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Highly reliable hybrid nano-stratified moisture barrier for encapsulating flexible OLEDs

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ABSTRACT

Herein, a novel thin-film encapsulation for flexible organic light-emitting diodes (FOLEDs) is proposed, and its long-term reliability in tensile stress conditions was tested. The hybrid nano-stratified moisture barrier consists of 2.5 dyads of an Al_2O_3/ZnO nano-stratified structure and a S-H nanocomposite organic layer. The nano-stratified structure is prepared by low-temperature atomic layer deposition and the S-H nanocomposite by spin-coating at a thickness of 30 and 120 nm, respectively. An optical transmittance of 89.05% was measured with the 2.5-dyad hybrid nano-stratified moisture barrier with a total thickness of 330 nm. A low water vapor transmission rate (WVTR) of 1.91×10^{-5} g/m^{2}day was recorded based on an electrical Ca test at 30 °C and 90% R.H. without losing its properties after a bending test. With this highly reliable hybrid nano-stratified moisture barrier, FOLEDs were successfully encapsulated. After 30 days under conditions of 30 °C and 90% R.H. with tensile stress, the J-V-L performances of the FOLEDs were comparable to those of the initial state without dark spots. These results suggest that this hybrid nano-stratified moisture barrier is an excellent method for encapsulating FOLEDs.

1. Introduction

From cathode ray tubes (CRTs) to flat panel displays such as AC plasma display panels (AC PDPs), liquid crystal displays (LCDs), and organic light emitting diodes (OLEDs), the display market has constantly developed over the years. Nowadays, the development in display technology is becoming faster, and as such, the display paradigm is rapidly shifting to flexible displays. Especially in the case of OLEDs, OLEDs are considered the most promising candidate for the next generation of flexible displays because of the flexibility property of organic materials. Even though OLEDs have many advantages, there are some significant disadvantages. The organic materials in OLEDs are very sensitivity to moisture and oxygen which cause reliability problems [1,2]. Moisture and oxygen from the external environment easily oxidize and crystalize organic materials which lead to the formation of dark spots [3–5]. To solve these problems, Burrows et al. examined an encapsulation method using a glass-lid with desiccant materials [6]. However, the brittle nature of glass hinders the application of this method to flexible displays.

For flexible encapsulation, various kinds of studies have been done previously [7,8]. In particular, thin-film encapsulation technology has been regarded as a promising technology. Unlike barrier foil technology, thin-film barriers have the strong advantage of eliminating edge-permeation. Among them, multi-barrier and nanolaminate barrier are popular technologies. The multi-barrier system has been reported by Vitex Inc, called the BARIX-system [9], which has a configuration of organic-inorganic alternating stacks (dyads). The inorganic layer has high chemical and thermal stability and a low water vapor transmission rate (WVTR) [10,11], however, there are defects that act as main diffusion channels in this technology formed by the limitation of the vacuum process. Adding an additional organic layer can help to prevent the formation of defects [12–14] and provide flexibility. This multi-barrier permeation mechanism has been discussed by Graff et al. [15]. In contrast, the nanolaminate barrier just uses inorganic layers which are laminated by other kinds of inorganic materials on a nanoscale level [16]. Because of its excellent gas barrier property, it has a low WVTR at the same thickness of a single inorganic barrier [17].

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However, it is still quite challenging to overcome the brittle property of inorganic materials.

In summary, the moisture barrier for flexible OLEDs (FOLEDs) requires a complicated and longer diffusion path as well as flexibility. We strategically introduced a nanolaminate structure to the multi-barrier system to satisfy these conditions. With the nanolaminate barrier approach, each inorganic layer effectively blocks the pinholes in the layers adjacent to each other which are the main diffusion path of oxygen and moisture. Moreover, the multi-barrier approach provides better bending characteristics compared with a single inorganic layer. By introducing the nanolaminate structure with the same thickness as a single inorganic layer in a multi-barrier system, we fabricated an extremely complicated hybrid nano-stratified moisture barrier with a thickness of just 330 nm. The hybrid nano-stratified moisture barrier has not only a low WVTR compared to normal multi-barriers but also more flexibility than that of general nanolaminate barriers. Finally, we fabricated a FOLED with the hybrid nano-stratified moisture barrier encapsulation. The FOLED device had high reliability and flexibility and showed stable and identical performances.

2. Experimental setup

2.1. Electrical Ca test

The electrical Ca test, which is based on the electrical corrosion of Ca metal, was done to estimate the WVTR [18]. The procedure for the Ca test was identical to that in a previous study [19]. First, the Al electrode with a height of 100 nm was deposited onto a glass substrate (2.5 cm × 4 cm). Next, the Ca pad was also deposited onto the glass substrate by thermal evaporation which had a total area of 1.5 cm^2 and a thickness of 250 nm. In this part, the window area of the Ca pad was equal to the permeation area. On the other hand, the 125-μm thick PET coated by the barrier functioned as a test sample for the Ca test. With these Ca pad coated glass and test samples, the barrier-coated film was attached with the Ca sensor using a UV-curable sealant (XNR5570-Ba, Nagase Chemtex). As a support, an additional guide glass-lid with a hole at the center was used on the barrier-coated film. A thin 2.5 mm UV-curable sealant line was applied with a syringe followed by the guide glass with a dispenser. During the UV-curing, the Ca test sample was pressured by large glasses for stable encapsulation. All processes were conducted in a glove box (climate chamber) in an N_2 environment which was connected to a thermal evaporator. Finally, the prepared Ca test samples were kept in the climate chamber at 30 °C and 90% R.H., and then, the change in resistance was recorded in situ using a four-point probe system (Keithley 2750).

2.2. Barrier coating and device fabrication

For the hybrid nano-stratified moisture barrier structure, Al_2O_3 and ZnO were used as the materials of nano-stratified structure. Al_2O_3 and ZnO were deposited with a thermal atomic layer deposition (ALD) system at a chamber temperature of 70 °C. Trimethylaluminum (TMA) and H_2O were used as a precursor and reactant for the Al_2O_3, while diethylzinc (DEZ) and H_2O were used for the ZnO. One cycle of the deposition process consisted of a 0.2 s precursor (TMA or DEZ) pulse, 10 s precursor (TMA or DEZ) purge, 0.2 s reactant (H_2O) pulse, and 10 s reactant (H_2O) purge, successively. Nitrogen gas was used as the carrier and purge gas.

A silica nanoparticle-embedded sol-gel organic-inorganic hybrid nanocomposite (S-H nanocomposite) was studied in a previous work [20]. Nanopox® E600 (Nanoresins, Germany), based on methyl-terminated silica nanoparticles dispersed in a reactive diluent of 3,4-epoxycyclohexyl methyl 3,4-epoxycyclohexane carboxylate (EMEC) was mixed with UV-curable cycloaliphatic-epoxy hybrid materials (hybrimer) and synthesized via a sol-gel reaction between [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (ECTS) and diphenylsilanediol (DPSD) which was prepared in a previous study. The organic layer comprised of S-H nanocomposite was spin-coated at 4000 RPM for 3 s and subsequently UV-cured by I-line UV light (λ = 365 nm, optical power density = 20 mW/cm^2) for 100 s. With this method, 120 nm S-H nanocomposite layer was spin-coated, and the thickness of the layer was measured with a surface profiler (Dektak-8, Veeco, USA). To remove the residual solvent, the barrier film was kept in a vacuum chamber with a high purity N_2 gas flow (99.99999%, 100 sccm) for 30 min after the deposition. When storing the samples in the vacuum chamber, the vacuum level was maintained at 1.2 Torrs during the drying time. All organic and inorganic layers were alternately coated onto a 125-μm thick PET substrate.

Bottom-emitted type FOLEDs were also fabricated on 125-μm thick PET substrates. The FOLED devices had the following structure: ZnS (25 nm)/Ag (7 nm)/MoO_3 (5 nm)/NPB (50 nm)/Alq_3 (50 nm)/Liq (1 nm)/Al (100 nm). A multi-layer electrode (ZnS/Ag/MoO_3) was used for the anode because of its flexibility [21]. Meanwhile, molybdenum trioxide (MoO_3) and N, N′-bis(1-naphthyl)-N, N′-diphenyl-1,1′-biphenyl - 4, 4′-diamine (NPB), respectively, functioned as a hole-injection layer (HIL) and a hole-transport layer (HTL). The emitting layer was deposited with a green emitting material, tris(8-hydroxyquinolinato)aluminum (Alq_3), which was also used as an electron-transport layer (ETL). Finally, 8-hydroxyquinolinolato-lithium (Liq) and Al were used as an electron-injection layer (EIL) and as the cathode, respectively. Finally, the devices were passivated by thin-film encapsulation (TFE) comprised of a hybrid nano-stratified moisture barrier with an identical barrier coating method. The J-V-L characteristics were measured with a source meter (Keithley 2400) and a spectrophotometer (Minolta CS-2000).

3. Results and discussion

3.1. Fabrication and WVTR performance of hybrid nano-stratified moisture barrier

The hybrid nano-stratified moisture barrier consists of an Al_2O_3/ZnO nano-stratified stack and S-H nanocomposite. The thickness of each layer is 30 nm and 120 nm, respectively. In the case of the nano-stratified stack, 5 pairs of Al_2O_3 (3 nm) and ZnO (3 nm) are included which is optimized by Ca test described in the Fig. S1 and Table S1. The Fig. 1a shows one dyad stack comprised of a nano-stratified structure and an organic layer with nano-stratified structure. This dyad stack is used as a basic unit for fabricating the hybrid nano-stratified moisture barrier. With these layers, the hybrid nano-stratified moisture barrier consists of a 2.5 dyad stack with a total thickness of 330 nm. Fig. 1b shows a high-resolution transmission electron microscope (HRTEM) image of 2.5 dyads of the hybrid nano-stratified moisture barrier on a Si wafer. A specific image of a one dyad stack is shown in Fig. 1c, and all the layers are well deposited in the whole structure. The HRTEM image was taken with a FEI company instrument (USA, Tencai TF30 ST).

The normalized conductance change with the time duration of the hybrid nano-stratified moisture barrier was measured with the electrical Ca test, and a detailed method of the Ca test is described in section 2.1. The inset in Fig. 2b is a schematic diagram of the Ca pad. With a normalized conductance vs time graph, the WVTR of the barrier can be calculated [16]. Fig. 2a and Table 1a show the WVTR values for various 30-nm single layer, Al_2O_3, ZnO, and nano-stratified structures comprised of 5 pairs of Al_2O_3 (3 nm) and ZnO (3 nm). The Al_2O_3 is known as the best material for a homogeneous