The effect of fullerene on the device performance of organic light-emitting diodes

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Abstract

In this paper, we describe a versatile use of fullerene(C60) as a charge transporting material for organic light-emitting diodes. The use of fullerene as a buffer layer for an anode, a doping material for hole transport layer, and an electron transport layer was investigated. Fullerene improved the hole injection from an anode to a hole transport layer by lowering the interfacial energy barrier and enhanced the lifetime of the device as a doping material for a hole transport layer. In addition, it was also effective as an electron transporting material to get low driving voltage in the device.

1. Introduction

C60 has been used in solar cells because photoinduced charge transfer between C60 and conducting polymers leads to photovoltaic effect[1,2]. It has been found that the C60 can be used as a weak electron acceptor dopant in conducting polymers and the enhancement of photoconductivity was observed in C60/conducting polymer system[3]. However, the charge transfer between C60 and conducting polymers induces the electroluminescence quenching in C60/conducting polymer systems, which leads to little electroluminescescence in C60 containing devices. Therefore, C60 cannot be used with light emitting materials in OLED. Instead, it can be applied in other charge transport layers to modify the charge transporting properties of the device[4].

In this work, C60 was used as a charge transporting material or an additive to the charge transporting layer. It was applied as a buffer layer for an anode and as a dopant for a hole transporting layer. In addition, it was also used as an electron transporting material and the device performances of organic light-emitting diodes(OLEDs) was investigated.

2. Results

In general, the lowest unoccupied molecular orbital(LUMO) of C60 measured was only 3.6 eV, which is low enough to accept electrons from common charge transport materials. Therefore, C60 can form a covalent bond with some metals by charge transfer and the properties of the C60 and metal are modified by the bonding formation between C60 and metals. In case of C60 and Al, the covalent bond formation between C60 and Al was observed by charge transfer and the work function of the C60 monolayer adsorbed on Al was changed from 4.3 eV to 5.2 eV, which is suitable for the application as an anode for the light-emitting devices. Therefore, it is expected that Al and C60 can form a covalent bond at the interface between Al and C60 and the thin interface layer resulted from the complex formation can have positive effect on the hole injection from Al to hole transport layer by lowering the large energy barrier between Al and organic hole transport layer.

The chemical bond formation at the Al/C60 interface was studied using XPS to confirm the covalent bond formation at the interface. C60 was evaporated on Al surface to observe the change of the chemical bonding state of the interface. Figure 1 (a) and (b) show the Al2p and C1s XPS spectra of Al and Al/C60. Pure Al has a metallic Al2p 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. Al/C60 also shows two peaks at the same binding energy, but the intensity of the peak at 75.2 eV which corresponds to the oxidation of Al or Al-C bond formation greatly increased. Assuming that the relative intensity of the pure Al and aluminum oxide remains the same after evaporation of C60 on Al, the relative increase of the peak at 75.2 eV can be due to the chemical bond formation between Al and C60 by charge transfer from Al to C60. The C1s peak of C60 also confirms the chemical bond formation at Al/C60 interface. C60 shows a carbon peak at 286.0 eV and weak shoulder at 287.0 eV, while Al/C60 has an additional peak at 289.0 eV which is assigned to the Al-C bond. The Al-C bond leads to the formation of new peak at high binding energy due to the chemical interaction between the orbital of C60 and Al.

The chemical bond formation at the interface between Al and C60 is expected to give positive effect on the hole injection from Al to hole transport layer because the interfacial energy barrier can be lowered by the formation of interface dipole which changes the work function of Al. The work function value of the interfacial layer was estimated from the work function value of the mixed Al:C60 composite, giving work function value of 5.2 eV. Considering that the energy barrier between Al(4.3 eV) and NPB(5.5 eV) is 1.2 eV, the interfacial energy barrier of the Al/NPB devices can be decreased up to 0.3 eV by inserting C60 buffer layer at the interface. The energy level shift at the interface is described in Fig. 2. The charge transfer between Al and C60 leads to the interface dipole formation, which causes the work function shift from 4.3 eV to 5.2 eV.

Fig.3 shows the I-V and L-V curves of top emitting devices with different C60 thicknesses. The current density of the devices with C60 buffer layer on top of Al was much higher than that of the devices without C60, indicating that the interfacial charge transfer reaction between Al and C60 was effective to reduce the barrier for hole injection from Al to hole transport layer. The turn on voltage of the device with C60 was 5.5 V compared with 11 V for the device without C60. Comparing the current density of the devices with C60 at different C60 thicknesses, the current density increased up to thickness of 30 Å and then decreased at a higher thickness. This behavior can be explained by postulating that the Al surface can be effectively covered by depositing C60 up to 30 Å and then further evaporation of C60 on the surface slows down the hole transport from Al to hole transport layer because C60 is not a good hole conducting material. Hole injection barrier at the interface dominates the total hole injection from Al to NPB at a low C60 thickness range, while the poor hole transport through the C60 buffer layer contributes to the less hole flow at a high thickness range.

Fullerene was also effective as a dopant for the hole transport layer to get improved lifetime in the device. Figure 4 shows the lifetime curves of phosphorescent devices with C60 doped hole transport layer. It is clear from the figure that the lifetime increases as the C60 concentration in the TDAPB layer increases. The extrapolated lifetime, which is defined as the time at which the luminance of the device reaches 50% of initial luminance, is about 700 h at 2000 cd/m2 for pure TDAPB device, whereas the 3% C60-doped device showed a lifetime of 1400 h at 2000 cd/m2. The lifetime improvement in the C60-doped device can be explained by the electron trapping function of the C60 molecule. There are several factors to determine the long-term stability of OLEDs, which includes thermal and chemical stability of the material, electrochemical stability, balanced charge injection, and interfacial stability. Among these factors, electrochemical stability and charge balance of the material are critical to the lifetime of OLEDs. Common hole transport materials are open to electron attack and electron transport materials are open to hole attack, which may degrade the device performance. Therefore, it is essential to confine the electrons and holes in the light-emitting layer to get high long-term stability. Another way to get a long lifetime is to add a compound that can trap excess holes and electrons injected from the light emitting layer to stabilize the charge transporting layers. In the case of C60, it can absorb six electrons per molecule and it can play a role of an electron-trapping agent in the HTL. Excess electrons injected from the light-emitting layer are deactivated by the C60 molecule and the HTL can be stabilized against electron attack. The C60 can protect the TDAPB, which is also open to electron attack from electroninduced degradation. The hole trap effect that is observed in a rubrene-doped device cannot contribute to the lifetime improvement considering that the hole injection from the HTL to the light-emitting layer was enhanced in the C60-doped device.

Figure 5 shows the current density-voltage curves of the devices with C60 as an electron transport layer. The current density was increased greatly by using fullerene as an electron transport layer due to its high electron mobility and low energy barrier for electron injection from cathode to electron transport layer.

Another application of C60 is its use as an additive to Al to get enhanced hole injection in the device. The current injection in the devices with Al:C60 composite anode was investigated at different C60 concentrations. Fig. 6 shows the current density of the Al:C60 devices according to the C60 content in the devices. The current density increases as the C60 content in the anode increases and the turn-on voltage was also lowered by the addition of C60 in the anode. The turn-on voltage of the pure Al device was 10 V, while the turn-on voltage of Al:C60 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 anode and NPB in Al:C60 facilitates the hole flow from anode to hole transport layer, resulting in the decrease of turn-on voltage in the device. The current density was proportional to the C60 content because the relative faction of the chemically bonded Al-C60 was high in Al:C60 with high C60 content.

3. Conclusion

C60 was useful as an additive and a buffer layer to an anode to get improved hole injection and it improved the lifetime of organic light emitting diodes. In addition, it was also very effective as an electron transporting material due to its high electron mobility.

4. References

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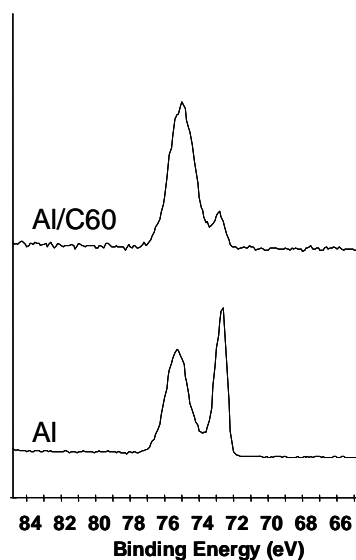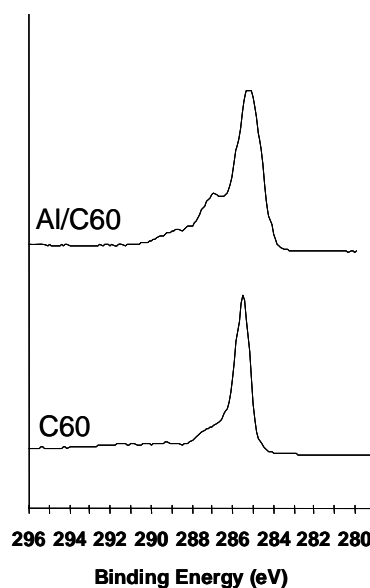
(b)

Figure 1. X-ray photoelectron spectra of Al, C60, and Al:C60

(a) Al2p spectra of Al and Al:C60

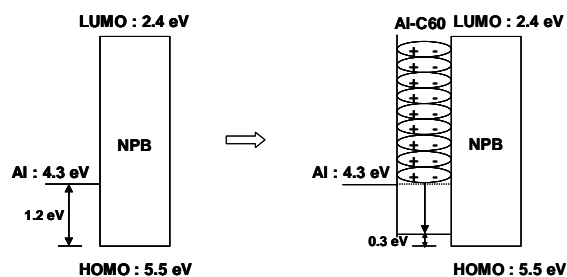(b) C1s spectra of C60 and Al:C60

(a)

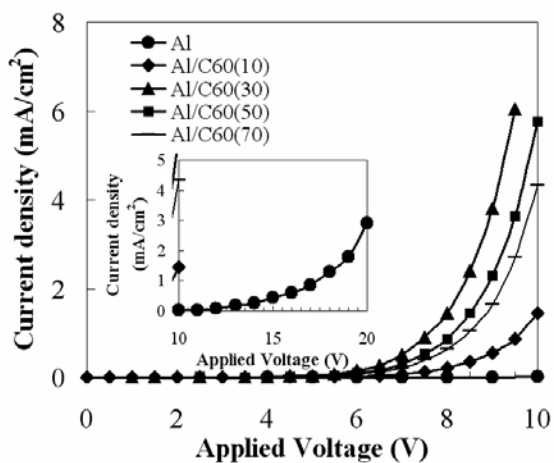Figure 2. The schematic diagram for the interfacial energy barrier shift

Figure 3. Current density-voltage curves of top-emitting organic light-emitting diodes according to the thickness of fullerene buffer layer.
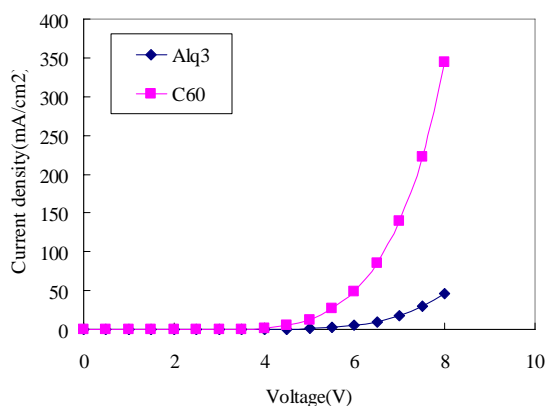

Figure 5. Current density-voltage curves of the devices with C60 as an electron transport layer.
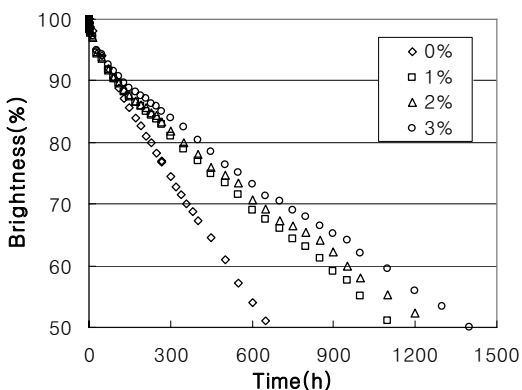

Figure 4. Lifetime curves of phosphorescent devices according to doping concentration of C60 in the hole transport layer.
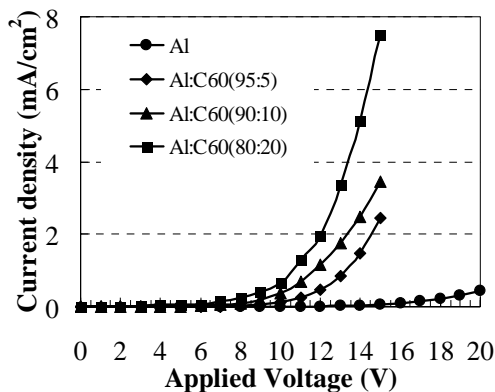

Figure 6. Current density-voltage curves of the devices with C60 as an additive to Al.