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Feasibility test of spray-coating method for patterning of vapor phase-polymerized poly(3,4-ethylenedioxythiophene) thin film

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ABSTRACT

In this study, spray-coating has been opted to prepare patterned Poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes for an organic thin film transistor (OTFT). The conducting polymer was grown *via* the vapor phase polymerization (VPP) method. The film quality of VPP-PEDOT critically relies on the uniformity of oxidant film selectively patterned on a thermally oxidized Si-wafer surface prior to the polymerization. Therefore, to improve the uniformity of the oxidant film, this study tried to discover best conditions of spray-coating. Several different temperatures of Si-wafer substrate, distances from nozzle to wafer, and spray times were tested during the spray coating process. Then, sprayed oxidant films and vapor phase-polymerized PEDOT patterns were characterized by several thin film analyzing tools such as FE-SEM and optical microscope. The characterization found that the best conditions of spray coating are room temperature, 18 cm, and 50 s of substrate temperature, spray distance, and time, respectively.

1. Introduction

To realize large-area with low-cost application, various deposition techniques, such as inkjet [1] and screen printing [2] or doctor blading [3], have been demonstrated. Nowadays, among them, spray-coating technique has attracted attention from numerous researchers. Spray coating method is well established in graphic arts, industrial coatings, and painting [4]. Thus, this simple, low-cost and high-throughput large-area deposition technique with integration of polymer electrodes into TFT ensures ideal coating on a variety of surfaces, which can be applied to many of fields such as organic thin-film transistors (OTFTs), organic photovoltaic cells (OPVs), and organic light-emitting diodes (OLED) [5–7].

A few recent publications introduced conventional spray coating as a polymer deposition method for organic solar cells (OSCs) [8]. Vak et al. showed that an optimized organic bulk heterojunction solar cell fabricated by using spray deposition performed comparably to devices, which were fabricated by spin coating [9]. Since then, some of the work has been conducted on examining the choice of solvents and the effects of annealing on performance of devices prepared by spray coating [10], the influence of the airbrush settings on the film morphology [11], the reproducibility of fully spray-coated organic photodetectors with low dark current densities [12], and the surface morphology of spray-coated films based on pristine solvents and multiple solvent systems [13]. However, most of the conductive films were sprayed directly by using polymer solution, which is difficult to control the thickness and roughness of film even if those films showed reasonably good electrical conductivities.

Among several conducting polymers used in practical applications, poly-3,4-ethylenedioxythiophene (PEDOT) has been known as a particularly robust and well conducting system [14]. PEDOT is available from H.C. Starck as an aqueous suspension (Baytron P) that can be conveniently coated onto a number of different surfaces by different coating techniques [14]. On the other side, very recent studies [15–17] successfully demonstrated that PEDOT can be prepared as a highly pure and homogeneous thin film. For example, Winther-Jensen and West [15], and Kim et al. [17], showed that 3,4-ethylenedioxythiophene (EDOT), a monomer of PEDOT, can be vaporized simply via temperature elevation, and can be quickly self-assembled and easily polymerized on an oxidizing agent pre-coated substrate, thereby producing a highly pure and homogeneous PEDOT thin film.

Since the above-mentioned advantages of spray coating and VPP methods are mostly complimentary to each other, in this study, both methods were combined together to prepare a selectively patterned PEDOT thin film. For example, the thickness and roughness of PEDOT thin film can be precisely controlled

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during the VPP process but not during spray coating, while the patterning can be realized by the spray coating method but not by the VPP method alone. However, a major potential hurdle of this synergistic combination is how the oxidant solution can be uniformly sprayed and coated on the substrate of interest since the quality of PEDOT thin film has a great dependence on the morphology of spray-coated oxidant film. Therefore, to search an optimum condition of uniform oxidant coating, various important parameters of spray-coating, e.g., spray distance, spray time, and substrate temperature were carefully investigated. Finally, PEDOT film prepared by spray-coating method was compared to the film prepared by spin-coating method.

2. Experimental

2.1. Preparation of oxidant solution and cleaning of substrate

Butanol and Fe(III)Cl_3 were received from Aldrich Chemical Company (USA). Polyethylene glycol-polypropylene glycol-polyethylene glycol (PEG-PPG-PEG) was purchased from Junsei Chemical Company (Japan). Polyurethane diol solution (concentration of 88 wt% in water, DUDO) was received from Aldrich Chemical Company (USA). Si-wafer (15 mm × 15 mm) was purchased from Silicon Technology Corporation (Japan).

DUDO of 1.0 wt% and PEG-PPG-PEG of 0.1 wt%, and Fe(III)Cl_3 of 2.1 wt% were dissolved in butanol of 30 g. This solution was used for spray coating. Wafer was cleaned in ethanol ultrasonically for 30 min and then further purified by argon plasma treatment with argon pressure of 0.3 Torr and power of 32 W for 2 min.

2.2. Spray coating and patterning of oxidant film

A spray gun (GP-1) was purchased from Fuso Seiki Corporation (Japan). The spotless wafer was placed on either heated or unheated support plate. The spray gun was backed up with nitrogen gas at 10 psi. 10 psi is a verified pressure that can minimize the loss of the droplets already piled up on the wafer by strong collisions of vapor streams. Tested spray distances from nozzle to wafer range from 16 cm to 20 cm. Spray times of 45–52 s were tested to find out a uniformly coated condition without any blank space. Additional control of the deposition condition was achieved by varying the solution flux. Two different oxidant films (whole and patterned oxidant films on Si-wafer) were simply separately prepared for comparison. In particular, oxidant pattern was prepared by using a metal shadow mask. Fig. 1 shows a schematic view of the spray coating process.

Oxidant films were also prepared by spin-coating method. The films were coated on Si-wafer surfaces at 2500 rpm during 30 s.

2.3. VPP and patterning of PEDOT thin films

EDOT was purchased from Aldrich Chemical Company (USA). Thermal evaporator system used in this study was manufactured by DaDa TG Company (Korea).

The oxidant-patterned wafer sample was transferred into a vacuum chamber. Then the EDOT monomer was placed in a quartz beaker within the chamber. The beaker temperature was set to 70 °C through thermal evaporation system. When the temperature reaches 70 °C, EDOT vapors started to hit the oxidant film, and it was maintained for 30 min. After the polymerization was terminated, the chamber was pumped down to 3.0×10^{-2} Torr and then the samples were annealed at 60 °C for 60 min. A schematic of the process is shown in Fig. 1.

2.4. Characterization of PEDOT thin films

Surface and cross section images of oxidant and PEDOT films were obtained by an optical microscope (BX-51, Olympus Corporation, Japan) and field emission scanning electron microscope (FE-SEM; Sirion 200, FEI Company, America). The thickness of PEDOT films was also obtained by FE-SEM.

3. Results and discussion

3.1. Effect of substrate temperature

3.1.1. Effect of Si-wafer temperature to the patterned shape of oxidant film

Patterned shape of oxidant is greatly affected by the substrate temperature. When the droplets were sprayed out of nozzle and hit the surface of wafer, solvent is quickly vaporized at high temperature, which is good for pattern generation [7]. Accordingly, the patterns become sharper and clearer as the substrate temperature increases.

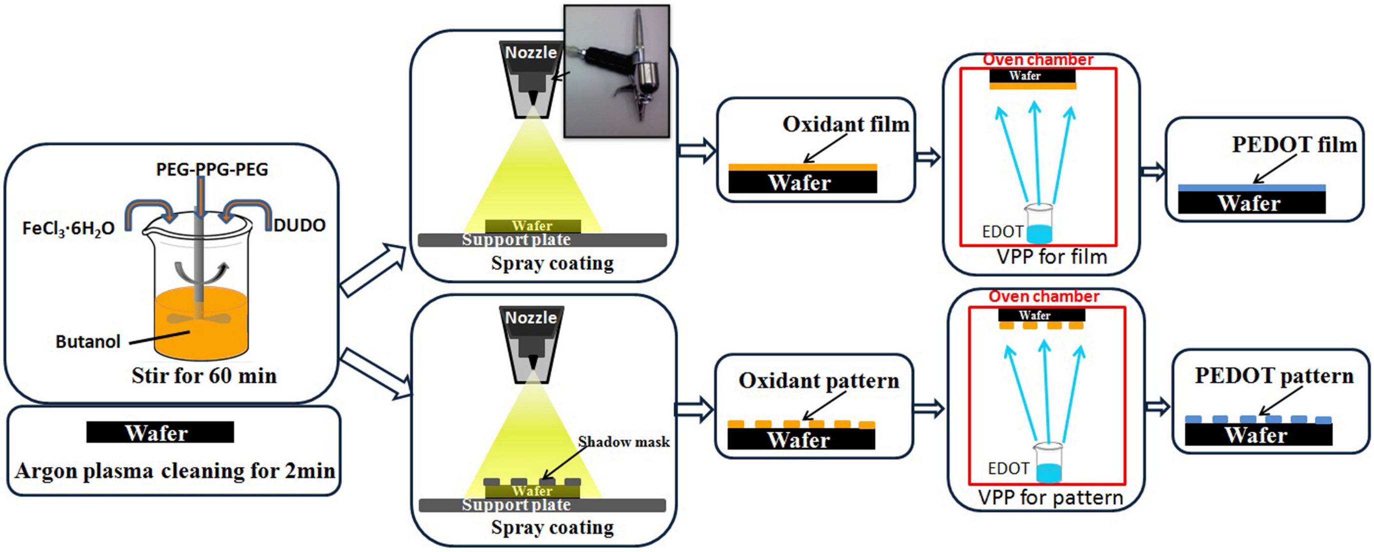

Fig. 1. A schematic of PEDOT patterning process and the synthesis of VPP-PEDOT thin film.