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Effect of HF and Plasma Treated Glass Surface on Vapor Phase-Polymerized Poly(3,4-ethylenedioxythiophene) Thin Film : Part I

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Abstract

In this study, in order to investigate how consecutive treatments of glass surface with HF acid and water vapor/Ar plasma affect the quality of 3-aminopropyltriethoxysilane self-assembled monolayer (APS-SAM), poly(3,4-ethylenedioxythiophene) (PEDOT) thin films were vapor phase-polymerized immediately after spin coating of FeCl3 and poly-urethane diol-mixed oxidant solution on the monolayer surfaces prepared at various treatment conditions. For the film characterization, various poweful tools were used, e.g., FE-SEM, an optical microscope, four point probe, and a contact angle analyzer. The characterization revealed that HF treatment is not desirable for the synthesis of a high quality PEDOT thin film via vapor phase polymerization method. Rather, sole treatment with plasma noticeably improved the quality of APS-SAM on glass surface. As a result, a highly dense and smooth PEDOT thin film was grown on uniform oxidant film-coated APS monolayer surface.

Keywords: Poly(3,4-ethylenedioxythiophene), Vapor Phase Polymerization, 3-Aminopropyltriethoxysilane, Water Vapor/ Argon Plasma

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. Highly conductive PEDOT thin film is generally synthesized via two different but consecutive procedures, i.e., oxidant spin-coating and oxidative vapour phase polymerization (VPP). Electrical characteristics of the film prepared by the serial process 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-amonopropyltriethoxysilane 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 oxidized silicon wafer surface. It suggests that APS-SAM helps to improve the PEDOT film quality, thereby improving the electrical characteristics of the film. Therefore, in the same context, it is reasonable to believe that the quality of APS monolayer self-assembled on a bare glass surface is critical for smooth and uniform coating of the oxidant on the same surface. In general, silanol (Si-OH) density on a silicon oxide type surface is a crucial factor in highly dense and uniform self assembly of alkylsilane monolayer. Accordingly, in this study, to maximally introduce silanol groups to glass surface, the substrate surface was consecutively treated with hydrofluoric acid and water vapor/Ar plasma. Then, APS monolayer was self assembled on various surfaces treated under different conditions. Quality of oxidant and PEDOT films on the monolayer surfaces was investigated and the effect of HF and plasma treatments on the film quality was also verified.

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2. Experimental Section

Glass samples (1.5 cm×1.5 cm) were purchased from Hyunil Lab-Mate Corporation, Korea. 3-Aminopropyltriethoxysilane (APS), Iron(III) Chloride hexa-hydrate ($FeCl_3$-$6H_2O$), Polyurethane diol (DUDO), and 3,4-Ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich Inc., USA and their purities are at least 97% or higher. 1-Butanol was purchased from Junsei Chemicals, Japan. Toluene (99.5%) and sodium metal were purchased from Samchun Chemicals, Korea. Hydrofluoric acid (Extrapure, DC Chemical Co.) and absolute ethanol (J. T. Baker Co.) were used as received. Toluene was further purified by distillation in sodium metal under N_2. Ultrapure water (18 MW resistivity) was supplied by using a Barnstead ultra-pure water system. Glass surface was treated by using a plasma cleaner (PDC-32G, Harrick Plasma). Water contact angles were measured by using a SEO contact angle analyzer.

Glass substrate was soaked in an ultra- sonicator (20 minutes) including acetone for cleaning, and then blown dried with N_2. The cleaned glass samples were treated with HF solution (HF 10 mL + Ultra-purewater 100 mL) at six different conditions (no treatment, 1 second, 3 seconds, 5 seconds, 10 seconds, and 20 seconds). And then the samples were washed with ultra-pure water and blown dried with N_2. As a final step of the surface treatment, HF-treated glass surface was further treated with Ar plasma under water vapor stream (32 W RF power; 500 mtorr vacuum pressure) for 5 minutes. The fully treated glass sample was dipped into APS solution (APS 0.12 mL + dry toluene 60 mL) for 1 hour to coat APS self-assembled monolayer (SAM) on the sample surface. Then, the sample was blown dried with N_2 and further dried by heat for 5 mins. All of the SAM preparation was carried out in a glove box (Relative Humidity ~<19%). The APS-SAM surface was spin-coated with a mixed oxidant solution (3 wt% $FeCl_3$ 1.5 g, and DUDO 0.2 g as a base inhibitor in 1-butanol 30 mL) at 1,500 rpm for 30 seconds. The mixed oxidant film was enclosed in an evaporation chamber and then EDOT molecules were vaporized at 70°C for 30 minutes, and hit the film surface to polymerize them on the surface. After that, the polymer thin film was annealed at 60°C under vacuum for 1 hour. Fig. 1 shows a schematic diagram of overall experimental procedure. In order to ascertain the film quality of APS-SAM, a contact angle of a water droplet on the monolayer was measured as a function of time up to 2 hours. In order to investigate the characteristics of PEDOT thin films, an optical microscope (Olympus, BX-51), Field Emission-Scanning Electron Microscope (FEI, Sirion 200), and 4-point probe (MStech, 4000) were used.

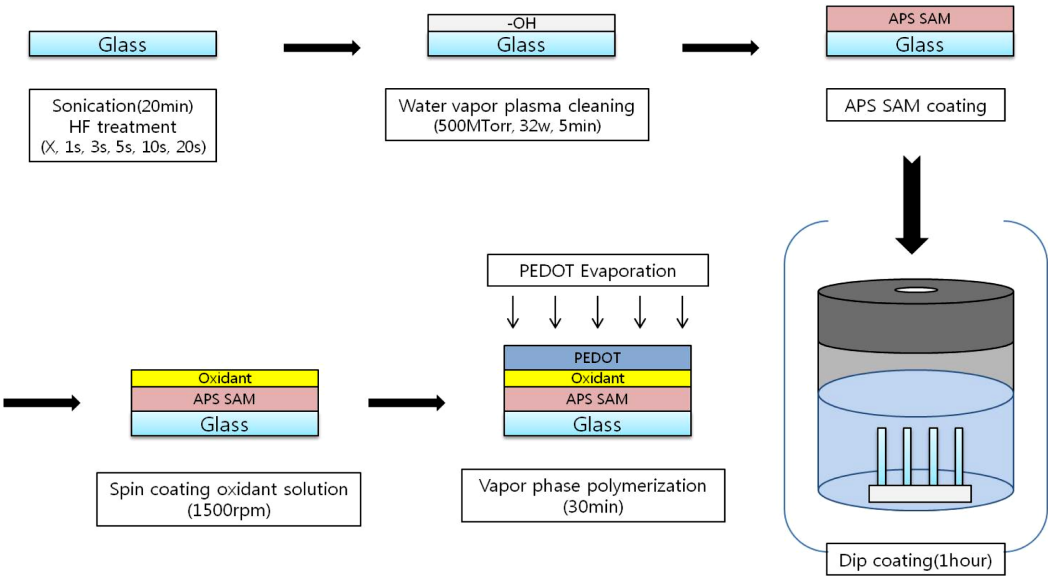

Fig. 1. Schematic diagram of experimental procedure.

3. Results and Discussion

Our previous study showed that the growth morphology and interfacial adhesion of PEDOT thin film is highly dependent upon the quality of APS-SAM[3]. That is, APS-SAM helps $FeCl_3$ solution to uniformly coat SiO_2 surface and also to promote adhesion between PEDOT thin film and Si wafer substrate, thereby resulting in improved film quality. Therefore, in this study, in order to prepare PEDOT thin film on a completely amorphous glass substrate, APS monolayer was self-assembled on the substrate prior to the polymerization. In order to secure the quality of APS monolayer on glass surface, the maximum concentration of surface silanol groups is highly required. One of promising methods to introduce hydroxyl groups on glass surface is water vapor/Ar plasma treatment. Several previous studies[4,5] have reported its good efficiency. A previous report from Polizzotti et al.[4] showed that water vapor/Ar plasma-treated glass surface increases surface silanol concentration nearly up to 50%. In an effort to increase the concentration more, the glass surface was treated with 10%(v/v) hydrofluoric (HF) acid at various exposure time since HF can activate SiO_2 surface before plasma treatment. Fig. 2 shows several optical microscope images of $FeCl_3$ (3 wt%; 1.5 g) + polyurethane diol (DUDO 0.2 g) oxidant films spin-coated (spin rate=1500 rpm for 30 seconds) on consecutively HF- and plasma-treated, then APS monolayer self-assembled glass surfaces.

Images in Fig. 2 represent oxidant-coated APS monolayer surfaces on HF-untreated (A), 1 second (B), 3 seconds (C), 5 seconds (D), 10 seconds (E), and 20 seconds (F) HF-treated glass surfaces, respectively. These images revealed an important fact. Only APS-SAM on no HF-treated but water vapor/Ar plasma- treated glass surface (Fig. 2(A)) has a relatively more uniform and less exposed oxidant coating than those on every HF-treated surfaces. It reflects that APS monolayer on HF-untreated surface has a much better film quality. In fact, a water contact angle in HF-untreated case was close to 23°, which means that the monolayer is highly dense and uniform[3]. However, contact angles on the monolayer in all HF-treated cases could not be measured because of complete wetting. It means that APS-SAM was very poorly formed or even not formed at all.

Similarly, APS monolayer was not coated on two differently pre-treated glass surfaces, i.e., only plasma-treated surface, and HF-treated for 1 second and then plasma-treated surface. On these two different surfaces, VPP-PEDOT films were grown immediately after the oxidant solution was spin-coated as shown in Fig. 3(A) and 3(B). These images commonly show a number of huge holes. It suggests that the oxidant films were not uniformly coated on two differently treated bare glass surfaces. That is, PEDOT was grown only on oxidant-coated surface areas, thereby generating many sinkholes within the films. As expected, such poorly grown films were nearly nonconductors. On the other side, Fig. 3(C) and 3(D) show top and cross-section views of PEDOT thin film, respectively. This 90 nm thick film was grown on $FeCl_3$ oxidant + DUDO-coated APS-SAM surface. The monolayer was prepared only on plasma-treated glass surface without HF treatment (refer to Fig. 2(A)). This polymer thin film is considerably smooth and, more importantly, there are no holes within the film even though there exist many $FeCl_3$ crystals on the film surface. It reflects that the oxidant film was uniformly coated on a highly dense and smooth APS-SAM sur-

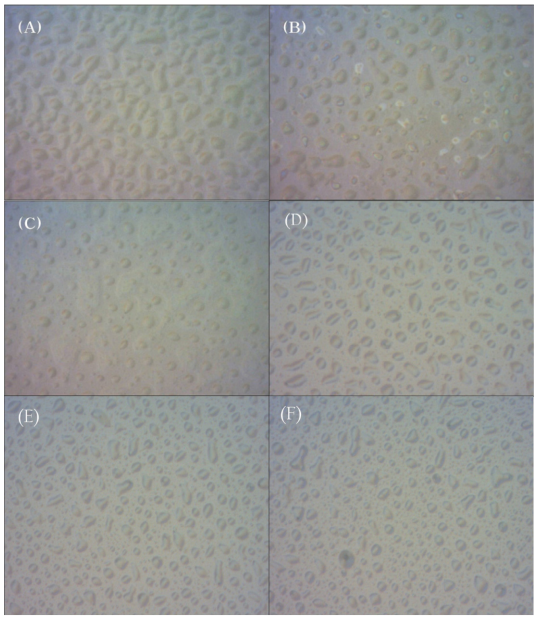

Fig. 2. Microscope images of oxidant films spin-coated from n-butanol (30 ml) solution including $FeCl_3$(1.5 g) and DUDO(0.2 g) on APS-SAM surfaces without HF treatment (A), and with HF treatments for 1s (B), for 3s (C), for 5s (D), for 10s (E), and for 20s (F) (Magnification = 500x).

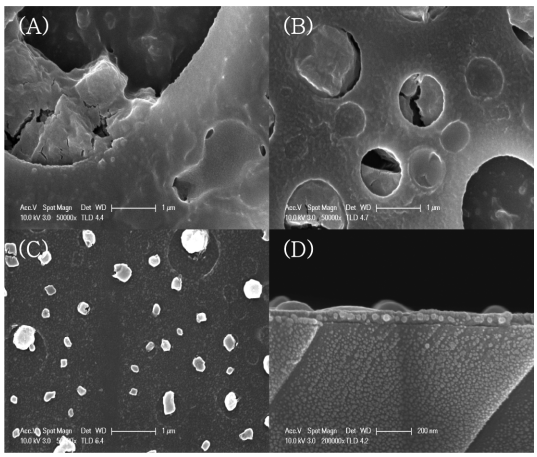

Fig. 3. FE-SEM images of PEDOT films on a H_2O/Ar plasma-treated bare glass surface (A), and on a HF-treated for 1s and then plasma-treated bare glass surface (B), and on APS-SAM surface only with H_2O/Ar plasma treatment (C) and (D).

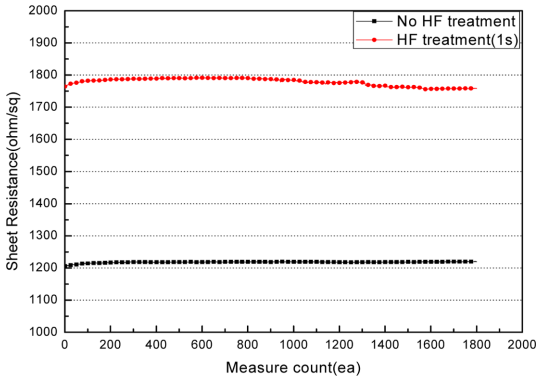

Fig. 4. Sheet Resistance (Ω/cm) of PEDOT thin films on APS-SAM surfaces only with H_2O/Ar plasma treatment (black symbol), and with both HF treatment for 1second and plasma treatment (red symbol).

face. It clearly supports that a good quality of APS-SAM is highly necessary for the synthesis of a highly conductive PEDOT thin film.

Sheet resistance of PEDOT thin film in Figure 3(C) and 3(D) was also measured, and it was 1217.91 Ω/cm as shown in Fig. 4. Even if this value is not high enough for the film to be electrically conductive, Fig. 4 shows there is a distinct difference in sheet resistance values between HF-untreated and -treated (1778.35 Ω/cm for 1 second) cases. It strongly suggests that HF treatment is not a good method for uniform coating of $FeCl_3$ and DUDO oxidant mixture on glass surface.

4. Conclusions

This study revealed that consecutive treatments of glass surface with hydrofluoric acid and water vapor/Ar plasma are not desirable for the vapor phase polymerization of PEDOT thin film. Rather, sole treatment with plasma noticeably improved the quality of APS-SAM on glass surface resulting in uniform coating of $FeCl_3$ + DUDO oxidant film on the monolayer surface. As a result, a highly dense and smooth PEDOT thin film could be grown on glass surface.

Acknowledgments

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