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A study of thin film encapsulation on polymer substrate using low temperature hybrid ZnO/Al_2O_3 layers atomic layer deposition

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ABSTRACT

Hybrid ZnO/Al_2O_3 layers grown by atomic layer deposition (ALD) at extremely low temperature (60 °C) have been investigated as thin film encapsulations (crystalline ZnO and amorphous Al_2O_3 films) on polymer substrates. All single and laminated film thicknesses are approximately 60 nm. As the thickness of ZnO layer decreased from 60 nm to 0 nm, the physical properties of laminated structures were systematically manipulated such as film crystallinity, surface roughness, density, transmittance and stress. The multi-laminated structure with 10 nm thick ZnO and 10 nm thick Al_2O_3 layers exhibited very lower crystallinity, smoother surface (root mean square ~ 0.2 nm), higher transmittance (over 90% at 550 nm wavelength) and similar film stress, to compare with these of a single ZnO film. As a transparent gas barrier layer, the multi-laminated structure with a thinner ZnO and Al_2O_3 had better barrier property than that of single ZnO and Al_2O_3 layers, showing that the water vapor transmission ratio of multi-laminated ZnO/Al_2O_3 layer was 10 times lower than that of the single layer.

1. Introduction

The OLEDs (organic light-emitting diode devices) have great potentials such as vivid full color, perfect video capability and thin form factor [1]. A major problem for the development of OLEDs on polymers is highly susceptible to the permeation of water and oxygen [2]. The water vapor and oxygen gas can oxidize the low work function alkali-metal cathode in the OLEDs [3]. Also OLED materials and polymer substrates should be carried out at low process temperature, compromising the electronic device performance [4].

Atomic Layer Deposition (ALD) can be employed at sufficient low temperatures to deposit various films on thermally fragile substrate for exciting new applications, ranging from food packaging to microelectronics to biomaterials. Among several exciting applications, a key application of ALD on polymers is the thin film encapsulation technology, serving as gas diffusion barriers in food packaging and extending for flexible electronics or OLEDs, because the continuous and pinhole-free nature of ALD films leads to high quality gas diffusion barriers [5]. Recently, multi-barrier stacks (laminated structure) are proposed for ultralow gas diffusion barrier films application [6]. Generally, thin Al_2O_3 ALD film is chosen for diffusion barrier applications, and usually applied as a multi-layer structure because Al_2O_3 has excellent O_2 and water vapor permeation barrier layer [7].

In this work, we investigated the hybrid ZnO/Al_2O_3 laminated films as a thin film encapsulation, using atomic layer deposition method at extremely low temperature (below 100 °C). In terms of film structures, Al_2O_3 and ZnO are amorphous and polycrystalline, respectively. But the ZnO film has higher density than the Al_2O_3 film [8]. It will be discussed the correlation between the water permeation and physical/structural properties as a function of laminated structure, including various ZnO/Al_2O_3 nano-layer thicknesses at low temperature.

2. Experimental details

Thin ZnO and Al_2O_3 films are deposited on polyethersulfone (PES, 150 μm thickness) substrate and Silicon (100) wafers at 60 °C in a viscous flow ALD reactor using diethylzinc (DEZ) and trimethylaluminum (TMA), respectively. Nitrogen (N_2, 99.999%) was used as a carrier gas on the DEZ, TMA and H_2O lines. The process pressure was 0.3 Torr in the reactor. The DEZ and H_2O were maintained at 10 °C and TMA was done at 25 °C. The Al_2O_3 ALD sequence was given by TMA pulse time (0.1 s) – N_2 purge (20 s) – H_2O pulse (1sec) – N_2 purge (20 s) and the ZnO ALD sequence was

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DEZ pulse (0.1 s) – N_2 purge (20 s) – H_2O pulse (1sec) – N_2 purge (20 s).

The structure of laminated layers was fixed with the out-surface ZnO and the intermediate Al_2O_3 layers for a gas barrier structure because the water absorption property of the Al_2O_3 is hydrophilic surface [9]. The thickness of thin films was measured by spectroscopy ellipsometry (SE, J. A. Woollam Co.). The crystal structures of thin films were examined by X-ray diffraction (XRD) using CuK_α radiation (λ = 1.5418 Å) in a Rigaku diffractometer. The microstructure of films was measured using cross-sectional transmission electron microscopy (TEM). The surface morphology was observed by using an atomic force microscope (AFM, Digital Instruments; Demension 3100). The thickness, density and roughness of each layer in the ALD multi-layer films were determined by X-ray reflectivity (XRR) analysis using CuK_α radiation (λ = 1.5418 Å). The XRR data was fit by using the LEPTOS fitting software to extract thickness, density, and roughness of each layer independently. The transmittances of all films were measured in the wavelength range from 300 to 800 nm by ultra violet visible spectroscopy (UV–VIS). To determine the effective water vapor transmission ratio (WVTR) of films, the Ca test method was conducted in an environmental chamber under 85 °C/85% relative humidity (RH) [10,11].

3. Result and discussion

Fig. 1 shows the dependence of ZnO and Al_2O_3 ALD growth rates as a function of the substrate temperature. As the deposition temperature decreases below 100 °C, both of ALD growth rates gradually decreases due to the incomplete surface reaction [12], reporting that similar tendencies were for ZnO ALD (DEZ and water system) [13–15] and Al_2O_3 (TMA and water system) [16,17]. In addition, the film thickness increases linearly as the number of cycles increase even at 60 °C, suggesting the conventional ALD behavior (not shown here). Although the growth rate is very low at 60 °C, all films processes are prepared in this work because there low temperature process on plastic substrates is needed to adjust thin film encapsulation for flexible OLEDs [1].

To investigate the effect of material and structure as a thin film encapsulation, various samples are prepared as depicted in Fig. 2. All samples are fixed with a 60 nm thickness: a ZnO (60 nm) single layer (#1), a ZnO (30 nm)/Al_2O_3 (30 nm) laminated layer (#3), a [ZnO (10 nm)/Al_2O_3 (10 nm)] × 3 laminated layers (#4), and an Al_2O_3 (60 nm) single layer (#2).

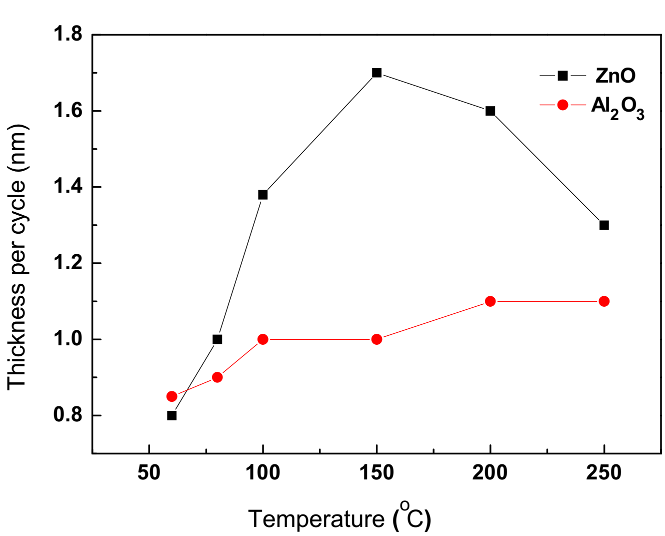

Fig. 1. The growth rates (thickness per cycle) of ZnO and Al_2O_3 thin films depending on growth temperatures.

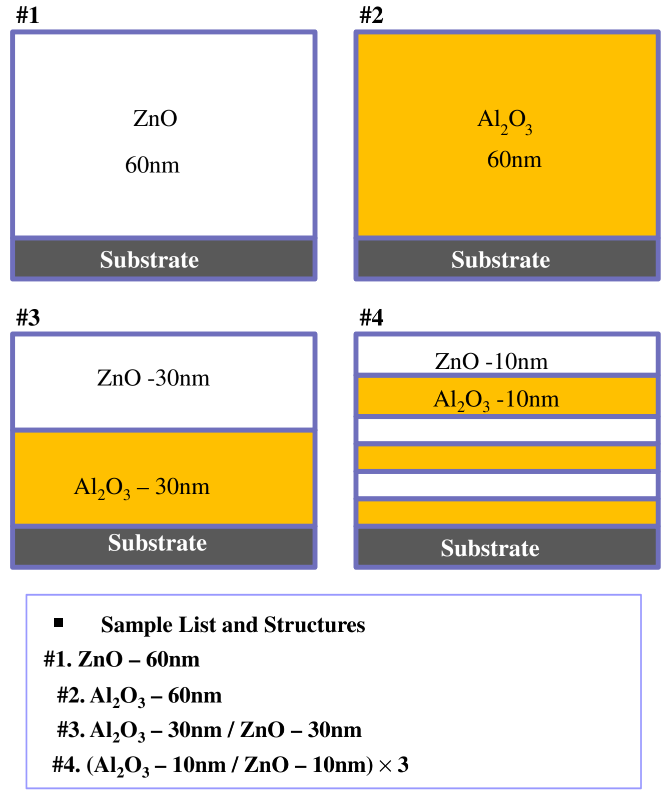

Fig. 2. A schematic diagram of prepared structures: #1 60 nm ZnO, #2 60 nm Al_2O_3, #3 ZnO/Al_2O_3 laminated layer (30nm/30 nm), #4 ZnO/Al_2O_3 multi-laminated layers [(10nm/10 nm) × 3 layers].

To elucidate the nature of the ordering in the individual layers, XRD measurements for #1–4 samples are shown in Fig. 3. The most prominent reflection, which was readily differentiable from Si substrate, was the ZnO(002) peak. Although no diffraction peaks are observed from an Al_2O_3 layer, ZnO(002) peak is observed at the others. Interestingly, the ZnO/Al_2O_3 laminated films showed not only the preferred ZnO(002) orientation but also different crystallinity, depending on the laminated structures. It suggests that ZnO

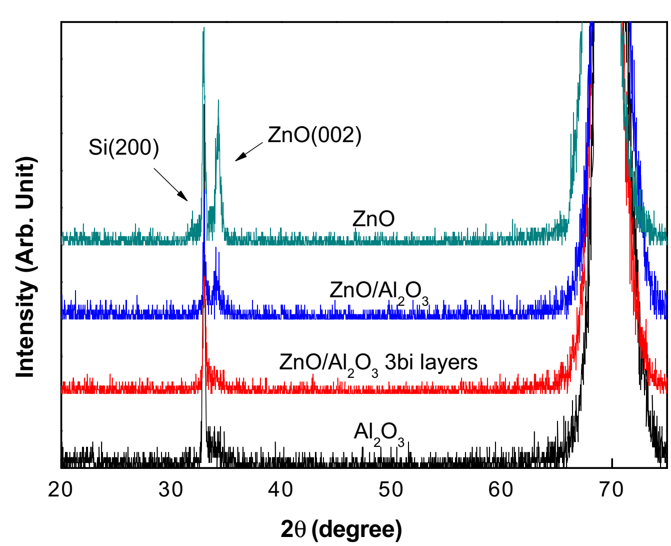

Fig. 3. XRD patterns of 60 nm thick ALD-ZnO, Al_2O_3 films and ZnO/Al_2O_3 laminate films grown on Si substrates.

layer growth may depend on substrate-sensitive, indicating the role of the surface structure in the deposition process. In addition, the intensity of the observed ZnO(002) peak decreases with increasing number of layers. This tendency could be explained that ZnO growth in the direction normal to the sample surface is affected by the thickness of the constituent Al_2O_3 layer [8].

As shown in Fig. 4, the micro-structure of all samples was examined by using cross-sectional high resolution transmission electron microscopy (HRTEM) in order to observe the growth of nano-laminated structures. These TEM images may have confirmed the expectations for the ZnO, Al_2O_3 films and individual ZnO and Al_2O_3 layers in terms of a laminate structure. As shown Fig. 4 (a) and (b), 60 nm thick ZnO and Al_2O_3 layers were deposited on Si, respectively. It showed a polycrystalline ZnO film and an amorphous Al_2O_3 film. As also shown in Fig. 4 (c) and (d), the formations of multi-layer and laminated structure can be effectively built up and show excellent conformality. In fact, J. M. Jensen et al. reported that the ZnO layer is thinner than the expected when Al_2O_3 layer couldn't have enough thickness [8], because ZnO deposition is less favorable at an Al_2O_3 surface, hindering the ZnO flim growth [18]. Thus, we confirmed that 10 nm Al_2O_3 layer of laminated structures is enough to deposit ZnO film uniformly. Thus, the crystallinity of films could be manipulated through different structure-organization despite of identical thickness and/or composition.

As mentioned above, the laminated structures may systematically control other physical properties such as surface roughness, film stress, density, and transmittance. Fig. 5 showed AFM images of all films, indicating that the RMS values were summarized in Table 1. The roughness of ZnO film is higher than that of Al_2O_3 film due to the ZnO crystallinity. Also, RMS values in the laminated structures gradually decreased with the increase number of layers.

On the other hand, the stress test is investigated to clarify how to change film stress by altering constitutions. The film stress values and type are summarized in Table 1. The film stresses of single ZnO and Al_2O_3 layers are 1.24 GPa (tensile) and 7.72 GPa (tensile), respectively. Surprisingly, there is a certain correlation between a film structure and stress when the film constitution is changed. As the ZnO layer in the laminated structure decreased below 30 nm, the multi-laminated structure showed the reducing stress value, which is close to that of polycrystalline ZnO film. Consequently, the multi-laminated structure may provide superior physical properties (lower crystallinity, surface roughness, and film stress) as a thin film encapsulation.

The film density was measured by XRR analysis as shown in Fig. 6 (a). The densities of single ZnO and Al_2O_3 layers are calculated to 4.49 g/cm^3 and 3.56 g/cm^3, respectively. The film densities of each single film were lower than the previous report [19] because the deposition is conducted at extremely low temperature (60 °C). The density of laminated structures was located between 4.49 g/cm^3 and 3.56 g/cm^3.

UV–VIS measurement was also performed from 300 nm (UV) to 800 nm (Visible) to determine the film transmittance. All films

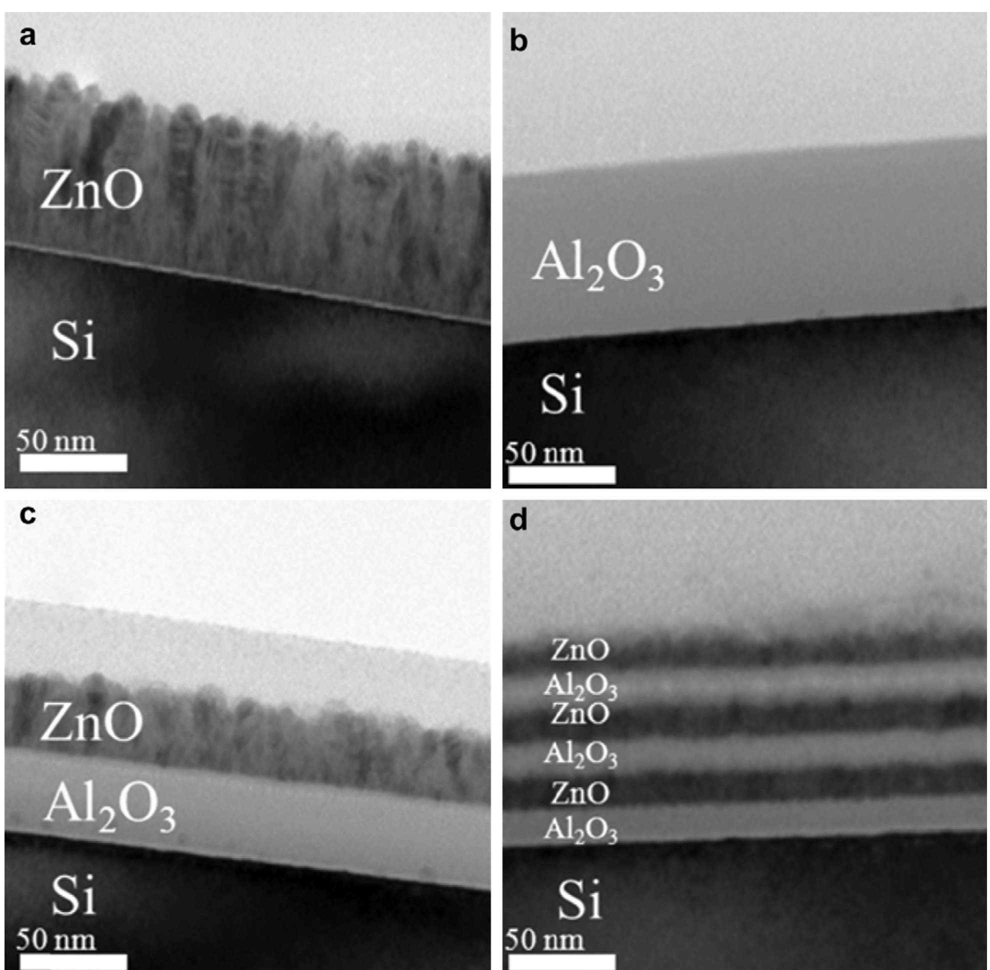

Fig. 4. Cross-sectional HRTEM images of (a) ZnO 60 nm films, (b) Al_2O_3 60 nm films, (c) ZnO/Al_2O_3 laminated layer, and (d) ZnO/Al_2O_3 multi-laminated layers.

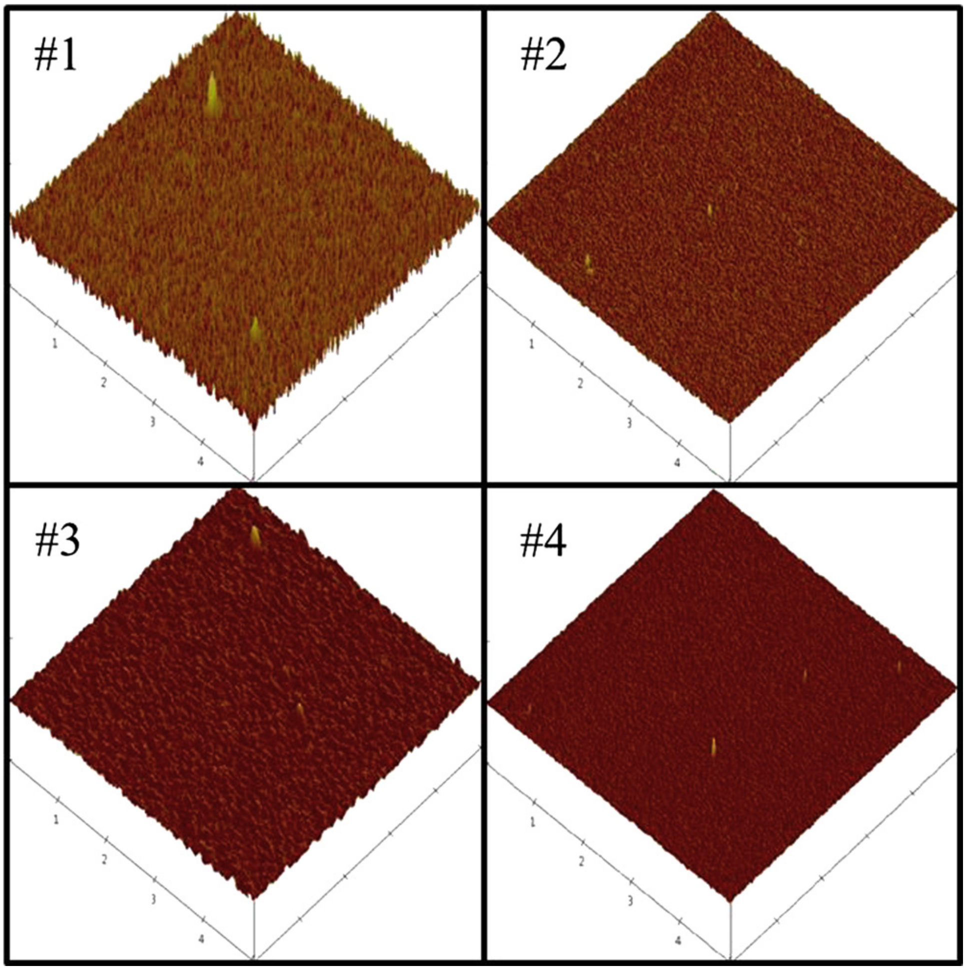

Fig. 5. AFM surface images of (#1) ZnO 60 nm films, (#2) Al_2O_3 60 nm films, (#3) ZnO/Al_2O_3 laminated layer, and (#4) ZnO/Al_2O_3 multi-laminated layers.

showed a transmittance over 75% on whole spectral range and over 90% at 550 nm. As shown Fig. 6 (b), transmittance of Al_2O_3 is higher than that of ZnO because Al_2O_3 has amorphous structure and high optical bandgap, since the crystalline structure generally tends to scatter the light at grain boundaries. Surface morphology also has a strong influence on the optical properties of the films [20]. Thus, the transmittance in multi-laminated structures may increase due to decreasing optical scattering, caused by decreasing the roughness and crystalline. It is quite consistent with above results. However, it is very hard to obtain the transmittance value as low as a single Al_2O_3 layer because the interface layer between ZnO and Al_2O_3 may result in the scattering problem.

To evaluate the permeability of multi-laminated structures as a gas diffusion barrier, WVTRs were measured by calcium (Ca) test for all prepared films. The permeability is characterized by using the calcium degradation by monitoring a resistive change in an ohmic behavior [21,22]. Fig. 7 showed the conductance changes of Ca layer as a function of the water exposure time under acceleration conditions (85 °C and 85%RH). The Ca measurement structure was depicted in Fig. 7 (inset). To compare with single layers, the conductance of ZnO ALD layer drastically decreased before 0.5 h, indicating the significant degradation of Ca metal due to water permeations. But the Al_2O_3 layer kept the conductance of Ca metal by 3hr, suggesting that Al_2O_3 layer (5×10^{-1} g/m^2 day) as a gas diffusion barrier is better than ZnO layer (1.28 g/m^2 day). It implies that a critical factor of gas diffusion properties might be the film crystallinity rather than film density. In a previous Al_2O_3 ALD result [23], Park et al. also reported that Al_2O_3 ALD layer exhibit low quality diffusion barrier films (0.1 g/m^2 day @ 38 °C) due to low deposition temperature.

To evaluate the effect of ZnO/Al_2O_3 laminated structures, #3–4 samples with a 60 nm thickness are fabricated on PES. Interestingly, WVTRs of a ZnO/Al_2O_3 (30/30 nm) layer and a multi-laminated ZnO/Al_2O_3 layer are 2.39 g/m^2 day and 2.8×10^{-1} g/m^2 day under 85 °C/85% RH, respectively. This result indicates that the adjustment of ZnO/Al_2O_3 laminated structures affects to the gas diffusion barrier property WVTR values, showing that increasing the number of ZnO/Al_2O_3 laminated layer may improve the gas diffusion barrier property. In particular, the laminated structures may provide unique and improved film properties as a gas diffusion barrier because the physical properties such as crystallinity, film stress, density and surface roughess, can be manipulated by the laminated structures. In terms of a permeability mechanism, the laminated structures may also offer to minimize the cracks, grain boundary and pinhole defects in the inorganic films [7].

Table 1
Summaries of surface roughness and film stress on various structures.

Sample ID	Film structures	Surface roughness RMS (Å)	Stress and type (GPa)
#1	[ZnO 60 nm]	15.37	1.24 (tensile)
#2	[Al_2O_3 60 nm]	3.26	7.72 (tensile)
#3	[ZnO 30 nm/Al_2O_3 30 nm]	5.55	9.09 (tensile)
#4	[ZnO 10 nm/Al_2O_3 10 nm] $\times$ 3	2.28	1.45 (tensile)

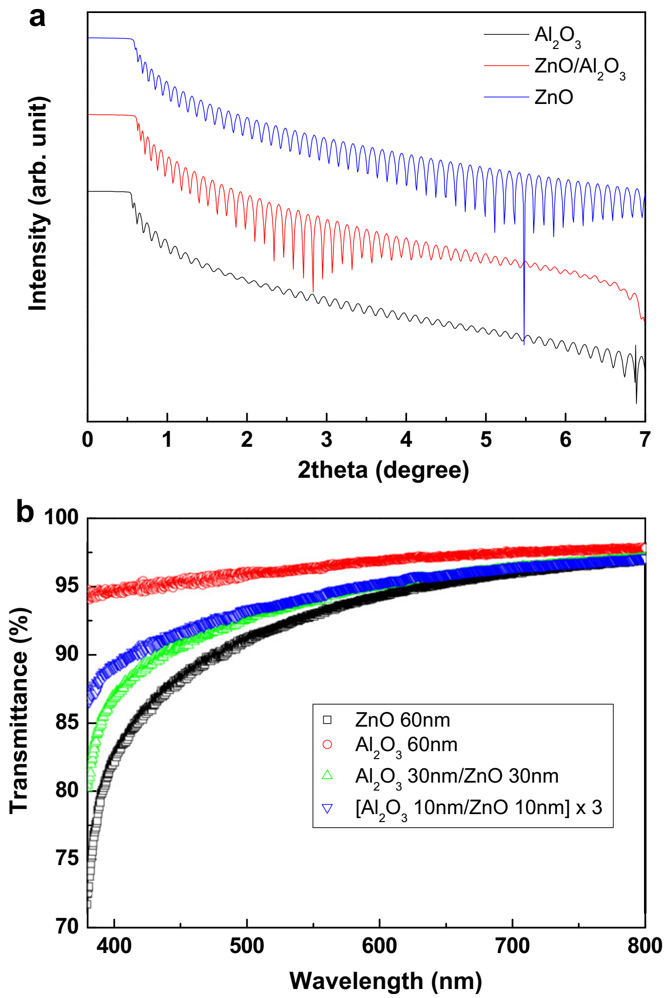

Fig. 6. (a) X-ray reflectivity curves for samples ZnO, Al_2O_3 and ZnO/Al_2O_3 multi-laminated layers and (b) UV–Visible spectra of 60 nm thick ALD-ZnO, Al_2O_3 and ZnO/Al_2O_3 laminated layers on a glass substrate.

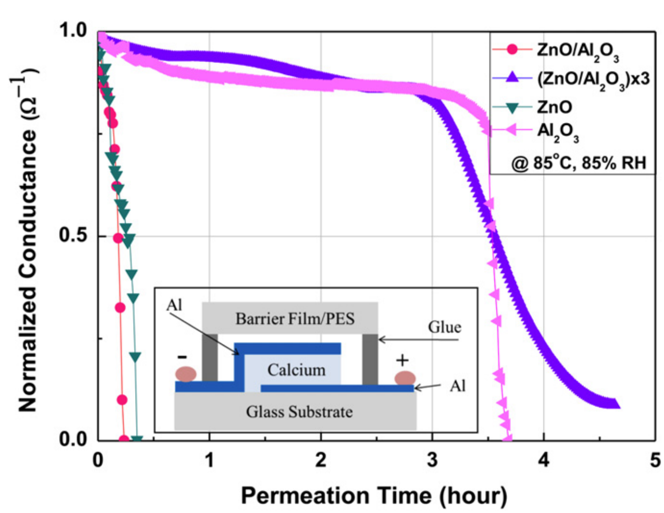

Fig. 7. Electrical curves induced by Ca degradation due to moisture permeation: All barrier films deposited on PES substrate (thickness of 150 μm).

4. Conclusion

Single ZnO, Al_2O_3 films and ZnO/Al_2O_3 laminated films on PES, deposited by ALD process at extremely low depsotion temperature (60 °C) were investigated. Through XRD and TEM measurement, it confirmed that it is possible to manipulate the crystallinity by using the different organizations structurally. In addition, the surface roughness and film density are also handled by changing the structure. The laminated structures are very transparent under visible range and reduced the film stress significantly as decreasing the ZnO thickness in the laminated structure. As a transparent gas barrier layer, the multi-laminated structure with a thinner ZnO and Al_2O_3 had better barrier property than that of single ZnO and Al_2O_3 layers, showing that the water vapor transmission ratio of multi-laminated ZnO/Al_2O_3 layer was 10 times lower than that of the single layer. The hybrid laminated layers by using low temperature ALD process can manipulate the physical properties to improve gas diffusion barrier properties. Therefore, it might be a promising candidate of thin film encapsulation applications, including from food packaging to electronics device (OLEDs etc.).

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