

Polyimide as a Plastic Substrate for the Flexible Organic Electroluminescent Device

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ABSTRACT

In this work, transparent flexible substrates based on polyimides (PI) with indium tin oxide (ITO) thin films for organic electroluminescent devices have been prepared. 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropanedianhydride (6FDA) and 2,2'-bis-(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) PI films were used for transparent flexible substrates. ITO thin films were prepared at two substrate deposition temperatures of 25°C and 150°C with a typical radio-frequency (r.f.) planar magnetron sputtering system. The sheet resistance and the optical transmission properties of the fluorinated PI substrate were comparable with those for the slide glass substrate. The substrate properties are better when the deposition temperature is higher. SiO₂ coating onto the fluorinated PI substrate by sol-gel reaction was also attempted to improve the optical transmission of the ITO/PI substrate. It was found that the coating of SiO₂ affected on the morphology of the PI substrates.

INTRODUCTION

In recent years, interests of transparent flexible plastic substrates with a transparent conducting oxide (TCO) layer such as ITO have been increased in the fields of portable devices, roll-up displays, or conformable displays. So far, the use of the flexible substrates for organic electroluminescent devices (OELDs) has been restricted mainly to the polyester films due to their excellent transparent property. However, the plastic substrates till now can be severely damaged at high temperature during deposition process, mainly due to their intrinsic low thermal and mechanical properties compared with other inorganic or metal substrates. Consequently, reduced electrical resistivity and long-term stability of the ITO surface cannot be achieved and maintained, which is directly related to the performance of applied devices. In this sense, wholly aromatic polyimides (PI's) are one of the best candidates for the substrate because of their excellent thermal stability and good mechanical, optical, electrical, chemical properties [1]. However, most aromatic PI's are highly colored polymers with colors ranging from yellow to brown, as well as poor processability and low solubility. Structural modification of PI's, therefore, has been attempted including the incorporation of flexible bridging units [2], bulky substituent groups [3], and aliphatic moieties [4] into the PI backbone.

In this work, colorless fluorinated polyimide substrate was prepared with ITO thin films. On the other hand, some inorganic materials, such as SiO₂ were recently introduced to OELDs to

balance the number of holes and electrons injected to the emitter layer to achieve high recombination efficiencies. In this work, therefore, the effect of the SiO₂ buffer layer on the morphology of the colorless polyimide substrate was also investigated. The SiO₂ buffer layer was inserted between the polyimide substrate and ITO layers by sol-gel reaction.

EXPERIMENTAL DETAILS

Fluorine-containing aromatic PI was derived from 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) [5]. The 6FDA-TFDB polyamic acid(PAA) precursor solution of dimethylacetamide with 15 wt.% concentration was coated onto a clean dry glass substrate by the solution casting method and dried at room temperature under reduced pressure. The spin-coated films were soft-baked at 80°C for 1 hour in a drying oven and dried at 150 °C for 1 day in a vacuum dry oven. The thermal imidization was performed under nitrogen atmosphere. The thickness of the fluorinated PI substrate was 250µm. ITO thin films were deposited onto the PI plastic substrates at 25°C and 150°C using a typical r.f. (13.56 MHz) planar magnetron sputtering system (a background pressure; 10⁻⁷ Torr, back filled with argon to 2.6 mTorr; 100 W, 10 min). The composition of the ITO target was 10 wt.% SnO₂ and 90 wt.% In₂O₃, and the distance of the target to the PI substrate was fixed at 60 mm. There were no post-deposition annealing treatments of ITO thin films.

For silica coating on the fluorinated PI substrate, proper amounts of tetraethoxy silane (TEOS) and colloidal silica (solid contents 30wt%, water dispersion) were slowly poured into 4-necked flask. On adding 0.5wt% of HCl slowly with stirring, the solution was controlled at pH 4.7 and stirred for 24 hours at 30°C for enough hydrolysis reaction. Then, to this solution excess amounts of water and ethanol were added, followed by heating at 40°C under reduced pressure with stirring. To make coating agents, isobutyl alcohol and ethylene glycol mono ethyl ether were added as diluents solvents with 0.2 wt% of a curing catalyst, tetramethyl ammonium formate. The coating solution of 40 wt% solid content was spin coated onto 6FDA-TFDB PI films at 2000 rpm for 2 min. The surface morphology and root-mean-square (RMS) roughness of these films were measured at 2×2 µm² scan areas by atomic force microscopy (AFM; Nanoscope IIIa (Digital Instruments Co.)). The optical transmission spectra were measured with an UV-visible-near IR spectrophotometer (CARY 5E, Varian Co.). The sheet resistance of the films was measured using the four-point probe method.

DISCUSSION

The fluorinated PI derived from 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) has high glass transition and decomposition temperature, low water absorption, good transmission and low optical loss. The electrical sheet resistance, optical transmission, grain size and structural orientation significantly depended on the substrate temperatures [6].

The sheet resistance of the ITO film deposited at 150°C was much higher than that

prepared at the substrate deposition temperature of room temperature. It can be considered that interfacial properties between the organic polymer substrate and the metal oxide film, such as contacts, adhesions, morphologies, and interactions may be efficiently activated and improved with the increase of the substrate temperature.

It is noteworthy that the sheet resistance of the ITO film deposited onto the fluorinated PI substrate at 150°C is about 26.7 $\Omega/\text{sq.}$, which is higher than that of the commercial high-quality glass substrate (9.28 $\Omega/\text{sq.}$) but much lower than that of a glass substrate reported in a literature (62.0 $\Omega/\text{sq.}$) [7]. Most of all, the sheet resistance value was much lower than the ITO films coated onto other polymer substrates which have been reported in the previous literatures [6,8,9].

Using the dependence of the sheet resistance on the grain size, it was considered that the predominant scattering mechanism limiting the mobility is the grain boundary scattering mechanism for the ITO films deposited onto the PI substrates[6]. The values of the figure of merit in table 1 show the potential abilities of the PI substrate as transparent flexible substrates with transparent conductive oxide thin films for optical and electrical applications, especially, flexible display devices. It was found that the electrical sheet resistance was slightly proportional to the surface roughness of the ITO films[6]. Table 1 also shows the better sheet resistance value of the fluorinated PI in comparison to that of the alicyclic PI when the deposition temperature is 150 °C, which has been synthesized from bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCOEDA) and 4,4'-oxydianiline (ODA) [10, 11].

The optical transmission of the ITO/PI film in the visible light range was higher as the substrate temperature was higher. Table 1 shows the comparison of the optical transmission as well as the sheet resistance of the fluorinated polyimide substrate with those of our previous alicyclic PI substrate[4,10]. The optical transmission of the fluorinated polyimide (at the deposition temperature of 150°C) was about 76% at the wavelength of 550 nm, which was higher than that of the alicyclic PI substrate (63 %). Table 1 indicates, however, that the optical transmission of the fluorinated PI substrate as well as the alicyclic PI substrate is still lower than that of the glass substrate regardless of whether it is commercial or home-made. Thus, the improvement of the optical transmission is needed.

Table 1. The sheet resistance of the ITO films deposited onto the fluorinated and the aliphatic cyclic polyimide substrates prepared at two different deposition temperatures.

Substrate	Growth Temp. (°C)	Avg. Transmission (400-700 nm) (%)	Sheet resistance ($\Omega/\text{sq.}$)	Figure of merit F_{TC}^* ($\times 10^{-3} \Omega^{-1}$) [12]
Alicyclic PI [10]	25	60.1	69.2	8.6
	150	63.0	34.6	18.2
Fluorinated PI[6]	25	66.2	126.5	5.23
	150	76.0	26.7	28.5
Glass [6] (commercial ITO)	-	83.4	9.28	89.8
Glass [7] (sputtering)	130	85.0	62.0	14.0

* $F_{TC} = T$ (optical transmission) / R_s (electrical sheet resistance)

Recently some inorganic materials, such as SiO_2 were introduced to OLEDs to balance the number of holes and electrons injected to the emitter layer to achieve high recombination efficiencies [13]. An attempt to obtain better electric conduction properties has been made by insertion of a SiO_2 buffer layer between the poly (ethylene terephthalate) (PET) and ITO layers (ITO/ SiO_2 /PET) [14]. Increasing the adhesion between the PET and ITO by the inserted SiO_2 anchor layer also enhanced scribbling durability when the ITO / PET substrate was used for a resistive touch panel [14, 15]. In this work, therefore, we also attempted to insert SiO_2 buffer layer in between ITO and the colorless fluorinated PI substrate in order to enhance the optical transmission performance of the flexible transparent substrate prepared.

To apply a thin SiO_2 layer onto the fluorinated PI substrate, nano-sized colloidal silica was mixed with TEOS, which was hydrolyzed and condensed with the silanol groups on the surface of silica. Coating films are made from these solutions on the fluorinated PI substrate.

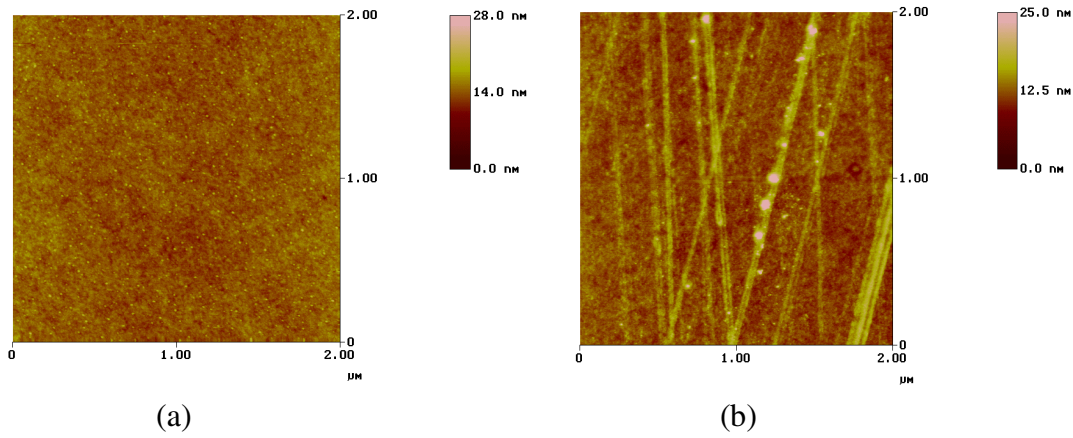


Figure 1. The AFM 2-D images ($2\ \mu\text{m} \times 2\ \mu\text{m}$ scan area) of the 6FDA- TFDB polyimide film (a) and polyimide film coated with SiO_2 (b).

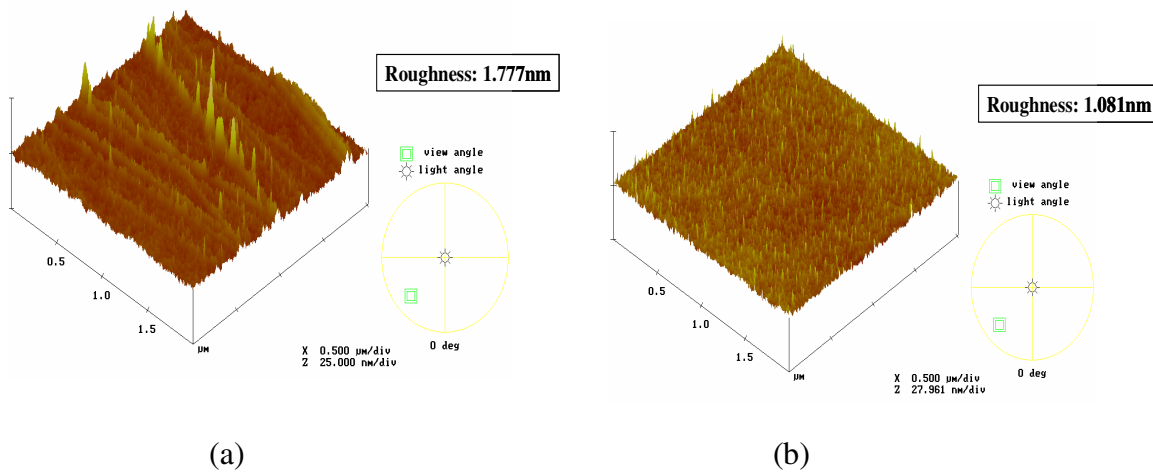


Figure 2. The AFM 3-D images ($2\ \mu\text{m} \times 2\ \mu\text{m}$ scan area) and root-mean- square (RMS) roughness of the 6FDA-TFDB polyimide film (a) and polyimide film coated with SiO_2 (b).

Figure 1 shows the AFM 2-D images of the fluorinated PI film and the SiO₂ coated PI film. The bare PI substrate shows a typical surface morphology of uniform flat amorphous polymers without any crystalline or agglomerate formation. Pinholes of PI's are, however, observed here and there during film preparation. It is noteworthy that the surface morphology of PI coated with SiO₂ is much better than uncoated PI because pinholes of PI are occupied by SiO₂. Figure 2 shows the AFM 3-D images and root-mean-square (RMS) surface roughness of the fluorinated PI film and the PI film coated with SiO₂. It is important to note that the surface roughness of the PI coated with SiO₂ film decreased because of the smoother surface in comparison to the PI film without SiO₂ layer.

Smooth surface with unevenness of less than about 0.7nm was obtained for the PI film coated with SiO₂. This low surface roughness may affect on the sheet resistance for sputtered ITO film. It was reported that better electric conductivity properties were observed by insertion of a SiO₂ anchor layer between the PI substrate and ITO layers [15]. Noda and Tanimura reported that the presence of SiO₂ anchor layer may induce a vitreous state of the PI surface, which has an affinity with ITO [16].

The optical transmission of the SiO₂ coated 6FDA-TFDB PI film reached to about 89% when optimized, while the average optical transmission of the 6FDA-TFDB PI substrate without SiO₂ was lower in the visible light range, as shown in table 1. It was mentioned that the synthesized aromatic PI substrate is optically colorless, transparent, and inactive, overcoming a major disadvantage of typical aromatic PI's as well as extending application fields [4,6]. These results are attributed to the minimization of the formation of the intra- and/or intermolecular charge transfer complex (CTC) in the PI molecules. It is important to note that the optical transmission of the PI film coated with SiO₂ increased slightly (over 2%) compared with uncoated 6FDA-TFDB PI film. The results suggest that very smooth surface of coating agents composed of TEOS and colloidal silica reduced light scattering on the film surface.

Future studies will focus on the deposition of ITO onto the SiO₂ coated 6FDA-TFDB PI substrate will be described elsewhere. It may be expected that the PI substrate coated with SiO₂ thin film can be a suitable candidate for flexible display devices with high transparency and good electrical properties.

CONCLUSIONS

In summary, the performance of the ITO film with the 6FDA-TFDB PI substrate such as optical transmission and sheet resistance was sufficiently comparable with that of the glass-substrate ITO film, and the PI substrate might be an excellent candidate for transparent flexible substrates in the flat panel display or other electronic applications. ITO thin films were prepared at two substrate deposition temperatures of 25°C and 150°C with a typical radio-frequency planar magnetron sputtering system. The sheet resistance and the optical transmission properties of the fluorinated PI substrate were comparable with those for the slide glass substrate. The substrate properties are better when the deposition temperature is high. The effect of the SiO₂ coating on the morphology of colorless fluorinated polyimide substrates for OLEDs was also investigated. To coat a thin SiO₂ layer, suspensions containing colloidal silica and TEOS were applied on the PI substrate by sol-gel reaction. Optical transmission of the SiO₂ coated 6FDA-TFDB PI film was significantly increased compared with the uncoated PI film, due to the decrease of surface

roughness.

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