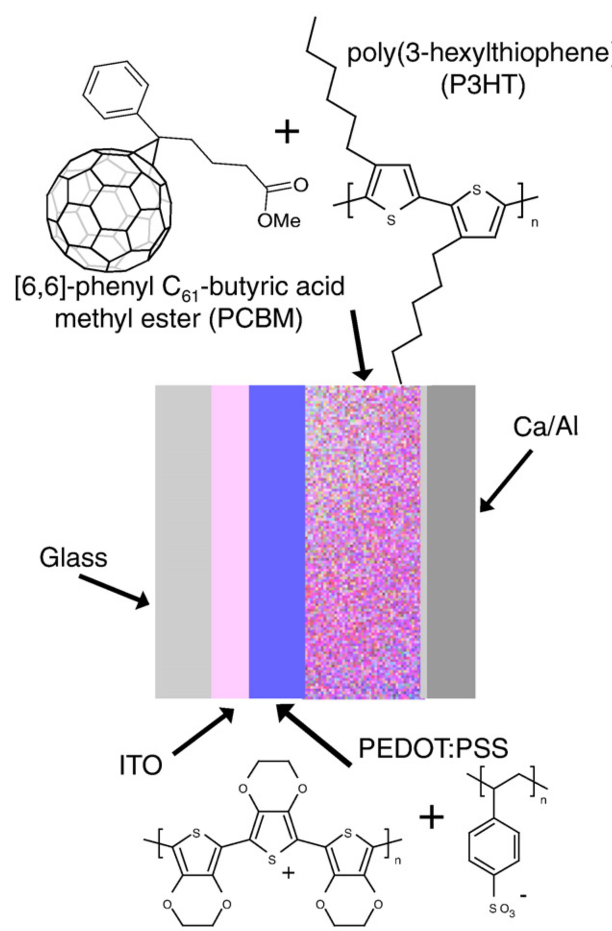

Fig. 2. Schematic of bulk heterojunction architecture used in testing PEDOT:PSS layers deposited by spin coating, inkjet printing and ultrasonic spray deposition.