● Development of a liquid organosilane precursor, TG-4E, for high gas barrier film

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We have developed a novel precursor, TG-4E, for high gas barrier film deposition by plasma enhanced chemical vapor deposition (PECVD). Colorless, transparent, and flexible gas barrier films were obtained, and furthermore, the water vapor transmission rate (WVTR) of the three-layer coated film achieved 4.1×10^{-5} g/m^2/day under 40℃, 90%RH condition.

1. Introduction

Recently flexible organic light emitting diode (OLED) devices have attracted much attention. Since OLED devices are easily degraded by moisture and oxygen, transparent and flexible films with high gas barrier property are strongly needed to encapsulate the devices. Although plastic films are transparent and flexible, these films are not suitable for this application because of their poor water vapor barrier property. To improve the barrier property, various gas barrier layers deposited on plastic films have been studied [1,2,3,4,5].

Inorganic gas barrier layers such as silicon dioxide and aluminum oxide deposited by sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD) have been widely investigated for this application. However, these layers have some problems such as their barrier property, color, deposition rate, crack, use of explosive gas, and process complexity.

In this paper, we report high gas barrier layers deposited by PECVD using a novel precursor, TG-4E. These gas barrier layers have enough gas barrier property and are colorless, transparent, and flexible.

2. Experiment

[1] Gas barrier film deposition

TG-4E was examined to deposit an 800 nm thick gas barrier layer by PECVD using oxygen gas on a polyethylene naphthalate (PEN) film with a hard coat layer as shown in **Fig. 1**. TG-4E was also used to deposit multilayer as shown in **Fig. 2**, and the three layers were deposited by PECVD using the same precursor under different deposition conditions. The first and third gas barrier layers were deposited under the same condition as the gas barrier film illustrated in **Fig. 1** was deposited. The second layer was deposited under relatively lower plasma power condition compared to the first and third ones for adjusting the internal stress of the multilayer. The total thickness of the three layers was 2000nm.

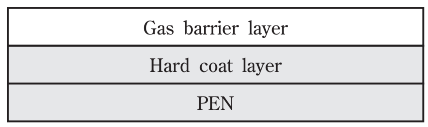

Fig. 1 A cross-sectional view of the gas barrier layer deposited on PEN substrate

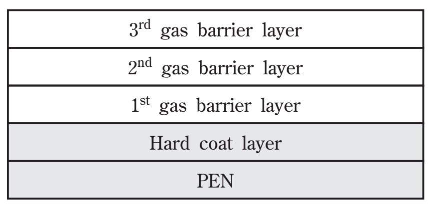

Fig. 2 A cross-sectional view of the gas barrier layers stacked on PEN substrate

[2] Evaluation of thin film properties

Film thickness was calculated approximately by cross-sectional scanning electron microscopy (SEM) image. The WVTR was evaluated by a gas chromatography method and Ca test. Film composition and average surface roughness, Ra, were measured by X-ray photoelectron spectroscopy (XPS) and by atomic force microscopy (AFM) using Nano Scope IIIa (Bruker AXS Co., ltd.) respectively. Visible light transmittance and haze value were analyzed by spectrophotometer U-4100 (Hitachi High-Technologies Corporation) and haze meter, respectively.

3. Results and discussions

Film deposition experiment under various conditions was examined, and the results of deposition rate and WVTR of the films varied up to 450nm/min and range from 10^{-1} g/m^2/day to 10^{-5} g/m^2/day, respectively. More details of high gas barrier films whose deposition rate and WVTR were range from 70nm/min to 100nm/min and from 10^{-4} g/m^2/day to 10^{-5} g/m^2/day, respectively, were discussed.

Film properties of an 800 nm thick gas barrier layer deposited from TG-4E on PEN substrate were evaluated and the results are summarized in **Table 1**.

Gas barrier film composition measured by XPS was SiO_2. Carbon and nitrogen contents were under their detection limit.

The surface roughness of the gas barrier film and PEN film were measured by AFM, and the surface images were illustrated in **Fig. 3**(a) and (b). Ra value of the gas barrier film surface was 0.68 nm, and that of PEN substrate was 0.71nm. It shows that the film deposited from TG-4E is flat enough.

Optical transparency was evaluated by the average value of transmittance range from 380 nm to 780 nm. The average value is in **Table 1**, and experimental data of PEN substrate and PEN substrate with gas barrier layer from TG-4E was shown in **Fig. 4**. The average visible light transmittance value of the gas barrier layer

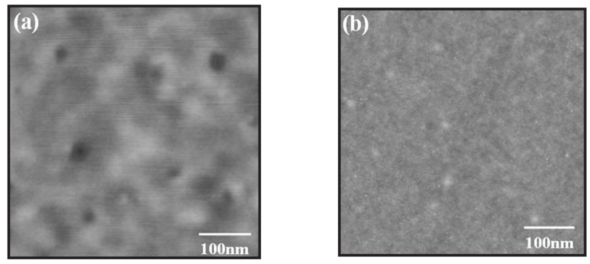

Fig. 3 AFM images of the gas barrier film surface deposited on PEN substrate (a) and the surface of PEN substrate (b)

on PEN substrate and PEN substrate were 88.2% and 88.3%, respectively.

The haze value was also measured and compared to that of PEN substrate. The results of gas barrier layer on PEN and PEN substrate were 0.86% and 1.03%, respectively. These results imply that the gas barrier layer deposition did not change the optical transparency.

Bending test with 10 mm ϕ glass stick was examined for the gas barrier film from TG-4E. After bending 20 times, WVTR value did not change. This result indicated that the gas barrier film has enough flexibility for flexible devices.

To improve the gas barrier property, three layers were deposited instead of the single 800 nm gas barrier layer using the same precursor under different plasma conditions as shown in **Fig. 2**. Total thickness of the three layers was 2000 nm and its appearance was colorless and transparent. As a result of Ca test, WVTR of the film with three gas barrier layers achieved 4.1×10^{-5} g/m^2/day under 40℃, 90%RH condition.

Table 1 Gas barrier film properties

		Gas barrier layer on PEN film	PEN film
Precursor	—	TG-4E	—
Thickness (gas barrier layer)	nm	800	—
WVTR (GC method)	g/m^2/day	$<2.0\times10^{-4}$	10^0–10^1
Film composition (XPS)	—	SiO_2	—
Ra	nm	0.68	0.71
Average light transmittance (380–780nm)	%	88.2	88.3
Haze	%	0.86	1.03
Appearance	—	colorless and transparent	colorless and transparent
Bending durability (10mm ϕ)	times	>20	—

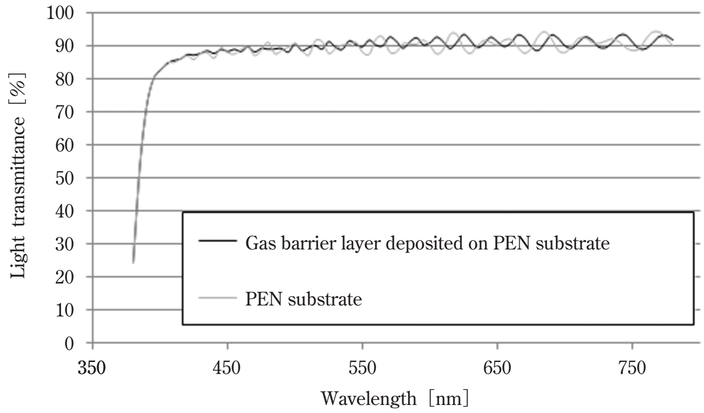

Fig. 4 Visible light transmittance of gas barrier layer deposited on PEN substrate and PEN substrate

4. Conclusions

We have developed a novel precursor, TG-4E, for high gas barrier film deposition by PECVD, and the gas barrier films deposited from TG-4E showed excellent gas barrier properties. Colorless, transparent, and flexible films with a single gas barrier layer deposited from TG-4E were obtained. Furthermore, WVTR of the three-layer coated film achieved 4.1×10^{-5} g/m^2/day under 40℃, 90%RH condition. We believe that the three-layer gas barrier film has enough property to be applied to OLED devices.

5. References

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