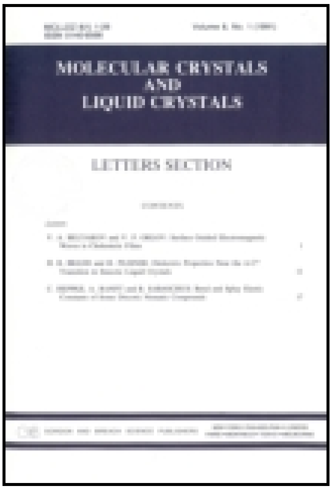

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Flexible organic light emitting diodes (OLEDs) have been studied actively for the potential application to OLED display and OLED lighting. One of the key materials for flexible OLED is the flexible and transparent film substrate which can substitute ITO glass in flat panel OLEDs.

In this work we deposited silicon and aluminium oxide and nitride single layer thin films on different flexible substrates such as poly(polyethylene terephthalate) (PET) and poly(polyethylene naphthalate (PEN) to investigate the gas barrier properties. After selecting the polymer film substrate and thin inorganic layer material, the inorganic/organic/inorganic multiple gas barrier was formed on film substrate by using roll-to-roll sputter and their property was examined from the viewpoint of multilayer structure and gas barrier properties for application to flexible substrate of OLED devices.

Keywords Flexible OLED; gas barrier layer; roll-to-roll sputtering; thin film; WVTR; multi-layer

1. Introduction

Flexible OLEDs have been studied actively for their potential application to both large size OLED display and decorative lighting [1, 2]. The efficiency and life time of flexible OLED are still major problem to overcome compared to the OLED devices based on glass substrate [3–5].

The short life time of flexible OLEDs are attributed to the increased penetration of oxygen and water vapor to the thin organic layer of OLED device through the flexible polymer film substrate. Therefore the fabrication of transparent thin gas barrier layers on the polymer film is important issue for the production of flexible OLED devices [6–10].

We used poly(ethylene naphthalate) (PEN) film as flexible substrate since it had a balanced property such as high transmittance, high thermal and mechanical property

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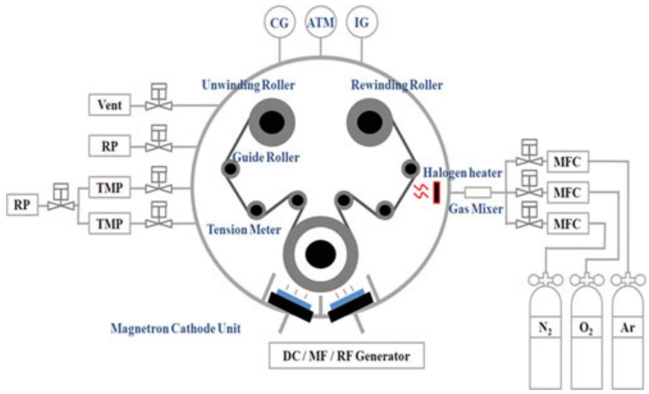

Figure 1. Diagram of roll-to-roll sputtering system.

and good gas barrier property with base polymer itself. The material selection of inorganic/organic/inorganic multilayers and thickness of layers were also found to affect the gas barrier property and robustness of flexible OLED devices to the bending stress.

2. Experimental

Fabrication of Gas Barrier Layers by Reactive Sputtering

The thin film of SiN_x was deposited on polymer film substrate as gas barrier layer by using roll-to-roll sputtering system shown in Fig. 1. First pre-sputtering was conducted for about 10 min at base pressure of 1×10^{-5}torr in the roll-to-roll sputter to clean the surface of Si or Al target and to stabilize the plasma state. The reactive sputtering of SiN_x and AlN_x thin films was then carried out by varying the partial pressure of N_2 gas with the mass flow controller (MFC). The reactive sputtering condition of the SiN_x thin film is

Table 1. Deposition condition of SiN_x layer on PEN film by reactive sputtering

Base pressure	1×10^{-5}[torr]	
Working pressure	3[mtorr]	
Power	DC pulse 600[W]	
Winding speed	0.05[m/min]	
Gas flow rate $=N_2(O_2)/Ar+N_2(O_2)$	SiO_x and AlO_x 0~20[%]	SiN_x and AlN_x 0~75[%]
Target	Si or Al (99.99%), $(250\times100\times6)$mm	

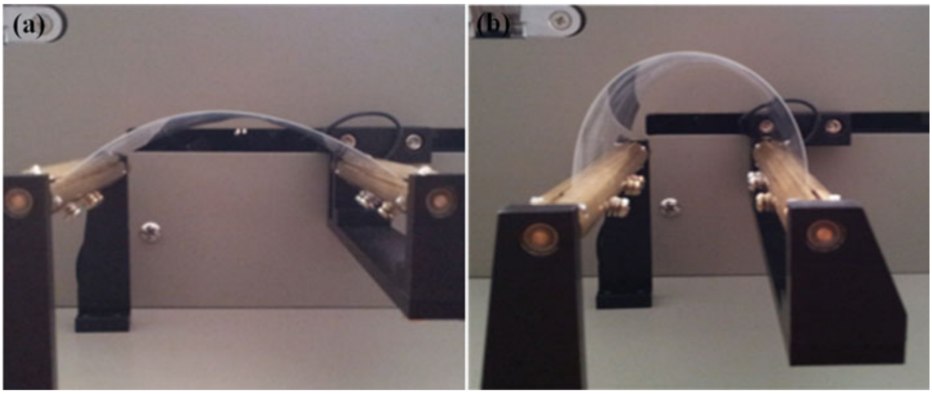

Figure 2. Bending tester (a) maximum width (b) minimum width.

shown in Table 1. We also used several different polymer films such as PET (poly ethylene terephthalate) and PEN (poly ethylene naphthalate) supplied by Kolon Industries (Korea) and Lintec Co. (Japan), etc.

Measurement

The thickness of the gas barrier layers and the light transmittance of the substrate film with gas barrier layers were measured by Nanoview (Nanosystem, NV-E1000) equipment and UV-vis spectraphotometer (CM-3600d, Konica Minolta Co., Japan). The water vapor transmission rate (WVTR) of the gas barrier films were measured by Mocon (Permatran-W^R 3/33MA) equipment under the condition of 37.8°C, RH 100%, and N_2 gas rate of 10 ± 0.2 sccm for 24 hrs. The surface of gas barrier thin film was examined by both scanning electron microscope (SEM, Hitachi S-4800, Japan) and XRD (Bruker, D8 Advance A25). The bending test of PEN film with gas barrier layers was conducted by bending machine (Zeetech, ZBT-200, Korea) shown in Fig. 2. The gas barrier film size was 100 × 100 mm and the test conditions were 10,000 cycles under 100 mm/sec speed in the range of 40 – 80 mm.

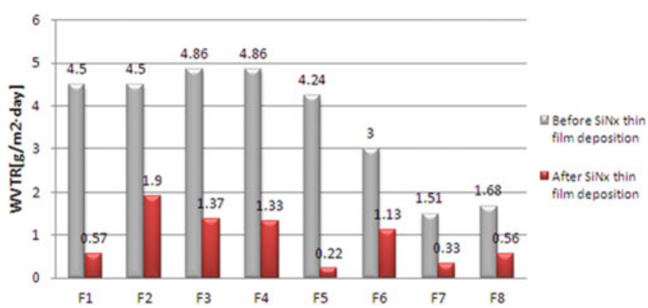

Figure 3. The WVTR values (gm/[m^2-day]) of PET and PEN films without and with SiN_x gas barrier layer.

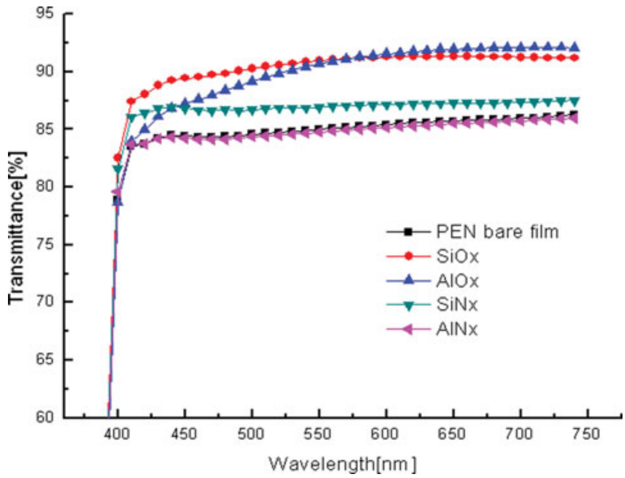

Figure 4. The transmittance of oxide and nitride thin films deposited on PEN film.

3. Results and Discussion

Selection of Substrate Films

In the preliminary experiment the WVTR of several PET and PEN films were checked after depositing SiN_x thin film to 50 nm thickness as gas barrier layer. As shown in Fig. 3 the PEN film exhibited lower WVTR values than PET films with same SiN_x as gas barrier layer. It was of interest because some PET films had hard coating layer while PEN film had no hard coating (bare film).

This suggest that the glass transition temperature of the polymer film (PET, T_g 78°C; PEN, T_g 120°C) is an important factor affecting the WVTR properties [10–12]. This means that gas permeation could be effectively blocked at the ambient temperature by the decreased

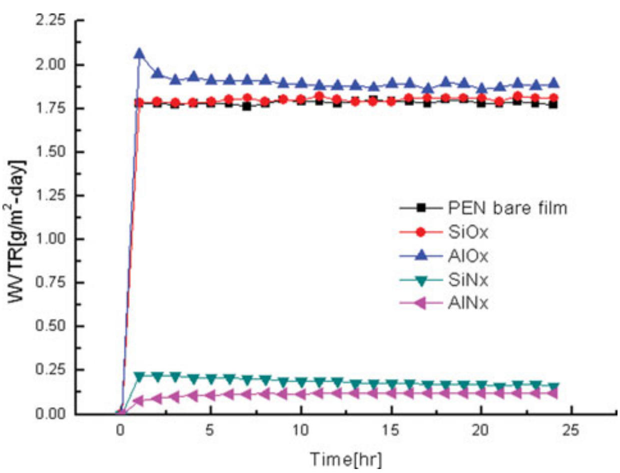

Figure 5. The water vapor transmission rate(WVTR) of oxide and nitride thin films deposited on PEN film.

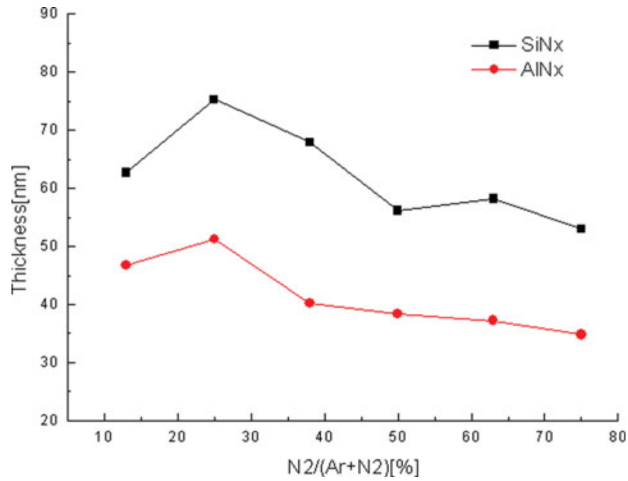

Figure 6. The thickness of SiN_x and AlN_x thin films deposited on PEN film with the N_2 partial pressure in the sputter.

segmental motion of polymer chains. It was also noted in our previous work that the flexible OLEDs made on PEN film substrate could withstand higher applied voltage than the one on PET film substrates. Therefore we chose the K-1 PEN film as flexible substrate for the further experiments [13–16].

Comparision of Single Gas Barrier Layers

The deposition of SiO_x, SiN_x, AlO_x, AlN_x gas barrier films were conducted by the reactive sputtering method utilizing Si and Al targets and O_2 and N_2 gas flowmeter equipped in the roll-to-roll sputter.

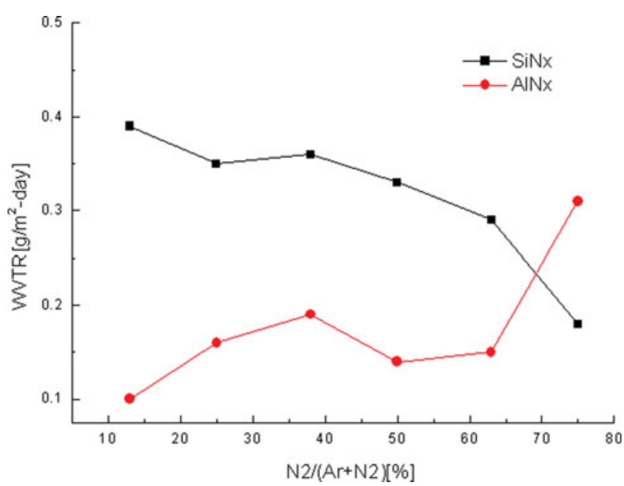

Figure 7. The water vapor transmission rate (WVTR) of the SiN_x and AlN_x thin films deposited on PEN film with the N_2 partial pressure in the sputter.

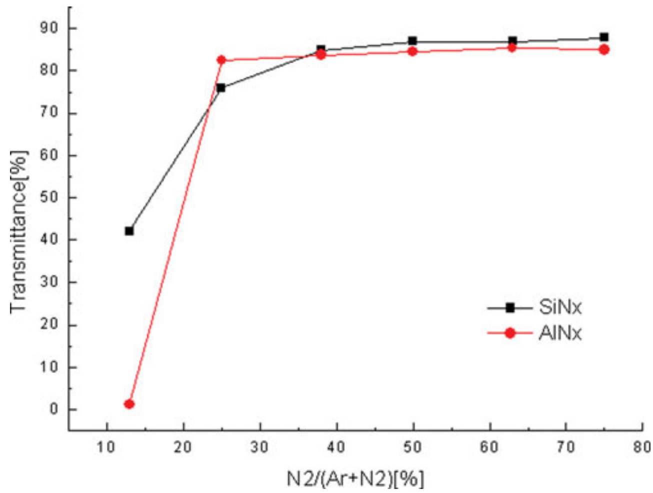

Figure 8. The light transmittance of the SiN_x and AlN_x thin films deposited on PEN film with the N_2 partial pressure in the sputter.

In order to compare the gas barrier property of the SiO_x, SiN_x, AlO_x and AlN_x thin films on PEN film, the thickness of the gas barrier layer should be controlled as constant as possible. The optimum operation condition of rolling cycle and the measured thickness of the SiO_x, SiN_x AlO_x, AlN_x thin films on PEN film were; (x2)75.58 nm, (x1)56.17 nm, (x5)43.11 nm and (x2)51.11 nm, rolling cycle in roll-to-roll sputter and thin film thickness respectively. From Fig. 4 the light transmittance of the oxide thin films (SiO_x and AlO_x) were higher than the nitride thin films, but the difference was not so much. However, the water vapor transmission rate (WVTR) of the nitride thin films (SiN_x, AlN_x) were much lower than those of the oxide thin films (SiO_x, AlO_x). Oxide thin films are known to have good gas barrier property over 100 nm thickness [13–16], however the WVTR of oxide

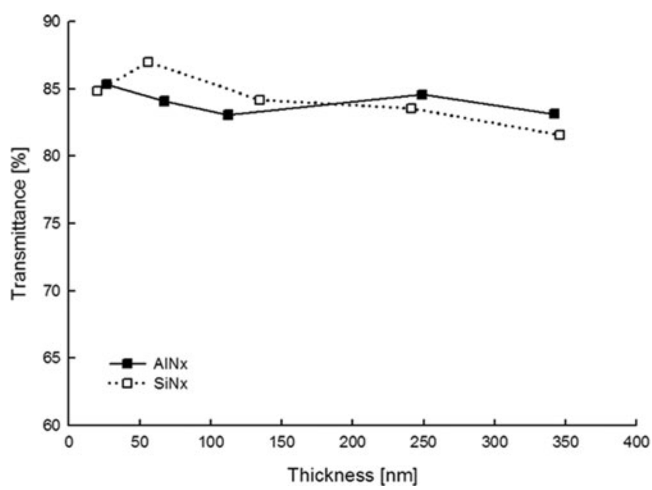

Figure 9. The optical transmittance of SiN_x and AlN_x thin films on PEN film with the thin film thickness.

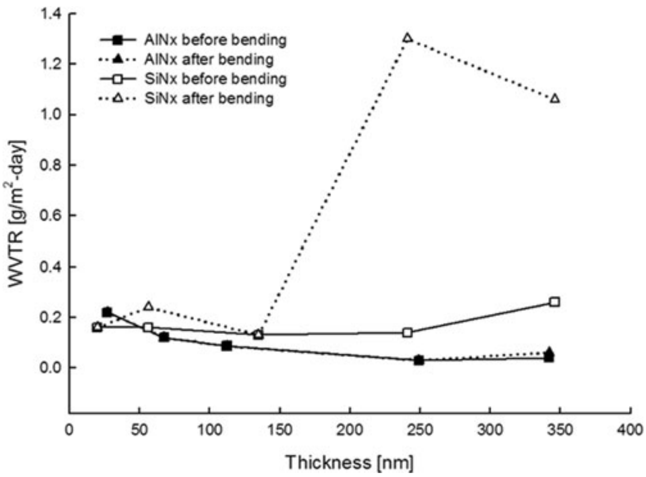

Figure 10. The WVTR plot of SiN_x and AlN_x thin films on PEN film with the thin film thickness.

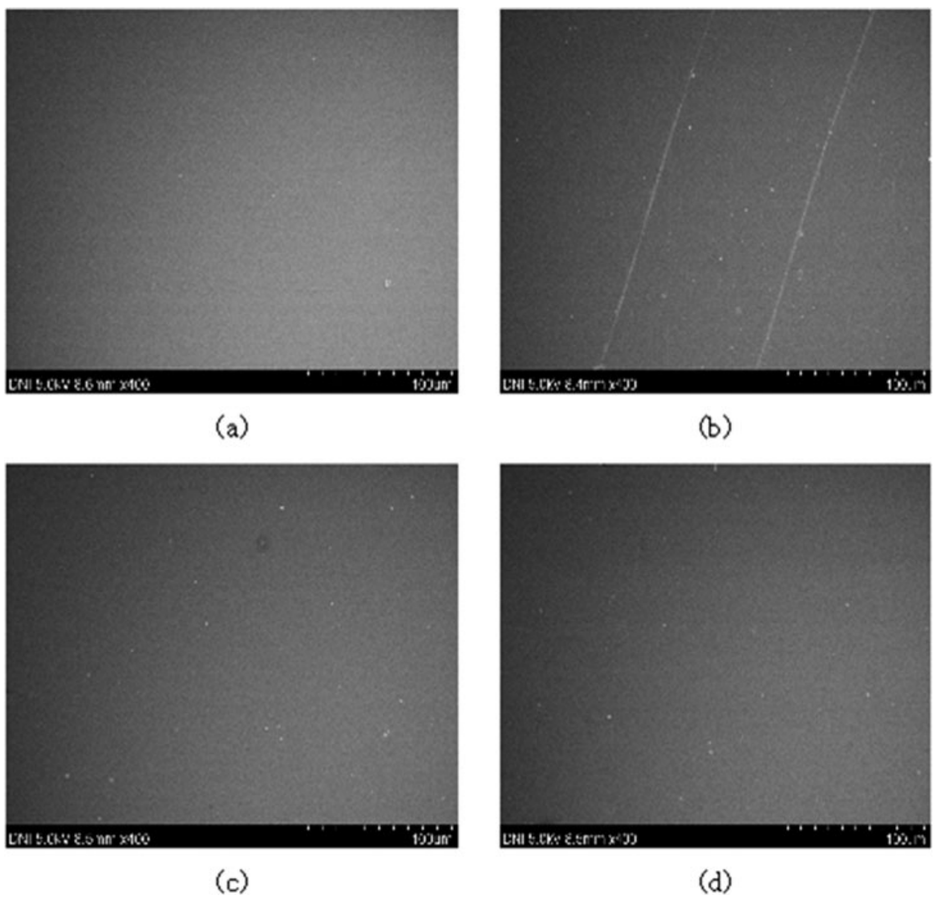

Figure 11. The SEM images before and after bending of PEN films with SiN_x and AlN_x thin films as gas barrier layer (a) SiN_x thin film before bending (b) SiN_x thin film after bending (c) AlN_x thin film before bending (d) AlN_x thin film after bending.

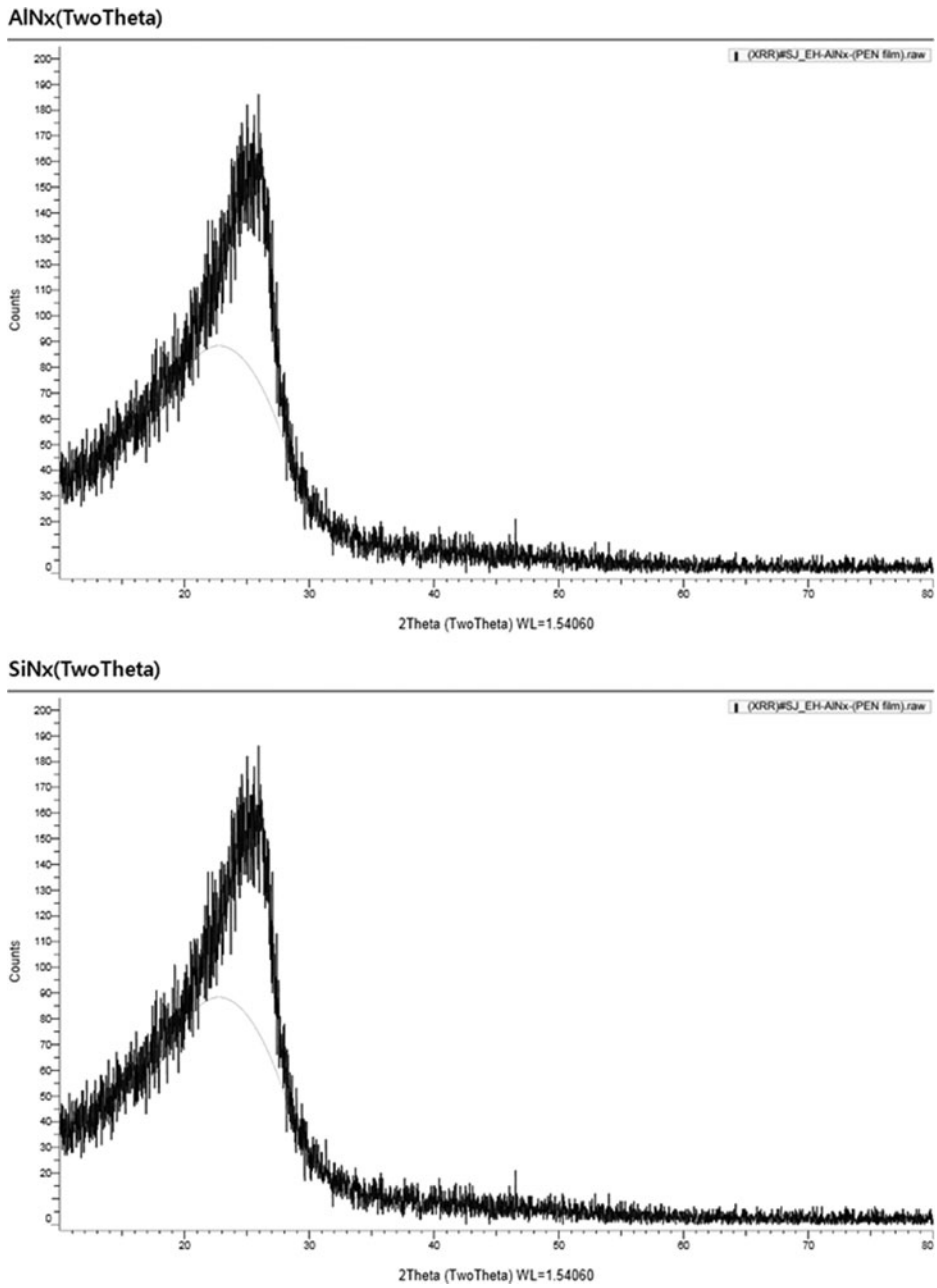

Figure 12. The XRD patterns of SiN_x and AlN_x thin films deposited on PEN film.

thin films were higher than those of the nitride thin films at about 50 nm thickness. The thickness of the gas barrier film should be as low as possible, since the light transmittance of the substrate film with multiple gas barrie layers usually decreases with the addition of each layer either organic or inorganic thin film [17–19].

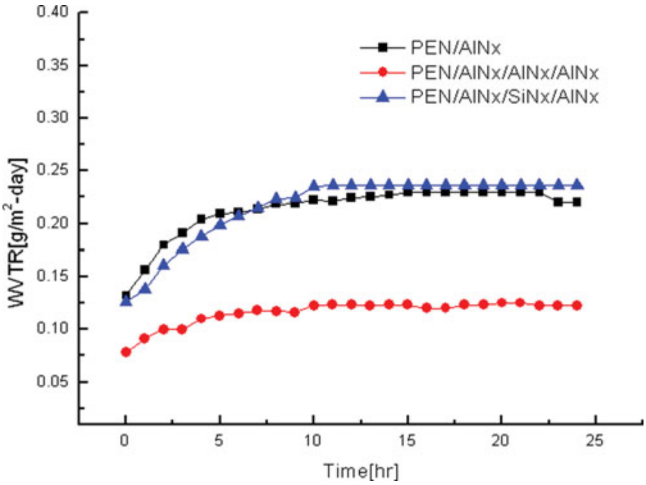

Figure 13. The WVTR plot of PEN film with multiple gas barrier layers with different layer structure.

Next we compared the nitride gas barrier layers (SiN_x and AlN_x) on PEN film. As shown in Figs. 6 and 7 the WVTR values of the SiN_x gas barrier layer were higher than those of the AlN_x layers although the thickness of the SiN_x layer was larger than the AlN_x layer when both layers were deposited under same N_2 partial pressure condition. However the light transmittance of the two layers were almost same as shown in Fig. 8. These results suggest that AlN_x thin films may have platelike structure and packed more densely than the SiN_x thin films.

We also studied the effect of thickness of SiN_x and AlN_x thin films on the light transmittance and on the bending stress tests. From Figs. 9 and 10 the light transmittance of the SiN_x and AlN_x thin films were not much different but the WVTR values of SiN_x thin film increased sharply above 150 nm thickness after bending stress tests.

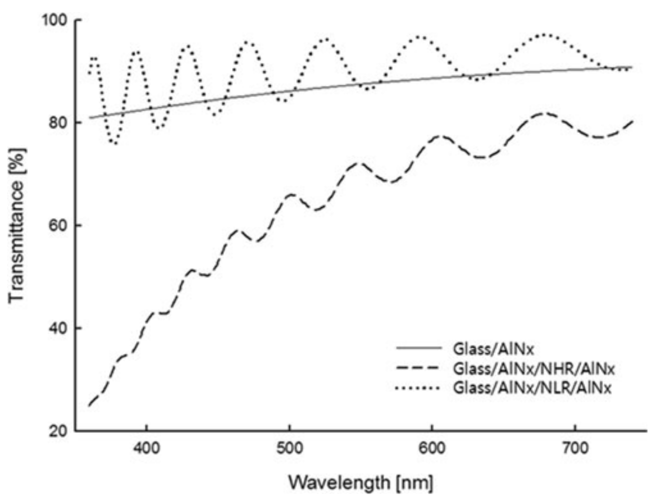

Figure 14. Optical simulation of gas barrier layers deposited on glass substrate by using Macleod Software.

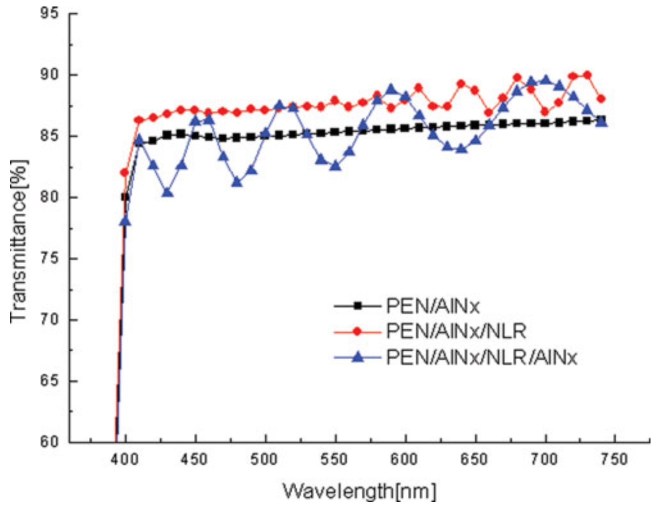

Figure 15. The optical transmittance of multiple inorganic/organic gas barrier layers deposited on PEN film.

However the WVTR values of AlN_x thin films were not dependent much on the thickness and bending stress. These data also suggest that the AlN_x thin films had strong adhesion to the film substrate and suitable layer structure resistant to the bending stress. When we checked the surfaces of the SiN_x and AlN_x thin films on PEN film before and after bending tests the scratch patterns were found on the surface of SiN_x thin film after bending stress test as shown in Fig. 11. We also checked the XRD patterns as shown in Fig. 12, but no crystalline regions were observed in both thin films.

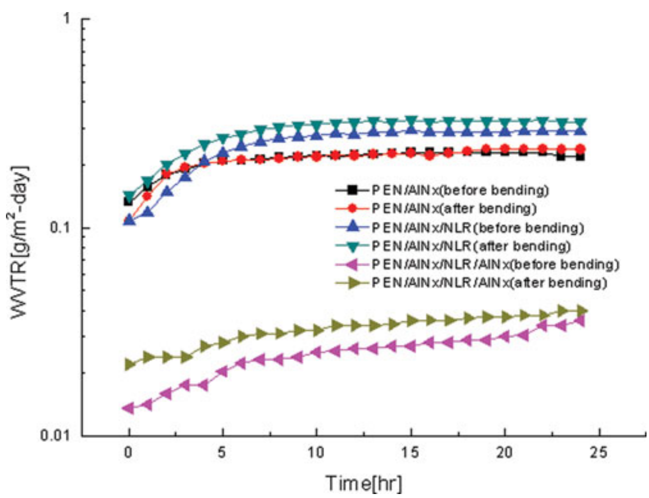

Figure 16. The WVTR plot of multiple organic/inorganic gas barrier layers deposited on PEN film with bending stress time.

Comparison of Multilayer Gas Barrier Films

The multilayer inorganic films with the structure of PEN/AlN_x/SiN_x/AlN_x and PEN/AlN_x/AlN_x/AlN_x were fabricated with each layer thickness of about 20 nm. The WVTR plots in Fig. 13 could be explained as following; (1) The PEN/AlN_x/AlN_x/AlN_x gas barrier film had lowest WVTR due to homogenous composition and increased thickness effect. (2) The PEN/AlN_x/SiN_x/AlN_x gas barrier film showed higher WVTR compared to the PEN/AlN_x/AlN_x/AlN_x film due to the presence of SiN_x middle layer. (3) Actually the WVTR value of the PEN/AlN_x/SiN_x/AlN_x gas barrier film was nearly same as that of the PEN/AlN_x single layer film.

We then examined the effect of inorganic/organic/inorganic multilayer gas barrier films on the WVTR and transmittance properties. First optical simulation of multiple gas barrier layers on glass substrate was conducted in order to select the refractive index range of the organic layer, that is, polymer layer. As shown in Fig. 14 the glass/AlN_x/NLR/AlN_x sample with the low refractive index polymer (NLR06, $n_d = 1.47$) as middle layer exhibited higher transmittance than the glass/AlN_x/NHR/AlN_x sample with the high refractive index polymer (NLR04, $n_d = 1.76$). In the optical simulation the glass had $n_d = 1.47$ and AlN_x thin film had $n_d = 1.92$.

Then the gas barrier films were made with structures of PEN/AlN_x, PEN/AlN_x/NLR and PET/AlN_x/NLR/AlN_x. As shown in Fig. 15 the three gas barrier films exhibited all high transmittance as expected from the optical simulation. After securing the optical transmittance of the multiple inorganic/organic/inorganic gas barrier layers on PEN film, we studied their WVTR properties under bending stress tests.

As shown in Fig. 16 the PEN/AlN_x/NLR/AlN_x gas barrier film showed low WVTR values before and after bending stress while the PEN/AlN_x/NLR and PEN/AlN_x films exhibited higher WVTR values, suggesting that the flexible polymer thin film (NLR) could withstand the flexural stress well and contribute to the WVTR property.

4. Conclusion

In this work we deposited multiple gas barrier layers on polymer film substrates utilizing roll-to-roll sputter and examined their properties from the view of application to the flexible OLED devices. As for the substrate films, the PEN film exhibited lower WVTR values than the PET film due to the low T_g value and incorporation of platelike naphthalene group in the polymer chain. In the comparison of single gas barrier layer the AlN_x thin film on PEN substrate showed lower WVTR value than the SiN_x thin film. In case of inorganic/organic/inorganic gas barrier layer the multilayer film with the structure of PEN/AlN_x/NLR/AlN_x exhibited low WVTR value, high visible light transmittance and high endurance to the bending stress test.

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