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Direct evidence of n-type doping in organic light-emitting devices: N free Cs doping from CsN₃

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Cesium azide (CsN_3) is confirmed to be decomposed during thermal evaporation. Only Cs could be deposited on tris(8-hydroxyquinolinato)aluminum (Alq₃) and n-type doping is easily achieved. Organic light-emitting devices with CsN₃ show highly improved current density-luminance-voltage characteristics compared to the control device without CsN₃. To understand the origin of the improvements, *in situ* x-ray and UV photoemission spectroscopy measurements were carried out and a remarkable reduction in electron injection barrier is verified with successive deposition of Al on CsN₃ on Alq₃. CsN₃ has a potential as alternative to doping the electron transport layer by replacing the direct deposition of alkali metals. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4718017]

Organic materials have expanded their application in areas such as organic light-emitting devices (OLEDs), organic thin-film transistors, sensors, and organic solar cells. OLEDs are the most widely studied devices since they are already matured as a commercial product. Numerous studies have been conducted in many aspects including materials, carrier injection and transport, luminance and luminous efficiencies. It has been a basic strategy to fabricate the OLEDs with multilayer structures after Tang et al. showed efficient devices with multilayered architecture.¹ Such successes of multilayers used to be achieved with the help of adequate energy level alignments at interfaces.^{2,3} Therefore, interfacial energy level alignments in devices have been a critical issue to achieve high performance of OLEDs because charge carriers have to overcome the energy barriers at multilayer interfaces from respective electrodes to the emissive layer. Mostly, electron injection has been an issue because the typical electron mobility and injection barrier are unfavorable compared to those of holes. To reduce this mismatch between two carriers, electron injection barriers should be reduced at the interface and thus this is one of the most widely studied issues.

There are two conventional methods to reduce electron injection barriers, which are the insertion of either an alkali metal itself^{4–7} or an alkali metal compound^{8–10} between the cathode and the electron transport layer (ETL). These methods have several weak points: (1) difficulties in deposition and handling due to high reactivity, (2) limited deposition rate, e.g., the alkali metal dispenser, (3) insulating nature of the compound, (4) high evaporation temperature which would not be compatible with pre-deposited organic layers. If alkali metals could be deposited from a conventional ther-

mal evaporator at moderate temperature, it would ease the difficulties of n-type doping with alkali metals.

Cesium azide (CsN₃) is also an alkali metal compound but it has been thought to possess the unique property that it decomposes into Cs and N₂ during the thermal evaporation process, and so it was applied to dope an ETL.¹¹ Very recently, Yang *et al.* used it as an n-type dopant in an interconnector layer.¹² Another advantage of CsN₃ is the low evaporation temperature (\sim 300 °C) which is similar to that of organic materials. In addition, it can be deposited with a conventional thermal evaporator and it is stable in ambient. Therefore, only the Cs metal could be deposited from a conventional thermal evaporator with ease of handling. These unique properties make CsN₃ a potential alternative as an alkali metal source for device fabrication.

Surprisingly, in spite of recent frequent applications of CsN₃, there are no direct/detailed reports that confirm the N free Cs deposition and its n-type doping mechanism except simplistic measurements.¹¹ It should be confirmed prior to the device application whether CsN₃ is actually decomposed and only Cs is deposited on the substrate and improves device characteristics as well. To address such issues practically, we fabricated OLEDs with CsN₃ as an n-type dopant and measured photoemission spectra at the interface of ETL/CsN₃/cathode to see the interfacial electronic structures as well as the N free Cs deposition from a CsN₃ source. CsN₃ insertion showed highly improved device characteristics and lowered the electron injection barrier just like the Cs deposited directly from an alkali metal dispenser.

OLEDs with CsN_3 were fabricated with conventional structures of indium-tin-oxide (ITO, 150 nm)/N,N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'diamine (NPB, 60 nm) /tris(8-hydroxyquinolinato)aluminum (Alq₃, 84 nm)/CsN₃ (0, 0.3, 0.5, 0.7, 1.0, 1.3 nm)/Al (100 nm). ITO patterned glass substrates were cleaned successively with ultrasonication in detergent, methanol, acetone, and deionized water. Organic

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materials and CsN₃ (Aldrich, purity > 99.99%) were thermally evaporated with a pressure of 1.0×10^{-8} and 1.0×10^{-5} Torr at the rates of 0.1 and 0.02 nm/s, respectively. The Al cathode was finally deposited at the rate of > 0.1 nm/s with a pressure of 1.0×10^{-6} Torr. Current density-voltage (J-V) and luminance-voltage (L-V) were measured with a Keithley 237 source measure unit and an optimized Si photodiode with Keithley 2400 source meter. All measurements were done in dry nitrogen ambiance at room temperature.

X-ray and UV photoemission spectroscopy (XPS and UPS) measurements were performed *in situ* to understand the working mechanism of CsN₃. A pristine Alq₃ film was prepared on a clean ITO substrate and CsN₃ and Al were deposited on Alq₃ in a stepwise manner. Before and after each deposition step, the sample was transferred to the analysis chamber without breaking the vacuum and XPS and UPS measurements were conducted. The base pressure of the deposition and analysis chamber were 2×10^{-8} and 5×10^{-10} Torr, respectively. A PSP RESOLVE 120 electron spectrometer was used with UV (He I, 21.22 eV) and standard x-ray (Mg K α , 1253.6 eV) sources. During UPS measurement, a -10 V bias was applied to the sample to obtain the true sample work function.

First, we checked if the CsN₃ is decomposed and only Cs is deposited. CsN₃ was deposited on an ITO substrate and *in situ* XPS measurement confirmed the decomposition. Fig. 1(a) shows the N 1*s* core level spectra before and after the CsN₃ deposition on ITO. No trace of N-related emission is observed upon the CsN₃ deposition. Instead Fig. 1(b) shows the clear Cs 3*d* core level spectrum after the CsN₃ deposition on ITO. The $3d_{5/2}$ peak is located at 725.74 eV, which is close to the value for metallic Cs, not CsN₃.¹³ Therefore, it is demonstrated clearly that the CsN₃ deposition occurs, nitrogen is removed, and only metallic Cs is deposited on the substrate.

To see the effect of CsN_3 as an n-type dopant in OLEDs, J-V and L-V measurements were carried out. Figs. 2(a) and 2(b) show the measured J-V and L-V characteristics, respectively. We varied the CsN_3 thickness to find optimal device performance and a CsN_3 layer of 0.7 nm showed the best characteristics in both current density and luminance. At 11.95 V, the optimal device shows current density and luminance of 2495.6 mA/cm² and 3387.3 cd/m², respectively.

FIG. 1. (a) XPS spectra of the N 1*s* level. There are no traces of nitrogen before or after the CsN_3 deposition. (b) XPS spectra of the Cs 3*d* level measured after CsN_3 (0.7 nm) deposition. It shows the metallic Cs deposited on the substrate.



FIG. 2. (a) Current density versus voltage (b) luminance versus voltage (c) luminous efficiency versus current density. All data were obtained from the device of ITO (150 nm)/NPB $(60 \text{ nm})/\text{Alq}_3$ $(84 \text{ nm})/\text{CsN}_3$ (x nm)/Al (100 nm) with different CsN₃ thickness.



FIG. 3. UPS spectra of (a) normalized secondary electron cutoff and (b) HOMO region after background removal during the interface formation of Alq₃/CsN₃/Al (unit: eV).

Comparing them with those of a control device without CsN₃, CsN₃ shows more than 20 and 70 times enhancements in current density and luminance, respectively. This enhancement can be explained by the typical n-type doping with Cs deposition on Alq₃ because only Cs is deposited on Alq₃ due to the CsN₃ decomposition confirmed above. Fig. 2(c) shows luminous efficiency versus current density of the same devices. The device with a CsN₃ layer of 0.5 nm showed better efficiency than that with a CsN₃ layer of 0.7 nm because the charge imbalance between holes and electrons is accomplished at the NPB/Alq₃ interface. That is, in the device with a CsN₃ layer of 0.7 nm, the amount of electrons far exceeds the amount of holes and the extra electrons do not contribute to the recombination process. This tendency of efficiency also confirms the efficient doping with CsN₃ clearly. The device performance would be much improved if an appropriate hole injection layer is used together with the CsN₃ dopant by improving charge balance.¹⁴

To understand the origin of the improvements in OLEDs with CsN_3 , *in situ* UPS and XPS measurements were carried out. We prepared a pristine Alq₃ layer having sufficient thickness (10 nm) to exclude any possible interacting region with the ITO substrate. Then we studied the interface formation between Alq₃ and Al upon the insertion of CsN_3 . The multilayered structures of ITO/Alq₃ (10.0 nm)/CsN₃ (0.03, 0.1, 0.3, 0.7 nm)/Al (0.02, 0.07, 0.2, 0.7, 2.0 nm) were used for the photoemission measurement. We chose a final CsN₃ thickness of 0.7 nm as the OLED with the same thickness shows the highest electron injection. We also measured the control interface without CsN₃ insertion (spectra not shown).

Fig. 3(a) shows the secondary electron cutoff (SEC) region of the UPS spectra. The SEC shifts to higher binding energies by 1.18 eV during the CsN₃ deposition. It gradually approaches to the work function of Al with an Al deposition,

resulting in total shift of 1.44 eV back to lower binding energies. Fig. 3(b) shows the highest occupied molecular orbital (HOMO) region during the step-by-step deposition. The HOMO onset of pristine Alq₃ is seen at 2.03 eV below the Fermi level. As soon as CsN₃ is deposited on Alq₃, all the energy levels including the HOMO shift toward high binding energy from the very first CsN₃ deposition. The total HOMO shift during the deposition of a CsN₃ layer of 0.7 nm is 1.18 eV. This shift is the same as the total shift observed in the SEC, implying a rigid level shift without an interface dipole (eD). This rigid high-binding shift is contributed to the n-type doping by charge donation of the deposited Cs. Successive Al deposition shifts the HOMO level further due to the extra charge transfer with Al. Al could interact with Alq₃ further through the thin Cs layer since a Cs layer of 0.7 nm is smaller than the one monolayer thickness of Alq₃.¹⁵ In addition to these shifts, a new gap state emerges in the original gap of Alq₃, indicating strong interactions with the deposited Cs. The initial onset of the gap state is at 1.22 eV (determined from a CsN₃ layer of 0.1 nm) below the Fermi level, which shifts 0.40 and 0.37 eV toward high binding energies during CsN₃ and Al deposition, respectively. This n-type doping and gap state formation is consistent with previous results with direct deposition of alkali metals.^{5,7} Therefore, CsN₃ works in the same way as the Cs metal is deposited directly. This confirms again the N free Cs deposition from the CsN₃ source.

Combining all information obtained from spectral changes, the energy level diagrams of $Alq_3/CsN_3/Al$ and Alq_3/Al were drawn. In the diagram, the lowest unoccupied molecular orbital (LUMO) level was estimated from the transport gap of Alq_3 .¹⁶ Fig. 4(a) shows the control interface of Alq_3/Al (spectra not shown) and the LUMO level of Alq_3 shifts downward by 0.89 eV with Al deposition. This LUMO



FIG. 4. Energy level diagrams of (a) Al on Alq₃ and (b) Al on CsN₃ on Alq₃ (unit: eV). E_F is the Fermi level, E_{ion} the ionization energy, E_{vac} the vacuum level, eD the interface dipole, V_b the level shift, Φ_e the electron injection barrier, and Φ_{Al} the work function of the final surface.

shift (V_b) is not the same as the vacuum level shift, indicating the existence of an eD. These shifts result finally in an electron injection barrier (Φ_e) of 0.71 eV. In Fig. 4(b), as seen in Fig. 3, no eD is induced but a rigid level shift results with CsN₃ deposition. The level shift (V_b) caused by n-type doping of Cs is 1.18 eV and the following Al deposition makes a further downward level shift. As a result, the final Φ_e is 0.15 eV, which is much smaller than that without CsN₃. Therefore, ohmic contact between the Al cathode and Alq₃ is achieved and the device characteristics are highly improved.

In summary, CsN_3 was used as an n-type dopant in OLEDs due to its unique properties. The decomposition of CsN_3 and N free Cs deposition on a substrate was confirmed. OLEDs with CsN_3 showed highly improved device characteristics compared to the device without CsN_3 . This improvement originates from the n-type doping effect of Cs decomposed from CsN_3 . XPS and UPS measurements clearly showed the level shift corresponding to the n-type doping and this shift resulted in the reduction of the electron injection barrier. Cs deposited from CsN_3 works in an identical way as Cs directly deposited from a metallic source, e.g., alkali metal dispenser. These make CsN_3 a potential source for n-type doping in organic devices.

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