Characterization of Aluminum Oxide Thin Film Grown by Atomic Layer Deposition for Flexible Display Barrier Layer Application

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Abstract

Aluminum oxide thin films were grown on a poly ethylene naphthalate (PEN) substrate at the temperature of 100°C using atomic layer deposition method. The film showed very flat morphology and good adhesion to the substrate. The visible spectrum showed higher transmittance in the range from 400 nm to 800 nm than that of PEN. The water vapor transmission value measured with MOCON for 230nm oxide-deposited PEN was 0.62 g/m^2/day @ 38°C, while that of PEN substrate was 1.4g/m^2/day @ 38°C.

1. Introduction

The flexible thin display has attracted much attention as the future display goal.[1,2] Organic light emitting diodes (OLEDs) are considered promising candidate for the flexible displays because most of materials used in the OLED device are flexible. Although the efficiency and the lifetime of OLED device using the glass substrate are in the stage of commercial production, encapsulation technology should be developed intensively to achieve long lifetime of a flexible display. Besides, the development of barrier layers for OLED device and flexible substrates of OLED would be the key technology for the realization of flexible display.

Although the requirement of barrier layer for OLED display is not elucidated clearly, it has been recognized that long-lived OLEDs need a moisture barrier layer which transmits $<10^{-5}$ g/m^2/day of water.[3] A layer of glass or metal is commonly used for the encapsulation of OLED fabricated on glass substrate. For a flexible and thinner OLED, however, thin encapsulation methods for the OLED devices and flexible substrates should be developed.

Lots of thin encapsulation methods have been developed for food and medical packaging,[4] and the methodologies used for these packaging would be useful in the development of barrier layer of OLED devices. It has been reported that three layer combination of polymer and oxide, namely plastic substrate/ polymer smoothing layer/ oxide layer/ polymer layer can be more than three orders of magnitude less permeable to water and oxygen than a single layer of inorganic oxide.[3,5] Several groups reported vacuum deposition methods of polymer films including so called the polymer multiplayer (PML) process.[6] In spite of similarly growing interests in oxide film coating for the barrier layer of OLEDs, however, relatively little research are carried out.

Among the vacuum deposition method of oxide thin film for the application of barrier layer of OLEDs, plasma enhanced chemical vapor deposition (PECVD) is known as the competing technique that allows industrial-scale deposition of high quality oxide barrier material with good uniformity and adhesion to the substrate.[7]

In this paper, we report a new approach to the oxide barrier layer of flexible OLED substrates using atomic layer deposition (ALD) technique. Since ALD is based on the chemical reactions, the structural imperfection in the films and substrate damage can be minimized. We investigated the characteristics of aluminum oxide (AlO_x) film on PEN substrate deposited at 100°C using ALD method for the application of barrier layer of the flexible display substrate.

2. Experimentals

Aluminum oxide thin films of 230 nm thickness were grown on Si and PEN substrate in a 12 x 16 inch large traveling wave ALD reactor with nitrogen as carrier gas at 100°C. The AlO_x film is also grown on Si substrate at 350°C for the comparison of Rutherford backscattering spectrometry(RBS) and secondary ion mass spectrometry(SIMS) data. Trimethylaluminum (TMA) and H_2O were used as precursor. TMA and H_2O bottles were held at 16°C and 18°C, respectively.

The transmission of water vapor for 24 hrs was measured for both PEN substrate and aluminum oxide coated sample on a 100 cm^2 active sample area, at 38±2 °C, 100% RH using MOCON permatran-W1A. Morphological properties were examined by scanning electron microscope (SEM) and the incorporation of impurities was characterized using SIMS (Cameca ims-4f). RBS was used for the areal density and stoichiomerty analysis. The refractive index and the film thickness were determined by the spectroscopic ellipsometry. UV-vis spetrum was taken using Hitachi U-3501 spectrophotometer.

3. Results and Discussion

The composition of AlO$_x$ thin film evaluated from RBS spectrum was Al 1.71 and O 3.29, indicating oxygen rich film compared to that of Al$_2$O$_3$ film grown at 350°C. The relative concentration of C and H incorporated during the film growth was estimated by the SIMS analysis. The SIMS data in Fig. 1 showed the O, H contents were higher than those of film grown at 350°C. It is not clarified so far whether the incorporation of extra amounts of O and H into the film indicates the residual water from the precursor. The SIMS data also showed higher C content than that of film grown at 350°C.

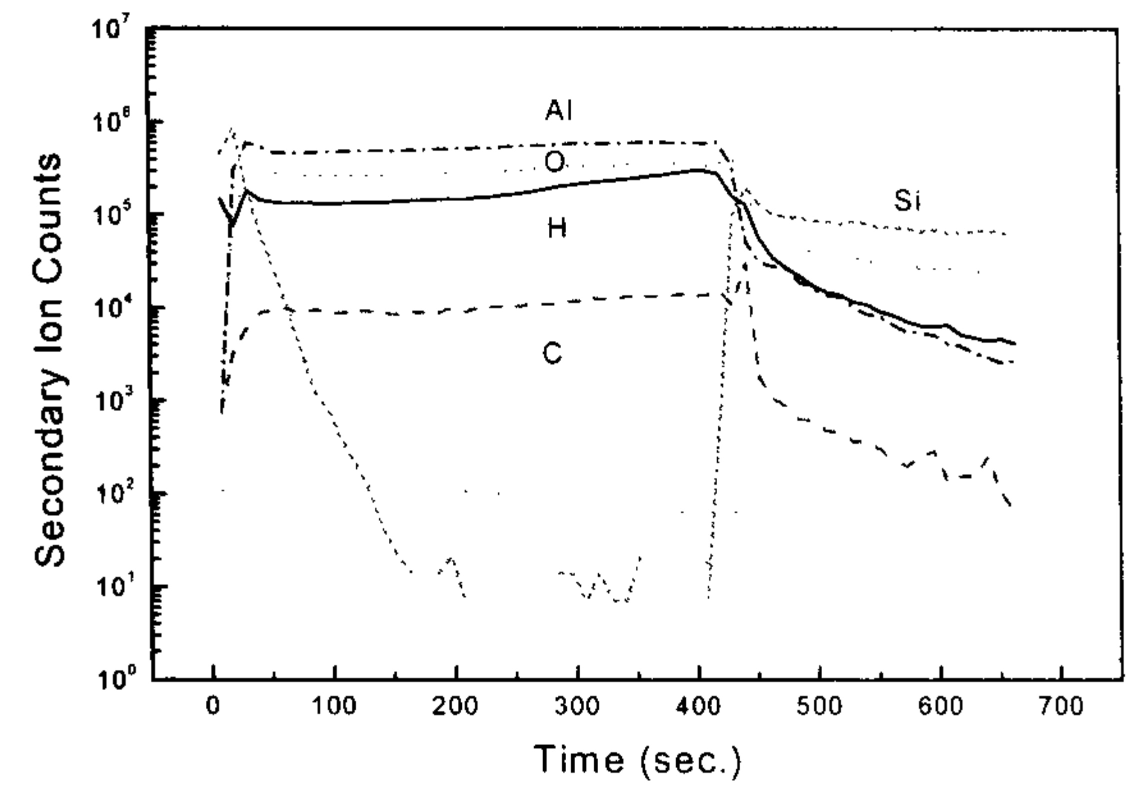


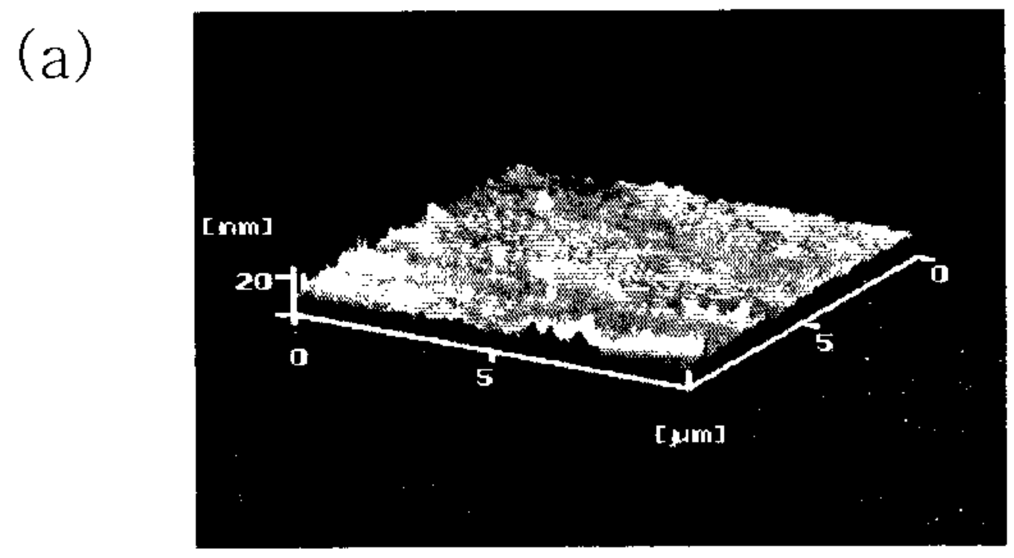
Fig. 1. SIMS data of AlO$_x$ thin film grown at 100°C

The density of film was estimated from the refractive index, areal density (atoms/cm^2) calculated from RBS analysis, and etch rate of film at the acid solution. Table 1 summarized the characteristics of AlO$_x$ film grown by ALD at the growth temperature of 100 and 350°C. The AlO$_x$ film grown at 100°C showed more porous characteristics than the film grown at 350°C as expected.

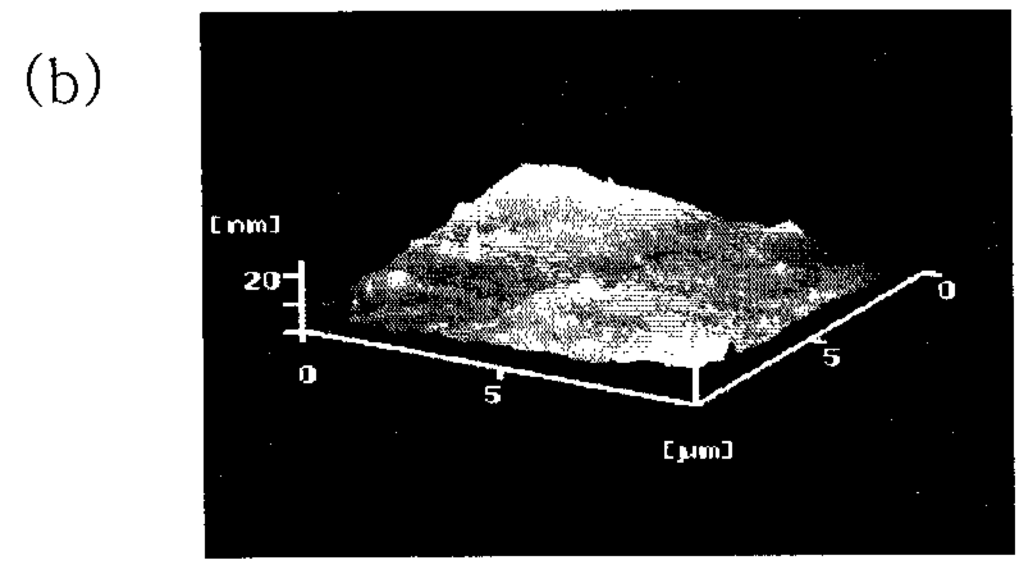
Table 1. Characteristics of AlO$_x$ films grown by ALD.

Growth Temp.	Refractive index @ 632.8 nm	Etch rate[a] (nm/sec.)	Areal density (atoms/cm^2)
100°C	1.583	4.18	1.823E18
350°C	1.629	1.14	2.074E18

[a] etch rate was measured by etching in the diluted HF solution (HF:H$_2$O=1:10)



R $_{p-v}$	Rms rough.	Ave. rough.	Surface area
26.8nm	1.66 nm	1.219 nm	100.8 μm^2



R $_{p-v}$	Rms rough.	Ave. rough.	Surface area
19.0 μm	1.89 nm	1.396 nm	100.8 μm^2

Fig. 2. AFM images of (a) PEN substrate; (b) aluminum oxide coated PEN.

Fig.2 showed atomic force microscope (AFM) images of a PEN substrate and aluminum oxide coated PEN substrate. The RMS surface roughnesses of substrate and aluminum oxide coated one were 1.66 and 1.89 nm, respectively. The RMS roughness of the substrate was slightly increased by the deposition of 230 nm-thick oxide film. On the contrary, the morphology below nano-scale was rather smoothed by the oxide deposition as shown in Fig. 2(b).

To examine the possibility for the application of barrier layer, water transmission value was measured. It has been reported that the permeation properties of oxide film varies with the thickness of film and there is a critical film thickness for the best barrier characteristics.[7] In this research, we primarily focused on the characteristics of AlO_x film grown by ALD at low temperature and the dependence of the transmission characteristics of water and oxygen on the film thickness is still under investigation. The uncoated PEN substrate showed water vapor transmission (WVTR) of 1.4g/m^2/day @ 38°C, while aluminum oxide coated substrate showed 0.62 g/m^2/day @ 38°C. The WVTR of SiO_x film deposited by PECVD method on a 50cm^2 active sample has been reported to be 0.3 g/m^2/day at 33°C/100% RH.[7] It is hard to compare directly to previously reported WVTR values because of the different measurement conditions. Although the water permeation value seemed to be not better than the earlier result of SiO_x film, this result showed the applicability of ALD grown AlO_x film for barrier layer.

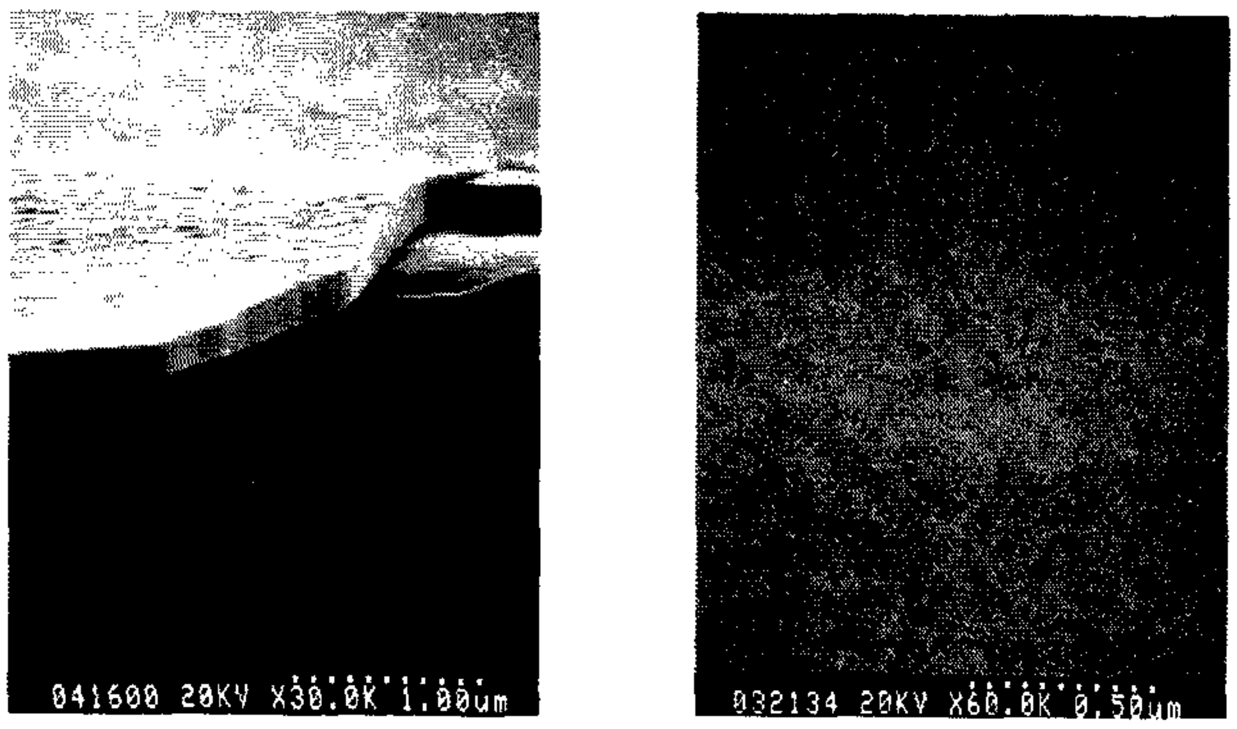


Fig.3. SEM micrographs of the AlO_x-deposited PEN substrate; (a) cross-section, (b) surface morphology

The SEM photographs of the aluminum oxide on PEN are shown in Fig.3. ALD grown aluminum oxide thin film showed flat morphology and also good adhesion to the plastic substrate. The SEM micrographs did not show any crack in the film.

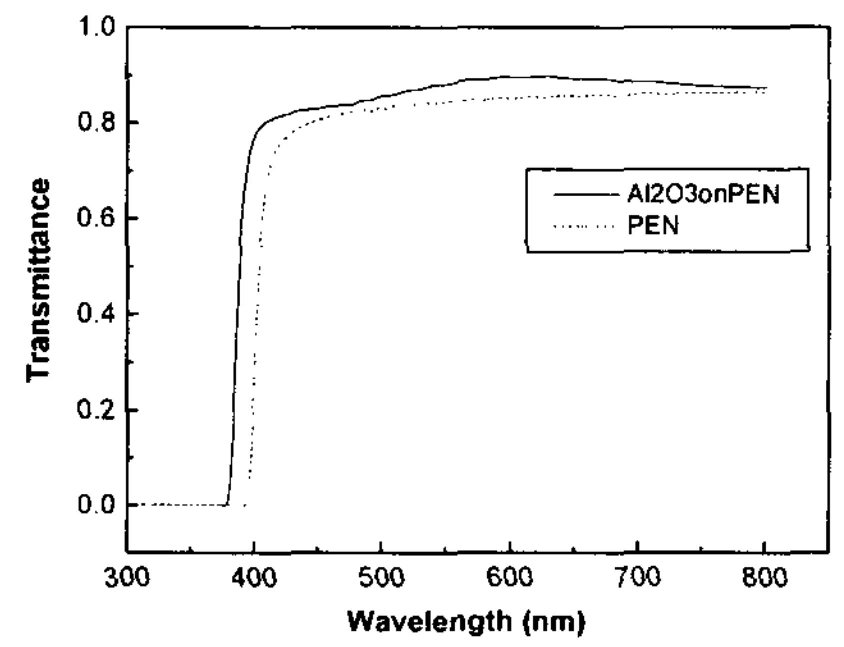


Fig. 4. Transmittance of PEN substrate and aluminum oxide coated PEN

For the application of barrier layer for the flexible substrate, the transmittance is also very important. The transmittance for the visible light is exhibited in Fig. 4. The coated one has higher transmittance than that of bare PEN substrate. The increase of transmittance of visible light might be induced by the improvement of the morphology below nano-scale illustrated in Fig. 2(b).

4. Conclusion

Aluminum oxide thin film grown using ALD method was investigated with regard to the characteristics of barrier layer for flexible display substrate. We introduced ALD technology for the deposition of oxide thin film as a barrier layer of flexible display for the first time. The film grown on the PEN substrate at the temperature of 100°C showed very flat morphology and good adhesion to the substrate. The visible spectrum showed higher transmittance in the range from 400 nm to 800 nm than that of PEN. The film showed the C, H count rates of SIMS higher and the refractive index lower than those of the film grown at 350°C. The results indicate that the films grown at 100 °C are less dense than the film grown at 350°C. The WVTR of 230 nm-AlO_x coated PEN measured with MOCON was 0.62 g/m^2/day @ 38°C, while that of PEN substrate was 1.4g/m^2/day @ 38°C. The present study shows that the AlO_x film grown at 100°C by ALD is a potential candidate for the barrier layer and the water vapor transmission characteristics can be further improved by the optimization of film thickness and ALD process condition.

5. Acknowledgements

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6. References

1. B. Comiskey, J. D. Albert, H. Yoshizawa, and J. Jacobson, Nature (London) 394,p.253, 1998
2. E. Lueder, proc. SPIE, 64, p.3297, 1998
3. P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. K. Shi, M. Hall, E. Mast, C. Bonham, W. Bennet, and M. B. Sullivan, Displays, 22, p.65, 2001
4. H. Chatham, Surface and Coatings Technology, 78, p.1, 1996 and references therein
5. J. D. Affinito, US Patent 6,268,695
6. J. D. Affinito, M. E. Gross, P. A. Mounier, M. -K. Shi, and G. L. Graff, J.Vac.Sci.Technol. A 17(4), p.1974, 1999
7. A. S.da S. Sobrinho, M. Latreche, G. Czeremuszkin, J. E. Klemberg-Sapieha, and M. R. Wertheimer, J. Vac. Sci. Technol. A 16(6), p.3190, 1998