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Doping Level Control and Thermoelectric Property of Vapor Phase Polymerization PEDOT thin films

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Abstract

PEDOT thin films were prepared by vapor phase polymerization (VPP) of 3.4-ethylenedioxythiophene (EDOT) monomer using $FeCl_3$ oxidant. Structural and electrical properties of VPP-PEDOT films were investigated by Raman spectroscopy, X-ray photoelectron spectroscopy, and four-terminal electrical conducting measurement. The doping revel and the electrical conductivity of VPP-PEDOT thin films increased in the first 20 min of polymerization at 60°C; and they became constant after 20 min. Thermoelectric property was observed in VPP-PEDOT thin films, and the Seebeck coefficient is estimated to be 18.7 µV/K.

1. Introduction

Poly (3.4-ethylenedioxythiophene) (PEDOT) is received a great deal of attention because of its high conductivity, outstanding chemical stability at ambient condition and transparency. PEDOT is of wide application such as organic thin film transistor, light emitting diodes and organic solar cells owing to its tuning of the conjugation length and doping levels. [1.2]. In addition, recently, the thermoelectric power of PEDOT has been reported. Thermoelectric conversion, which generate electric power from wasted heat or natural energy such as sunlight and body temperature, is one of most attractive technology for sustainable energy society. It has been reported that the thermoelectric property of PEDOT is improved by controlling its oxidation level with anion dopants. [3,4].

In this study, we focused on the vapor phase polymerization (VPP) technique which is a bottom-up processing method for preparation of PEDOT thin films. We prepared VPP-PEDOT thin films using $FeCl_3$ oxidant, and tried to control of doping level of Cl under various polymerization conditions. The relationship between the doping level and the conductivity of VPP PEDOT thin films was investigated. The thermoelectric property of these films is also discussed.
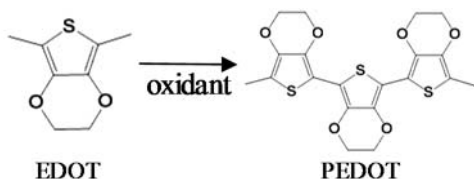

Fig. 1 Reaction scheme of PEDOT

2. Experimental

The PEDOT films are prepared by the vapor phase polymerization techniques using $FeCl_3$ oxidant. $FeCl_3$ was dissolved in ethanol at a concentration of 5 wt%. $FeCl_3$ solution were deposited on substrates by the spin-coating method at room temperature. Then, the as-spun $FeCl_3$ film was annealed at 80°C for 30 seconds to remove ethanol. The substrate was mounted into the quartz chamber immediately where EDOT monomer was allowed to evaporate at 60°C for 10-60min, allowing the polymerization reaction to occur directly on the surface of the oxidant layer. Finally the sample was rinsed in the ethanol for 10 min to remove the unreacted oxidant and monomer.

VPP-PEDOT films were characterized by Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The electrical conductivity was measured by the standard four-terminal method and the Seebeck coefficient using our homemade setup at 298K in vacuum.

3. Results and discussion

Figure 2 shows the Raman spectrum of the VPP-PEDOT thin film prepared at 60 ºC for 60 min. The sample exhibit a strong absorption in the 1423 cm^{-1} region that is characteristic of symmetric $C_\alpha=C_\beta$ stretching and indicative of a high level of oxidation. The band from the asymmetric C=C stretch at 1501 cm^{-1}, the C_β- C_β stretch at 1365 cm^{-1}, the C_α-C_α inter-ring stretch at 1260 cm^{-1}, the oxyethylene ring deformation peak at 990 cm^{-1} and the symmetric C-S-C deformation at 693 cm^{-1} are all characteristic of PEDOT[5].
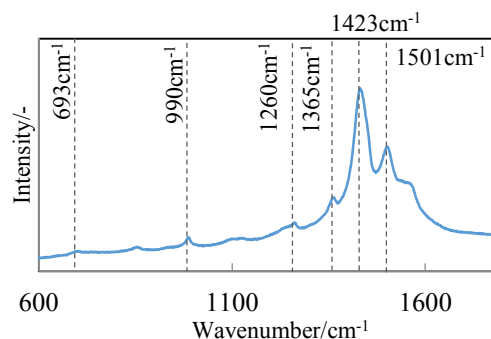

Fig.2 Raman spectrum of VPP-PEDOT thin film.

The XPS spectrum obtained from the VPP-PEDOT thin film displays the characteristic peaks for carbon, oxygen, sulfur and chlorine, as shown in Fig. 3. The atomic concentrations for C, O, S, and Cl are 67.69%, 18.67%, 6.57%, and 5.64%, respectively. These results consistent with that of the atomic ratio of PEDOT. $FeCl_3$ was oxidant of polymerization, Fe was removed by ethanol washing after polymerization, however the Cl counteranions remained in the PEDOT thin film. These results suggested that Cl-doped PEDOT thin films were prepared by VPP method. Here, the doping level is estimated from the area ratio of S 2p to Cl 2p with XPS data. [6].
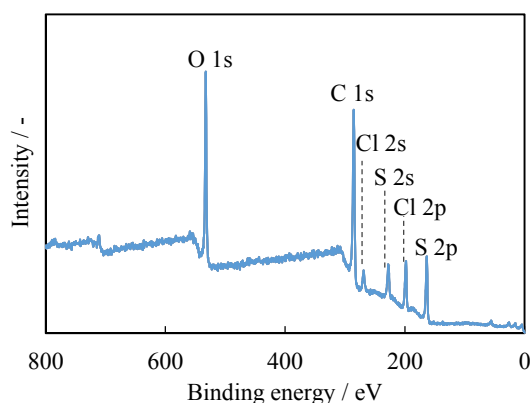

Fig. 3 XPS spectrum of VPP-PEDOT thin film.

Figure 4 shows reaction time dependence of electrical conductivity and doping level of VPP-PEDOT thin films. The doping level remarkably increased from 0.013 to 0.21 in first 20 min, and is approximately constant at 0.2 after 20 min. The conductivity similarly increased in first 20min and became constant. These results suggested that the doping level is able to be controlled by changing reaction time and temperature, thus, the electric conductivity of the VPP-PEDOT thin films is also controllable.
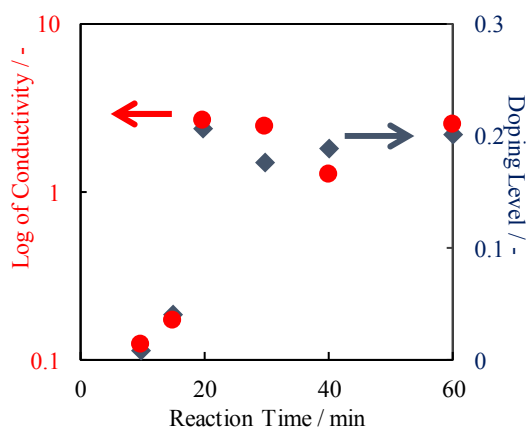

Fig. 4 Time dependence of conductivity and doping level of VPP-PEDOT thin films.

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The thermoelectric measurement of the film reacted for 60 min. was conducted, as shown in Fig. 5. The linear output voltage versus temperature difference, which shows thermoelectric property, was obtained. The Seebeck coefficient was estimated to be 18.7 µV/K, with a positive value indicating p-type semiconductor.
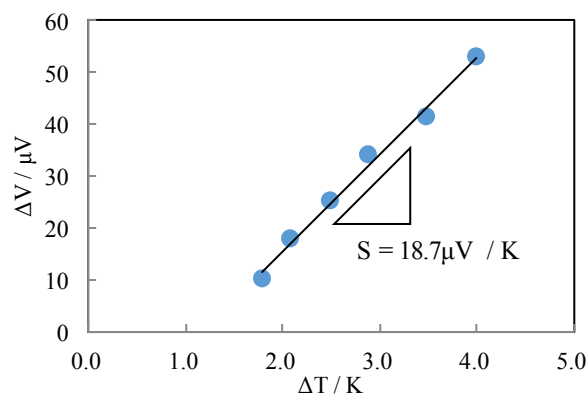

Fig. 5 Seebeck coefficient measurement of VPP-PEDOT thin films.

4. Conclusions

In this study, Cl-doped PEDOT thin films were fabricated by the vapor phase polymerization of EDOT using $FeCl_3$ as oxidant. The electrical conductivity and doping level of VPP-PEDOT thin films behave similarly depending reaction time. Thermoelectric power was observed in VPP-PEDOT thin films and the Seebeck coefficient was 18.7 µV/K. Thus, VPP technique is useful for directly fabrication PEDOT thin films on various substrates; and controlling of doping level of PEDOT films has potential to improve these thermoelectric property.

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