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Electrospray aerosol deposition of water soluble polymer thin films

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ABSTRACT

We report the fabrication and characterization of thin films from the water soluble polymer sodium poly[2-(3-thienyl)-ethyloxy-4-butylsulfonate] (PTEBS) by electrospray deposition (ESD). Contiguous thin films were created by adjusting the parameters of the electrospray apparatus and solution properties to maintain a steady Taylor cone for uniform nanoparticle aerosolization and controlling the particle water content to enable coalescence with previously deposited particles. The majority of deposited particles had diameters less than 52 nm. A thin film of 64.7 nm with a root mean square surface roughness of 20.2 nm was achieved after 40 min of ESD.

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1. Introduction

An electrospray is a fine aerosol produced when electrical forces overcome surface tension forces in a liquid resulting in nebulization. While electrospray aerosols can be formed in a number of ways, the most common method is to apply a high electrical potential to a liquid inside of a metallic capillary tube. The liquid at the tip of the capillary forms a Taylor cone, formed by the competition between the electric force and surface tension. A fine jet of liquid is emitted from the tip of the Taylor cone and this jet breaks up into a fine aerosol of charged droplets. [1]. The droplets may be on the order of 10's of nanometers and ideally can be controlled by controlling the electric potential [2]. Electrospray deposition (ESD) has become a viable technology for preparing polymer thin films of less than 100 nm from a precursor solution for organic optoelectronic (OE) devices such as photovoltaic cells [3–5], light emitting diodes [6,7], and surface acoustic wave (SAW) sensors [8,9].

Laboratory-scale OE devices are commonly prepared by the spin casting method. However, spin casting is a low throughput and high waste process where much of the polymer is lost due to the high rotational speeds. A second problem is the inability for consecutive layering from common solvents. In order to add multiple layers of polymer, a solvent orthogonal to the previous layer is needed to prevent dissolution. Another potential disadvantage associated with the spin casting of a bulk solution is the presence of a vertical phase gradient due to the penetration of less soluble components [10,11]. These obstacles hinder simple, low-cost, commercially favorable solution based processes.

ESD is a method of depositing thin films which can overcome the problems associated with spin coating. First, ESD is inexpensive, efficient (minimal waste), and has a relatively high throughput [2] making it practical for large scale commercialization. Second, it overcomes the solubility issue between two adjacent layers. ESD generates nebulized aerosol particles which, depending on solvent volatility, can be nearly dry upon deposition so that prior layers do not dissolve. ESD can also be advantageous for controlled vertical (uniform and gradient) deposition of thin-films.

In this work we have developed and characterized thin films of the water soluble polymer sodium poly[2-(3-thienyl)-ethyloxy-4-butylsulfonate] (PTEBS) (Fig. 1) from ESD for use in polymer solar cells (PSC). PTEBS thin films deposited by spin coating and drop casting have successfully been used as the electron donor in the fabrication of PSCs [12–18]. Water soluble polymers are advantageous in that their solvent is cheap and environmentally friendly. Water soluble polymer thin films have also been used in the fabrication of organic transistors [19,20], LEDs [21], and fluorescent CdTe/polymer films [22]. The aim of this study is to understand the evolution of thin, nanoscale films from charged electrospray aerosols.

2. Experimental

Transparent conductive FTO (fluorine doped tin oxide) coated glass substrates of 8–12 Ω sheet resistance were purchased from Hartford Glass Company. A highest grade V1 AFM mica disc (purchased from Ted Pella) was then adhered to the center of the FTO

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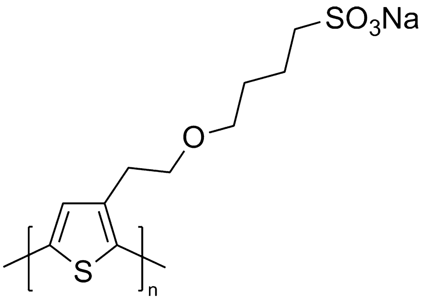

Fig. 1. Molecular structure of PTEBS [23].

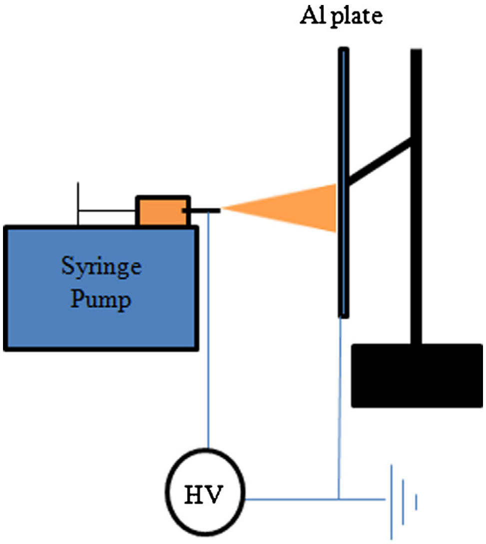

Fig. 2. Schematic of horizontal ESD apparatus used in experiments.

glass substrate. The mica disc was cleaved immediately before sputtering with a 2.7 nm platinum film.

The water-soluble polythiophene PTEBS was purchased from QCR Solutions. A stock solution of PTEBS was created by dissolving in DI water at a concentration of 2% by weight. The solution was stirred for three days at room temperature. Water and ethanol were added to dilute the stock solution to 0.5% with a solvent ratio of 1:1. The diluted solution was then sonicated for 15 min immediately before being loaded into a 1 ml syringe with a 30 gauge hypodermic needle.

Fig. 2 is a schematic of the horizontal electrospray configuration used to deposit the PTEBS thin films. The distance between the needle tip and the grounded aluminum plate was 10 cm. The flow rate through the needle, controlled by a syringe pump, was 1.5 μl/min and the applied voltage was 8–9 kV. The FTO substrate was grounded to the aluminum plate using copper tape before the syringe pump and voltage were activated. Films were analyzed using a Veeco Icon Dimension AFM, Ambios XP-1 profilometer, and a Lambda 35 UV-Vis spectrometer.

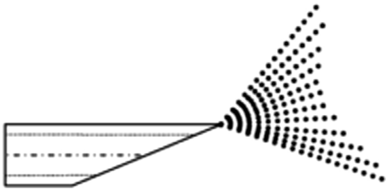

Fig. 3. ESD spray formation from 30 G hypodermic needle [24].

3. Results and discussion

One of the most important requirements for creating a uniform thin film from ESD is to maintain a stable Taylor cone at the tip of the spraying capillary. Steady Taylor cones result from the proper balance of the following parameters (achieved at the values listed above): distance between spray tip and grounded substrate, flow rate through the needle, applied voltage, and solution properties. The best films are achieved through a careful balance of these parameters. Interruptions in steady flow from the tip of the Taylor cone can result in the emission of large droplets which degrade film quality. Ethanol was added to the solution to reduce the liquid surface tension compared to a pure water solution. A solution concentration of 0.5% was found to result in good Taylor cone stability. The syringe pump flow rate was adjusted to replenish the fluid removed by the aerosol and such that the ESD process remained electrostatically driven. The applied voltage was varied between 8 and 9 kV depending on the flow rate and distance between the needle and grounded substrate. For the PTEBS polymer at these applied voltages, a tip-substrate distance of 10 cm was found to provide the best films. This may be due in part to the amount of time needed for evaporation of the solvent in droplets. Longer distances result in dry particle deposition which leads to rough surfaces. Shorter distances result in wet particle deposition causing the film to run or drip. The voltage was increased from 0 kV and held constant once a stable Taylor cone was present at the tip of the beveled edge of the hypodermic needle (Fig. 3). Other authors have also reported Taylor cone stability at the orifice of the nozzle apex [24,25]. Chen et al. reported a decrease in deposited particle size with a sharper needle tips [26].

Fig. 4 shows optical microscope images of PTEBS thin films from ESD where an unstable (left) and a stable (right) Taylor cone were

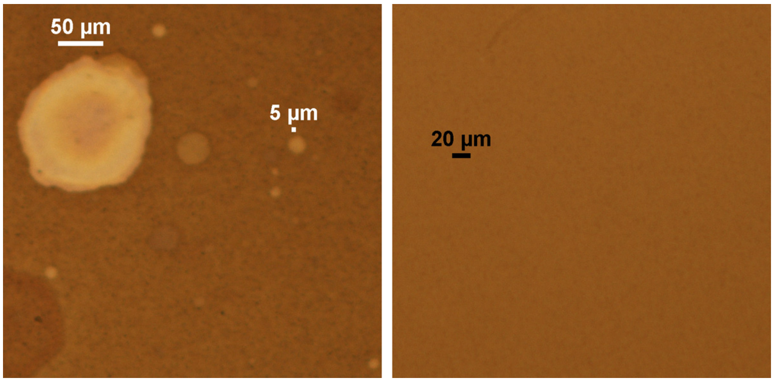

Fig. 4. Optical microscope image at 10× of PTEBS films where a Taylor cone was (left) unstable and (right) stable.