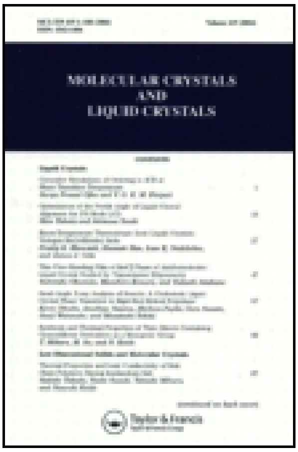

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Fabrication and Performance of Flexible OLEDs with AGZO/Ag/AGZO Multilayer Anode on Polyethersulfone Film

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In this study, we made flexible OLED's based on polyethersulfone(PES) film which has high transmittance in visible region and high glass transition temperature(Tg 223°C). UV hand coating was conducted on the PES base film followed by SiO_2 gas barrier layer and aluminium gallium Zinc Oxide(AGZO)/Ag/AGZO transparent multi layer anode by roll-to-roll sputtering. The SiO2 gas barrier was found to be more effective than the UV hand coating as well as enabling the AGZO/Ag/AGZO multilayer anode deposition by roll-to-roll sputter. The relatively high luminance and current efficiency of the flexible OLED with AGZO/Ag/AGZO multilayer anode could be explained by the decreased energy level close to that of NPB hall injection Layer as well as the micro cavity effect of the multilayer anode and gas barrier layer.

Keywords Flexible; OLED; Microcavity; Multilayer Anode; ITO; PES; AGZO

Introduction

Flexible OLEDs have been studied actively for their potential application to both large size OLED display and decorative lighting[1,2,3]. The efficiency and life time of flexible OLED are still major problem to overcome compared to the OLED devices based on glass substrate[4]. In this study, we made flexible OLED's based on polyethersulfone(PES) film which has high transmittance in visible region and high glass transition temperature(Tg 223°C). UV hand coating was conducted on the PES base film followed by SiO_2 gas barrier layer and aluminium gallium Zinc Oxide (AGZO)/Ag/AGZO transparent multi layer anode by roll-to-roll sputtering. The effects of UV hand coating, SiO_2 gas barrier layer and AGZO/AG/AGZO anode on the performance of OLED device are discussed.

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Experimental

Materials for the Flexible Substrates

As for the base film of flexible OLED devices polyethersulfone (PES) film obtained from i-Component (Korea) was used. The PES film did not have hard coating and had the following specifications; thickness 170 μm, width 210 mm, transmittance 88.7%, haze 1.4%, coefficient of thermal expansion (CTE) 60 ppm/K and glass transition temperature (Tg) 223°C.

The UV curable hard coating resin was synthesized by free radical polymerization. The UV oligomers and high refractive index monomer 2-phenoxyethanolacrylate(M-140) were obtained from Miwon Commercial Co., and UV photoinitiators (I-184, I-189) were from Ciba Specialty Chemicals of which structures are shown in Fig. 1.

Gas Barrier and Transparent Conductive Layer Deposition by Sputtering

On top of the UV hard coating layer of PES film, thin SiO_2 gas barrier layer was deposited by using roll-to-roll type sputter. The sputtering conditions were RF power 500 W, base

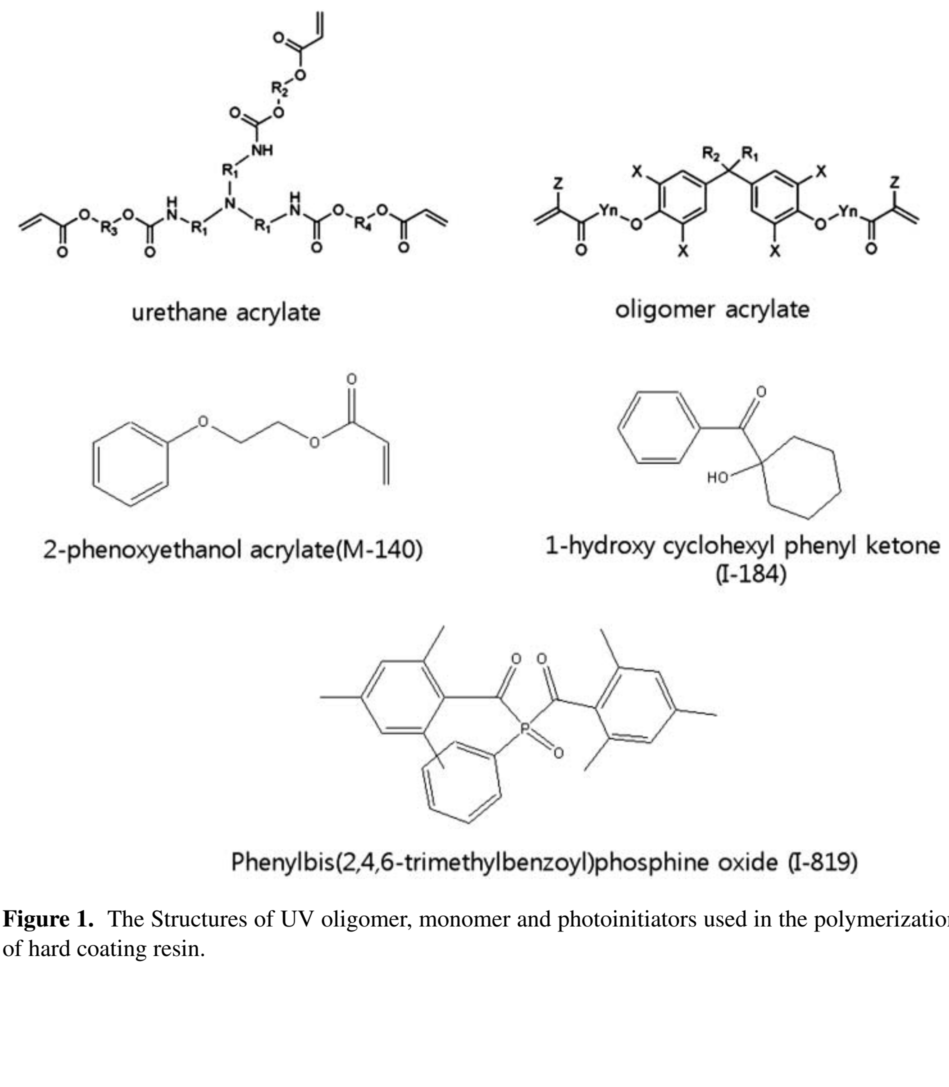


Figure 1. The Structures of UV oligomer, monomer and photoinitiators used in the polymerization of hard coating resin.

pressure 1 × 10^{-5} torr, operation pressure 3 × 10^{-3} torr and Ar gas flow 220 sccm with SiO_2 target(Size 200 × 100 × 6 mm) made by TS Solution Co., in Korea.

As for the transparent conductive layer, AGZO/Ag/AGZO multilayer was deposited on top of the UV hard coating layer of PES film. Aluminium gallium zinc oxide (AGZO) thin film has been known as a substitute for indium tin oxide (ITO) thin film due to the forecasted shortage of indium source. First the bottom AGZO thin layer were deposited by roll-to-roll sputter under the condition of RF power 500 W, Ar gas flow 220 sccm and same base and operating pressure as SiO_2 with AGZO target (Al_2O_3 1.903 wt%, Ga_2O_3 0.254 wt%) made by TS Solution Co., (Size 200 × 100 × 6 mm). The silver(Ag) interlayer was deposited to about 8 μm thickness by using DC 210W power under same condition as AGZO underlayer and then followed by AGZO top layer deposition.

The PES flexible substrate with UV resin coating, SiO_2 and AGZO/Ag/AGZO transparent conductive layer were subjected to the stress relaxation simulation under bending force by using ABAQUS program.

Fabrication of OLED Device on AGZO/Ag/AGZO Conductive Multilayer Formed PES Film

The fabrication of OLED devices with AGZO/Ag/AGZO multilayer anode was started from the patterning of AGZO/Ag/AGZO anode layer. First the AGZO/Ag/AGZO transparent conductive anode layer was patterned by photolithographic process utilizing a positive PR (DS-i1000, Dongjin Chemical Co.) followed by etching of multilayer anode with an etching solution (DA-300, Dongjin Chemical Co.). The insulator layer was also patterned by photolithographic method by using an acrylate type photoresist (DS-i1000) instead of the polyimide type photoresist commonly used in order to increase the visible light transmittance. The fabrication of OLED device on the AGZO/Ag/AGZO multilayer anode patterned on the PES flexible substrate was carried out with Sunic EL Plus 200, a cluster type OLED panel fabrication system.

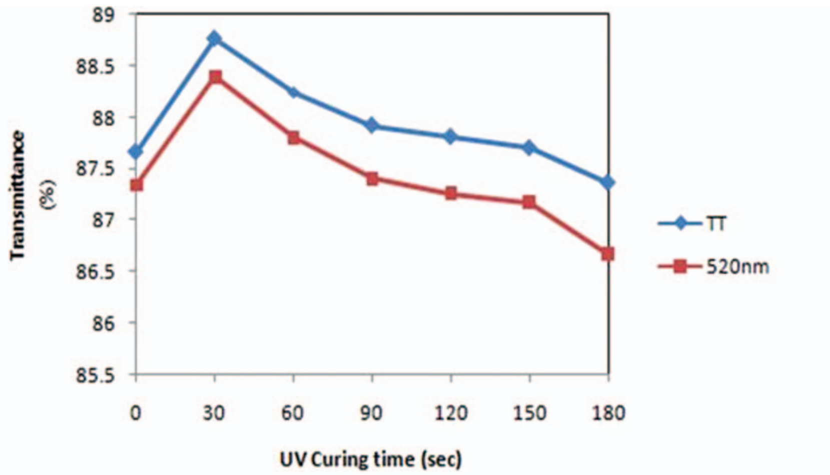
Results and Discussion

Effect of UV Hard Coating Layer

UV hard coating was conducted on top of PES base film to make a buffer layer before depositions of SiO_2 gas barrier and AGZO/Ag/AGZO multilayer anode by sputtering process. Table 1 shows the dependence of viscosity and refractive index of the UV hard

Table 1. Formation and properties of UV coating resin

Composition/Sample No.	BL-1	BL-2	BL-3	BL-4	BL-5	BL-6
Urethan acrylate	-	10	25	35	47	57
Acrylate oligomer	57	47	32	22	10	-
M-140	40	40	40	40	40	40
I-184	2	2	2	2	2	2
I-819	1	1	1	1	1	1
Viscosity (cP)	2200	1100	980	830	780	710
Refractive index	1.571	1.563	1.550	1.542	1.538	1.534



Curing Time(sec.)	PES	30	60	90	120	150	180
Total Transmittance(%)	87.6	88.7	88.2	87.9	87.8	87.7	87.3
Transmittance at 520nm(%)	87.3	88.4	87.8	87.4	87.2	87.1	86.6

Figure 2. Transmittance of UV hard coating buffer layer on PES film by varying UV exposure time at 40 mW intensity.

coating layer after curing on the formulation of the UV coating resin. As shown in Table 1 both the viscosity and refractive index values were increased with the increasing content of acrylate UV oligomer in the UV coating resin. The formulation BL-2 was selected from the view point of the optimum viscosity in coating process. The BL-2 formulation was coated on the PES base film to 30 nm thickness and then UV cured at 40 mW power while varying the UV exposure time. As shown in Fig. 2 the optimum UV cure time was obtained at 30 sec at which the transmittance of the UV hard coating layer was over 88% in the visible region.

The surface roughness of the UV hard coating layer was checked by AFM analysis. As shown in Fig. 3 the surface roughness was improved to 0.39 nm after UV hard coating from 0.72 nm of the PES base film. The performance of the synthesized UV coating resin was also compared with the commercial one by checking the mechanical property of the UV hard coated PES film. The PES film coated with the BL-2 UV coating resin exhibited increased toughness compared to the typical commercial UV coating resin (CH-SR33, CC Tech Co.) in the stress-strain curves of the two films measured by UTM mechanical tester as shown in Fig. 4.

SiO_2 Gas Barrier Layer Formation by Roll-to-Roll Sputtering

The BL-2 UV hard coated PES film was subjected to the gas barrier and transparent conductive layer formation by using the roll-to-roll sputtering system shown in Fig. 5. The

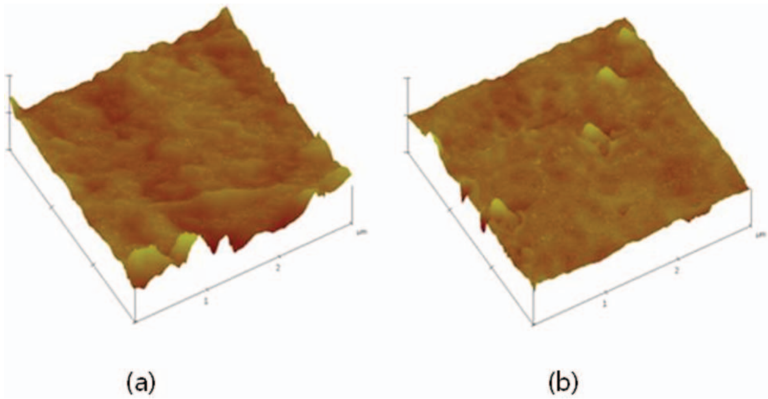


Figure 3. AFM surface images of (a) PES base film (Ra : 0.72 mm) and (b) UV hard coated PES film (Ra : 0.39 mm).

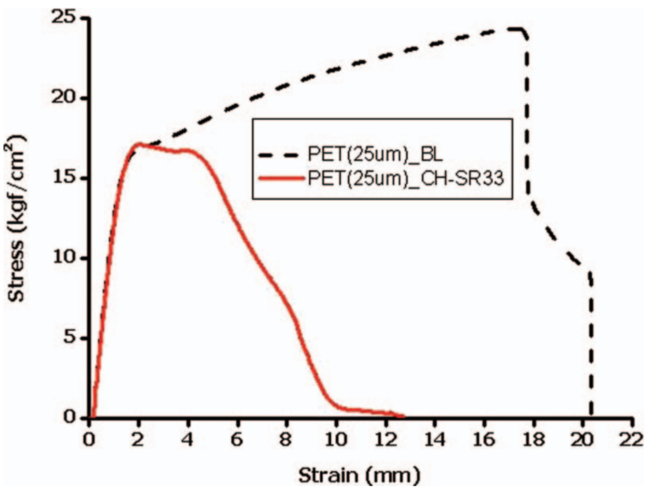


Figure 4. Mechanical properties of UV hard coating PES film (a) BL-2 UV resin and (b) commercial CH-SR 33 UV resin.

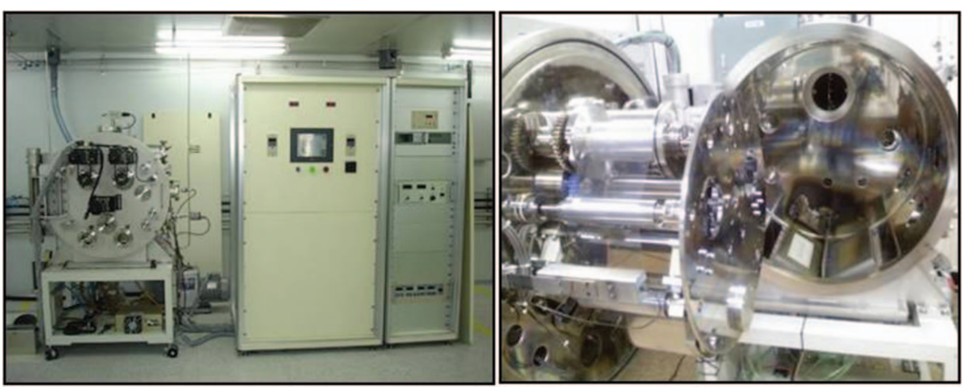


Figure 5. Roll-to-roll sputtering equipment used in the gas barrier and conductive transparent layer on PES film.

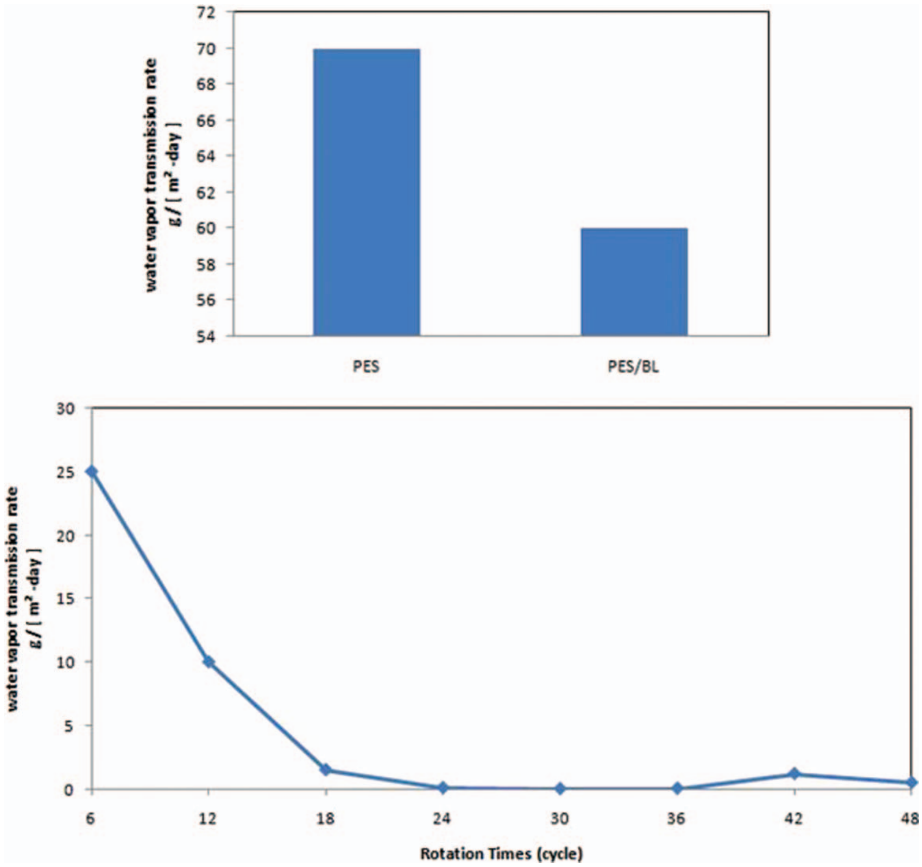


Figure 6. Gas barrier property of SiO2 layer deposited by roll-to-roll sputter on BL-2 UV hard coating PES film.

gas barrier property of the SiO_2 thin film deposited on top of the BL-2 UV hard coated PES film improved significantly with the thickness of the SiO_2 film. The water vapor transmission rate (WVTR) of PES base film was 70 g/m^{2}day which was decreased to 60 g/m^2·day by BL-2 UV hard coating (300 nm thickness). However the WVTR value was decreased to 1×10^{-2} g/m^2·day by SiO_2 barrier coating to about 125 nm (30 cycles) by roll-to-roll sputtering process as shown in Fig. 6. The visible light transmittance of the SiO_2 gas barrier coated PES film was checked with the cycle time of the roll-to-roll sputter. As shown in Fig. 7 the transmittance showed peak at about 125 nm of SiO_2 layer corresponding to 30 cycle time of roll-to-roll sputter. It was noted that the gas barrier property of PES film was much improved by the thin SiO_2 layer (125 nm) than the thick UV hard coating (300 nm) layer. It was also noticed that the SiO_2 thin film as gas barrier layer on PES film had certain limitation (125 nm) above which the barrier property was not improved. This suggested that the inorganic-organic multilayers should be coated to achieve 1×10^{-6} g/m^2·day WVTR required for the long life time of flexible OLED's based polymer film substrate. The balance of the gas barrier and visible light transmittance should also be carefully checked for the high luminance of flexible OLED devices based on flexible polymer films.

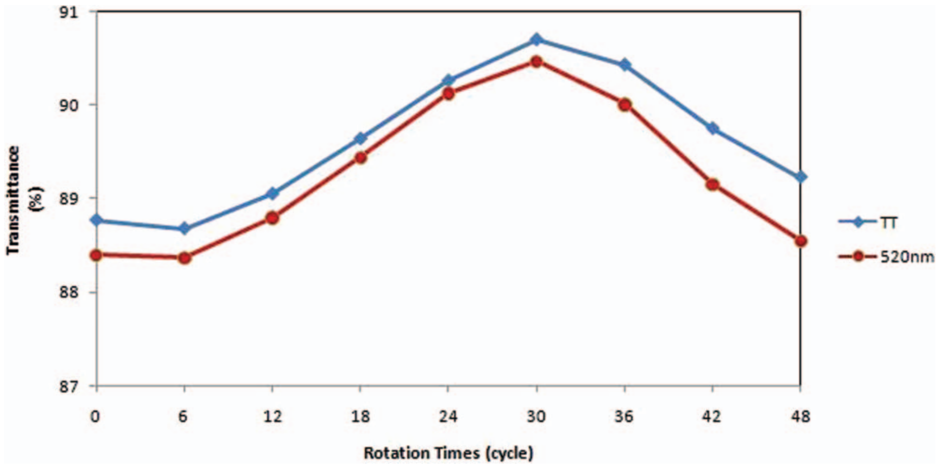


Figure 7. Visible light transmittance vs. SiO2 gas barrier layer thickness (roll-to-roll sputter cycle time) deposited by sputtering on BL-2 UV hard coating PES film.

AGZO/Ag/AGZO Multilayer Anode and OLED Performance

Aluminium gallium zinc oxide(AGZO)/Ag/AGZO multilayer was deposited on top of the SiO2/UV hard coating/PES film by roll-to-roll sputtering method to make a transparent conductive substrate for flexible OLED's. Figure 8 shows the dependence of sheet resistance

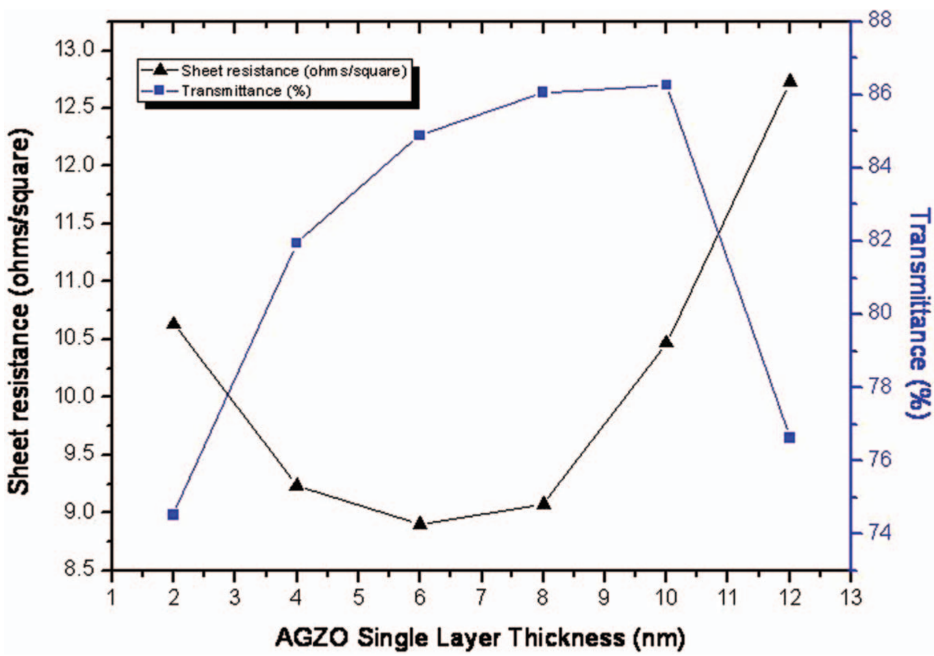


Figure 8. Sheet resistance and transmittance of AGZO/Ag/AGZO multilayer anode as a function of AGZO single layer thickness.

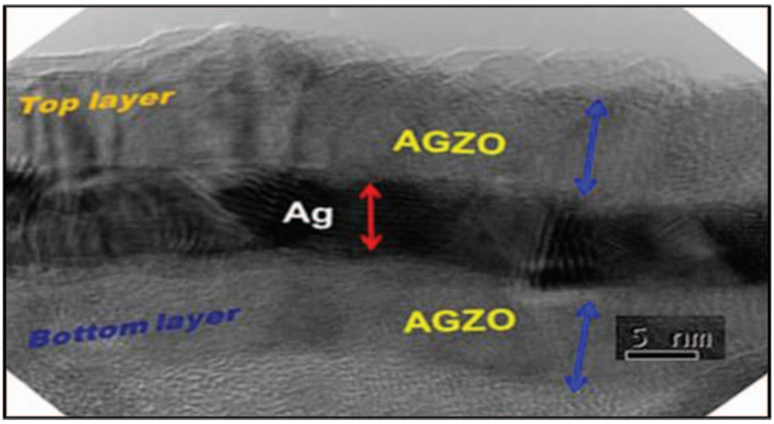


Figure 9. Cross section TEM image of AGZO/Ag/AGZO multilayer anode deposited on SiO2/UV hard coating/PES film by roll-to-roll process.

and visible light transmittance on the AGZO single layer thickness in the AGZO/Ag/AGZO multilayer anode while maintaining the Ag interlayer thickness at about 8 nm which was confirmed in the preliminary experiments. When the top and bottom AGZO layer was deposited to about same thickness as Ag interlayer, both the visible light transmittance and the sheet resistance of the AGZO/Ag/AGZO multilayer were found to be optimized. The TEM image of the cross section of the AGZO/Ag/AGZO transparent conductive layer is shown in Fig. 9. The AGZO/Ag/AGZO multilayer anode formed under optimum condition showed low sheet resistance of 9 Ω/□ comparable to that of the conventional ITO glass used to make OLED devices.

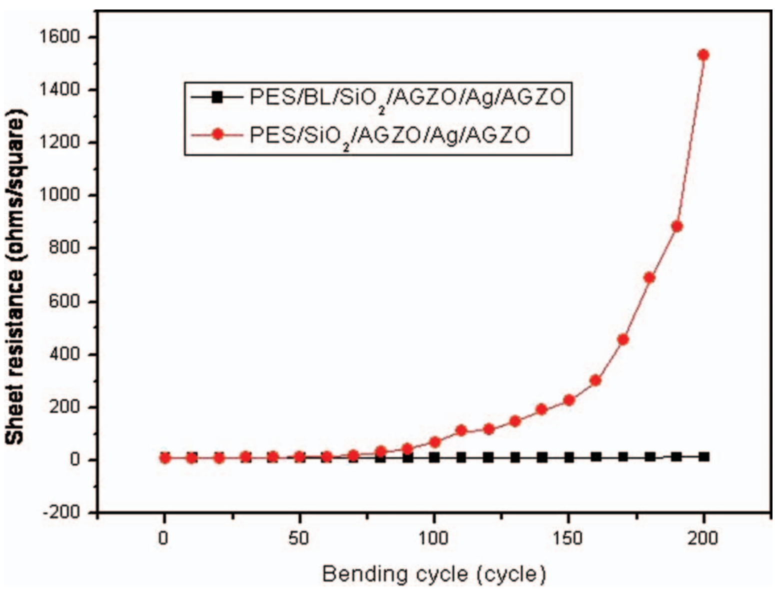


Figure 10. Variation of sheet resistance of AGZO/Ag/AGZO multilayer anode with bending cycle.

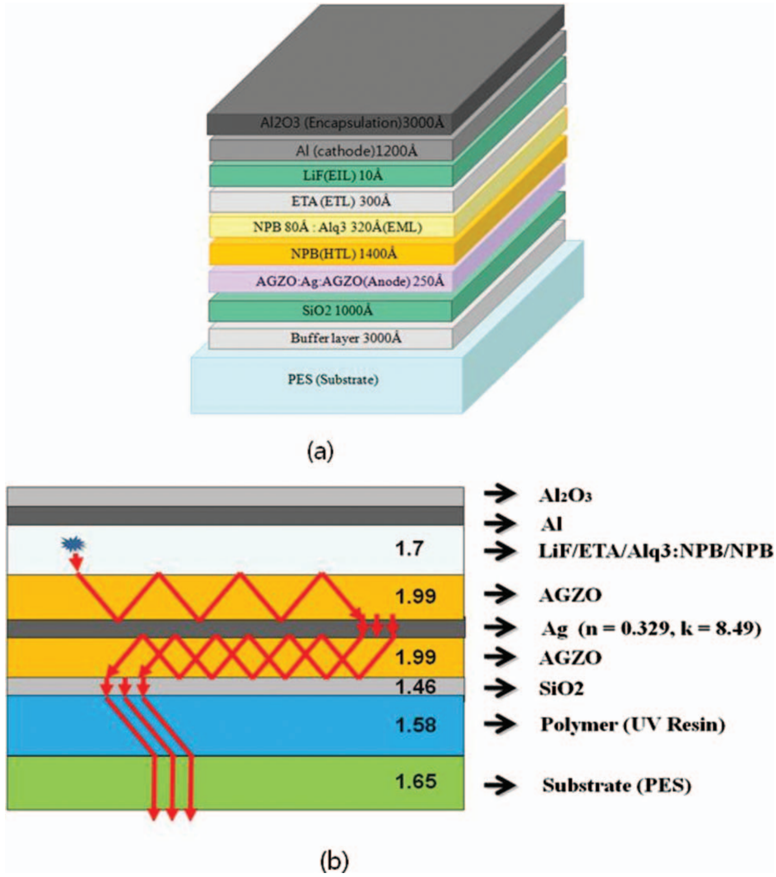


Figure 11. Structure of OLED's (a) layer configuration and (b) refractive indices of layers

Figure 10 shows the variation of sheet resistance with the bending cycle of the AGZO/Ag/AGZO anode layer deposited on SiO2 deposited PES film and on the SiO2 deposited on UV resin coated PES film. Both films maintained low sheet resistance up to 70 cycles, however, the sheet resistance of AGZO/Ag/AGZO multilayer anode increased sharply above 70 bending cycles in the case of PES film without UV resin coated buffer layer. This was in accordance with the mechanical property of the BL-2 coated PES film which exhibited increased toughness as shown in Fig. 4. After hard coating of synthesized UV curable resin and subsequent deposition of SiO2 gas barrier layer and AGZO/Ag/AGZO transparent conductive layers by roll-to-roll sputtering method, the flexible PES substrate was subjected to the OLED device fabrication. The fabricated OLED device had configuration of HIL(1400 Å)/EML(400 Å)/ETL(300 Å)/LiF(10 Å)/Al(1200 Å) as shown in Fig. 11(a) and the refractive index values of each layer are shown in Fig. 11(b).

The performance of the OLED with AGZO/Ag/AGZO multilayer anode is shown in Fig. 10. The relatively high values of luminance (2500 cd/m2) and current efficiency (5.13 cd/A) of the flexible OLED device shown in Fig. 12(a) seemed to be due to the decreased energy level (5.21eV) of the AGZO/Ag/AGZO multilayer anode as shown in Fig. 12(b) as well as the microcavity effect of the OLED device with the multilayer anode and the SiO_2 gas layer as shown in Fig. 11(b).

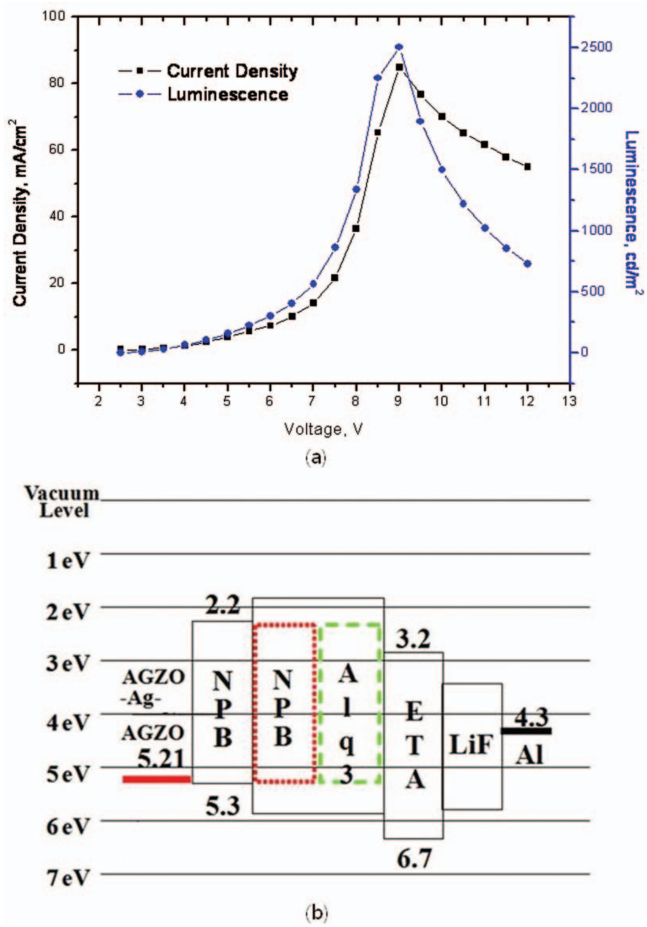


Figure 12. The performance of OLED device fabricated on AGZO/Ag/AGZO multilayer (a) LIV curve and (b) energy band diagram.

Conclusions

In this work flexible OLED was fabricated with UV hand coated polyethersulfone(PES) film as substrate on which SiO2 gas barrier and AGZO/Ag/AGZO transparent anode layers were deposited by roll-to-roll sputtering method. UV had coating utilizing synthesized BL-2 resin improved both the mechanical property and surface flatness of the PES film. The SiO2 gas barrier was found to be more effective than the UV hand coating as well as enabling the AGZO/Ag/AGZO multilayer anode deposition by roll-to-roll sputter. The relatively high luminance and current efficiency of the flexible OLED with AGZO/Ag/AGZO multilayer anode could be explained by the decreased energy level close to that of NPB hall injection Layer as well as the micro cavity effect of the multilayer anode and gas barrier layer.

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