Examination of Treatment Methods for a PEDOT:PSS Transparent Conductive Film Produced Using an Inkjet Method

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Abstract

Flexible devices manufactured using printed electronics have attracted the attention of many researchers. A high-performance transparent conductive film exhibiting high flexibility and elasticity is expected to be developed because of its need for the creation of flexible devices. An indium tin oxide (ITO) thin film, which has generally been used, has weaknesses such as fragility to bending stress and depletion of the resource. This study focused on poly (3, 4-ethylenedioxythiophene)/poly (styrenesulfonate) (PEDOT:PSS), a conductive polymer material, and examined improvement in the resistivity and transmittance of the transparent conductive film produced using an inkjet method. The present study improved the electrical and optical characteristics of the thin film by examining the annealing temperature between printing operations and the application method of a polar solvent. As a result, the resistivity and transmittance of a PEDOT:PSS thin film were $1.49 \times 10^{-3}$ Ω·cm and 89.2%, respectively. This film was obtained by annealing at 90°C for 30 min and applying a polar solvent, using an inkjet printer, between printing operations. The printing was performed three times.

Keywords

PEDOT:PSS, Inkjet Printing, Transparent Conductive Film, Flexible Devices

1. Introduction

Currently, ITO thin film is used as a standard material for transparent electrodes in electronic devices such as solar cells and displays [1] [2]. However, because an
ITO thin film contains indium, a rare metal, depletion and increased price of the resource have become issues. Therefore, materials that can be substituted for ITO have been actively studied [3]-[8]. Since ITO thin films are produced using the sputtering method and a dry process, a material and a method which can form a thin film using a wet process, which has a higher production efficiency than that of the dry process, are required. By overcoming these weaknesses and developing a material that can be a substitute for ITO, for the creation of transparent conductive films, inexpensive devices can be stably manufactured.

By analyzing the latest research on flexible electronic devices, it can be determined that the development of a flexible transparent conductive film is urgently required because ITO thin films show fragility to bending stress. To this end, various materials such as organic materials, metallic nanoparticles, carbon nanotubes (CNTs) and oxide-based materials (including zinc oxide), have been studied [9] [10] [11] [12] [13]. Organic materials are noteworthy because a transparent conductive film can be formed using simple processes such as printing and coating [14] [15] [16]. Since organic materials possess excellent flexibility and elasticity, they are suitable for flexible displays and thin-film solar cells [17] [18].

Recently, there has been a significant increase of studies conducted on flexible devices manufactured by printed electronics [19] [20] [21] [22]. By using printing technologies for device manufacturing, complicated circuits can be easily formed, and the apparatus used for manufacturing a device can be made smaller and the cost of manufacturing a device can be reduced.

If a practical, transparent conductive film can be produced using a simple and inexpensive method, such as a printing method, not only electrodes, but also flexible devices can be manufactured using only printing.

However, to use printing technologies, a material must be prepared in the form of ink, the prepared ink must be optimized, and the surface of the film must be even during printing. Moreover, the performance of organic, transparent conductive films must be improved; otherwise, the films cannot be practically used.

Because of these necessary characteristics, this study focused on PEDOT:PSS, an organic electroconductive material exhibiting high flexibility and conductivity, as a substitute for ITO. The aim was to produce a cheap and flexible organic transparent conductive film by forming the film on a plastic-film substrate using an inkjet printer.

In previous studies, it has been revealed that cleaning of the plastic-film substrate with UV/O₂, annealing of the film after it was deposited on the substrate and dipping of the film into a polar solvent were useful to improving the characteristics of the thin film [23] [24]. In the present study, the effects of the removal of a polar solvent by annealing each time after a layer was printed, the changes in the surface state of the film due to the aggregates of PEDOT:PSS particles and the differences in the homogenization of the film surface, according to
the application method of a polar solvent after annealing, on the improvement in the characteristics of the thin film were examined.

2. Experimental

2.1. Ink Material for a Transparent Conductive Film

In the present study, CLEVIOS (Clevios™ PH500) was used as PEDOT:PSS. CLEVIOS PH500 possesses excellent conductivity, permeability, and flexibility. Since the mechanical flexibility of CLEVIOS PH500 is high, it can be used as a material for printed electronics. Figure 1 shows the molecular structure of PEDOT:PSS, and Table 1 shows its physical properties. By adding an additive to PEDOT:PSS, the characteristics of the obtained thin film can be improved. By adding a low-boiling point solvent to PEDOT:PSS, the surface tension of ink is reduced and the wettability of the substrate is improved. When a high-boiling point solvent is added, the secondary doping effect on PEDOT is exerted and conductivity is improved due to the coupling of conductive regions [25]. It was reported that when ethylene glycol, a high-boiling point solvent, was added, insulative PSS was removed, and a conductive region consisting of conductive PEDOT was formed [26]. Like a previous study, the ink composition of PEDOT:PSS:ethanol:ethylene glycol = 70:20:10 wt% was adopted in the present study [24].

![Figure 1. The molecular structure of the PEDOT:PSS.](image)

<table>
<thead>
<tr>
<th>Table 1. Material properties of the PEDOT:PSS.</th>
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<tr>
<td>Typical values</td>
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<tr>
<td>PEDOT:PSS ratio</td>
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<tr>
<td>Viscosity at 20°C</td>
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<tr>
<td>pH at 20°C</td>
</tr>
<tr>
<td>Density at 20°C</td>
</tr>
<tr>
<td>Average particle size</td>
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<td>Boiling Point</td>
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</table>
2.2. Production and Evaluation of a Thin Film

To produce a PEDOT:PSS thin film, a piezo-type, pigment-based, inkjet printer (PX-105; Seiko Epson CO.) was used. During printing, the printer was set to [Inkjet paper, Best quality]. For the printing pattern of the PEDOT:PSS thin film, 40 mm (length) × 15 mm (width) was adopted. A heat-resistant, transparent film possessing excellent transparency, heat resistance, and chemical resistance (Teonex Q65-FA; Teijin DuPont Films Co., Ltd.) was used as the substrate. The surface of the substrate, before film formation, was cleaned using a UV/O₃ cleaning and modifying apparatus (ASM401N; Asumi Giken, Ltd.). For the conditions of UV/O₃ cleaning, the UV radiation distance was 30mm, the output of a low-pressure mercury lamp was 40 W, and the cleaning time was 20 min. Like a previous study, PEDOT:PSS thin films were formed by printing two to four times [24]. To evaporate the additives that remained in the thin film as impurities after it was formed and adversely affected the conductivity, the thin film was annealed for 30 min after each time a layer was printed and for 60 min after the entire printing process was completed, using a constant-temperature drying oven (EOP-300B; As One Co., Ltd.). Ethylene glycol was used as a polar solvent. The thickness of the produced PEDOT:PSS thin film was measured using a stylus-type surface roughness tester (NanoMap-PS; AEP Technology Co.). The resistivity was measured using a digital multimeter (VOAC7521H; Iwatsu Electric Co., Ltd.). The transmittance was measured using a spectrophotometer (U-3900; Hitachi High-Technologies Co.). The surface state of the thin film was observed and its roughness was measured using a microscope (VHX-1000; Keyence Co., Ltd.) and an atomic force microscope (NaioAFM; Nanosurf Co.).

3. Results and Discussion

3.1. Ink Material for a Transparent Conductive Film

Annealing is required after each time of printing. Annealing can remove ethanol which decreases conductivity. Unlike with other film formation methods such as the spin coating and roll-to-roll methods, the viscosity of ink affects the ejection of the ink used during the inkjet method. Although the viscosity of ink used for an inkjet printer is generally 5 - 15 mPa-s, the viscosity of PEDOT:PSS (CLEVIOS PH 500) is 25 mPa-s. Therefore, the viscosity of PEDOT:PSS was decreased by adding ethanol. However, if ethanol remains on a thin film after it is formed, its conductivity will decrease. Therefore, annealing is required. In previous studies, annealing was performed at 80˚C, 100˚C, and 150˚C. The best thin film characteristics were obtained at 100˚C [23]. In the present study, the annealing temperatures used after each time a layer was printed were changed to 80˚C, 90˚C, and 100˚C. Figure 2 shows changes in the resistivity according to the annealing temperature and the number of printing times. The resistivity was lowest at 90˚C when the number of printing times was three. When the number of printing times was four, the resistivity increased at each annealing temperature. The interface of the thin film increased with the number of printing times.
The increase in the interface has the great influence on resistivity. Table 2 shows differences in the thin film thickness, according to the annealing temperature, when the number of printing times was three. The thin film thickness was thinner when the annealing temperature was 100°C compared to when the annealing temperatures were 80°C and 90°C. Therefore, the thin film was revealed to have evaporated because the boiling point of PEDOT:PSS is approximately 100°C. If PEDOT:PSS evaporates after a thin film is formed, the thin film thickness is difficult to control. Figure 3 shows changes in the visible light transmittance according to the annealing temperature and the number of printing times. Transmittance was measured at the wavelength of 550 nm. The visible light transmittance was highest when the annealing temperature was 100°C. This is probably due to the decrease in film thickness. Figure 4 shows images of the surfaces of the PEDOT:PSS thin films, observed using a microscope. In this figure, Figure 4(a) shows that because the aggregation of the thin film was large when the annealing temperature was 80°C, a state in which the thin film seemed to be blurry was observed. Therefore, it was revealed that ethanol remained on the film, it was not sufficiently removed. Also, in this figure, Figure 4(b) and Figure 4(c) show that because the aggregation state of the thin film did not change when the annealing temperatures were 90°C and 100°C, respectively. In these thin films, ethanol was sufficiently removed. When difficulty in controlling the film thickness due to the residence of ethanol and the evaporation of PEDOT:PSS was taken into consideration, the optimal value of the annealing temperature was 90°C.

3.2. Examination of the Application Method of a Polar Solvent

Drying a PEDOT:PSS thin film again, after dipping it into a polar solvent, was reported to facilitate the arrangement of PEDOT molecules, resulting in improvement of the conductivity of the PEDOT:PSS thin film [27]. In a previous study, by spraying the polar solvent on a PEDOT:PSS thin film after each time a layer was printed, the characteristics of the PEDOT:PSS thin film were improved in terms of resistivity and transmittance [24]. However, there was a limitation in uniformly applying a polar solvent by artificially spraying it. Therefore, the aim
Figure 3. Transmittance as a function of annealing temperature and the number of printing times.

Figure 4. Microscope image of the surface of a PEDOT:PSS (3 timesprinting, 100×). (a) 80°C; (b) 90°C; (c) 100°C.
Table 2. The film thickness of PEDOT:PSS at each annealing temperature (3 times printing).

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Thickness [nm]</th>
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<tr>
<td>80</td>
<td>222.2</td>
</tr>
<tr>
<td>90</td>
<td>234.4</td>
</tr>
<tr>
<td>100</td>
<td>181.1</td>
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</table>

was to improve the homogeneity of a PEDOT:PSS thin film by applying the polar solvent using an inkjet printer. Figure 5 shows changes in the resistivity, according to the number of printing times, when the application method of the polar solvent was changed. The resistivity of a thin film largely decreased when the polar solvent was applied using an inkjet printer. The increase in the resistivity was also small when the number of printing times was four.

Figure 6 shows images of the surfaces of the PEDOT:PSS thin films, observed using a microscope. In this figure, Figure 6(a) shows the film surface obtained when not treated using the polar solvent. In the inkjet method, an aggregation of ink is observed, which is not reported as observed in other film formation methods [23] [28]. It is then considered that in the aggregation of ink, PEDOT molecules are unevenly distributed. Consequently, the formation of a conductive region is hindered. Also, in this figure, Figure 6(b) shows the film surface obtained by spraying the polar solvent on each layer. The unevenly generated aggregates of PEDOT:PSS particles were fractionated and distributed. Figure 6(c) shows the film surface obtained by applying the polar solvent to each layer using an inkjet printer. The number of gaps between aggregates was smaller in Figure 6(c) than in Figure 6(b). Since the thin film of Figure 6(c) was smallest in surface roughness Sa, the aggregates of PEDOT:PSS particles were more evenly distributed.

Figure 7 shows the surfaces of the PEDOT:PSS thin films observed using an AFM. In this figure, Figure 7(a) shows the film surface obtained when not using the polar solvent and Figure 7(b) shows the film surface obtained by spraying the polar solvent onto each layer. When Figure 7(a) was compared with Figure 7(b), the unevenness on the film surface was larger in Figure 7(b) than in Figure 7(a). This is probably because the polar solvent was not evenly applied to each layer when it was sprayed. Also, in this figure, Figure 7(c) shows the film surface obtained by applying the polar solvent to each layer using an inkjet printer. As shown in Figure 7(c), the unevenness on the film surface was reduced. Thus, it was revealed that improvement in the homogeneity of the film surface inhibited an increase in the resistivity when the number of printing times was four.

Figure 8 shows changes in the visible light transmittance, according to the number of printing times, when the application method of the polar solvent was changed. The transmittance was improved by applying the polar solvent to each layer. Due to the fractionation of the aggregates of PEDOT:PSS particles, the bi-
Figure 5. Resistivity as a function of annealing temperature and the number of printing times.

Figure 6. Microscope image of the surface of a PEDOT:PSS (annealing temperature: 90°C, 3 times printing, 100×). (a) No treatment; (b) Spraying treatment; (c) Printing treatment.
Figure 7. AFM image of the surface of a PEDOT:PSS (annealing temperature: 90˚C, 3 times printing, ×100). (a) No treatment; (b) Spraying treatment; (c) Printing treatment.

Figure 8. Transmittance as a function of annealing temperature and the number of printing times.

as in the distribution of PEDOT:PSS particles caused by the printing pattern was reduced. Consequently, visible light transmittance increased. By uniformly applying the polar solvent using an inkjet printer, uniformity that could not be obtained by spraying it, the aggregates of PEDOT:PSS particles were fractionated and the surface state of the thin film homogenized. Consequently, visible light transmittance was improved.

4. Conclusions

In the present study, PEDOT:PSS was used as a substitute for ITO. A thin film was formed on the plastic-film substrate using an inkjet printer. To further improve the characteristics of the PEDOT:PSS thin film, annealing temperature and polar solvent application methods were examined.

At the annealing temperature of 80˚C, the solvent which decreased conductivity could not be sufficiently removed. At the annealing temperature of 90˚C, the solvent could be sufficiently removed. Consequently, the resistivity was improved. When the annealing temperature was 100˚C, PEDOT:PSS evaporated so film thickness was difficult to control.

When the polar solvent was applied using an inkjet printer, the resistivity decreased and the visible light transmittance increased. Moreover, the fractionation of the aggregates of PEDOT:PSS particles and the homogenization of the film surface were facilitated. When the number of printing times was three, the
resistivity was low under all conditions. This is because the interface of the thin film increased with the number of printing times. By homogenizing the film surface, increase in the resistivity could be inhibited.

The resistivity and transmittance of a PEDOT:PSS thin film were $1.49 \times 10^{-3}$ Ω·cm and 89.2%, respectively. This film was obtained by annealing at 90°C for 30 min and applying the polar solvent, using an inkjet printer, between printing operations. The printing was performed three times. However, in comparison with the commonly used ITO thin film, there is room for improvement in the performance.

In the future, we are planning to homogenize the film surface by studying additives and ink composition.

**References**


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