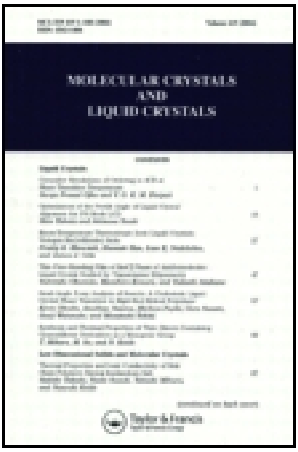

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ITO/Ag/ITO Multilayer Polymer Films by Roll-to-Roll Process and Performance of Flexible OLED Devices

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ITO/Ag/ITO Multilayer Polymer Films by Roll-to-Roll Process and Performance of Flexible OLED Devices

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In this study polyethylene naphthalate(PEN) and polyethersulfone(PES) films were chosen as a flexible substrates for fabrication of organic light emitting diode(OLED) devices. Hard coating was applied on both PEN and PES films utilizing UV curable resin. The transparent conductive ITO/Ag/ITO multilayer was deposited by the roll-to-roll sputter on the polymer films with hard coating. The UV hard coating of thin film on the polymer films improved both the surface roughness (50% in case of PEN film) and the transmittance in the visible region. In the subsequent multilayer transparent conductive layer formation, the optimum condition was obtained in the ITO(50 nm)/Ag(17 nm)/ITO(50 nm) multilayer structure. The OLED's fabricated with the optimized multilayer conductive films exhibited high luminance and current efficiency under low operation voltages.

Keywords OLED; flexible OLED; roll-to-roll process; TCO film; flexible substrate

Introduction

Flexible OLEDs have been studied actively for their potential application to low cost OLEDs and large area displays [1,2]. However the flexible substrates in case of polymer films require combination of properties such as chemical stability, optical clarity, low surface roughness and good thermo-mechanical properties. [3,4] Fabrication of OLEDs on flexible substrates is greatly dependent on the process temperatures and coefficient of thermal expansion (CTE) of the flexible polymer films. Of the polymer films available we chose polyethylene naphthalate (PEN) and polyethersulfone (PES) as the substrates for the fabrication of flexible OLEDs. In order to increase the optical and thermal property of the PEN and PES base films, thin layer of hard coating was conducted on the polymer films utilizing the UV curable resin. The transparent conductive oxide (TCO) thin films of the ITO/Ag/ITO structure were deposited on top of the hard coated base films by roll-to-roll sputtering system and the resulting films were subjected to the fabrication of OLED

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Table 1. Deposition conditions for ITO/Ag/ITO multilayers by roll-to-roll sputtering process.

Condition	ITO	Ag	ITO
Power(W)	RF 1400	DC 240	RF 1400
Flow gas rate(sccm)	Ar 30	Ar 20	Ar 30
Base pressure(torr)	1.0×10^{-5}	1.0×10^{-5}	1.0×10^{-5}
Working pressure(torr)	5.0×10^{-3}	3.0×10^{-3}	5.0×10^{-3}

devices [5]. The performance of flexible OLEDs was examined in terms of the effect of the hard coating, surface roughness and ITO/Ag/ITO multilayer deposition on polymer film by roll-to-roll process.

Experimental

Hard Coating on PEN and PES films

UV curable resin (CH-SR33) obtained from CC-Tech Co. was used as hard coating material. The resin had low viscosity of 7.5 cP and solid content of 50 wt% in MEK : Toluene = 1 : 1 mixture solvent. The resin was coated on both sides of PEN and PES films to 10 μm thickness by bar coater and then cured by exposure to the UV light with maximum peak in the 350 $\sim$ 440 nm range.

Multilayer TCO Deposition by Roll-to-Roll Sputtering System

ITO/Ag/ITO multilayer thin films were sequentially deposited on the hard coated PEN and PES polymer films by RF sputtering (ITO layer) and DC sputtering (Ag layer) utilizing roll-to-roll sputtering system at room temperature [6]. Table 1 lists the detailed deposition conditions for ITO/Ag/ITO multilayers on polymer films. First a bottom ITO layer was deposited to 50 nm thickness with an ITO target containing 5 wt% SnO_2. Silver(Ag) thin interlayer was deposited on top of the bottom ITO layer to variable thickness in the range of 15 $\sim$ 20 nm by using metallic Ag (99.999% purity) target in order to investigate the dependence of both sheet resistance and transmittance to visible light of the ITO/Ag/ITO

Table 2. Physical properties of PEN and PES film before and after hard coating.

Properties	PES	PES with HC	PEN	PEN with HC
Film Thickness μm	170	–	110	–
HC Thickness μm	–	10	–	10
Transmittance (at 550 nm)%	87.6	89.2	86.1	88.9
L*	95.2	96.4	94.7	96.1
a*	−0.0	−0.1	0.3	0.5
b*	1.0	−0.5	−0.2	−2.2
Hardness	–	$2H$	–	$2H$

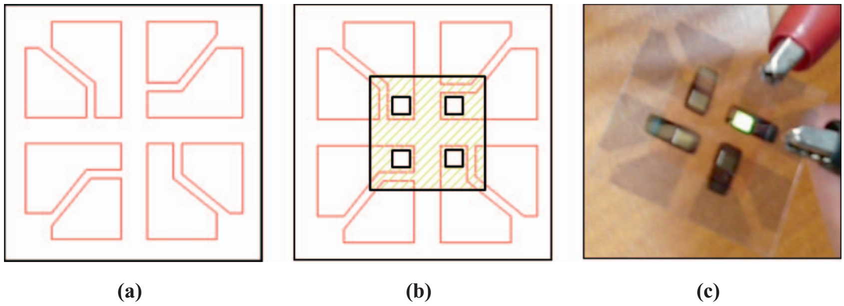


Figure 1. The back plane of 4 pixel structure flexible OLED (a) patterned TCO layer (b) patterned TCO layer with insulator layer (c) working flexible OLED device.

multilayers as transparent conductive flexible substrates for OLED devices. Subsequently the top ITO layer was deposited on top of the Ag/ITO layer to 50 nm thickness under the same deposition conditions used for the bottom ITO layer.

Fabrication of Flexible OLEDs

After the hard coating of UV curable resin and subsequent deposition of ITO/Ag/ITO transparent multilayers by roll-to-roll process, the flexible substrates were subjected to the OLED device fabrication. For the patterning of ITO/Ag/ITO multilayer anode on flexible substrates the photolithographic processes have to be modified from the usual ITO glass or ITO film used in the OLED device fabrication.

First positive-PR (DS-i1000, Dongjin Chemical Co.) was spin coated stepwise under the condition of 200 rpm (10 sec), 1800 rpm (20 sec) and 2000 rpm (20 sec) followed by soft bake at 90°C for 3 min. The positive-PR thin film was subjected to UV exposure (MDA-12000, Midas System) at 6 mW/cm^2 for 15sec followed by developing in TMAH 2.38 wt% solution (80 sec), D.I. water washing and hard bake at 100°C for 5 min. The ITO/Ag/ITO multilayer anode was then etched by dipping in an etchant solution (DA-300, Dongjin Chemical Co.) for 10min followed by deionized water washing. After etching of ITO/Ag/ITO anode the remaining positive PR was stripped in an aqueous alkaline solution (Remover PG, Microchem Co.) by dipping for 5 min followed by D.I. water washing. After patterning of ITO/Ag/ITO anode the insulator layer was also patterned by photolithographic

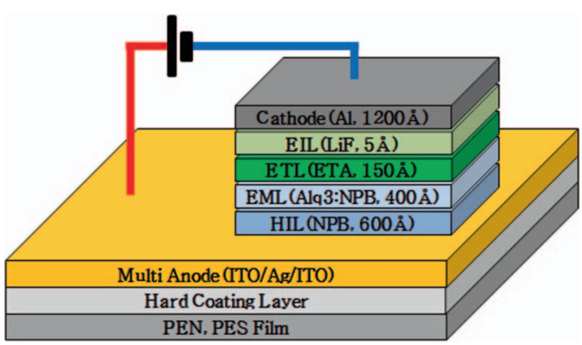
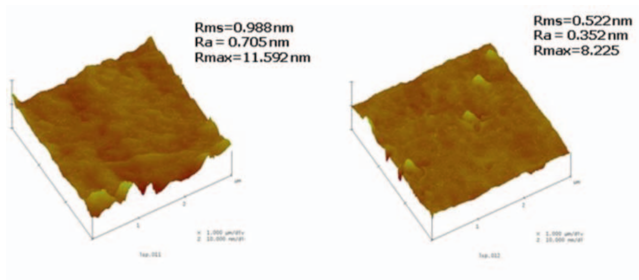


Figure 2. Structure of flexible OLED device with multilayer anode.



(a) (b)

Figure 3. Comparison of surface roughness (a) PEN base film, (b) hard coated PEN film.

process. Here we used a new insulator layer that is the same positive PR (DS-i1000, Dongjin Chemical Co.) used in the ITO/Ag/ITO anode pattering instead of the usual polyimide PR due to the higher process temperature of the latter photoresist. The back plane of flexible OLED substrate after ITO/Ag/ITO multilayer anode etching and insulator patterning is shown in Fig. 1(a) and Fig. 1(b), respectively.

The fabrication of OLED device on the flexible substrate with patterned ITO/Ag/ITO multilayer anode and a new positive PR insulator layer was carried out with the Sunic EL Plus 200, a cluster type OLED panel fabrication system. The OLED device had configuration of HTL(NPB, 600 Å)/EML(Alq3:NPB, 400 Å)/ETL(ETA, 150 Å)/EIL(LiF, 5 Å)/Cathode(Al, 1200Å) as shown in Fig. 2.

Results and Discussion

Properties of ITO/Ag/ITO Multilayer Flexible Substrate

Since the surface property of a new ITO/Ag/ITO transparent conductive flexible substrate affects the performance of the resulting OLED device, the surface roughness (Ra) of PEN and PES flexible substrates was measured by AFM after the thin film hard coating utilizing UV curable resin. In case of PEN film the Ra value was decreased to about 50% from 0.705 mm to 0.352 nm as shown in Fig. 3. Table 2 shows the physical property changes of the PEN and PES films before and after UV hard coating. As shown in Table 2 the UV hard coating improved both the visible light transmission and roughness of the PEN and PES base films. These are very important for the OLED devices since the active layer(HTL, EML, ETL and Al cathode) of OLED device is usually less than 150 nm in total and sensitive to the status of the transparent conductive surface. The surface of the UV hard

Table 3. Electro-optical properties of PEN and PES with ITO/Ag/ITO multilayer.

Layer	ITO/Ag/ITO	
Base film	PEN	PES
Sheet Resistance(Ω/□)	7.2	6.7
Total transmittance(%)	81.0	82.5
Transmittance at 550 nm(%)	82.1	83.2

Table 4. Performance of OLED devices with ITO/Ag/ITO conductive layer on PEN and PES film.

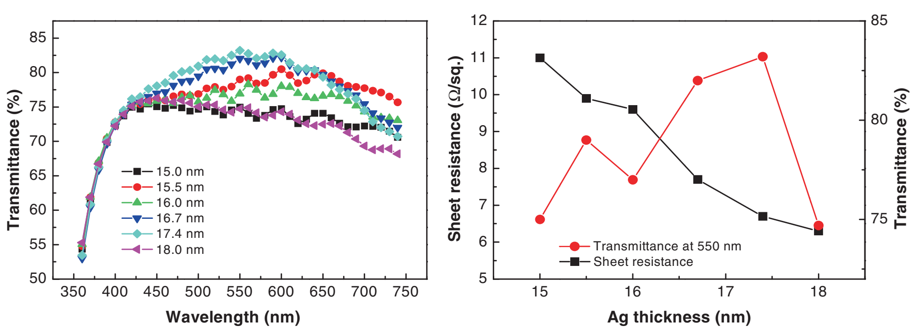
Film	PEN	PES
Turn on Voltage	2.5 V	2.5 V
Voltage(at Max Luminance)	5.5 V	5.0 V
Max Luminance	15640 cd/m2	7176 cd/m2
Max Current efficiency	2.772 cd/A	2.503 cd/A

coated polymer films are also important from the view point of the ITO/Ag/ITO multilayer deposition in the roll-to-roll sputtering process which require good thermal and mechanical properties.

Figure 4(a) shows the UV visible spectra of ITO/Ag/ITO multilayer polymer films with different Ag interlayer thickness. The optical transmittance of ITO/Ag/ITO multilayer films were remarkably increased in the visible region compared to those of Ag/ITO multilayer films. The highest transmittance of 83.2% at wavelength of 550 nm was observed in ITO/Ag/ITO multilayer films with Ag interlayer thickness of about 17 nm, as shown in Table 3 [7,8]. This transmittance value corresponds to that of 50 nm thickness of ITO single layer polymer film fabricated by roll-to-roll sputtering process. However further increase of Ag interlayer above 17 nm resulted in sharp decrease in the transmittance even though ITO/Ag/ITO multilayer films showed lower sheet resistance as shown in Fig. 4(b). The analysis of sheet resistance based on the parallel circuit model was also consistent with experimental sheet resistance results of the ITO/Ag/ITO multilayer films. It was noted that the low sheet resistance (6.7Ω/□) of ITO/Ag/ITO multilayer films (total thickness 117 nm and Ag interlayer 17 nm) was better than that of the commercial single layer ITO films available and quite suitable for the fabrication of flexible OLED devices [9].

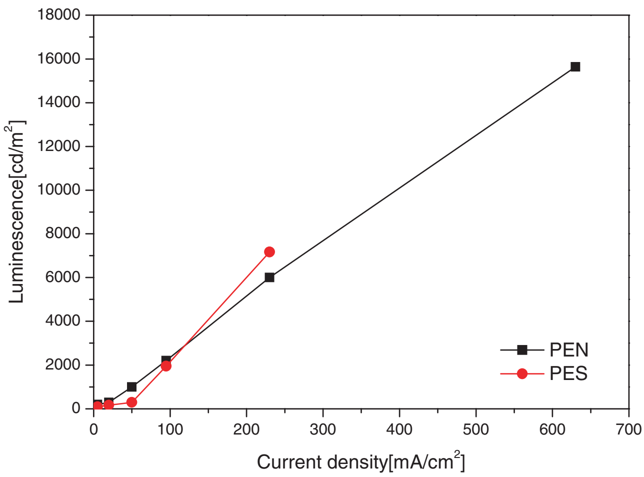
Performance of flexible OLED devices

The luminance and current efficiency vs. current density plots of flexible OLEDs fabricated on ITO/Ag/ITO multilayer transparent conductive films are shown in Fig. 5 and Table 5.

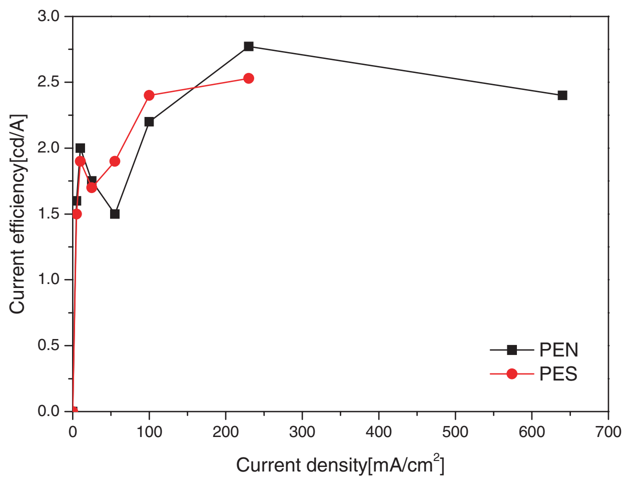


(a) (b)

Figure 4. Optical transmittance spectra of ITO/Ag/ITO multilayer films (a) as a function of Ag interlayer thickness, (b) sheet resistance and optical transmittance as a function of Ag interlayer thickness.

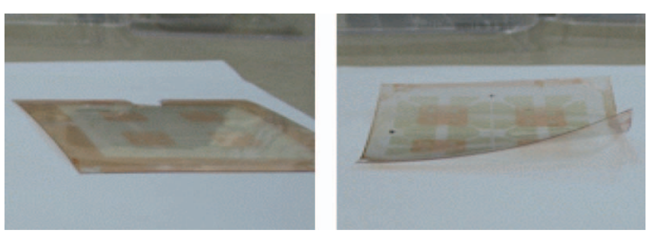


(a)



(b)

Figure 5. Performance of flexible OLEDs (a) luminescence and (b) current efficiency vs. current density.



(a) (b)

Figure 6. Curling of (a) PEN film and (b) PES film after ITO/Ag/ITO multilayer formation.

Table 5. Properties of polymer films for flexible substrate of OLEDs.

Property	PET	PEN	PC	PES	PI
Thickness(μm)	125	125	150	200	100
Tg(°C)	78	120	150	223	$\sim$ 340
CTE(ppm/°C)	15	13	70	54	$\sim$ 50
Refractive Index	1.66	1.74	1.59	1.65	—
Transmission(%)	91	87	90	88	$\sim$ 30
Retardation	68	*High*	< 1	$\sim$ 10	—
Density(g/cm3)	1.4	1.36	1.2	1.37	1.4
Water uptake(weight)	0.3	0.3	0.3	1.4	1.8
Young's modulus(Gpa)	5.3	6.1	3	2.2	2.5
Tensile strength(Mpa)	225	275	—	83	$\sim$ 200

PC : polycarbonate, PI : polyimide, PET : polyethylene terephthalate.

The turn-on and maximum luminance voltages of flexible OLEDs were in the range of 2.5 and 5.0 $\sim$ 5.5 volt, respectively. These low voltage driving characteristics were close to those of the OLEDs based on ITO glass as substrate. These indicate that the surface smoothness and uniformity of the ITO/Ag/ITO multilayer were suitable for the flexible OLEDs.

The difference between the PEN and PES film based flexible OLEDs were the unstability of the OLEDs based on PES flexible substrate compared to the PEN film. The failure of operation of OLEDs based on PES substrate above 200 mA/cm^2 current density might be due to the high thermal expansion property of PES film compared to the PEN film. These are exhibited in Fig. 6(b) in which the PES based multilayer film showed curling phenomenon while PEN film maintained the flat shape after the deposition of the ITO/Ag/ITO transparent conductive films as shown in Fig. 6(a). These could also be confirmed from Table 5 in which the coefficient of thermal expansion (CTE) value of PES film was about 4 times larger than that of PEN film although other properties were similar or even better than PEN film

Conclusions

In this study the UV hard coating and ITO/Ag/ITO multilayer transparent conductive layer were formed on the PEN and PES films and then these flexible substrates were used in the fabrication of flexible OLED devices. The UV hard coating of thin film on the polymer films improved both the surface roughness (50% in case of PEN film) and the transmittance in the visible region. In the subsequent multilayer transparent conductive layer formation by roll-to-roll sputtering method, the optimum condition was obtained in the ITO(50 nm)/Ag(17 nm)/ITO(50 nm) multilayer structure. The OLEDs fabricated with the optimized multilayer conductive films exhibited high luminance and current efficiency under low operation voltages. The PEN base film exhibited better performance in the flexible OLEDs than PES film probably due to the low coefficient of thermal expansion of the former film.

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