

Study on Poly(3,4-ethylenedioxythiophene) Thin Film Vapour Phase-Polymerized with Iron(III)Tosylate on AcOH-Catalyzed 3-Aminopropyltriethoxysilane Self-Assembled Monolayer

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Abstract

In this study, PEDOT thin films polymerized with Iron(III)tosylate ($\text{Fe}(\text{PTS})_3$) and grown on acetic acid-catalyzed 3-aminopropyltriethoxysilane self-assembled monolayer (APS-SAM) surfaces by VPP method have been investigated. PEDOT thin films were synthesized on APS self-assembled SiO_2 wafer surface at two different concentrations (20 wt% and 40 wt%) and growth time (3 and 30 minutes), and then they were compared. PEDOT vapour phase-polymerized with 40 wt% $\text{Fe}(\text{PTS})_3$ oxidant completely formed a thin film on acetic acid-catalyzed APS-SAM surface while with 20 wt% $\text{Fe}(\text{PTS})_3$ did not at all. It means that the oxidant can be uniformly coated on acetic acid-catalyzed APS-SAM surface at the 40 wt% concentration, which gives rise to the uniform growth of PEDOT thin film on it.

Key words: Poly(3,4-ethylenedioxythiophene), 3-Aminopropyltriethoxysilane, Vapor Phase Polymerization, Iron(III)tosylate

1. Introduction

For decades, conductive π -conjugated polymers have fascinated many scientists with their great potential for applicability to the next-generation flexible display device such as organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs)^[1]. Among these polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been particularly focused on as a potential component of OTFT or OLED devices due to its superb material characteristics^[2]. PEDOT is electrochemically very stable, and it has a low bandgap energy (1.5~1.7 eV) and a considerably high electrical conductivity. PEDOT thin film is generally synthesized via two different methods, i.e., spin-coating or oxidative vapour phase polymerization (VPP). Electrical characteristics of the thin film prepared by those methods are critically affected by its growth morphology. In particular, our recent study showed that the morphology of PEDOT thin film polymerized with FeCl_3 and grown on a high quality 3-aminopropyltriethoxythiophene self-assembled

monolayer (APS-SAM) is noticeably different from that of the thin film grown on a relatively low quality APS-SAM^[3]. The film grown on the high quality SAM by vapour phase polymerization (VPP) method is denser (or less porous) and more robustly adhered to silicon oxide surface. It suggests that APS-SAM helps to improve the PEDOT film quality, thereby improving the electrical characteristics of the film. It means that the film morphology is considerably affected by APS-SAM, itself as well as its quality. Therefore, in this study, in order to improve electrical characteristics of PEDOT thin film vapour phase-polymerized and then doped with $\text{Fe}(\text{para-toluenesulfonate})_3$ ($\text{Fe}(\text{PTS})_3$), the thin films were grown on two differently prepared (both high and low quality) APS-SAM, and they were compared in terms of oxidant concentration and growth time.

2. Experimental Section

Chemicals used in this experiment, iron(III)tosylate (or Iron (III) *para*-toluenesulfonate), 3-aminopropyltriethoxysilane (APS), 3,4-ethylenedioxythiophene, were purchased from Sigma/Aldrich company, USA, and toluene (reagent grade) was refluxed under Na metal and further distilled under N_2 . Oxidized silicon wafer

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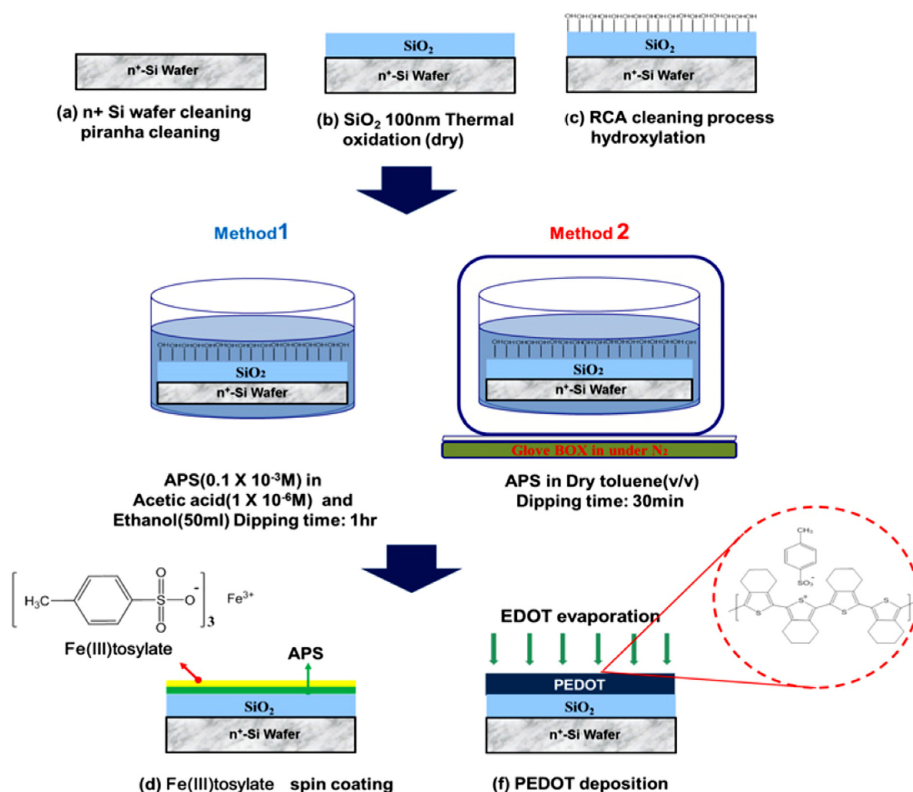


Fig. 1. Schematic diagram of PEDOT vapour phase polymerization (VPP) method. Fe(PTS)₃ was used as a dopant as well as an oxidant for the VPP process.

(1.5 cm×1.5 cm) was ultra-sonicated in ethanol for 30 min. after ethanol wash. And then, the wafer was repeatedly treated with piranha solution and DI water to remove organic/inorganic contaminants on it. After that, to remove water molecules adsorbed on the wafer surface, it was dried in a vacuum oven at 70°C for 30 min. On the cleaned wafer, two different samples of APS monolayer were self-assembled at completely different conditions. First sample is a monolayer prepared in a glove box under a strictly controlled humidity (<10 %RH). And also completely anhydrous toluene was used as a solvent throughout the preparation. The wafer substrate was dipped into APS (120 μL) solution dissolved in 60 mL of anhydrous toluene for 30 min. Second one is a APS monolayer self-assembled in atmospheric environment without any suppression of humidity. The monolayer was self-assembled in APS (0.1×10⁻³ M) solution mixed with acetic acid (1×10⁻⁶ M) in 50 mL of ethanol for 1 h. Two different oxidant solutions for the growth of PEDOT thin film were prepared with

20 wt% and 40 wt% iron(III)tosylate 6H₂O dissolved in ethanol. Oxidant films were spin-coated on the wafer substrates at 2500 rpm for 90 s. And then, as shown in Fig. 1, PEDOT was vapor phase-polymerized in an oven at 70°C for 30 min. In order to characterize APS-SAM and PEDOT thin film, AFM (VEECO, Nanoman, U.S.A) and FE-SEM (FEI, Sirion model, Netherlands) were used, and sheet resistance of PEDOT thin film were measured using a 4-point probe (A.I.T, CMT-SR2000).

3. Results and Discussion

Our previous study showed that the growth morphology and interfacial adhesion of PEDOT thin film is highly dependent upon APS-SAM^[3]. That is, APS-SAM helps FeCl₃ solution to uniformly coat SiO₂ surface and also to promote adhesion between PEDOT thin film and Si wafer substrate, thereby resulting in improved film quality. PEDOT thin film is vapour

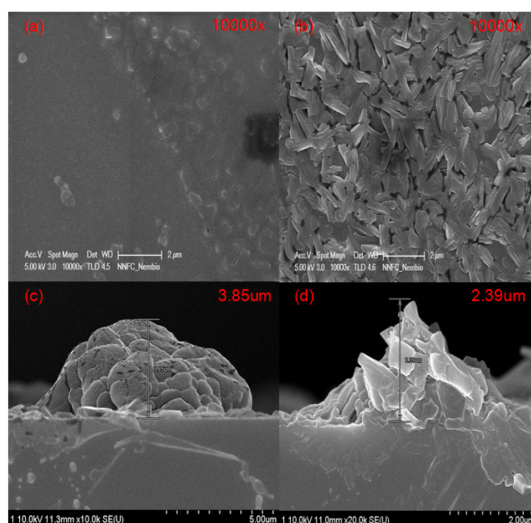


Fig. 2. FE-SEM images of PEDOT thin films grown on acetic acid-catalyzed APS-SAMs. All of the films used 20 wt% $\text{Fe}(\text{PTS})_3$. The films in (a) and (c) images were grown for 3 min and those in (b) and (d) images for 30 min.

phase-polymerized generally via two different oxidants, i.e., FeCl_3 and $\text{Fe}(\text{PTS})_3$. Both oxidant have their own merits. However, unlike FeCl_3 , $\text{Fe}(\text{PTS})_3$ is more advantageous to the deposition of less porous film. Thus, as the first section of these serial publications, PEDOT thin films polymerized with the $\text{Fe}(\text{PTS})_3$ oxidant and grown on acetic acid-catalyzed APS-SAMs by VPP method have been mainly investigated. Fig. 2 shows FE-SEM images of PEDOT thin films grown on acetic acid catalyzed APS-SAM surface via only 20 wt% $\text{Fe}(\text{PTS})_3$. In general, it has been known that 40 wt% $\text{Fe}(\text{PTS})_3$ is used for the synthesis of highly conductive VPP-PEDOT.^[4] However, such concentration is too high for the oxidant to over-dominate the physico-chemical properties of the polymer, itself. Therefore, this study tried to reduce the concentration of $\text{Fe}(\text{PTS})_3$ to the half (20 wt%) of currently known optimal one when a base inhibitor is used for the VPP reaction.^[4] However, as shown in Fig. 2, PEDOT didn't form films at both 3 and 30 minutes of growth time. It may suggest that the oxidant solution was not uniformly coated on the acetic acid-catalyzed and thus very rough APS-SAM surface, which is a poor quality^[3]. Thereby, it resulted in such incompletely formed PEDOT films. Or more convincingly, less amount of the oxidant and rough and quite hydrophobic APS monolayer surface, they both play

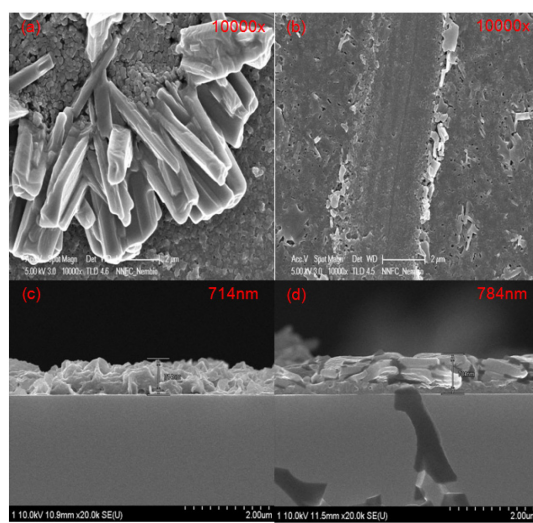


Fig. 3. FE-SEM images of PEDOT thin films grown on acetic acid-catalyzed APS-SAMs. All of the films used 40 wt% $\text{Fe}(\text{PTS})_3$. The films in (a) and (c) images were grown for 3 minutes and those in (b) and (d) images for 30 minutes.

important roles at the same time in very poorly formed PEDOT films. Indeed, FE-SEM images shown in Fig. 3, clearly support the latter conjecture. In other words, VPP-PEDOT on 40 wt% $\text{Fe}(\text{PTS})_3$ -coated SiO_2 surface at two different growth time (3 and 30 minutes) completely formed films. It means that the 40wt% oxidant solution is uniformly coated on acetic acid-catalyzed APS-SAM surface. As a result, PEDOT also uniformly grows on the oxidant-coated surface even at the relatively short growth time of 3 minutes as shown in Fig. 3c. In addition, FE-SEM images in both Fig. 2 and Fig. 3 indicate that PEDOT grows faster on $\text{Fe}(\text{PTS})_3$ -coated APS-SAM surface than on the same oxidant-coated bare SiO_2 surface. It is clearly supported by the fact of which PEDOT thin film was nearly completely formed even at very short growth time of 3 minutes. Such growth time is as short as that of the PEDOT thin film polymerized with only 3 wt% FeCl_3 even if the FeCl_3 -doped film grows usually much faster than $\text{Fe}(\text{PTS})_3$ -doped one does^[3,4]. More detail kinetic and crystallographic studies are underway.

4. Conclusion

This study demonstrated that PEDOT vapour phase-

polymerized with 40 wt% Fe(PTS)₃ oxidant completely forms a thin film on acetic acid-catalyzed APS-SAM surface while PEDOT polymerized with 20 wt% oxidant does not at all. It means that the oxidant can be uniformly coated on acetic acid-catalyzed APS-SAM surface at the 40wt% concentration, which gives rise to the uniform growth of PEDOT thin film on it.

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