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Translated structural morphology of conductive polymer nanofilms synthesized by vapor phase polymerization

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ABSTRACT

Vapor phase polymerization (VPP) is at the forefront for synthesizing highly conductive poly(3,4-ethylenedioxythiophene) (PEDOT). However, little attention has been directed towards the factors affecting chain growth in solid-state polymerization. In this study, we revealed the VPP growth mechanism of a PEDOT film and thus provided a link to the structure-property relationship. Our results show that the monomers are activated on the oxidant layer and the chain growth is guided by the substrate morphology *via* diffusion into the oxidant layer, producing a thin PEDOT-stuffed layer. Further film growth proceeds through diffusion of the monomer into the oxidant layer following the structural texture of the oxidant film. This reaction-diffusion process generates a propagating PEDOT-stuffed/oxidant interface (with a constant velocity), thus leading to the film growth. As a result, the film grows linearly with EDOT evaporation time and the structural texture of the oxidant film was translated to the PEDOT film, thus determining the critical properties, such as the morphology, conductivity, and transparency of the film.

1. Introduction

Direct depositing of conducting polymers onto a variety of substrates and nanostructures has offered unprecedented opportunities in optoelectronics, biomedical and energy applications [1–6]. Poly(3,4-ethylenedioxythiophene) (PEDOT), in particular, has received great attention by several advantages, such as high conductivity [7], excellent transparency [8] in the visible range, photocatalytic [9] and electrocatalytic activities [10], and thermoelectric properties [11,12]. Methods to fabricate high-quality PEDOT films (*i.e.*, a highly conducting, transparent film) are of intensive research interest as these films show great promise for applications in the relevant fields. However, many of the current fabrication strategies have significant limitations. For example, solution-phase processing with water-soluble polyelectrolyte or direct oxidative growth of the polymer commonly suffers from inhomogeneity and reproducibility issues [13], while electro-polymerization requires a conductive substrate to start with. Among all fabrication strategies, vapor phase polymerization (VPP) of conducting polymers offers a fast and facile production of pure, uniform and highly conducting polymer thin films on a wide range of substrate materials with process compatibility [14–16].

In principle, VPP of PEDOT is a simple and straightforward method: 3,4-ethylenedioxythiophene (EDOT) monomers are exposed to a Fe-oxidant layer, which are then absorbed by the oxidant layer, leading to PEDOT film growth *via* oxidative polymerization reaction. Continuous research effort has been devoted to understanding the chemical reaction dynamics in order to control the film growth. Winther-Jensen moderated the pH of the reaction media with organic base, leading to a four-fold increase in PEDOT conductivity (as high as 1000 S/cm) [17]. Fabretto reduced the reactivity of Fe-oxidant by incorporating an amphiphilic co-polymer, poly(ethylene glycol-*ran*-propylene glycol), resulting in a highly conductive and transparent film [18]. We previously

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reported the effects of solvent and oxidant on the PEDOT film structure and conductivity [2,19–21]. While there are many studies on the chemical reaction dynamics during the film formation, there is insufficient information into how the oxidant and monomer interact in the solid state and lead to chain growth.

Controversial debate persists within the literature as to how the film grows and where the nucleation starts, [20–23] *i.e.*, whether the film formation follows a top-down process [24] (diffusion of monomers through the initially formed layer to reach the oxidant layer for polymerization), or a bottom-up process [25] (diffusion of oxidants outward through the initially formed layer for oxidation of the adsorbed monomer). Understanding the film growth mechanism is thus a critical subject, due to this knowledge being required to precisely tailor the film properties. In this paper, we reveal the film growth mechanism by probing the initial film growth profile and the diffusing species at the nucleation stage and correlate the growth mode with the physical properties of the PEDOT film. $FeCl_3$ was used as the oxidant to produce PEDOT films, as it provides good elemental contrast from the PEDOT film, thereby enabling easy probing of the diffusing species.

2. Experimental

100 nm-thick SiO_2-coated Si substrates were cleaned by immersing them into piranha solution (2:1 mixture of 98% aq. sulfuric acid and 30% aq. hydrogen peroxide) for 10 min. They were then exposed to UV illumination (wavelength = 184 nm and 254 nm) for 20 min to produce hydroxyl (−OH) groups on the surface of the substrate in order to facilitate siloxane bond formation to a (3-aminopropyl) trimethoxysilane (APS) monolayer. The samples were then dipped into 50 mL of an ethanol solution containing 0.1 mM APS (97% purity) and 1 μM acetic acid for 1 h to form the APS monolayer. They were then rinsed by ethanol and dried by blowing N_2. The use of an APS monolayer provided a uniform distribution of $FeCl_3$ on an APS-coated SiO_2 surface, possibly due to the lone pair interaction of the Fe(III) to -NH_2 surface groups in the APS monolayer. This led to the formation of a uniform and homogeneous PEDOT film on SiO_2.

A solution containing $FeCl_3$ oxidant in ethanol was spun onto the substrates at 3000 rpm with a spin coater for 60 s. The concentration of this solution varied from 1 wt.% to 20 wt.% to investigate the concentration effects on the growth rate, diffusion and final thickness of PEDOT. The oxidant-coated samples were placed in an oven at 80 °C for 1 to 30 min, in which EDOT vapor (1 g of EDOT monomer placed in a 10 mL container) was evaporatively deposited on the oxidant-coated layer, as shown in Fig. 1(a). Finally, the PEDOT-stuffed films were washed with methanol to remove unreacted species and by-products.

The sheet resistances were measured by a four-point probe (CMT-series, Changmin Co. Ltd., Korea). The morphologies of the deposited films were analysed by field-emission secondary electron microscopy (FE-SEM, Jeol-7401F) and by atomic force microscopy (AFM, SPA 400 Seiko, Japan). AFM characterization was performed in air, at room temperature, and in standard semi-contact mode using commercial silicon cantilevers. Depth profiling of the elements in the samples was conducted by Auger electron spectroscopy (AES) and the compounds were identified by X-ray photoelectron spectroscopy (XPS, PHI 5800

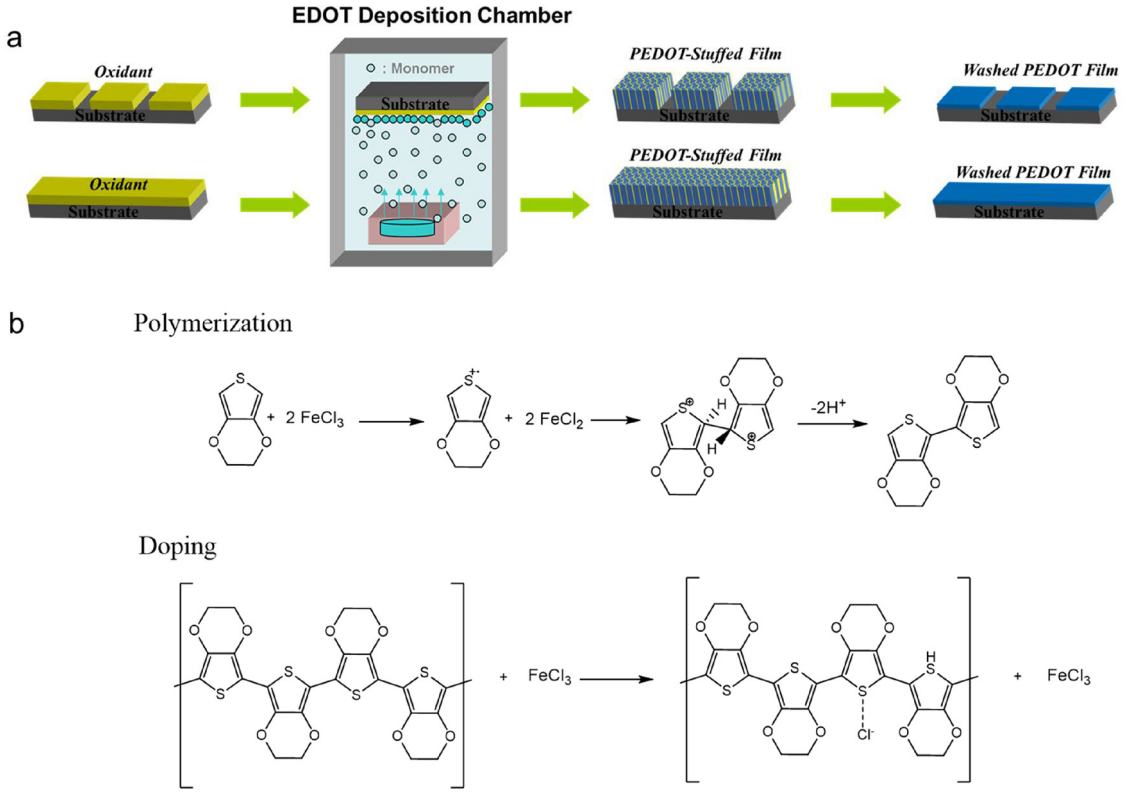

Fig. 1. (a) Schematic diagram showing a vapor phase deposition of EDOT monomer on oxidant layer, leading to PEDOT film. (b) A series of oxidation and deprotonation steps leading to the oxidative polymerization of conjugated PEDOT. The doping step also occurs simultaneously.