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 electron-ohmic contact at 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.

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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 organic-metal 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 (EF) 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$_3$, WO$_3$), 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$_3$ is frequently used as an electron injecting layer (EIL), forming an electron ohmic contact with a lithium fluoride (LiF)/Al bi-layer cathode.

As the n-type dopant, Feng et al. first reported that fullerene (C$_{60}$) acts as a highly conductive electron-injecting layer (EIL), forming an electron ohmic contact with a lithium fluoride (LiF)/Al bi-layer cathode. Recently, alkali-metal carbonates such as rubidium carbonate (Rb$_2$CO$_3$) and cesium carbonate (Cs$_2$CO$_3$) have been introduced as additional n-type ohmic dopants. In the n-mixing system of Rb$_2$CO$_3$-mixed 4,7-diphenyl-1,10-phenanthroline (Bphen), ultraviolet and X-ray photoemission spectroscopy (UPS and XPS) showed that n-type mixing effects, which are an electron charge transfer from Rb$_2$CO$_3$ to Bphen and the metal-induced gap states (MIGSs) created by aluminum (Al) deposition, are both the same as the improved carrier injection efficiency.

Here, 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, square, Geomatec 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-x nm)/[Rb$_2$CO$_3$-mixed C$_{60}$ (x%)]/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. The OLED was fabricated with a Rb$_2$CO$_3$-mixed C$_{60}$ layer at various mixing concentrations and thicknesses and was investigated according to the ohmic property in the organic-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.

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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 Rb$_2$CO$_3$-mixed NB 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 Rb$_2$CO$_3$-mixed C$_{60}$ (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 Rb$_2$CO$_3$-mixed C$_{60}$ was designed to obtain a resistance-free contact.

Figure 1a shows the J-V characteristics of the electron-only devices with the ITO/Rb$_2$CO$_3$-mixed C$_{60}$/Al structure, as a function of the Rb$_2$CO$_3$ mixing concentration at a fixed thickness of 10 nm. Compared to the electron-only device with a mixing concentration of 5% Rb$_2$CO$_3$, 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 electronic 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 Rb$_2$CO$_3$ 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 Rb$_2$CO$_3$ mixing concentration. Figure 1b exhibits the J-V characteristics when the thickness of the Rb$_2$CO$_3$-mixed C$_{60}$ layer was changed at the Rb$_2$CO$_3$ mixing concentration of 75%. The results show the ohmic-contact characteristic of the electron-only device when the thickness of the Rb$_2$CO$_3$-mixed C$_{60}$ layer was 30 nm and below. However, the bulk resistance of the Rb$_2$CO$_3$ thin films was increased at the thickness of 30 nm above. The electron ohmic-contact property of the EIL layer without the Rb$_2$CO$_3$-mixed C$_{60}$ was increased at the thickness of 30 nm above.

Figure 2 shows the UPS spectra of pristine C$_{60}$ and C$_{60}$ mixed with various Rb$_2$CO$_3$ mixing concentrations were investigated using UPS. Figure 2a shows the onset of the valence band spectra, representing the WF of the surface. Initially, as the Rb$_2$CO$_3$ mixing concentration was increased to 25%, WF was slightly increased to 0.2 eV compared to that of pristine C$_{60}$ (4.7 eV), but as the concentration was further increased above 25%, WF was significantly decreased to 1.2 eV and 2.8 eV for 75% and 100% Rb$_2$CO$_3$, respectively, compared to that of pristine C$_{60}$. The shifts of these WF is estimated to be relative to the structural change when the Rb$_2$CO$_3$ mixing concentration is changed in the Rb$_2$CO$_3$-mixed C$_{60}$ films.

Figure 2b and Fig. 2c show the valence band spectra and the region around the EF of the Rb$_2$CO$_3$-mixed C$_{60}$ 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 C$_{60}$. The difference between the onsets of the HOMO level and EF are nearly not shifted as 1.5, 1.3, 1.3, 1.5, and 1.6 eV for 0, 10, 25, 50, and 75%, respectively. The ionization energy of C$_{60}$, which is the sum of WF (4.7 eV) and HOMO (1.5 eV), is measured as 6.2 eV in Fig. 2b, which is consistent with a previous report. Here, the energy level of the HOMO is the distance from EF to the onset of HOMO in UPS. In addition, the C$_{60}$ has a bandgap of about 2.5 eV. In the UPS spectra of Fig. 2b, the Rb$_2$CO$_3$-mixed C$_{60}$ 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 C$_{60}$. 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 C$_{60}$, starts to appear at about around 0.7 eV. The intensities of the peaks in HOMO-1, HOMO, and new FLCSs are increased as the Rb$_2$CO$_3$ mixing concentration is increased to 25%. At the mixing concentration of 50%, the intensities of HOMO-1 and HOMO features are decreased, as shown in Fig. 2b, and the width and intensity of the FLCSs in Fig. 2c grows significantly at the
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 Rb1C60 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 Rb1C60 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.30

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 Rb1C60 with the NaCl structure and it functions as a conductor. Rb3C60 with a face-centered cubic structure is a superconductor with a relatively high critical temperature. Rb6C60 is a non-conducting material with a body-centered cubic structure, and Rb4C60 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 C60.28 The observed characteristic changes as the mixing concentration was increased from 10 to 25% indicated the increase of Rb1C60 domains in the Rb2CO3-mixed C60 thin film. The Rb1C60 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 Rb1C60 phase. The characteristics for the Rb1C60 (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 FLCSs intensity near the EF at the Rb2CO3 mixing concentration of 50% or higher are believed to be related to the formation of the Rb1C60 phase. The characteristics for the Rb1C60 (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

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Figure 4. (a) AFM images of the surfaces of pristine C₆₀ and Rb₂CO₃-mixed C₆₀ (x%, x = 10, 25, 50, and 75 and pristine Rb₂CO₃ thin films) deposited on p-type Si wafers. (b) RMS roughness as a function of the Rb₂CO₃ mixing concentration in C₆₀. The thickness of all films was maintained at 10 nm.

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 FCLSs 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 FCLSs 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, and 75%, 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 was increased from 0 to 50%, the RMS roughness of the Rb₂CO₃-mixed C₆₀ thin film 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 Rb₆₀ to Rb₆₀. 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 NPB 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 characteristics 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/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. 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...
structure, showed the highest light-emitting characteristics of η compared to 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 ηPr of 3.4 lm/W at 5.2 V as a function of mixing concentration of the Rb2CO3-mixed C60 electron ohmic layer.

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 Ef, 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.

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References

1. K. Leo, Nature Photonics, 6, 716 (2011).