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C60 Modification of Al Anode for Efficient Hole Injection in Organic Light-Emitting Diodes

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An Al:C60 composite anode structure was developed to improve hole injection in organic light-emitting diodes. Work function of Al was shifted from 4.3 eV to 5.2 eV by the addition of C60 because of complex formation between C60 and Al. The current density in the device was improved by 10 times by using a composite anode structure because of low hole injection energy barrier between the composite anode and hole transport layer.

Keywords: C60:Al; composite anode; light-emitting diode

INTRODUCTION

Organic light-emitting diodes (OLEDs) were developed over 20 years ago and are now used in many applications, such as mobile displays, monitors, and flat screen televisions. Bottom emission-type devices have been commercially available in passive and active matrix devices for many years, but the use of top emission-type devices with reflective anodes and semi-transparent cathodes are still under development for use in active matrix devices.

Considerable research has been devoted to the development of anode and cathode structure in top-emission organic light-emitting diodes (TOLEDs). Currently, several different metal electrodes are being developed as reflective anodes for TOLEDs [1–12]. In order to be used as an anode for TOLEDs, metals, such as Ni, Cr, Ag, and Al, must possess a high degree of reflectivity and a high work function. Chen *et al*. reported that by modifying the Ag surface with UV/ozone,

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Ag could be used as an anode in top-emitting OLEDs [11]. Ozone treatment of Ag was able to shift the work function of Ag from 4.6 eV to 5.1 eV. Therefore, the hole injection from the Ag anode to the hole transport layer can be greatly improved by oxygen plasma treatment. Ni can also be used as an anode for TOLED due to its high work function of 5.2 eV and its high reflectivity. Al can also be used as an anode for TOLED. However, its relatively low work function of 4.3 eV limits its use to systems with p-type hole injection material [12]. The energy barrier of 0.7 eV with common hole injection materials and the driving voltage of the device was over 10 V. Therefore, Al is not a suitable anode for TOLEDs due to its poor hole injection efficiency and low light-emitting efficiency, in spite of its high reflectivity.

In this work, the work function of Al was modified by co-evaporation of Al with C60, which has a highest occupied molecular orbital (HOMO) of 6.2 eV. The composite anode of Al and C60 is expected to shift the work function of Al through the chemical interaction between Al and C60. The chemical interaction and current injection in the Al:C60 devices were investigated by changing the composition of the Al:C60 composite anode.

EXPERIMENTAL

Fabrication of OLED

OLED configurations used in this study were Al:C60 (200 nm)/NPB (50 nm)/CBP:Irppy$_3$ (30 nm, 5% doping)/Balq (5 nm)/Alq3 (25 nm)/LiF (1 nm)/Mg:Ag (20 nm). Glass substrates used for deposition of composite anodes were produced by Samsung Corning Company. N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine (NPB) was used as a hole injection and hole transport material. Light emitting material was a mixture of (4,4′-N,N′-dicarbazole)biphenyl (CBP) and tris(phenylpyridine) Iridium(Irppy$_3$). Biphenoxy-bi(8-hydroxy-3-methylquinoline) aluminum(Balq) was used as a hole blocking material and tris (8-hydroxyquinoline) aluminium(Alq$_3$) was used as the electron transport material. A LiF/Mg:Ag double layer was used as a cathode system.

Glass substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 15 min each and were dried at 120°C for 2 hr before use. Al:C60 anodes were deposited on the glass substrates at a thickness of 200 nm and at a pressure of 10^{-7} Torr. The composition was controlled by changing the evaporation rate of metal and C60 and by varying the concentration of C60 from 0% to 15%. Al and Al:C60 electrodes were exposed to UV-ozone for surface treatment and the glass substrate was subsequently transferred to the evaporation chamber. NPB was evaporated at a thickness of 50 nm as a hole transport layer and CBP:Irppy$_3$ phosphorescent light emitting layer was evaporated at a thickness of 30 nm and doping concentration was 5%. Balq thickness was 5 nm and Alq was evaporated at a thickness of 25 nm. LiF thickness was 1 nm and Mg:Ag was evaporated at a thickness of 20 nm. The organic materials were deposited at a base pressure of 5×10^{-7} Torr at a rate of 1 Å/s. After cathode deposition, the devices were encapsulated with glass lids.

Measurements

The current-voltage-luminance (I-V-L) characteristics of the devices were measured with Keithley 2400 source measurement unit and PR 650 spectrometer. Work function of the anode was measured with surface analyzer (Riken-keiki AC2).

RESULTS AND DISCUSSION

In general, C60 has extended surface orbitals and a bandgap of 2.6 eV. The lowest unoccupied molecular orbital (LUMO) of C60 was only 3.6 eV, which is low enough to accept electrons from common charge transport materials. C60 can be readily reduced and six-reversible one-electron reductions can be observed. Therefore, C60 can form covalent bonds with some metals and the properties of the C60 and metal can be modified by the chemical bond formation between C60 and the metals. Covalent bond formation was observed between C60 and Al, resulting in a change in the work function of the Al from 4.3 eV to 5.2 eV, which is suitable for anode applications in light emitting devices [13,14]. Therefore, the composite of C60 and Al is expected to play a role as an anode for OLEDs through chemical bond formation between Al and C60.

The chemical bond formation in Al:C60 was studied using X-ray photoelectron spectroscopy (XPS) to confirm the covalent bond formation in co-evaporated Al:C60 composite. Figures 1(a) and (b) show the C_{1s} and Al_{2p} XPS spectra of Al:C60 according to the C60 content in the composite. Pure Al has a metallic Al_{2p} peak at 72.4 eV and aluminum oxide peak at a high binding energy of 75.2 eV, which is due to the oxidation of surface Al. As the C60 is co-evaporated with Al, the peak intensity at 75.2 eV was increased, which is attributed to the aluminum oxide and Al-C bond. Assuming that the degree of oxidation of the Al and Al:C60 is similar, the increase of peak intensity at 75.2 eV may be ascribed to the chemical bond formation between Al and C60. The C_{1s} peak of C60 also confirms the chemical bond formation in Al:C60. C60 shows a strong carbon peak at 285 eV, while

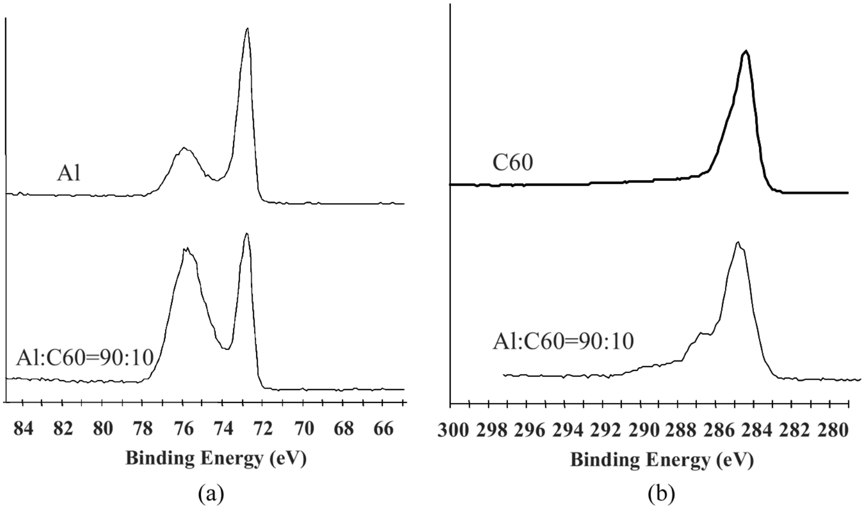


FIGURE 1 X-ray photoelectron spectra of Al:C60 (a) Al_2p spectra of Al and Al:C60; (b) C1s spectra of C60 and Al:C60.

Al:C60 has additional peaks at 287 eV and 289 eV which are assigned to the Al-C bond. The Al-C bond leads to the formation of a new peak with high binding energy due to the chemical interaction between the π orbital of C60 and Al.

The chemical bond state of Al:C60 greatly affects the electron density of Al and C60. This would have an impact on the work function of Al. The work function of Al was shifted from 4.3 eV to 5.2 eV by addition of C60, as measured with a surface analyzer (Fig. 2). The

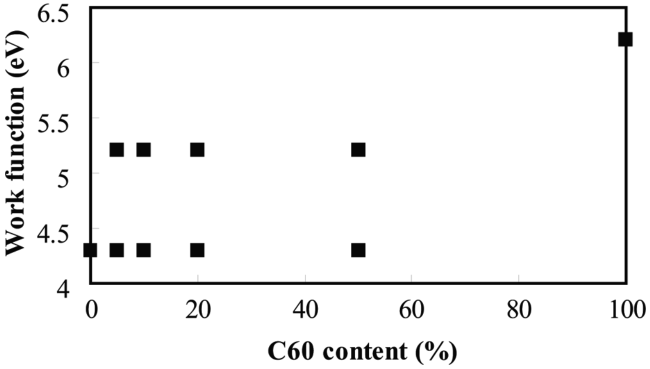
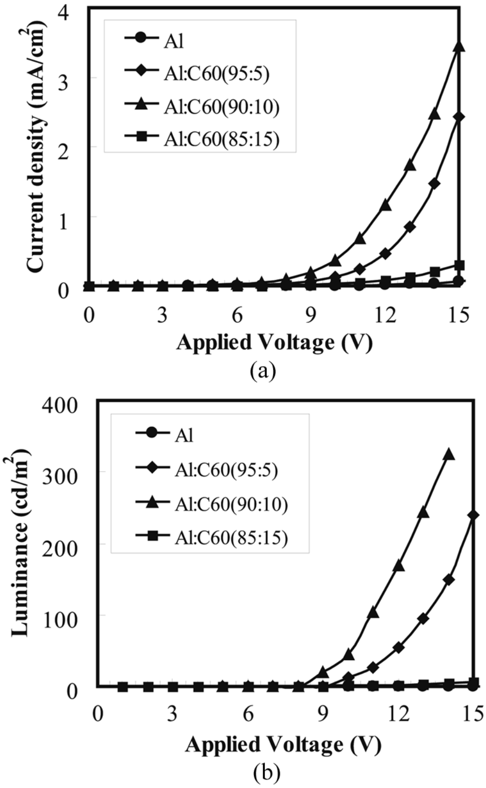


FIGURE 2 Work function levels of Al:C60 anodes according to C60 content.

Al:C60 composite showed two work function levels of 4.3 eV and 5.2 eV due to the coexistence of both pure Al and Al:C60 composite in the Al:C60 anode films. The work function of 4.3 eV is assigned to Al and the work function level of 5.2 eV is assigned to Al:C60. This result is in agreement with our results reported in previous paper about the Al (200 nm)/C60 (1 nm) double layer [14]. An identical work function level of 5.2 eV was obtained for the Al/C60 thin film, which indicates that the new work function level is due to Al-C60 complex formation. The position of the work function was independent of the C60 content in the Al:C60 anodes, while the change in relative intensity of the two energy levels was due to the composition of the anodes. The intensity of the peak at 5.2 eV was increased at high C60 concentrations. The evolution of the new work function level of 5.2 eV in Al:C60 composite



(a)

(b)

FIGURE 3 Current-voltage-luminance characteristics of Al:C60 devices. (a) Current-voltage curves of Al:C60 devices; (b) Luminance-voltage curves of Al:C60 devices.

anode would be beneficial to the hole injection from the anode into hole injection or hole transport layer because of low energy barrier between the anode and organic layer.

The relationship between current injection in the devices with the Al:C60 composite anodes and C60 concentration was also investigated. Figure 3 shows the current density and luminance of the Al:C60 devices according to C60 content in the devices. The current density of Al:C60 devices increased as the C60 content increases up to 10% and then decreased at 15%. In addition, the turn-on voltage was also lowered by the addition of C60 up to C60 content of 10%. The turn-on voltage of the pure Al device was 10 V, while the turn-on voltage of Al:C60 devices was 7 V. The low turn-on voltage in Al:C60 devices is closely related with the work function shift in the Al:C60 anode. The energy barrier between Al and NPB is 1.3 eV, while the energy barrier between Al:C60 and NPB is only 0.3 eV. The reduced energy barrier between the Al:C60 anode and NPB facilitates hole injection from anode to hole transport layer, resulting in the decrease of turn-on voltage [15–16]. The current density was high in the devices with high C60 content because the relative fraction of the chemically bonded Al-C60 was higher in Al:C60 with high C60 content. However, current density was decreased greatly at high C60 content over 10% because of high resistance and low reflectivity of Al:C60 composite anode. Even though work function of 5.2 eV could be obtained in the composite anode, sheet resistance of Al:C60 composite with 15% C60 was 800 Ω/□ compared with 4 Ω/□ of pure Al anode. In addition, reflectance of Al:C60 was only 70% of pure Al compared with 90% of Al:C60 with C60 less than 10% due to light absorbing character of C60. Therefore, 10% addition of

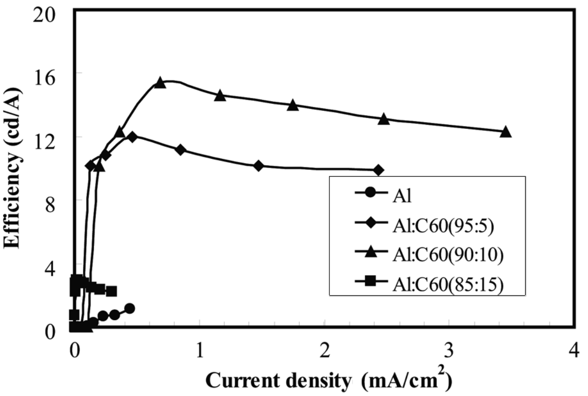


FIGURE 4 Current efficiency of Al:C60 devices.

C60 in Al anode was optimum to get high current density and luminance in C60 modified Al OLEDs. Luminance of Al:C60 devices showed the same tendency as current density and high luminance value was observed in 10% C60 containing Al:C60 anode structure.

Figure 4 shows current efficiency-current density curves of Al:C60 devices. Current efficiency calculated from the current density and luminance of Al:C60 devices was 15.4 cd/A compared with 1.1 cd/A of pure Al device. Efficient hole injection from Al:C60 composite anode to organic layer balanced hole and electrons in the emitting layer, resulting in high efficiency in the emitting layer.

CONCLUSIONS

In summary, the addition of C60 in Al improved the hole injection of OLED by chemical interaction between C60 and Al. Work function of Al was shifted from 4.3 eV to 5.2 eV by C60 modification and turn-on voltage of Al devices was lowered from 10 V to 7 V. The Al:C60 anode is promising as an anode structure for the OLED due to efficient hole injection from anode to hole transport layers.

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