A flexible transparent gas barrier film employing the method of mixing ALD/MLD-grown $\text{Al}_2\text{O}_3$ and alucone layers

Wang Xiao, Duan Ya Hui, Chen Zheng, Duan Yu*, Yang Yong Qiang, Chen Ping, Chen Li Xiang and Zhao Yi

Abstract

Atomic layer deposition (ALD) has been widely reported as a novel method for thin film encapsulation (TFE) of organic light-emitting diodes and organic photovoltaic cells. Both organic and inorganic thin films can be deposited by ALD with a variety of precursors. In this work, the performances of $\text{Al}_2\text{O}_3$ thin films and $\text{Al}_2\text{O}_3$/alucone hybrid films have been investigated. The samples with a 50 nm $\text{Al}_2\text{O}_3$ inorganic layer deposited by ALD at a low temperature of 80°C showed higher surface roughness ($0.503 \pm 0.011$ nm), higher water vapor transmission rate (WVTR) values ($3.77 \times 10^{-4}$ g/m$^2$/day), and lower transmittance values (61%) when compared with the $\text{Al}_2\text{O}_3$ (inorganic)/alucone (organic) hybrid structure under same conditions. Furthermore, a bending test upon single $\text{Al}_2\text{O}_3$ layers showed an increased WVTR of $1.59 \times 10^{-3}$ g/m$^2$/day. However, the film with a 4 nm alucone organic layer inserted into the center displayed improved surface roughness, barrier performance, and transmittance. After the bending test, the hybrid film with 4 nm equally distributed alucone maintained better surface roughness ($0.339 \pm 0.014$ nm) and barrier properties ($9.94 \times 10^{-5}$ g/m$^2$/day). This interesting phenomenon reveals that multilayer thin films consisting of inorganic layers and decentralized alucone organic components have the potential to be useful in TFE applications on flexible optical electronics.

Keywords: Thin film encapsulation; Water vapor transmission rate; Molecular layer deposition; Low-temperature atomic layer deposition

Background

Organic electronics is an emerging technology that has potential uses in highly efficient lighting, super-bright displays, novel photovoltaic devices, and integrated smart systems [1-3]. Furthermore, it offers promising opportunities for the development of new products that utilize the special features of organic electronics such as flexibility, bendability, and transparency [4-6]. However, one major impediment to the mass production of organic devices is insufficient product lifetimes caused by their inclination to stop functioning when exposed to water vapor, oxygen, and other detrimental compounds present in air. Encapsulation layer, also known as barrier film, is a necessary and often overlooked part of the organic device architecture. Furthermore, polymer substrates, often used in flexible devices, provide better flexibility and toughness properties, but possess insufficient barrier properties against water vapor and oxygen permeation [7]. Since oxide films have to be of high quality to provide superior barrier performance, atomic layer deposition (ALD) is being pursued as an alternative to traditional chemical and physical vapor deposition methods. Reducing the number of defects (pinholes, grain boundaries, etc.) can reduce the layer thickness and/or number of layers required to achieve the required water vapor transmission rates (WVTR, g/m$^2$/day). Recently, this type of thin film encapsulation (TFE) has attracted great attention in order to overcome the air-sensitive issue [8-10]. The inorganic/organic encapsulation method based on ALD and molecular layer deposition (MLD), respectively, has demonstrated better barrier performance and mechanical properties than single inorganic layers [11-13]. On the one hand, the organic layer could potentially decouple any defects and prolong the permeation path, leading to lower WVTR values [14,15].
the other hand, single inorganic encapsulation films are 
brittle in general, but the hybrid inorganic/organic stucture 
reduces the internal stress of inorganic films generally 
improving flexibility [16,17].

It is therefore important to consider the development 
of high-barrier functionalities as well as the mechanical 
properties of TFE samples. In this study, samples with 
Al$_2$O$_3$ (ALD) or alucone (MLD) layers were grown and 
characterized. All encapsulation films were deposited at 
a low temperature of 80°C [18,19]. We investigated 
single Al$_2$O$_3$ films with Al$_2$O$_3$/alucone hybrid laminate 
before and after a bending test. The gas barrier and 
mechanism performances were both optimized [20] 
upon Al$_2$O$_3$ samples incorporating a 4-nm transparent 
organic component of the same nominal thickness. From 
this analysis, some important insights were determined, 
demonstrating that the performance of TFE with hybrid 
inorganic-organic structure could be optimized by pru-
dent selection of certain design parameters.

Methods
In the experiments, we fabricated a group TFE consisting 
of three different thin films. All films have nominal 
thicknesses of approximately 50 nm. As shown in Figure 1, 
film A was a 50 nm Al$_2$O$_3$ inorganic film. Films B and C 
consisted of approximately 46 nm Al$_2$O$_3$ and 4 nm 
alucone. For film B, 4 nm alucone was in the center of the 
hybrid film (23/4/23 nm). However, the alucone layer was 
divided into four equal parts in film C (9/1/9/1/9/1/9/1/9 nm). 
Both Al$_2$O$_3$ and alucone thin films were deposited 
by a LabNano 9100 ALD system (Ensure Nanotech Inc., 
Beijing, China) at 80°C, and all pipes were heated to 
120°C, while the pressure in the reaction chamber was 
1.5 × 10$^0$ Pa.

Table 1 summarizes the film deposition parameters 
during the ALD process. Al(CH$_3$)$_3$ (trimethylaluminum 
or TMA, Sigma Aldrich, St. Louis, MO, USA) and de-
ionized water were prepared as precursors for Al$_2$O$_3$ 
inorganic layer. During the growth process, high-purity 
N$_2$ (flow rate = 20 sccm) was used as carrier gas for these 
precursors. One reaction cycle included the following: 
0.02 s TMA dose, 30 s nitrogen purge, 0.02 s H$_2$O dose, 
and 30 s nitrogen purge. This sequence was repeated to 
obtain the desired thicknesses. For alucone organic layer, 
TMA and HO-(CH$_2$)$_2$-OH (ethylene glycol or EG, Sigma 
Aldrich) were reactants grown under identical condi-
tions. Before the deposition process, EG was preheated 
to 95°C to increase its vapor pressure [21]. The timing 
sequence was as follows: 0.02 s TMA dose, 30 s nitrogen 
purge, 0.07 s EG dose, and 120 s nitrogen purge. The 
growth mechanism for each type of film has been 
described previously [22]. WVTR measurements were

![Figure 1 A schematic diagram of prepared TFE structures. (a) Film A: Al$_2$O$_3$ 50 nm. (b) Film B: Al$_2$O$_3$/alucone/Al$_2$O$_3$: 23/4/23 nm. (c) Film C: Al$_2$O$_3$/alucone/Al$_2$O$_3$/alucone/Al$_2$O$_3$/alucone/Al$_2$O$_3$/alucone/Al$_2$O$_3$/alucone/Al$_2$O$_3$: 9/1/9/1/9/1/9/1/9 nm.](image-url)
carried out to test the barrier performance of the films through the calcium (Ca) corrosion method. The amount of water vapor permeating through the film was estimated with the following formula [11]:

$$\text{WVTR} \, \text{g/m}^2\text{/day} = -n \times \delta \text{Ca} \times \rho \text{Ca} \times \frac{d}{dt} \left( \frac{1}{R} \right)$$

$$\times \frac{M(\text{H}_2\text{O})}{M(\text{Ca})} \times \frac{\text{Ca}_{\text{Area}}}{\text{Window}_{\text{Area}}}$$

$\text{Ca}_{\text{Area}}/\text{Window}_{\text{Area}}$ represents the effective testing area to mask window area ratio. In this experiment, $\text{Ca}_{\text{Area}}/\text{Window}_{\text{Area}}$ is equal to 1. The root-mean-square roughness (RMS) and other surface features of the films were measured with a Veeco AFM. The thickness and refractive index of the thin films deposited on clean Si substrate were measured using a J.A. Woollam variable-angle spectroscopic ellipsometer (J.A. Woollam Co. Inc., Lincoln, NE, USA). The electrical characteristics of the devices were measured with an Agilent 2920 source meter (Agilent Technologies, Inc., Santa Clara, CA, USA) at room temperature.

**Results and discussion**

Table 2 summarizes some surface characteristics after thin film deposition by ALD at 80°C, including film thickness, normalized growth rate, RMS, and water contact angle.

| Film code | Thickness (nm) | Normalized growth rate (Å/per cycle) | RMS roughness (nm) | Contact angle (°) |
|-----------|---------------|--------------------------------------|-------------------|------------------|
| A         | 52.137 ± 0.034 | 0.947 ± 0.001                        | 0.503 ± 0.011     | 65.3 ± 3.7       |
| B         | 53.693 ± 0.156 | 1.161 ± 0.003                        | 0.492 ± 0.002     | 95.1 ± 3.3       |
| C         | 54.956 ± 0.067 | 1.153 ± 0.001                        | 0.465 ± 0.012     | 86.5 ± 1.4       |

Previous research by Dameron et al. reported that the alucone organic films showed a growth rate of 4 Å/cycle at 85°C, much faster than approximately 1 Å/cycle for $\text{Al}_2\text{O}_3$ at 80°C [23]. Here, a similar MLD deposition rate was achieved at 3.8 Å/cycle at 80°C, which further indicates that MLD alucone is typically a bifunctional monomer for...
fast stepwise condensation polymerization and yield completely organic films. Figure 2a,b shows the setup of the device for the investigation of the mechanism behavior of TFE under oscillatory bending. A square film sample was loaded between parallel plates. One of the plates was mounted on an oscillatory driven stepper motor. The number of revolutions performed by the motor controls the frequency. In the middle of the bend, the lowest radius of curvature \( r \) and the largest tensile strain at the \( y \)-axis (Figure 2c) were determined by the distance between parallel plates. In this study, the distance was fixed at approximately 2 mm and the radius of curvature \( r \) was 1.05 mm. The white circle in Figure 2b marks the maximum curved position where the AFM images were taken.

Figure 3 shows the surface topography and roughness of all thin films measured with AFM before and after the bending test. Before the bending test, a RMS of 0.503 ± 0.011 nm, 0.492 ± 0.002 nm, and 0.465 ± 0.012 nm was obtained for films A, B, and C, respectively. These values were almost equal to the bare PET substrate (RMS = 0.522 ± 0.007 nm). The highly conformal thin films were attributed to the use of ALD and MLD.
techniques. The slight negative trend from film A to film C might be due to the organic layer smoothing the surface [24]. However, film A (the single Al$_2$O$_3$ inorganic layer) exhibited an increase in RMS of 1.210 ± 0.034 nm after the bending test, while film B-C presented still lower values of 0.761 ± 0.021 and 0.339 ± 0.032 nm, respectively. We deduce that during the bending process, the alucone organic layer served as a stress buffer layer and might account for the lower RMS values. In the case of film C, the internal stress of Al$_2$O$_3$ layer was alleviated the most from separated organic layers [25]. Figure 4 shows the SEM image of film B deposited by ALD/MLD at 80°C. The Al$_2$O$_3$/alucone hybrid film appeared to be homogeneous with a smooth surface. The contact angle was found to be 95.1 ± 3.3° and 86.5 ± 1.4° for film B and C, respectively. This is higher than the value of single Al$_2$O$_3$ films (65.3 ± 3.7°). This phenomenon was attributed to the surface of the hybrid film being smoother than Al$_2$O$_3$, and this could be evidence for the possible dependence of the contact angle on the surface morphology.

To evaluate the permeability of Al$_2$O$_3$/alucone films as a water diffusion barrier, we studied the films before and after the bending test. The Ca sample wafers (Glass/Ca (200 nm)/Al (100 nm)) were deposited by thermal evaporation equipment at $5 \times 10^{-4}$ Pa without breaking the vacuum and were then transferred to a glove box. The area of Ca thin films was $1 \times 1 \text{ cm}^2$. The barrier films deposited by ALD/MLD on clean PET substrates were adhered to the Ca samples by UV sealant as shown in the inset of Figure 4 [26]. The calculated WVTR changes for different films before and after the bending test were shown in Figure 5. Before the bending test, the WVTR was found to be $3.77 \times 10^{-4}$ g/m$^2$/day (film A), $1.06 \times 10^{-4}$ g/m$^2$/day (film B), and $7.1 \times 10^{-5}$ g/m$^2$/day (film C). This was attributed to the fact that the alucone organic layer increases the permeation path for water vapor in the hybrid structure. It also reacts with the water vapor, decreasing the diffusion speed [11,27]. Figure 6 illustrates the water vapor permeation process for different thin film structures. With a 4-nm-thick alucone organic component divided into four equal layers, a 40% decrease in WVTR was obtained when comparing films B and C. As confirmed by our previous research [20], the increased proportion of Al$_2$O$_3$ in the hybrid structure leads to an improved barrier performance. However, after the bending test, the barrier performances demonstrated evidence of different degrees of damage. A notable increase from $3.77 \times 10^{-4}$ to $1.59 \times 10^{-3}$ g/m$^2$/day in WVTR was obtained for film A, while a more subtle increase from $9.94 \times 10^{-5}$ to $7.1 \times 10^{-5}$ g/m$^2$/day was achieved for film C. The results indicate that internal alucone organic layers improve flexibility under the same thicknesses. When the alucone organic layer was separated into separate layers, it leads to a more even distribution of stress in the laminates and reduced destruction [25].

In order to demonstrate the effect of the bending test on different films, we took some microscopic pictures for film A and film C in contrast to see if there were some damage after the bending test. As can be clearly
seen from Figure 7(a),(c) were taken from the surface of films A and C, respectively, before the bending test. There was no obvious difference between the two films. Figure 7b was film A after the bending test; we could clearly see some parallel stripes. On the contrary, there was no such phenomenon in (d) taken from film C after the bending test. We believe it was the alucone organic layer that served as buffer layer easing the stress under bending test. The cracks from the surface of film A were an evidence for the raising RMS and WVTR values.

Finally, the optical properties of TFE samples were measured as well as simulated. Figure 8 shows the simulated and experimental transmittance of Alq$_3$ (50 nm)/Ag (20 nm)/TFE/air structures on a PET substrate before carrying out the bend test. For all tests, no obvious change in transmittance was observed, even after 600 iterations of the bending test. Film C (maximum transmittance of 69%) showed a slightly higher transmittance at the region of 400-580 nm compared with film B (maximum transmittance of 65%) (Figure 8). In addition, simulated results predicted that the hybrid film would have similar transmittance values with the single Al$_2$O$_3$ film over the whole visible region. This optical characteristic is beneficial due to the fact that alucone has superior photo permeability [25] and this may potentially be useful for the TFE design in top emitting organic light devices or organic photovoltaics.

Conclusions
In summary, a hybrid ALD/MLD deposition technique has been used at a low temperature of 80°C in order to fabricate multiple stacked layers of Al$_2$O$_3$/alucone thin film encapsulations. Single Al$_2$O$_3$ film and Al$_2$O$_3$/alucone hybrid films have been investigated for the potential usage on flexible PET substrates. By introducing a 4 nm alucone organic layer inside and separating them into four equal layers inside the TFE structure, the hybrid structure delivers a considerably lower gas permeation (WVTR = 9.94 × 10$^{-5}$ g/m$^2$/day), higher flexibility, and transparency performance. This information will be useful for encapsulation structure engineering, to eventually enable optimal design of organic electronics.
Abbreviations
ALD: atomic layer deposition; TFE: thin film encapsulation; WVTR: water vapor transmission rate; MLD: molecular layer deposition; EG: ethylene glycol; AFM: atomic force microscopy; SEM: scanning electron microscopy.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
WX did the experiments and drafted the manuscript. DY is the corresponding author and had the first idea of MLD/ALD hybrid structure. CZ did the WVTR measurement for the encapsulation films and deposited the thin oxide films. YIQ performed the statistical analysis and characterized the optical performance for encapsulation film. CP helped to draft the manuscript. ZY is the expert in the field of organic electronics and provided SEM and AFM images. All authors read and approved the final manuscript.

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