Al₂O₃/Ag/Al₂O₃ multilayer thin film passivation prepared by plasma damage-free linear facing target sputtering for organic light emitting diodes

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**A B S T R A C T**

Al₂O₃/Ag/Al₂O₃ multilayer passivation prepared by plasma damage-free linear facing target sputtering (LFTS) was investigated as a function of inserted Ag thickness. Using antireflection effect of the Ag layer that is sandwiched between dielectric Al₂O₃ layers, we can obtain a transparent Al₂O₃/Ag/Al₂O₃ multilayer passivation for organic light emitting diodes (OLEDs). It was found that insertion of the Ag layer with optimized thickness between Al₂O₃ layers lead to improvement of the optical transparency and water vapor transmission rate of the Al₂O₃/Ag/Al₂O₃ multilayer. In addition, current density–voltage–luminescence of an OLED passivated with Al₂O₃/Ag (10 nm)/Al₂O₃ multilayer was similar to that of an OLED with nonpassivated sample, indicating that the performance of an OLED is not affected by high-density plasma during the LFTS process. Moreover, the lifetime to half initial luminance of an OLED passivated with Al₂O₃/Ag (10 nm)/Al₂O₃ multilayer was longer than that of a nonpassivated sample.

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1. Introduction

To fabricate high-performance organic light emitting diodes (OLEDs), it is essential to acquire high-performance encapsulation because both lifetime and performance of the OLEDs are critically affected by quality of the encapsulation [1]. For this reason, several types of encapsulation techniques have been extensively explored to improve long-term stability of OLEDs or flexible OLEDs [1–3]. In particular, thin film passivation has been considered as the most desirable encapsulation for OLEDs, due to its simplicity, thin thickness and flexibility. Although various SiNx, SiOₓ, SiOₓNₓ, AlOₓ, and Al₂O₃:N films have been investigated for transparent thin film passivation for OLEDs, a single inorganic thin film is not sufficiently dense to protect flexible optoelectronic devices from permeation by moisture and oxygen [4–8]. Thus, multilayer passivation, such as Barix coating, which is composed of alternating organic–inorganic multilayers, has been proposed as a means to achieve ultra high barrier properties for OLEDs or flexible OLEDs [1,9,10]. However, Barix coating still has not been employed in mass production of OLEDs due to its complicated process and long-process time. In addition, most reported deposition techniques for the inorganic films are based on a plasma process which is harmful to organic materials. Therefore, it is imperative to develop simple multilayer passivation prepared by plasma damage free process to substitute Barix coating for high performance OLEDs and flexible OLEDs. However, oxide/metal/oxide (OMO) multilayer has not been investigated for thin film passivation even though it has various advantages such as high transparency and simple process.

In this work, we report on the characteristics of transparent Al₂O₃/Ag/Al₂O₃ multilayer passivation prepared by a linear facing target sputtering (LFTS) as a function of inserted Ag layer thickness. Due to antireflection effect of the Ag and high density of Al₂O₃ layer, multilayer showed a high transparency and low water vapor transmission rate (WVTR) despite the very small thickness of the multilayer (~150 nm). Furthermore, the current–voltage–luminescence (I–V–L) characteristics of the OLED passivated with the Al₂O₃/Ag/Al₂O₃ layer were identical to that of an OLED with nonpassivated sample, indicating no damage by LFTS process. In addition, the lifetime of the OLED passivated by the Al₂O₃/Ag/Al₂O₃ multilayer was compared with that of the nonpassivated OLED.

2. Experimental details

Al₂O₃/Ag/Al₂O₃ multilayer passivation was fabricated by a LFTS and thermal evaporation as shown in Fig. 1(a). The 70 nm-thick bottom Al₂O₃ layer was reactively sputtered on a glass or polyethylene terephthalate (PET) substrate at a constant Ar/O₂ flow ratio of 8/2 sccm, a pulsed direct current (DC) power of 500 W and a working pressure of 133 × 10⁻³ Pa. Due to effective confinement of high-density plasma between Al targets, we can deposit Al₂O₃ layer on the substrate without substrate heating caused by bombardments of the energetic particles [11]. Fig. 1(b) shows schematics of linear facing sputter cathodes and picture of the effectively confined plasma between Al targets during LFTS process. Unidirectional magnetic fields between facing Al targets and negative voltage of cathodes lead to the confined plasma, which cannot affect the substrate like Fig. 1(b). In addition, the substrate position out of high-density plasma region makes it possible to deposit Al₂O₃ layers without severe plasma damage. After the deposition of
the bottom Al₂O₃ layer, an Ag layer was thermally evaporated onto the bottom Al₂O₃ layer at a constant deposition rate of 0.02 nm/section as a function of thickness (6–20 nm). Subsequently, the 70 nm-thick top Al₂O₃ layer was sputtered onto the Ag layer under deposition conditions identical to those for the bottom Al₂O₃ layer. The optical transmittance of AL₂O₃/Ag/AL₂O₃ multilayer fabricated on PET substrate was measured in a wavelength range from 350 to 800 nm using a UV/visible spectrometer as a function of Ag thickness. The surface morphology of the Ag layer grown on the bottom Al₂O₃ layer was analyzed as a function of Ag thickness using a field emission scanning electron microscope (FESEM) with operating voltage of 10 kV. To investigate structural properties of the Al₂O₃/Ag/Al₂O₃ multilayer, synchrotron X-ray scattering examination was carried out. The synchrotron X-ray scattering measurements were carried out at the 5C2 GIST beamline at Pohang Light Source. Water vapor transmission rate (WVTR) value for the Al₂O₃/Ag/Al₂O₃ multilayer at an initial luminance of 500 cd/m² was measured. To compare the lifetime of OLED with Al₂O₃/Ag/Al₂O₃ multilayer and some uncovered region. Due to agglomeration and connection of Ag islands. However, the Al₂O₃/Ag/Al₂O₃ multilayer with Ag thickness of 10 nm shows a significantly increase in the optical transmittance. The increased optical transmittance of the Al₂O₃/Ag/Al₂O₃ multilayer could be attributed to the antireflection effect which has been observed in dielectric/metal/dielectric structure [12]. As discussed by Berning and Turner, symmetry designs consisting of dielectric layer stacks around a central layer of a Ag film can be produced with very high transmittance in visible spectral range [13]. However, further increases of Ag thickness result in decreases in optical transmittance of Al₂O₃/Ag/Al₂O₃ multilayer passivation due to light absorption by Ag layer. Driven at 38 ± 2 °C, 100% relative humidity by MOCON (PERMATRAN-W 3/33 MA) for 72 h as shown in the inset picture of Fig. 4. We have used MOCON apparatus, model PERMATRAN-W 3/33 MA from MOCON Inc. To compare the lifetime of OLED with Al₂O₃/Ag/Al₂O₃ multilayer and nonpassivated sample (reference), we prepared conventional OLEDs. α-naphthylphenylbiphenyl (NPB) and tris-(8-hydroxyquinoline) aluminum (Alq₃) were employed as the hole transport layer and electron transport layer (Emission layer) layers, respectively. Finally, a 1 nm/100 nm-thick LiF/Al cathode was patterned on the Alq₃ layer using a shadow mask for an active device area 3 mm². After preparation of the OLED sample, it was passivated with an optimized Al₂O₃/Ag (10 nm)/Al₂O₃ multilayer. The current density–voltage–luminescence (J–V–L) characteristics of OLEDs were measured using a Photo Research PR-650 spectrophotometer driven by a programmable dc source. Driven at 2 mA/cm², the device lifetime of OLED passivated with the Al₂O₃/Ag/Al₂O₃ multilayer at an initial luminance of 500 cd/m² was measured.

3. Results and discussion

Fig. 2(a) shows the optical transmittance of the Al₂O₃/Ag/Al₂O₃ multilayer grown on PET substrate as a function of the inserted Ag thickness. The multilayer sample with Ag thickness 6 and 8 nm shows a low optical transmittance due to light absorption and scattering of the Ag islands. However, the Al₂O₃/Ag/Al₂O₃ multilayer with Ag thickness of 10 nm shows a significantly increase in the optical transmittance. The increased optical transmittance of the Al₂O₃/Ag/Al₂O₃ multilayer could be attributed to the antireflection effect which has been observed in dielectric/metal/dielectric structure [12]. As discussed by Berning and Turner, symmetry designs consisting of dielectric layer stacks around a central layer of a Ag film can be produced with very high transmittance in visible spectral range [13]. However, further increases of Ag thickness result in decreases in optical transmittance of Al₂O₃/Ag/Al₂O₃ multilayer passivation due to light absorption by Ag layer.

Fig. 1. (a) Schematics Al₂O₃/Ag/Al₂O₃ multilayer deposition process using LFTS and thermal evaporator. (b) Schematic of linear facing target to confine high density plasma between Al targets and picture showing confined plasma during LFTS process.
layer from island to completely covered film is similar to our previously reported works [14,15]. Considering barrier properties of the Al2O3/Ag/Al2O3 multilayer, it is desirable to insert thicker Ag layer between Al2O3 layers because the thicker Ag film densely covered the bottom Al2O3 layer as shown in Fig. 3(a). However, due to the transparency of the multilayer, optimization of Ag thickness is necessary in the Al2O3/Ag/Al2O3 multilayer. Fig. 3(b) shows the synchrotron X-ray scattering results of the Al2O3/Ag/Al2O3 multilayer as a function of the Ag thickness. Regardless of the Ag thickness, all of the top and bottom Al2O3 layers shows a very broad peak between Qz = 1.5 and Qz = 2.0 indicating their amorphous structure. As previously reported, the effective confinement of the energetic particles between the facing Al targets enables us to deposit an Al2O3 film with a completely amorphous structure at room temperature [11]. However, the microstructure of the Ag layer prepared by thermal evaporation was dependent on its thickness. Up to a thickness of 12 nm, there is no peak related to crystalline Ag at Qz = 2.66. This indicates that the structure of the islands and channel Ag layer is amorphous under the 12 nm thickness. A crystalline Ag peak of low intensity at Qz = 2.66 starts to appear an Ag thickness of 14 nm. Further increasing the Ag thickness leads to the clear appearance of a crystalline peak of fairly high intensity at Qz = 2.66.

Fig. 4 shows WVTR value of the Al2O3/Ag/Al2O3 multilayer samples which were grown on the PET substrate as a function of Ag thickness. WVTR value of the Al2O3/Ag/Al2O3 multilayer sample after MOCON test. Due to the small size of Al2O3/Ag/Al2O3 multilayer samples, WVTR value for all multilayer passivation were measured by packaging the samples like inset picture. Compared to the WVTR value (1.4 g/m²-day) of the single Al2O3 layer, the WVTR value of the Al2O3/Ag/Al2O3 multilayer is much lower. As the Ag thickness increases in the Al2O3/Ag/Al2O3 multilayer, the WVTR value monotonically decreases because the thicker Ag layer can effectively prevent the intrusion of water vapor. However, effect of the Ag thickness on the WVTR value is fairly small due to main barrier properties are related to the density of the Al2O3 film. Despite of the very small thickness of the Al2O3/Ag/Al2O3 multilayer (~150 nm), the WVTR of the multilayer passivation shows the fairly low WVTR value, which is 0.011 g/m²-day for a Ag thickness of 20 nm. Considering transparency and WVTR value, we decided the optimized thickness of Ag layer as 10 nm. Although the WVTR value (~10⁻² g/m²-day) of the Al2O3/Ag/Al2O3 multilayer is higher than the previously reported WVTR (10⁻³–10⁻⁴ g/m²-day) values of several thin film passivation [8–10], high transparency and very thin thickness could be merit of the Al2O3/Ag/Al2O3 multilayer. Fig. 5 shows X-ray photoelectron spectroscopy (XPS) depth profiles results obtained from the optimized Al2O3/Ag(10 nm)/Al2O3 electrode. It was shown that the individual layers of top Al2O3, Ag, and bottom Al2O3 layer exist without interfacial reaction. The constant atomic percent of Al and O atoms in the bottom and top Al2O3 layers shows
that both bottom and top Al₂O₃ layer were identically deposited on the glass substrate and Ag layer. However, the Ag layer shows asymmetrical feature due to rough and agglomerated surface morphology as shown in Fig. 3(a).

Fig. 6(a) shows J-V-L characteristics of the OLED passivated with a Al₂O₃/Ag/Al₂O₃ multilayer and the reference OLED (Nonpassivated sample). The J-V-L curve of the OLED passivated with a Al₂O₃/Ag/Al₂O₃ multilayer exhibits an similar turn on voltage, forward bias behavior and luminance to those of the reference OLED. These similar J-V-L characteristics of OLEDs passivated with a Al₂O₃/Ag/Al₂O₃ multilayer indicates that the electrical and optical characteristics of the OLED are not critically affected by exposure to the high density plasma during the Al₂O₃ deposition. Fig. 6(b) shows the lifetime for an OLED passivated with a Al₂O₃/Ag (10 nm)/Al₂O₃ multilayer and a reference OLED. The operating lifetime of both the OLED passivated with the Al₂O₃/Ag/Al₂O₃ multilayer and the reference OLED were measured at a dc-current drive of 2 mA/cm² with an initial luminance of 500 cd/m² at room temperature. The lifetime of the reference sample with an initial luminance of 500 cd/m² was approximately 40 h. The abrupt decrease in the luminance of the reference OLED is related to severe degradation of organic layers by direct intrusion of moisture and oxygen through the cathode layer. However, the lifetime of the OLED passivated with a Al₂O₃/Ag/Al₂O₃ multilayer is longer than that of the reference sample. The lifetime of the passivated OLED is approximately 140 h. It is noteworthy that the lifetime of the OLED could be prolonged by using a Al₂O₃/Ag/Al₂O₃ multilayer unlike other reported thin film passivation procedures, which use a thick film. The prolonged lifetime of the OLED verifies that Al₂O₃/Ag/Al₂O₃ multilayer grown by LFTS was very a good passivation layer. Therefore, the identical J-V-L data and prolonged lifetime of the OLED passivated with Al₂O₃/Ag/Al₂O₃ multilayer grown by LFTS sugests that the Al₂O₃/Ag/Al₂O₃ multilayer is a promising passivation scheme for high performance OLED and flexible OLEDs.

4. Conclusion

We reported on the characteristics of the antireflective Al₂O₃/Ag/Al₂O₃ multilayer passivation prepared by plasma damage-free LFTS. It was found that insertion of the Ag layer with optimized thickness between Al₂O₃ layers lead to improvement of the optical transparency and WVTR of the Al₂O₃/Ag/Al₂O₃ multilayer. However, effect of the Ag thickness on the WVTR value is fairly small due to main barrier properties are closely related to the density of the Al₂O₃ film. Using antirefection effect of the Ag layer that is sandwiched between dielectric Al₂O₃ layers, we can obtain a transparent Al₂O₃/Ag/Al₂O₃ multilayer passivation for OLEDs. The current density-voltage-luminance of an OLED passivated with Al₂O₃/Ag (10 nm)/Al₂O₃ multilayer was similar to that of an OLED with nonpassivated sample, indicating that the performance of an OLED is not affected by high-density plasma during the LFTS process. Moreover, the lifetime to half initial luminance of an OLED passivated with Al₂O₃/Ag (10 nm)/Al₂O₃ multilayer was longer than that of a nonpassivated sample.
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