Notes

Poly(3,4-ethylenedioxythiophene) Vapor-Phase Polymerization on Glass Substrate for Enhanced Surface Smoothness and Electrical Conductivity

Thuy Le Truong, Nguyen Dang Luong, and Jae-Do Nam*
Department of Polymer Science and Engineering, SKKU Advanced Institute of Nanotechnology (SAINT), Suwon 440-746, Korea
Youngkwan Lee
Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
Hyouk Ryeol Choi and Ja Choon Koo
School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
Huu Nieu Nguyen
Department of Materials Technology, Hochiminh City University of Technology, Vietnam

Received December 15, 2006; Revised April 3, 2007

Introduction

As with other conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is considered as a promising material for optoelectronic devices. In most of those optoelectronic applications as buffer or electrode layers, the surface and/or interface of the PEDOT coating layer substantially influences mobility, quantum efficiency and stability of charge carriers as well as assembled devices. Polythiophene structure and morphology have been reported to be important for obtaining high charge-carrier transport characteristics. Previous studies show that the effect of dielectric surface on charge mobility is due to surface-induced morphology of polythiophene. In particular, the surface roughness of the PEDOT thin films is often required not to exceed few nanometers (<5 nm), and a uniform composition is usually required in optoelectronic device. Therefore, the main issues of PEDOT in most electronic device applications are not only the electrical conductivity but also the film surface morphology such as film thickness, surface roughness, uniformity, etc.

In this sense, the vapor-phase polymerization (VPP) of PEDOT is a promising technology in various optoelectronic applications to provide a thin, uniform, and highly-conductive PEDOT coating. The VPP PEDOT coating has been reported to give conductivities of approximately 70 S/cm and light transmittance up to 95% below 40 nm of thickness using FeCl₃ as the oxidizing agent. Recently, a PEDOT film with a high conductivity, exceeding 1000 S/cm, was reported using pyridine as a base inhibitor during VPP of 3,4-ethylenedioxythiophene (EDOT). However, not only the conductivity enhancement but also the surface morphology of PEDOT VPP should be further explored to be adopted in optoelectronic device. In addition, the conductivity of the PEDOT coating in relation with surface smoothness and transparency should be identified to be used as thin film coating in optoelectronic devices.

In this study, VPP of PEDOT coating on the glass substrate was investigated by changing the polymerization rate using pyridine as a polymerization retardant. The polymerization rate was associated with the surface smoothness and conductivity to give a robust and transparent PEDOT coating in VPP.

Experimental

Fe(III) tosylate, (Fe(OTS)₃), 40% solution in n-butanol, Baytron C) as an oxidizing agent and dopant were received from Bayer AG. The 3,4-ethylenedioxythiophene (EDOT), all solvents and reagents such as butanol, ethanol, acetone, pyridine were purchased from Sigma-Aldrich and used as supplied. The substrate materials used in this study were plain glass plates, which were at 1 mm thickness and supplied by Corning, N.Y. 14830, USA.

The glass substrate was cleaned twice in acetone by sonication prior to use and then coated with a 20 wt% oxidant Fe(OTS)₃ solution in butanol by spin-coating. Various amount of pyridine was added to the Fe(OTS)₃ solution. After drying, the samples were transferred to a gas-phase polymerization chamber using a similar experimental setup and method as reported elsewhere. The chamber was flushed with nitrogen during polymerization, and heated to 50°C and the vapor-phase polymerization was carried out for 30 min in the atmospheric pressure, and the samples were then heated to 50-90°C for 30 min. The samples were then washed sequentially with ethanol and DI water. Finally, the PEDOT film was dried to remove the residual solvents at 80°C for 20 min.

The conductivity of the samples was measured using a
four-point probe (Jandel Engineering Ltd.) connected to a Keithly 2400 source meter. The probe was equipped with four spring-loaded tungsten carbide needles spaced 1 mm apart. The conductivity of the PEDOT film coated on the glass plate was calculated from the surface resistivity and the film thickness, which was measured by FE-SEM (a JEOL JSM-7000F FESEM, voltage of 5.0 kV). Atomic force microscopy (Auto Probe CP Research, Thermo Microscopes, USA) was used to analyze the film surface morphology. All data manipulations and image processing were carried out using Proscan 1.7 software. All surface roughness values used in this study are the root-mean-square roughness. The absorbance of the PEDOT films was measured using UV-VIS-NIR spectrophotometer (Varian Cary 5000).

Results and Discussion

The scanning electron microscopy (SEM) images show the cross sections of PEDOT coatings on glass substrates at various pyridine concentrations (Figure 1). The thickness of the PEDOT film decreases with increasing pyridine concentrations from 191 to 25 nm for 0 to 0.75 molar ratio of pyridine/Fe(OTs)$_3$, respectively. In addition to the thickness, it can be seen that the structural morphology of VPP-PEDOT is also influenced by the pyridine concentration. In Figure 1(A), large PEDOT grains are formed, which could possibly provide a void spaces in the PEDOT film when pyridine was not used in the VPP process. A well-defined structure is shown in Figures 1(B) and 1(C), where the structure of PEDOT films are dense and uniform without noticeable cracks or voids when pyridine is incorporated in VPP as a polymerization retardant.

Figure 2 shows the AFM images of the PEDOT produced at different pyridine/Fe(OTs)$_3$ ratios. Figure 2(A) shows the surface of PEDOT without pyridine, where the RMS roughness is 6.9 nm. A distinct improvement of the surface roughness is observed in Figure 2(B) at a pyridine/Fe(OTs)$_3$ molar ratio of 0.5. As summarized in Table I, the surface roughness is influenced considerably by the pyridine concentration, and a minimal RMS roughness was obtained as 2.1 nm at a pyridine ratio of 0.5. This suggests that pyridine has a substantial effect on the conductivity and surface roughness of the PEDOT films.

![Figure 1. The cross section of PEDOT coatings on glass substrates (B) at various molar ratios of pyridine/Fe(OTs)$_3$: ratios of (A) 0, (B) 0.25, (C) 0.5, and (D) 0.75.](image1)

![Figure 2. AFM images of PEDOT-coated glass substrates at different pyridine/Fe(OTs)$_3$ ratios of (A) 0 and (B) 0.5.](image2)

<table>
<thead>
<tr>
<th>Pyridine/Fe(OTs)$_3$ Ratio</th>
<th>0</th>
<th>0.25</th>
<th>0.5</th>
<th>0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>30</td>
<td>180</td>
<td>5.0×10$^3$</td>
<td>300</td>
</tr>
<tr>
<td>Surface Roughness Rms (nm)</td>
<td>6.9</td>
<td>3.8</td>
<td>2.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Transmittance (450 nm) (%)</td>
<td>18.95</td>
<td>60</td>
<td>80</td>
<td>86</td>
</tr>
</tbody>
</table>