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Characteristics of ITO and Overcoat Layer for Full Color Organic Light Emitting Diode with Color Filter

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In order to fabricate organic light emitting diode (OLED) on color filter layer for full color OLED, we estimated the property of water absorption of the overcoat (OC) layer and indium tin oxide (ITO) on the OC layer. During ITO patterning process, OC layer was exposed water and absorbed that. Due to property of water absorption of overcoat layer, devices on overcoat layer showed the low efficiency and short life time. Especially, in the device with overcoat, dark spot happened very seriously. To solve this problem, the heat treatment process was added to desorb water from OC layer and the SiO_2 *buffer layer was adopted as the blocking layer for water to sink through OC layer. Lifetime of device with suggested structure and process was improved dramatically over twenty times.*

Keywords: color filter; dark spot; full color; indium tin oxide (ITO); organic light emitting diode (OLED); overcoat (OC)

INTRODUCTION

Nowadays, full color organic light emitting diode (OLED) panels have been generally manufactured by vacuum evaporated patterning method with shadow masks. However, this process has serious problems by using the shadow masks, which are the limited aperture ratio, the limited substrate size and the high cost. In order to solve the serious problems by fine shadow mask, full color OLEDs with color filter (CF) have been suggested [1,2]. This method composed as the white OLED

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on the CF, where CF has a similar structure with liquid crystal display. So it has been expected to realize high resolution, large size and low cost process easily. However CF based OLED devices involve a problem of dark spots due to remaining moisture in the CF layer [3].

Dark spot is known as one of the major failure mechanism of OLEDs, however there are many different causes for the dark spot formation. The major origin of dark spot is the reaction between cathode material and moisture penetrated through cathode pinhole during operation [4,5]. Another cause is a local electrical short between the cathode and anode [6]. Also, lifetime of OLED is very sensitive to indium tin oxide (ITO) as anode [7,8]. By the way, in the OLEDs on color filter, ITO and device are deposited on the overcoat (OC) layer that is coated on the black matrix and red, green and blue color filer. Here, OC layer is a polymer material, polyacrylate. Therefore properties of ITO, such as roughness, work function, morphology and sheet resistance are varied to compare with ITO that is deposited on the bare glass substrate. Consequently, the absorbed moisture in the CF and OC could pass to OLED through pinhole and deteriorate device properties. And the incongruent ITO on OC deteriorates device properties and induced the dark spot [3].

To solve these problems, we estimated the water absorption and desorption of OC and investigated the properties of ITO on OC layer as process and buffer layer, SiO_2. And then we fabricated OLED on OC layer and analyzed effects of ITO and OC.

EXPERIMENTAL

We prepared various samples to estimate the properties of OC layer by process. Samsung Corning glass substrates (5×5 cm) were thoroughly cleaned with detergent and alkali cleaner in ultrasonic bath followed a rinse in deionized (DI) water and dried in N_2 blow before OC coating. To simplify process for estimation, we adopted OC/glass structure without CF below OC layer, because OC layer has enough thickness of 2.3 μm to ignore water absorption of CF. An OC (Dongjin Semichem, DOC-HA33) that was made of acrylic co-polymer was coated on the bare glass by a spin coater and baked in oven of 110°C for 20 min. Hard baking was done in oven of 230°C for 30 min after exposure with 100 mJ/cm^2. The morphology of OC as cleaning and drying after hard baking was analyzed by atomic force microscope (AFM, PSI, XE100). The water absorption was estimated by Ca test. Ca with 50 nm thickness was deposited on the pre-treated OC layer and then Ag with 200 nm thickness was deposited on Ca layer, sequentially. Sample was encapsulated in the glove box without being exposed to the air by a glass cap and UV curable sealant. On this occasion, getter was not included. Samples for Ca test were kept in a thermo-hygrostat chamber, 60°C/80% RH. The degree of oxidation of Ca in the sample was observed by microscopy.

We deposited on different substrates, the bare glass and the OC layer on the bare glass and then fabricated OLEDs. ITO was deposited on the OC layer at 200°C by super density arc plasma ion plating (SDAP-IP) method. ITO was patterned by photolithograph and wet etching. Fabricated devices were composed as this structure, ITO\2-TNATA\NPD\Alq3:C545T\Alq3\LiF\Al. Where 4,4′,4″-tris(N-(2-naphthyl)-N-phenyl-amino)-triphenylamine (2-TNATA) 4,4-bis[N-(1-naphtyl)-N-phenyl-amino]biphenyl (α-NPD), tris-(8-hydroxyquinoline)-aluminum (Alq3) and (10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one) (C545T) were used as hole injecting layer, a hole transporting layer, a host for the emission layer and electron transport layer and a dopant for the emission layer, respectively. Devices on the different ITO and OC layer were fabricated by thermal evaporation in vacuum. Devices were encapsulated with a glass cap and UV curable sealant and without getter. Current-voltage (I-V) characteristics were measured with an experimental set-up consisting of a Keithley 2400 source meter with calibrated photodiode. Measurements and data acquisition were controlled by National Instrument's LabVIEW software. A Spectroradiometer (Minolta CS1000) was employed for measurements of the electroluminescence spectrum. All the devices have the emitting area of $4 \times 6\,\mathrm{mm}^2$.

RESULTS AND DISCUSSION

For fabrication of full color OLED with CF, ITO on OC layer was patterned by wet process. This process makes OC layer to contact etchant in the solution state and DI-water. So, in this processes, OC layer is able to absorb water. In order to analyze water absorption of OC layer as process step and condition, four sample types were treated as follows.

Sample 1: OC was formed by standard process until hard baking.
Sample 2: OC of Sample 1 was rinsed with DI-water and blown by N_2.
Sample 3: Heat treatment was carried out using OC of Sample 2 at 150°C for 30 min.
Sample 4: Heat treatment was carried out using OC of Sample 2 at 230°C for 30 min.

We estimated the degree of water absorption by Ca test. Figure 1 shows the results of Ca test after storage for 60 h in a thermo-hygrostat

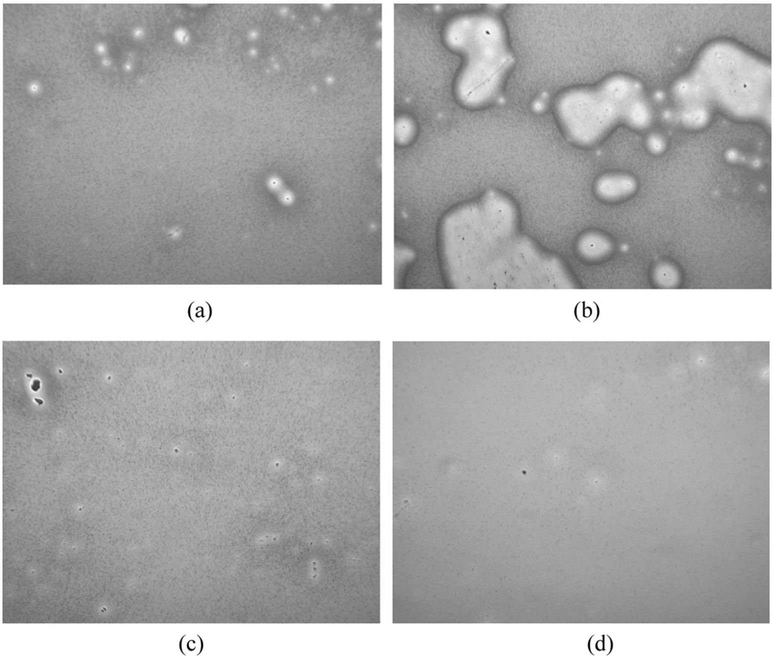

FIGURE 1 Image of Ca layer on OC layer after Ca test in 60°C/80%, RH (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.

chamber, 60°C/80% RH. Despite of encapsulation with UV epoxy and glass, oxidized Ca in the sample 1 is observed. In the case of sample 2, oxidized phenomena happen very seriously, so N_2 blow is the only limited method to eliminate water from the surface of water. However due to heat treatment, oxidation is dramatically decreased. And sample 4 is little detected oxidized region. It seems that OC layer absorbs much water during OC layer exposed to water. So it necessarily required to remove the absorbed water in OC layer. Most of absorbed water in OC layer are eliminated by the heat treatment at 230°C for 30 min that is same condition for initial hard baking of OC layer.

Table 1 represents the surface roughness of sample 1–4 by AFM measurement. The surface roughness characteristic of OC layer is measured by three definitions, R_a, R_{rms} and R_{pv}. Because the high R_{pv} is got by spike and the R_a and R_{rms} is by wrinkles, R_{pv} has a stronger influence than R_a or R_{rms} on the instability of OLED [8]. Sample 1 has the lowest R_{pv} of 4.03 nm. As OC is contacted to water, its surface becomes rougher. Heat treatment process improves the surface roughness in the sample 3 and 4, but does not recover as sample 1. R_a and

TABLE 1 Surface Roughness of Sample 1–4 by AFM Measurement

	R_{pv} (nm)	R_{rms} (nm)	R_a (nm)
Sample 1	4.030	0.513	0.409
Sample 2	4.983	0.530	0.419
Sample 3	4.893	0.457	0.363
Sample 4	4.749	0.618	0.498

R_{rms} become worse by a rinse of water, too. R_a and R_{rms} of sample 4 show highest values to compare other samples.

ITO is deposited at 200°C by SDAP-IP method. Before ITO deposition, OC layer is cleaned by cleaning solution, rinsed with DI-water and then heat treated in the loading chamber at 150°C for 30 min in vacuum. Surface roughness, R_{rms} of ITO on bare glass and OC is 0.553 nm and 1.015 nm, respectively. And etching rate for ITO with 150 nm on each other substrate is different 320 sec and 270 sec. But sheet resistance is little different, 9.8 Ω/sq and 10.1 Ω/sq.

Figure 2 shows these devices properties, voltage-current density and voltage-efficiency. After ITO patterning, sample was heat treated at 150°C for 30 min. The device on OC layer had higher current density at same voltage than without OC. And turn on voltage of device on OC is lower than OLED on bare glass. However device on OC shows lower

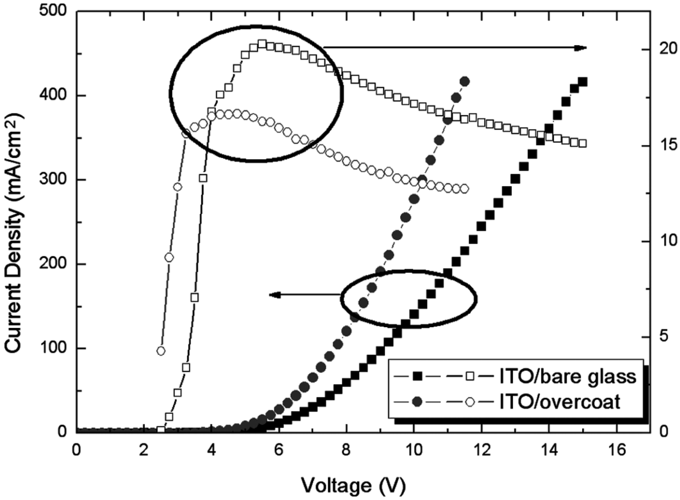

FIGURE 2 I-V-E curves of fabricated devices with/without overcoat layer.

brightness, so its peak efficiency of device on OC was 16 cd/A, it was lower value than without OC, 20 cd/A. Also device on OC shows the short lifetime and the serious dark spots. Dark spot occupies over 20% in the emitting area after working for 5 h.

To solve these serious problems, we deposited SiO_2 under ITO layer, where SiO_2 is an adhesive layer between OC and ITO and blocking layer for water to sink through OC layer. SiO_2 is deposited by sputtering and then ITO is done sequentially without break vacuum. We test two kinds of SiO_2 with 5 nm and 30 nm thickness.

Table 2 shows the roughness of ITO (150 nm)/SiO_2 (30 nm)/OC and SiO_2 (30 nm)/OC layer as a function of heat treatment. ITO is deposited on SiO_2 (15 nm and 30 nm)/OC and patterned by photolithography and wet etching. Sample 5 is the state after rinse with DI-water and N_2 blow. Heat treatment of sample 6 and 7 are done in oven at 150°C and 230°C for 30 min, respectively. As drying temperature is increased, surface roughness becomes deteriorate. Contrary to Table 1, as OC experiences a few heat treatment processes, such as baking, drying and photolithograph, its roughness is increased by steps. Although rough morphology could be lower properties of device, heat treatment process to remove water absorbed in OC must be required. Therefore, the trend-off to modify roughness and elimination of water must be needed.

Figure 3 shows life time of fabricated devices as buffer layer thickness and drying temperature. Drying was done after ITO patterning. Initial brightness is 1000 cd/m^2. In the case of absent buffer layer, device has a very short lifetime, about 5 h. Drying at 150°C for 30 min min improve lifetime as about 2.5 times. Masaru reported water penetrate by pinhole in the SiO_2 layer and reach the OC layer [3]. And this moisture induces explosive degradation due to the gasification. The lifetime of device with SiO_2 that is not carried out drying process is shorter than without SiO_2 and drying. So SiO_2 of 5 nm thick is not

TABLE 2 Surface Roughness of Patterned ITO and Exposed SiO_2/OC in the Sample 5–7 by AFM Measurement

		R_{pv} (nm)	R_{rms} (nm)	R_a (nm)
Sample 5	ITO/SiO_2/OC	12.377	1.645	1.310
	SiO_2/OC	10.362	1.194	0.946
Sample 6	ITO/SiO_2/OC	15.687	1.960	1.556
	SiO_2/OC	17.990	2.207	1.764
Sample 7	ITO/SiO_2/OC	15.543	2.006	1.578
	SiO_2/OC	27.418	3.365	2.454

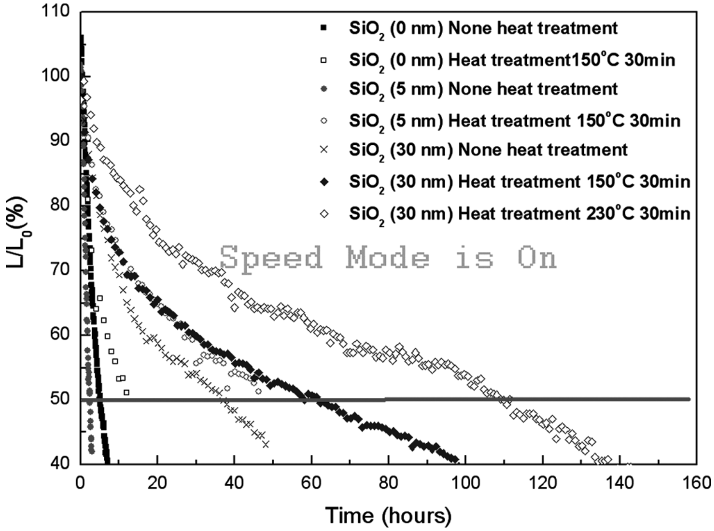

FIGURE 3 Life time of fabricated devices as a function of SiO_2 layer and heat treatment condition.

sufficient to block off water penetration to OC layer. And it is difficult to release absorbed water in OC layer without drying process. However it seems that the absorbed moisture gets out during working. Also the device has a short lifetime and many dark spots. However explosive degradation due to the gasification is not detected. The SiO_2 layer of 30 nm thick prevents water penetration into OC layer, so its lifetime is increased than without SiO_2 layer. The device with drying at 230°C shows the longest lifetime, about 110 h.

CONCLUSIONS

The development of OLED with color filter has been required to realize full color OLED with high resolution and large size. However for this method, ITO must be deposited on the polymer, OC layer, so ITO has different properties with ITO on the bare glass and it induces to short life time and the low efficiency. Especially, OC layer has the property to absorb water, so it induce dark spot and short lifetime. We tested the heat treatment process to desorb the water from OC and the SiO_2 buffer layer to prevent penetration of water to OC layer. Although heat treatment at high temperature deteriorates surface roughness, absorbed water could be eliminated by drying. In order to block infiltration of water, SiO_2 was required thick enough over

30 nm. Lifetime of device with these treatments was improved over twenty times.

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