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Letter

High barrier properties of transparent thin-film encapsulations for top emission organic light-emitting diodes

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ABSTRACT

This paper reported a low-temperature thin film encapsulation (TFE) process based on atomic layer deposition Al_2O_3 layer for top-emission organic light-emitting devices (TE-OLEDs). The barrier characteristics of both H_2O-based and O_3-based Al_2O_3 films were investigated. O_3-based Al_2O_3 TFE showed lower water vapor transmission rate (WVTR) of 8.7×10^{-6} g/m^2 day and longer continuous operation lifetime of 5 folds compared to the device with H_2O-based Al_2O_3 TFE under identical environmental and driving conditions. Furthermore, the extraction of emitting light of the devices with barrier layer was enhanced compared to the bared one. The theory simulation data were consistent with our experimental results and showed the potential for the design of TFE structures optimized for enhancing light transmission.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention recently because of their high efficiency, fast response time, flexibility and transparency, etc. Especially top emission organic light-emitting diodes (TE-OLEDs) have been widely studied for their application use in active matrix displays [1]. In a bottom-emitting OLED where light is emitted downward through the substrate, the overall area that can emit light is limited by the presence on the substrate of circuitry such as thin film transistors, which are opaque. Consequently the open area available for the light to emerge is reduced. In the TE-OLEDs structures where the light is made to emerge primarily through the top surface away from the substrate and thin film transistor (TFT) circuitry, are of great importance for achieving monolithic integration of OLEDs on a silicon chip. However, OLEDs are extremely sensitive to water vapor and oxygen, which may cause rapid degradation. Therefore, epoxy, cover glass and desiccant are commonly used to encapsulate bottom emitting OLEDs [2]. However, the transmittance of desiccant is opaque, therefore, it is not a viable option for TE-OLEDs. The requirements for TE-OLEDs encapsulation should include both effective high gas barrier and optical transmission properties.

Established deposition techniques for the preparation of dense, pin-hole free layers rely on elevated temperatures (>200 °C) or require highly reactive plasma-processes such as plasma-enhanced chemical vapor deposition (CVD). Most organic materials, however, are relatively fragile and have low glass-transition temperatures (<100 °C). Many of these processes are therefore not suitable for the encapsulation of organic electronic devices.

Recently, thin film encapsulation technologies employ physical vapor deposition (PECVD) and sputter for preparation of dense, pin-hole free layer [3,4]. However, a severe drawback of these techniques employed with plasma is or-

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ganic materials are susceptible to high-energy atoms impinging and flux of charge particles [5,6], which exists in plasma enhanced atomic layer deposition (PEALD). Particularly in TE-OLED, the cathode metal itself is a prerequisite of thinner. Therefore the plasma damage to the fragile organic layers will be more severe, as there is less protection for organic layer by electrode [7]. Atomic layer deposition (ALD) is one of the ideal deposition technologies. This technique is well-established in the processing of insulating films for gate dielectrics and capacitors [8]. ALD has the advantage of allowing the deposition of very dense films, and thus appears to be a promising technique suitable for preparing encapsulation layers on the top of OLEDs [9]. However the temperature window of ALD is about 200–400 °C, which leads to the completely damage on OLEDs. So the low temperature ALD process is essential to OLED encapsulation.

2. Experimental section

In this study, we presented the performance of encapsulation properties and optical transmittance of barrier films. Two types of ALD Al_2O_3 films, with H_2O and O_3 as the oxidant precursor deposited at a relative low temperature of 80 °C, were tested, and their water vapor transmission rate (WVTR) and microstructure were determined to improve their effectiveness as encapsulation films. The calculation demonstrates that Al_2O_3 encapsulation could enhance the light emission output, which was proved by experimental results. As expected, the device performance and stability were improved significantly with protection from ALD Al_2O_3 encapsulation. The Al_2O_3 films in this study were grown in the LabNano 9100 ALD system by Ensure Nanotech Inc. For the preparation of the Al_2O_3 layers, trimethylaluminum (TMA) were used as precursors, O_3 and H_2O were used as oxidant. The experiment parameters were list in Table 1. The relative encapsulation time per one cycle and total deposition time of H_2O-based TFE in our experiment conditions were 60 s and 15 h, respectively, and the encapsulation time per one cycle and total deposition time of O_3-based TFE were 40 s and 10 h. The deposition rate of the films was 0.9 Å/cycle. Here, O_3 was produced by an ozone generator. A mixture of oxygen (400 sccm, 99.999%) and catalytic nitrogen (5 sccm) was used to generate ~3.5 wt% O_3, and its concentration was about 50 mg/L. It should be addressed that the TMA was placed before the H_2O pulse to prevent incursion of H_2O or O_3 into the devices, as the adsorbed TMA molecules would rapidly consume the incoming oxidant molecules before they could permeate devices [10]. The thickness and refractive index of the ALD–Al_2O_3 films were determined by a J.A. Woolam variable-angle spectroscopic ellipsometer. The root-mean-square (RMS) of its films was measured by Vecco atomic force microscope (AFM). The refractive index and RMS were measured by testing the Al_2O_3 depositing on the Si substrates which were precision polished that can provide smooth surface (RMS: 0.6 ± 0.1 Å), thus, the impact of substrates could be negligible (see Table 2).

3. Results and discussion

Our previous study of ALD–Al_2O_3 showed the different film formation properties by using H_2O or O_3 as the oxidant [11]. The TMA + H_2O process had been extensively studied and the underlying reactions are well-understood. For TMA + O_3 process, we assumed that O_3 decomposes into O_2 and monatomic O, and that the latter is rather active species which could burn off organic ligands. The TMA and O_3 yield Al_2O_3 ALD according to self-limiting surface reactions, whose mechanism was shown in Eq. (1) [12]. This mechanism is approximate with the TMA + H_2O process Eq. (2). Both processes produce surface –OH, which is crucial reactive group to determine the succession of self-limiting reaction in the next cycle.

$$\text{surf-Al}(CH_3)_n + O_3(g) \rightarrow \text{surf-Al}(CH_3)_{n-1} + \text{surf-OH} + 1/2C_2H_4(g) + O_2(g) \quad (1)$$

$$\text{surf-Al}(CH_3)_n + H_2O(g) \rightarrow \text{surf-Al}(CH_3)_{n-1} + \text{surf-OH} + CH_4(g) \quad (2)$$

However, since O_3 has high reaction activation energy, it implies that the using of O_3 for the Al_2O_3 film can suppress the presence of bulk-OH compared to the H_2O-based process [13]. Thus, the O_3 oxidant can produce dense and homogeneous film. However, in the TMA + H_2O process, the water and by-product methane cannot be efficiently purged out under low temperature condition, resulting in incomplete chain-reaction and increasing voids [14]. Furthermore, H_2O molecule would penetrate inside these voids, it has been identified as the most significant drawback issue, which limited continuous and pinhole-free nature of Al_2O_3 ALD films of low temperature ALD process [15].

To further investigated the ALD films deposited by H_2O and O_3 as the oxidant sources under low temperature experimental conditions. The topographic information of the Al_2O_3 films was studied. The RMS of H_2O-based Al_2O_3 (film A) and O_3-based Al_2O_3 (film B) were measured over a scanned area of $0.5 \times 0.5\ \mu m^2$ by AFM. As displayed in Fig. 1(a) and (b), the RMS of film A is 0.331 nm, which was relative rough than film B, which RMS is 0.255 nm. This tiny RMS of O_3-based Al_2O_3 film implied atomically

Table 1
Parameters of films deposition processes of ALD in our experimental conditions.

Film code	Oxidant precursor	Oxidant precursor pulse time (s)	N_2 purge time (s) for oxidant precursor	Tg (°C)	Pressure (Pa)	Carrier gas	TMA pulse time (s)	N_2 purge time (s) for TMA
A	H_2O	0.02	30	80	3×10^{-2}	N_2	0.02	30
B	O_3	0.1	10	80	3×10^{-2}	N_2	0.02	30