Optoelectronic Characteristics of Organic Light-Emitting Diodes with a Rb$_2$CO$_3$-Mixed C$_{60}$ Layer as an Electron Ohmic-Contact

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A rubidium carbonate (Rb$_2$CO$_3$)-mixed fullerene (C$_{60}$) layer was used as the electron ohmic-contact layer and the effect of Rb$_2$CO$_3$ mixing concentration on the optoelectronic properties of organic light-emitting diodes (OLEDs) was investigated. The performance of an electron-only device, with a glass/ITO/Rb$_2$CO$_3$-mixed C$_{60}$ (10 nm)/Al structure, was strongly dependent on both the thickness and the mixing concentration of the Rb$_2$CO$_3$ layer in the Rb$_2$CO$_3$-mixed C$_{60}$ thin films. The ultraviolet photoemission spectra of the Rb$_2$CO$_3$-mixed fullerene (C$_{60}$) layer showed the formation of new Fermi level crossing states, below the Fermi level caused by a chemical interaction between Rb species and C$_{60}$, and which led the n-mixing effect to the contact. The emergence of new FLCSs contributed to the formation of an electron ohmic-contact between the cathode and the organic layer by increasing the number of electron carriers. The OLED device with Rb$_2$CO$_3$-mixed C$_{60}$ as an electron ohmic contact layer, and composed of a glass/ITO/MoO$_3$-mixed NPB (25%, 5 nm)/NPB (63 nm)/Alq$_3$ (39 nm)/Rb$_2$CO$_3$-mixed C$_{60}$ (75%, 3 nm)/Al (150 nm) structure, showed better optoelectronic properties than the OLED fabricated with C$_{60}$ (5 nm)/LiF (1 nm) as the electron ohmic-contact layer. © 2012 The Electrochemical Society. [DOI: 10.1149/2.03830jess] All rights reserved.

The electron-only device was separately fabricated with the structure of glass/ITO/MoO$_3$-mixed N, N'-diphenyl-N, N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB, 5 nm)/NPB (63 nm)/tris(8-quinolinolato)aluminum (III) (Alq$_3$, 42-nm)[/Rb$_2$CO$_3$-mixed C$_{60}$ (y%, x = 3 nm)] or C$_{60}$ (x = 5 nm)/lithium fluoride (LiF, 1 nm)/Al (150 nm). MoO$_3$-doped NPB was used as a hole-injecting layer (HIL), NPB as a HTL, Alq$_3$ as both a green emissive layer and an ETL, Rb$_2$CO$_3$-mixed C$_{60}$ or C$_{60}$/LiF as an electron ohmic-contact layer to improve the driving performance of the OLEDs. The n-mixing effect of the Rb$_2$CO$_3$-mixed C$_{60}$ layer at various mixing concentrations and thicknesses was investigated according to the ohmic property in the electron-only device, the electronic structure around the EF, and the morphological property. Finally, we discuss the correlation between the device performance of OLEDs with this electron-ohmic layer and the n-mixing effects.

Experimental

The structure of the all-carrier ohmic-contact OLEDs is glass/ITO (about 10 μm, Geomate Co., Ltd.)/MoO$_3$ (25%)-mixed N, N'-diphenyl-N, N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB, 5 nm)/NPB (63 nm)/tris(8-quinolinolato)aluminum (III) (Alq$_3$, 42-nm)/[Rb$_2$CO$_3$-mixed C$_{60}$ (y%, x = 3 nm)] or C$_{60}$ (x = 5 nm)/lithium fluoride (LiF, 1 nm)/Al (150 nm). MoO$_3$-doped NPB was used as a hole-injecting layer (HIL), NPB as a HTL, Alq$_3$ as both a green emissive layer and an ETL, Rb$_2$CO$_3$-mixed C$_{60}$ or C$_{60}$/LiF as an EIL, and aluminum (Al) as the cathode layer. Each layer was sequentially vacuum-deposited by using a thermal evaporator system. The MoO$_3$ and Rb$_2$CO$_3$ materials were co-evaporated with NPB and C$_{60}$, respectively. The fabricated devices were encapsulated by depositing a bead of epoxy around the edge of the substrate, sticking another piece of glass on the bead, and curing the epoxy in a dry nitrogen box. The emissive active area of the devices was 2.0 mm$^2$.

The electron-only device was separately fabricated with the structure of glass/ITO/Rb$_2$CO$_3$-mixed C$_{60}$ (y%, x = 3 nm)/Al (150 nm). The mixing concentration (y%) of Rb$_2$CO$_3$ was varied from 5 to 75% and the thickness of the Rb$_2$CO$_3$-mixed C$_{60}$ thin film was varied from 10 to 70 nm.

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Organic light-emitting diodes (OLEDs) are novel light sources that offer attractive applications for flat-panel displays, flexible displays, and general-purpose lighting. For various applications, OLEDs have recently received considerable attention due to their rapidly improving efficiency and performance. The efficiency of OLEDs is extremely dependent on the carrier-injecting ability, which is related to the formation of resistance-free or ohmic contacts at the metal-organic interfaces. This carrier-injecting probability is strongly influenced by both the injecting barrier heights and the number of carriers in the thin film. Here, the injecting barrier height is defined in terms of an energy difference between the Fermi levels ($E_F$) of the electrodes and the relevant levels for conduction in the OLED. Therefore, appropriate aligning of the relevant levels in organic (or inorganic)-metal contact is necessary to maximize the luminous efficiency and minimize the power consumption by developing a low-voltage carrier-injecting layer.

OLEDs contain almost no intrinsic charge carriers due to their weak intermolecular coupling. In order to enhance the performance of OLEDs, the extrinsic carrier concentration needs to be increased by mixing. Strong electron acceptor and donor materials have commonly been adopted as dopants in organic hole-transporting layers (HTLs) and electron-transporting layer (ETLs) in OLEDs. Mixing these materials into HTLs and ETLs causes a charge transfer between the host and dopant materials, which markedly increases the free carrier concentration in these mixed layers and promotes the formation of an ohmic contact at electrode-organic interfaces.

The recent reports of several materials that yield extremely low-voltage devices has excited renewed interest in developing the next generation of contacting electrodes. As a p-type dopant, transition-metal oxides such as molybdenum oxides (MoO$_3$), vanadium oxides (V$_2$O$_5$), and ReO$_3$ are promising candidates to replace the previous generation of organic hole injection layers at the anode, due to their stability and their high work function (WF). Among these p-type carrier-injecting layers, MoO$_3$ and Rb$_2$CO$_3$ materials were co-evaporated with NPB and C$_{60}$, respectively. The fabricated devices were encapsulated by depositing a bead of epoxy around the edge of the substrate, sticking another piece of glass on the bead, and curing the epoxy in a dry nitrogen box. The emissive active area of the devices was 2.0 mm$^2$.

The electron-only device was separately fabricated with the structure of glass/ITO/Rb$_2$CO$_3$-mixed C$_{60}$ (y%, x = 3 nm)/Al (150 nm). The mixing concentration (y%) of Rb$_2$CO$_3$ was varied from 5 to 75% and the thickness of the Rb$_2$CO$_3$-mixed C$_{60}$ thin film was varied from 10 to 70 nm.
The current density (J)–voltage (V)–luminance (L) characteristics were measured using a source-measure unit (2400, Keithley Instrument Inc.) while the emission intensities from the OLEDs devices were measured by using the photocurrent induced on a silicon photodiode (71608, Oriel) with a picoammeter (485, Keithley Instrument Inc.).

The Rb2CO3-mixed NPB interfaces were examined by using UPS at the 4B1 beam line of the Pohang Accelerator Laboratory in Korea. All the measurements and depositions were performed in an ultra-high vacuum system, consisting of a main analysis chamber (approximately $5 \times 10^{-10}$ Torr) and a sample preparation chamber (approximately $5 \times 10^{-8}$ Torr). For the analysis, the Rb2CO3-mixed C60 (10 nm) layers with various mixing concentrations were prepared in situ by sequential thermal evaporation on a p-type Si wafer in an ultra-high vacuum system which was connected to the beam line in vacuum. All thicknesses were determined by timed deposition calibrated using a quartz-crystal microbalance. In the UPS measurements, the He I (21.2 eV) line from an ultraviolet source was used. The photoemission onset reflecting the WF at the surface of all samples was measured by biasing the samples at $-5$ V. The incident photon energy was calibrated by measuring the Au 4f level of a clean Au surface. The surface roughness of the deposited thin films was observed by atomic force microscopy (AFM, SPA-300HV, SII Nano Technology Inc.).

Results and Discussion

The charge injection efficiency and interface stability can significantly affect the overall device performance and lifetime of OLEDs. Especially for a particular driving voltage, a robust interface is required with no potential barrier to carriers in order to prevent any Joule heating at the electrode interfaces. In order to explore a new robust electron-ohmic contact to the cathode, a series of electron-only device with the Rb2CO3-mixed C60 was designed to obtain a resistance-free contact.

Figure 1a shows the J-V characteristics of the electron-only devices with the ITO/Rb2CO3-mixed C60/Al structure, as a function of the Rb2CO3 mixing concentration at a fixed thickness of 10 nm. Compared to the electron-only device with a mixing concentration of 5% Rb2CO3, the devices with a mixing concentration of 10% and above exhibit perfectly linear J-V patterns that are characteristic of a true ohmic contact at both the top and bottom interfaces. The electrical conductivities of the devices with mixing concentrations of from 10% to 75% were calculated to be about $1.5 \times 10^{-6}$ S/cm. However, when the Rb2CO3 mixing concentration was either 5% or below, the J-V curves showed non-linear relationships, which revealed that these interfaces were typically not pinned at the EF of electrodes and were thus strongly dependent on the Rb2CO3 mixing concentration. Figure 1b exhibits the J-V characteristics when the thickness of the Rb2CO3-mixed C60 layer was changed at the thickness of 30 nm. As the thickness of the mixed C60 increased from 10 nm to 30 nm above, the electron-ohmic-contact property of the EIL layer without the Rb2CO3 mixing concentration in the Rb2CO3-mixed C60 films, the structural change when the Rb2CO3 mixing concentration is changed in the Rb2CO3-mixed C60 films.

Figure 2a shows the valence band spectra and the region around the EF of the Rb2CO3-mixed C60 layers, respectively. In Fig. 2b, the intensities of all curves are normalized to the incident photon flux. The bottom curve represents the photoemission spectrum for the pure C60. The difference between the onsets of the HOMO level and EF of the Rb2CO3-mixed C60 film presents both HOMO-1 (at around 3.5 eV) and HOMO (at around 2.2 eV) features, which reveal higher intensities than those of pristine C60. In Fig. 2c, a new Fermi level crossing state (FLCS) feature, which is aligned at the EF such as a general metal and is partially formed by the chemical interaction between Rb species and C60, starts to appear at about 75%. The bias voltage was applied to the bottom electrode in reference to the top grounding electrode.
mixing concentration of 50% or higher. At the mixing concentration of 75%, the width of the FLCSs grows to about 1.3 eV, from below the EF. The changes of the UPS spectra on the HOMO and FLCSs are believed to be attributed to the formation of charge transfer complexes between rubidium species as an electron donor and C₆₀ as an electron acceptor in the Rb₂CO₃-mixed C₆₀ thin film. We suppose that the intercalation compounds of RbₓC₆₀ could be formed by two steps when Rb₂CO₃ is co-deposited with C₆₀. First, Rb₂CO₃ could be decomposed into Rb metal as a trace amount, Rb₂Oₓ (1 < x), and carbon dioxide (CO₂) during the thermal evaporation. Second, the Rb metal may be diffused into the neighboring vacant sites of C₆₀, leading to the formation of the RbₓC₆₀ intercalation compounds, as reported by other researchers.²⁸,²⁹ In the case of cesium carbonate (Cs₂CO₃) deposition reported by other researchers, when Cs₂CO₃ is evaporated, almost all of the CO₂ was easily outgassed from the Cs₂CO₃ material, resulting in a formation of Cs metals or cesium oxide layers.²⁰

Meanwhile, the phases, properties, and electronic structures of the Rb-intercalated C₆₀ have been well characterized by several techniques.³¹ Four stable phases have been reported for the RbₓC₆₀ crystal: Rb₁C₆₀, Rb₃C₆₀, Rb₄C₆₀, and Rb₆C₆₀. The intercalation of Rb atoms into C₆₀ results in the formation of RbₓC₆₀ with the NaCl structure and it functions as a conductor. RbₓC₆₀ with a face-centered cubic structure is a superconductor with a relatively high critical temperature. Rb₄C₆₀ is a non-conducting material with a body-centered cubic structure, and Rb₆C₆₀ is a semiconductor with a body-centered tetragonal structure.³²,³³

In our experiment, the Rb-intercalated C₆₀ complexes (Rb₁−₃C₆₀) might be formed by chemical interaction during the mixing of Rb₂CO₃ to C₆₀. The increase of HOMO-1 and HOMO levels as the mixing concentration was increased to 25% could related to the formation of conducting Rb₁C₆₀, compared to the Rb-intercalated C₆₀ complexes formed by the reaction between pure Rb metal and C₆₀.³⁴ The observed characteristic changes as the mixing concentration was increased from 10 to 25% indicated the increase of RbₓC₆₀ domains in the Rb₂CO₃-mixed C₆₀ thin film. The RbₓC₆₀ phase, in which a highly conducting state (or superconductance) occurs when the triad of degenerated LUMO acquires three electrons forming a half-filled band,³⁴ started to form at the Rb₂CO₃ mixing concentration of 50% or higher as the spectral weight of the FLCSs at the EF increased. The change of HOMO-1 and FLCSs intensities and the significant increase of FLCSs intensity near the EF at the Rb₂CO₃ mixing concentration of 50% or higher are believed to be related to the formation of the Rb₃C₆₀ phase. The characteristics for the RbₓC₆₀ (x = 1 - 3) formation in the UPS spectra coincided well with the synthetic mechanism of Rb-intercalated metallic Rb₃C₆₀ reported by other researchers.²⁸,²⁹,³¹

Fig. 3 exhibits the onset of the energy levels (WF, FLCS, and HOMO) in the Rb₂CO₃-mixed C₆₀ film, obtained from the results of Fig. 2. The HOMO level of the Rb₂CO₃-mixed C₆₀ film was shifted within 0.2 eV, and thus did not exhibit any significant change as the mixing concentration was increased from 10 to 75%, when compared to that of the C₆₀ film. On the other hand, the combined effect of the WF lowering and phase transition, and the occurrence of a new FLCSs below a EF of 0.7 eV, due to chemical interaction between Rb species and C₆₀, not only reduced the electron injection barriers but also increased the electron concentration in the organic films, thereby explaining the improvement in the electron ohmic property, as shown in Fig. 1. These results demonstrated that Rb₂CO₃ can serve as an effective n-type mixant when mixed with C₆₀. In addition, the charge transfer complexes formed at the mixing concentration of 50% and
higher can also improve the electron-ohmic contact property of the Rb2CO3-mixed C60 film. Figure 3b shows the proposed energy band diagram at the Alq3/Rb2CO3-mixed C60/Al interfaces. The electrons were efficiently injected from the EF of Al to the FLCSs partially formed by chemical interaction between Rb species and C60, which exists as a little amount in Rb2CO3-mixed C60, and could be transported by hopping from the FLCSs of the Rb2CO3-mixed C60 layer to the LUMO level of Alq3. Figure 4a shows AFM images of the surfaces of pristine C60, Rb2CO3-mixed C60, and pristine C60 thin films deposited on p-Si wafer. The thicknesses of all films were maintained at 10 nm. The Rb2CO3 mixing concentration in the Rb2CO3-mixed C60 thin films was 0, 10, 25, 50, 75, and 100%, respectively. Figure 4b shows the change of root mean square (RMS) roughness as a function of the Rb2CO3 mixing concentration in C60. As the mixing concentration increased from 0 to 50%, the RMS roughness of the Rb2CO3-mixed C60 thin film was increased from 8.9 to 18.9 Å. At a mixing concentration of 75%, the RMS roughness decreased to a very smooth level of 4.6 Å. This abrupt change of RMS roughness may have been related to the phase transition occurring between the two materials from Rb1C60 to Rb3C60. This smooth morphological property at a mixing concentration of 75% was expected to contribute to the stable electron-injection at the electrode-organic interface in OLEDs.

To fabricate the all-carrier ohmic OLEDs, MoO3-doped NPB35 was used as a hole ohmic contact and Rb2CO3-mixed C60 as the electron ohmic contact, in line with the results in Fig. 1-4. Figure 5 shows the J-V-L characteristic of OLEDs to optimize the mixing concentration of the Rb2CO3-mixed C60 layers at a fixed thickness of 3 nm. The results of Fig. 5 are summarized in Table I. The structure of Devices II~IV was composed of glass/ITO/MoO3-doped NPB (25%, 5 nm)/NPB (63 nm)/Alq3 (42-x nm)/Rb2CO3-mixed C60 (y%, x = 3 nm)/Al (150 nm). The Rb2CO3 mixing concentrations in Devices II, III, and IV were 25, 50, and 75%, respectively. For comparison, the J-V curve of Device I, where Rb2CO3-mixed C60 as the EIL was replaced by C60 (x = 5 nm)/LiF (1 nm) in the same structure of the all-carrier ohmic OLEDs, is included in Fig. 5. As shown, Devices III and IV with a mixing concentration between 50 and 75% exhibited an operation voltage of 5.6 and 5.2 V at about 20 mA/cm², respectively. These voltages were less than the 6.6 V of Device I, used as the reference device, in which the C60/LiF layer has been previously reported as a good electron ohmic-contact.18 In contrast, Device II, with a mixing concentration of 25%, showed a higher operation voltage than Device I. Also, Devices III, and IV at a luminance of 1000 cd/m², showed a power efficiency of 0.6, 3.0, and 3.4 lm/W, respectively. Those results indicated that the EIL functioned as a good electron conductor and that the electron concentration was significantly increased at the Al/Rb2CO3-mixed C60 interface, as the mixing concentration of Rb2CO3 in the Rb2CO3-mixed C60 was increased from 25 to 75%. Meanwhile, the maximum luminance (Lmax) of Devices II~IV was 7700 (11.8 V), 51700 (10.2 V), and

Table I. J-V-L characteristics of the devices comprised of glass/ITO/MoO3-doped NPB (25%, 5 nm)/NPB (63 nm)/Alq3 (42-x nm)/[Rb2CO3-mixed C60 (y%, x = 3 nm)/C60 (x = 5 nm)/LiF (1 nm)]/Al (150 nm).

<table>
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<tr>
<th>Devices</th>
<th>EILs</th>
<th>V (V) at 20 mA/cm²</th>
<th>ηPE (lm/W) at 1000 cd/m²</th>
<th>Lmax (cd/m²)</th>
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<tr>
<td>I</td>
<td>C60 (5 nm)/LiF (1 nm)</td>
<td>6.6</td>
<td>1.9 at 7.0 V</td>
<td>508000 at 10.4 V</td>
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<tr>
<td>II</td>
<td>Rb2CO3-mixed C60 (3 nm, 25%)</td>
<td>7.6</td>
<td>0.6 at 7.6 V</td>
<td>7700 at 11.8 V</td>
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<tr>
<td>III</td>
<td>Rb2CO3-mixed C60 (3 nm, 50%)</td>
<td>5.6</td>
<td>3.0 at 5.6 V</td>
<td>51700 at 10.2 V</td>
</tr>
<tr>
<td>IV</td>
<td>Rb2CO3-mixed C60 (3 nm, 75%)</td>
<td>5.2</td>
<td>3.4 at 5.2 V</td>
<td>71000 at 9.6 V</td>
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71100 cd/m² (9.6 V), respectively. Clearly, at a given light-emitting property, Device IV had the lowest driving voltage among the Devices investigated. The driving voltage decreased monotonically as the mixing concentration was increased, indicating that the bulk resistance of the Rb₂CO₃-mixed C₆₀ layer was reduced due to the electrical n-mixing effect, which in turn reduced the hopping activation energy during the electron-injecting process in OLED. This result was in agreement with the n-mixing effect of Rb₂CO₃-mixed C₆₀ shown in Figs. 1–4.

Conclusions

The mixing of Rb₂CO₃ in the C₆₀ layer induced the partial formation of new complexes in the Rb₂CO₃-mixed C₆₀. Due to the chemical interaction between Rb species and C₆₀, a new FLCSs was formed below the E_cv as revealed by the UPS spectra. The generation of the new FLCSs markedly decreased the resistance contact and increased the electron carrier number. The electron-only device showed a good electron ohmic-contact property with increasing Rb₂CO₃ mixing concentration in the C₆₀ layer. The device performance of the OLEDs with this electron ohmic-contact layer was consistent with both the n-mixing effect and the RMS roughness of the films. Among the OLED devices investigated, the all-carrier ohmic-contact OLED which has a glass/ITO/MoO₃-doped NPB (25%, 5 nm)/NPB (63 nm)/Alq₃ (39 nm)/Rb₂CO₃-mixed C₆₀ (75%, 3 nm)/Al (150 nm) structure, showed the highest light-emitting characteristics of ηₑ, of 3.4 lm/W at 5.2 V as a function of mixing concentration of the Rb₂CO₃-mixed C₆₀ electron ohmic layer.

Acknowledgments

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