Al Top Cathode Deposition on OLED Using DC Magnetron Sputtering

Tae Hyun Gil,* Christian May, Hubert Lakner, Karl Leo, Stefan Keller

We fabricated OLEDs having the evaporated Yb cathode and the sputtered Al cathode. Magnetron sputtering is a versatile deposition method, but the energetic particles during sputtering process can damage the underlying organic layers. We applied various process parameters to explain the role of Ar neutrals quoting the former researches. OLEDs showed almost comparable degradation under the discharge voltage of 300 V, but serious degradations were found at the discharge voltage of over 300 V and the low process pressure. The degradations influenced on the lifetime of OLED, and the measured luminance decay was much larger than the OLED having the evaporated Yb cathode due to the high leakage currents.

Introduction

OLED are versatile self-emitting devices and their application for large-area lighting is being expected due to high brightness and relatively simple fabrication process. During the last decade, enormous efforts have been undertaken to improve OLED efficiency and develop more efficient materials. The most remarkable developments in organic materials were the utilization of organo-transition metal compounds consisting of triplet emitters[1,2] and the introduction of doped transport layers in order to enhance carrier transport property.[3] OLED structures are usually classified into bottom emission (BE), top emission (TE), and transparent OLED (TOLED) according to the combination of the sandwiched two electrodes. For realization of OLED lighting, currently the BEOLED structure is preferred. Homogeneous electrode properties are required for uniform luminance in lighting panels. OLED have two of electrodes: the anode where holes are injected into organic semiconductor and the cathode where electrons are injected. As an anode material, transparent conducting oxides (TCO) are widely used for optical transparency of generated light. The deposition method is usually magnetron sputtering using reactive gas. In case of cathode deposition on organic layers, vacuum evaporation is used because the organic materials are vulnerable to high energetic particles. However, vacuum evaporation has several demerits like high outgassing rate and limited material selection due to the different vaporizing temperature. A challenging issue of vacuum evaporation for large-area applications is to achieve a homogeneous film thickness. From this point of view, magnetron sputtering may help to overcome these problems. Many researchers have attempted to utilize magnetron sputtering for top contact deposition,[4,5] and the damage of organic materials from high energetic particles from sputtering was also reported.[6] However, a detailed approach to explain a degradation mechanism has not been performed yet, and results depending on sputtering process parameters were not reported.

Rossnagel has reported an effect of energetic particle bombardment of films.[7] According to this study, the local gas density near a magnetron cathode gives rise to large changes in sputtering process. The local gas density near the cathode is calculated according to Equation (1).

\[
n_g = \left( \frac{2n_0T_w}{E_uY \sigma} \right)^{1/2} I^{-0.5}
\]

where \( n_0 \) is the original gas density, \( T_w \) the wall temperature, \( K \) the thermal conductivity of the gas, \( E_u \)
the average kinetic energy of the sputtered atoms, $Y$ the sputter yield, $\sigma$ the cross-section for momentum transfer, and $f$ the number of mean free paths away from the cathode before the particle is considered “thermalized.” As seen in Equation (1), the local density is a strong function of discharge current $I$, and a significant percentage of the background gas may leave the near-cathode region as the discharge current increases. Consequently more neutralized energetic species can arrive at the surface of the substrate, and they can influence the structural properties of the film. If the surface is organic material, the Ar neutrals will destroy organic molecules and cause a significant defect inside the organic layers. The bombardment rate of energetic species is, however, almost constant as the chamber pressure increases, and only the deposition rate is decreased. This is a discrepancy to Equation 1, and can be explained by the collision cross-section. Energetic neutrals may have kinetic energy up to several hundred eV, whereas the sputtered atoms have energy of typically a few eV. Because of the different energies, their collision cross-sections are quite different. The collision cross-section of the sputtered atoms is usually much larger than those of the energetic neutrals. Hence the generated neutrals may not collide with gases in low pressure glow discharge keeping their arriving flux constantly. The sputtered atoms, however, collide often with gases, and fewer atoms contribute to film growth. As the pressure decreases, there is a gradual increase in the discharge voltage. The energy of neutrals is expected to become higher at lower pressure.

The object of this study is, therefore, to identify the role of energetic particles in sputtering process referring to the study of Rossnagel, and various sputtering parameters are applied to deposit aluminium on OLED. In terms of characterizing OLEDs, any changes of energetic particles are explained by phenomena in sputtering. The OLEDs are characterized and evaluated by typical I-V-L and lifetime measurements. Additionally, the surface roughness of deposited Al films is measured and compared with OLED results in order to explain the deposition mechanism more detail.

## Experimental Part

The OLEDs are fabricated in VES400 (Applied Materials, GmbH & Co. KG), worlds first vertical in-line OLED deposition system consisting of a lot of vacuum chambers as shown in Figure 1.[8,9] In-line type deposition machines have been using in many semiconductor and display mass-production lines due to their high throughput. The implementation of the vertical design has two main advantages: one is less particle contamination and the other is that for large area glass and masks, the problems of bending are avoided.

The anode ITO film of 90 nm is deposited on a glass substrate. The size of active area of 79.6 mm² is defined by the aperture of the passivation layer.

In the OLED stack, doped carrier transport layers (Novaled AG) were utilized to achieve low voltage operation, and emission layer consisted of $\alpha$-NPD (4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl) and Ir(MDQ)$_2$(acac) (Iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate)) as host and orange-red phosphorescent dye dopant was selected. The complete OLED stack for this study was ITO/NHT5:$\alpha$-NDP2/$\alpha$-NPD/$\alpha$-NPD:Ir(MDQ)$_2$(acac)/NET5/NET5:NDN1. The layer thicknesses were held constant for comparison. For a reference OLED, Yb was deposited on the organic layers by thermal evaporation in order to fabricate damage-free OLED. The Al cathode is deposited in the sputtering chamber (module 5 in Figure 1), and the target size is 88 x 478 mm². The results of deposition rate and current-voltage relations from the process parameters are tabulated in each following section.

## Results and Discussion

### Power Variation

Sputter power was varied from 100 to 500 W at fixed Ar flow rate of 500 sccm. The detailed process parameters and the corresponding dynamic deposition rates and current-voltage relations are indicated in Table 1.
The discharge current increases almost linearly as the power increases from 100 to 500 W, and the deposition rate increases at almost proportional rate of the discharge current while the sputter voltage increases from around 250 V. In this case, the substrate arrival rate of energetic neutral to atom condensing rate is balanced well, and the energy transfer from the neutrals to the condensing atoms has the same rate. Only the energy of neutrals can be varied by discharge voltage. The measured I-V-L characteristics are shown in Figure 2. The OLED having the evaporated Yb cathode shows very low current density at reverse voltage and high luminance which states low defect. The OLEDs having the sputtered Al cathodes show almost comparable current density over all voltage regimes, and they show higher current densities at reverse voltage which prevent degradation providing a current path through organic layers in OLED. Although the sputter voltage has been changed slightly according to the discharge power, the OLED does not exhibit a difference in I-V characteristics. It can be interpreted that the energy of Ar neutrals in cathode voltage range under 300 V may not be sufficient to result in a significant change. In order to identify any correlation between the energy of neutrals and the corresponding structural change on the surface, Al surface roughness of the fabricated OLEDs was measured by atomic force microscopy (AFM) within a area of $5 \times 5 \mu m$. The results and the AFM images are shown in Figure 3. From the AFM images, a change of the grain of Al film was observed, and the size of grain became larger as the power decreased. In conventional film growth mechanisms, grain size is increased as the deposition rate is decreased. However, the presence of hillocks means that a heat accumulation might exist in the film, which could result in a large strain. Considering the very long process time at DC power of 100 W, the thermal energy from the plasma could remain quite long in the layer system because there are not sufficient heat sink path. If the organic layers were degraded by this heat energy, the I-V curve should have shown a difference. Since no change was found, this result gives rise to a presumption that the degradation of OLED might occur mostly at the beginning of Al film deposition at the thickness range of few tenth of nanometers.

The OLED having the sputtered Al cathode show a driving voltage of 4.2 V, power efficiency of 7.7 lm/W, and current efficiency of 10.6 cd/A at 1000 cd/m² while the OLED having the evaporated Yb show lower driving voltage of 3.16 V, higher power efficiency of 12.14 lm/W, and current efficiency of 12.28 cd/A at 1000 cd/m².

The lifetime of the fabricated OLEDs were evaluated at different current densities of 10, 20, and 30 mA/cm². The results are shown in Figure 4. The luminance decays of the OLED having the sputtered Al cathode are much faster than the OLED having the evaporated Yb cathode as expected from higher leakage current.
Ar flow rates were varied from 100 to 500 sccm at a fixed discharge power of 500 W. The detailed process parameters and consequent dynamic deposition rate and current-voltage relations are indicated in Table 2.

An increase of the DC voltage and a decrease of discharge current are found as the pressure decreases from 0.5 to 0.1 Pa, and the deposition rate increases due to less collision with gases. As discussed above, the flux of energetic neutrals stays almost constant, and their energy can be varied as the discharge voltage. The measured I-V-L characteristics are shown in Figure 5. The pressure dependence on the deposition rate of sputtered atoms shows still clear results. Since the measurements of the flux and the energy of neutrals are difficult in our current system, we assume that the energy and the flux of energetic neutrals follow the explanation of Rossnagel. The measured leakage currents of the OLEDs exhibit a strong dependence of discharge voltage over 300 V despite of the higher deposition rate and the lower discharge current. The rate of the arriving flux of energetic neutrals to the condensing atoms might become lower as the pressure decreases. One may guess that the quickly deposited Al grains prevent the organic layers from energetic neutrals, but the results show an opposite tendency. When the higher energetic neutrals impinge onto the surface of organic layer due to the higher discharge voltage, they collide with condensed Al atoms transferring their high energy to Al atoms or penetrate through Al into the organic. During the collision procedure between Ar neutrals and Al atoms, Al atoms can scatter into the organic layers as well, which can result in an electrical short cut of anode and cathode as shown in the curve of Ar 100 sccm in Figure 5. Therefore the high reverse current density is attributed to the higher energy of neutrals, especially over discharge voltage of 300 V.

As discussed in Subsection 3.1, the degradation of OLED was also suggested to occur at the initial stage of Al deposition. In the pressure dependency, the degradation of organic layers seems to be formed early as well because the deposition rate is high at low process pressure. In other research, the maximum penetration depth of Ar neutrals of 400 eV existed at mostly around 20 nm from the surface of Al(111). This result also confirms the assumption of the time of OLED degradation.

We could not evaluate the lifetime of the fabricated OLEDs because the OLEDs processed at low pressure showed very short lifetime, generating quick short cuts so that they are not shown here.

**Table 2. Process parameters and deposition rates and current-voltage relations**

<table>
<thead>
<tr>
<th>DC power (W)</th>
<th>Ar (sccm)</th>
<th>Pressure (Pa)</th>
<th>Deposition rate (Arb. Unit)</th>
<th>Discharge voltage (V)</th>
<th>Discharge current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>100</td>
<td>0.1</td>
<td>24.86</td>
<td>364.4</td>
<td>1.37</td>
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<tr>
<td>500</td>
<td>300</td>
<td>0.3</td>
<td>18.7</td>
<td>320.5</td>
<td>1.56</td>
</tr>
<tr>
<td>500</td>
<td>500</td>
<td>0.5</td>
<td>14.75</td>
<td>308.8</td>
<td>1.62</td>
</tr>
</tbody>
</table>

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Conclusion

We successfully fabricated OLEDs having the evaporated Yb cathode and the sputtered Al cathode. The OLEDs were characterized by I-V-L and lifetime measurements. The OLED fabricated with sputtered Al cathode showed higher reverse current density and larger decay in luminance. In order to investigate the role of energetic neutrals, OLEDs were fabricated as various sputter process parameters. In the power dependence, the leakage currents of OLEDs were almost comparable under the discharge voltage of 300 V. From the Al surface roughness measurements, the point of time of degradation was identified to be in the initial stage of sputter deposition. In the pressure dependence, the I-V characteristics showed wide range of leakage currents over the discharge voltage of 300 V, and the leakage current increased as the discharge voltage increased. Such degradation might occur also at a initial stage of sputter deposition considering the quick organic surface covering by Al grains at low process pressure.

The OLEDs having the sputtered Al cathode showed a driving voltage of 4.2 V, a power efficiency of 7.7 lm/W, and a current efficiency of 10.6 cd/A at 1000 cd/m². The lifetime of the fabricated OLEDs were evaluated, and the results showed that the luminance decay of the OLEDs having the sputtered Al cathode was much larger than the OLED having the evaporated Yb cathode, which is due to the presence of high leakage currents from the energetic neutrals bombardment.

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Keywords: DC magnetron sputtering; organic light emitting diode; p-i-n OLED
