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Al_2O_3/TiO_2 multilayer thin films grown by plasma enhanced atomic layer deposition for organic light-emitting diode passivation

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A B S T R A C T

Aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2) films deposited on flexible polyethersulfone substrates by plasma-enhanced atomic layer deposition have been investigated for transparent barrier applications. The effects of the induced plasma power on the passivation properties were investigated as function of film thickness and substrate temperature. The optimum plasma power and substrate temperature were investigated through measurements of the refractive index and packing density of the Al_2O_3 and TiO_2 films. In this research, three different barrier structures were investigated for the purpose of improving water vapor barrier characteristics. A low water vapor transmission rate of approximately 5×10^{-3} g/m^2·day or below was achieved with two pairs of Al_2O_3/TiO_2 stacks with a total stack thickness of 40 nm deposited at 80 °C. The passivation performance of the multilayer film was investigated using an organic light-emitting diode. The coated device lifetime was 267 h, which was 41 times longer than that of an uncoated sample.

1. Introduction

Methods for improving the characteristics of passivation layers for organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and flexible display panels have been intensively studied, as polymer materials are easily degraded by water vapor, gaseous oxygen, and high process temperatures [1,2]. For flexible electronic applications, it is necessary to deposit passivation layers at low temperatures due to the low glass transition temperature of polymers. In OLED devices, the passivation layer requires a water vapor transmission rate (WVTR) of 10^{-6} g/m^2·day at 39 °C and 95% relative humidity (RH) to ensure reliable performance and durability [2,3]. Many research groups have proposed passivation layers deposited by chemical vapor deposition (CVD) [4] or sputtering [5]. However, inorganic passivation layer deposited by chemical vapor deposition (CVD) and sputtering methods has shown high water vapor transmission rates and thick layers, which are not suitable for flexible organic displays. The self-limiting atomic layer deposition (ALD) method enables conformal coating of a surface and allows for exact thickness control on an atomic level. Therefore, a passivation layer deposited using the ALD process can improve the conformality and uniformity of these films [6]. Moreover, plasma-enhanced ALD (PEALD) is a promising deposition technique for low temperature applications [7]. Energy from plasma gases can decompose precursors to more reactive species thereby increasing the reaction rate on a surface. Therefore, a high growth rate can be obtained even at low substrate temperatures [8]. Resistance to water vapor transmission is dependent not only on the size and density of nanoscale defects such as pinholes or pores, but also on chemical interactions between the passivation materials and water vapor [9]. The permeation of water vapor through barrier films is governed by 1) absorption into the film surface, 2) solubilization in the film, 3) diffusion through the film, and 4) desorption at the opposite surface of the film [10]. In recent years, low water vapor transmission rates (WVTRs) have been achieved using ALD-deposited aluminum oxide (Al_2O_3) thin films deposited at low temperatures, and these materials have been shown to produce improvements in OLED lifetime, and substrate protection against water vapor or gaseous oxygen [11–14]. And roll-to-roll ALD-deposited Al_2O_3 and TiO_2 barrier films on polymer (PET) films have been reported by E. Dickey et al. [15]. Very low permeation rates of 6.5×10^{-5} g/m^2/day at 60 °C and 85% RH (relative humidity) have been reported for Al_2O_3 films that were grown at 120 °C [13]. However, substrate temperatures above 100 °C may not be feasible because the glass transition temperatures of many functional OLED materials have been reported to be in this temperature range [16]. In previous studies, we investigated the water vapor permeation barrier properties of TiO_2 films fabricated via PEALD with radio frequency (rf) plasma at a substrate temperature of 90 °C [17]. As of yet, water vapor transmission rate values 5×10^{-3} g/m^2·day (WVTR measurement limit) have not been achieved for TiO_2 films. In this study, we describe the deposition of aluminum oxide (Al_2O_3) and titanium oxide (TiO_2) films onto poly(ether sulfone) (PES) substrates as the barrier structure instead of an organic/inorganic multilayered structure. Remote plasma

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source of electron cyclotron resonance (ECR) ALD was used to reduce plasma damage to the polymer materials and to deposit aluminum oxide and titanium oxide at low temperatures (80 °C). The resulting thin films have great potential for use as water vapor barrier layers in organic-based devices.

2. Experimental details

Al_2O_3 and TiO_2 films were deposited onto both a PES substrate and a Si wafer (001) using PEALD. A Si wafer (001) was used to investigate the chemical and physical properties of the oxide thin film. This Si wafer was dipped into a dilute HF (HF: H_2O = 1: 100) solution and rinsed in deionized water to obtain a hydrogen-terminated surface. In flexible electronic processing, not only raw substrate WVTR but also glass transition temperature (T_g) is important. Thus, we selected PES substrate instead of common PET or PEN. (T_g of PES: 223 °C, PET: 78 °C, PEN: 121 °C) Our PES substrate without oxide adhesion layer was 650 μm in thickness, surface roughness root mean square was 6.1 1 Å and raw substrate WVTR was 50 g/m^2·day. Unfortunately, we did not measure PES's particle/defect density. Furthermore, PES is a good candidate for flexible plastic substrates for optical transmittance (above 88% over the visible wavelength). Prior to the deposition of the passivation layer, the PES substrate was washed with isopropyl alcohol and methanol in an ultrasonic bath and then dried in a stream of nitrogen.

The precursors used in the PEALD of Al_2O_3 and TiO_2 films were trimethylaluminum (TMA) and tetrakis(dimethylamino)titanium (TDMATi), respectively. The TMA and TDMATi sources were injected without a carrier gas. The temperature of the TMA source was maintained at 20 °C by a cooling system, and the base pressure inside the reactor was 26.6 Pa. The sequence of pulses for one deposition cycle for an Al_2O_3 film was as follows: 1) a TMA source for 0.7 s, 2) an Ar purge for 20 s, 3) an O_2 reactant pulse with ECR plasma for 10 s, and 4) an Ar purge for 20 s.

The temperature of the TDMATi source was maintained at 40 °C by a heating system, and the base pressure inside the reactor was 26.6 Pa. The sequence of pulses for one deposition cycle for TiO_2 films was as follows: 1) TDMATi source for 1 s, 2) an Ar purge for 20 s, 3) an O_2 reactant pulse with ECR plasma for 10 s, and 4) an Ar purge for 20 s. ECR plasma was used for the deposition of the passivation layers onto polymer substrates using PEALD. The ECR plasma power and the substrate temperatures were varied from 100 to 700 W and from 40 to 100 °C, respectively. The substrate temperature that was controlled by thermocouple and thermometer connected to substrate holder. It was able to be measured by checking the thermocouple and thermometer.

WVTR measurement was carried out at 38 °C and 100% RH by using a permeation instrument (Permatran W 3/33, Mocon, Inc.). The samples were masked with aluminum foil to form 5 cm^2 gas exposure areas. X-ray reflectometry (XRR, PANalytical X'Pert PRO) was used to investigate the density of the deposited film, using Cu-Kα filtered radiation. The X-ray source was operated at the voltage of 40 kV and current of 20 mA. In order to determine the densities of the films from the XRR data, we used the following equation [17]:

$$\theta_c = \lambda\sqrt{\left(\frac{\rho_e\gamma_e}{\pi}\right)}. \quad (1)$$

When an X-ray beam is reflected at a grazing angle by a film, there exists a critical angle below which total external reflection of the radiation takes place. This critical angle, θ_c, can be approximated using the above equation, where ρ_e is the electron density or the number of electrons per unit volume of the material, λ is the X-ray wavelength, and γ_e = 2.818 fm is the classical electron radius. The electron density calculated using the above equation can be transformed to reflect the density of the sample by using N_A, A, and Z—Avogadro's number, atomic weight, and the number of electrons per atom, respectively.

Bending testing was carried out using a homemade machine. Samples were bent to a cylinder of radius 12.5 mm under compressive stress. We also investigated the passivation performance of the buffer layer and multilayer water vapor barrier film deposited directly on the OLED without lamination process by measuring the luminance of the devices. The OLED devices were prepared with following configuration by using vacuum thermal evaporation: indium tin oxide (ITO) glass substrate/copper phthalocyanine (CuPc) (20 nm)/*N*,*N*′-bis(naphthalene-1-yl)-*N*,*N*′-diphenylbenzidine (α-NPB) (40 nm)/8-hydroxyquinoline aluminum (Alq_3) (60 nm)/lithium fluoride (LiF) (0.5 nm)/Al (80 nm). The ITO glass substrate was used as the transparent anode, CuPc as the hole-injection layer (HIL), α-NPB as the hole-transport layer (HTL), and Alq_3 as the emitting layer (EL). The OLED performance was evaluated by measuring the electroluminescence spectra and the current density–voltage–luminance (J–V–L) characteristics using an IVL300 (JBS International) in a dry N_2 atmosphere at room temperature. And the OLED lifetime was measured by degradation from side.

3. Results and discussion

Fig. 1 shows the dependence of the growth rate and density of Al_2O_3 and TiO_2 films as a function of (a) the substrate temperature, which was varied over a range of 32.5 to 102.5 °C at a plasma power of 500 W, and (b) the plasma power, which was varied over a range of 100 to 700 W at a substrate temperature of 80 °C. The growth rate of the Al_2O_3 and TiO_2 films decreased when the substrate temperature was increased from 32.5 to 102.5 °C. Al_2O_3 and TiO_2 film densities were analyzed using X-ray reflectometry (XRR). It is evident from Fig. 1 that the film densities of Al_2O_3 and TiO_2 films increased with the substrate temperature. In addition, the growth rate and density of Al_2O_3 and TiO_2 films both increased when the plasma power was increased from 100 to 500 W. In contrast, the growth rate and density decreased at a plasma power of 700 W.

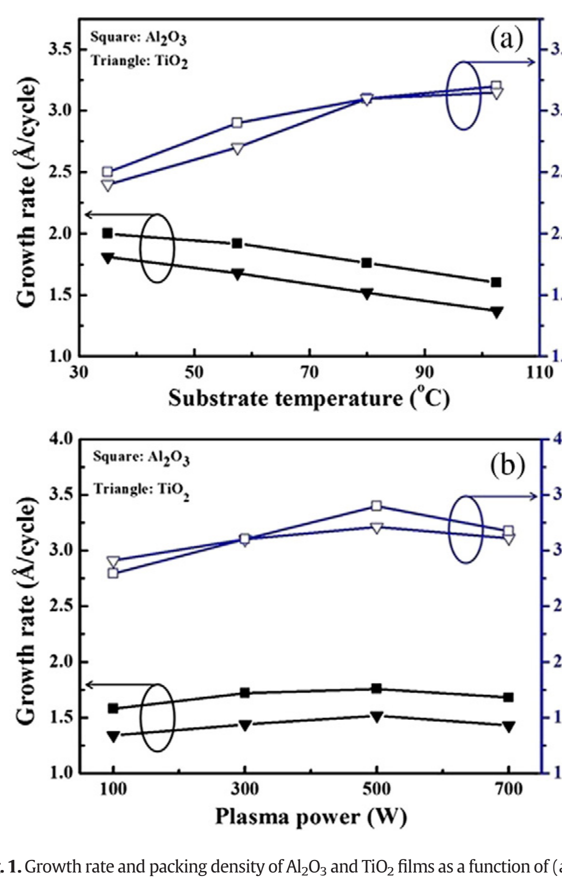

Fig. 1. Growth rate and packing density of Al_2O_3 and TiO_2 films as a function of (a) substrate temperature and (b) plasma power.