Enhancing Efficiency of Organic Light-Emitting Diodes Using a CsI-Doped Electron Transporting Layer

Tsang-Wei Kuo, Shui-Hsiang Su*, Chung-Ming Wu and Meiso Yokoyama

Department of Electronic Engineering, I-Shou University, 1, Section 1, Hsueh-Cheng Rd., Ta-Hsu Hsiang, Kaohsiung County, Taiwan 840, R.O.C. Phone: +886-7-6577257 *E-mail: shsu@isu.edu.tw

1. Introduction

Organic light-emitting diodes (OLEDs) have been widely recognized as a technology for flat panel display (FPD) products today and for potential future use in the lighting industry [1-2]. Recently, doping techniques, which been widely used in forming have inorganic semiconductors, have been applied for forming organic pand n-type materials [3]. A typical n-type doping electron transporting layer (n-ETL) consists of a low work-function metal doped in an organic material. The OLEDs with a Li-doped tris-(8-hydroxyquinoline) aluminum (Alg₃) n-ETL have been reported in our previous study [4]. However, Li, one of the reactive low-work-function metals, is air un-stable and requires special care or equipments for handling. In this study, cesium iodide (CsI) is co-evaporated with Alq₃ to form an n-ETL in the device to improve the electron injection ability and enhance the electroluminescence (EL) efficiency. Unlike reactive low-work-function metals, CsI is an air stable material and known to be robust and inert. An OLED, comprising a CsI-doped Alq₃ n-ETL, requires no extrinsic thin LiF film (~ 0.5nm), meeting commercial requirements with improved reproducibility.

2. Experiments

The inset of Fig. 1 shows the structure of devices studied in this work, in which indium-tin oxide (ITO) on glass acts as an anode and the Al as a cathode. ITO with a thickness of 150 nm and a sheet resistance of $7\Omega/sq$ was used as a substrate in the OLED. After the substrate was loaded into an evaporation system, organic layers were sequentially fabricated at a rate $1 \sim 2$ Å/s onto substrates by thermal evaporation from resistively heated tantalum boats, at a base pressure of $2 \sim 5 \ge 10^{-6}$ Torr. The evaporation rate and thickness of the film was determined using an oscillating quartz thickness monitor (Sycon STM-100). The active area of the devices, defined by the overlap of the ITO and the Al electrodes, was 0.4×0.6 cm². All devices were encapsulated in a dry nitrogen glove box. CsI-doped Alq₃.is the ETL and the doping concentration is 0%, 5%, 10%, and 15 %, respectively. The luminance-current density (L-J) and the current density-voltage (J-V) characteristics were measured using a Topcon PR-650 luminance meter at room temperature and a Keithley 2400 precision semiconductor parameter analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultrahigh vacuum system. The XPS spectroscopy, which consisted of a high power X-ray

source operating at the Mg K α line and an angle resolved electron energy analyzer, had an energy resolution of 1.2 eV.

3. Results and discussion

For an ITO/NPB (30 nm)/Alq₃ (30 nm)/X% CsI-doped Alq₃ (15 nm)/Al (150 nm) device, green EL was observed through the glass substrate. The current density-voltage characteristics of the OLEDs with various concentrations of CsI dopants in Alq₃ are shown in Fig. 1. Compared with the device without CsI-doped Alq₃, a dramatic increase of the current density was observed when CsI was doped into Alq₃ layer. The current density increased with an increased CsI doping concentration, indicating a strong n doping effect of CsI in Alq₃ and therefore the conductivity of the devices can be improved. Moreover, the un-doped device exhibited an operation voltage of 9.61 V at 2.5 mA/cm². In contrast, the operation voltage significantly reduced among the devices with a CsI-doped Alq₃ ETL. For example, the devices with 5%, 10% and 15% CsI-doped Alq₃ EML have the operation voltages of 7.48, 7.21, and 6.3 V, respectively. From these results, it can be expected that CsI doping can improve the electron carrier concentration, increasing the current density and decreasing the operation voltage. Table I summarizes the performance of the devices at a driving current density of 20 mA/cm². These results clearly reveal that the CsI doping in Alq₃ as an ETL is effective in lowering the operation voltages and to balance the recombination of hole-electron, resulting in high luminous efficiencies.

Cs(3d) core level spectra of the cesium atom in the Alq₃ upon various CsI doping concentration are shown in Fig. 2. It can be seen that the Cs $3d_{5/2}$ peaks of 5% CsI-doped Alq₃ appeal at binding energies of 726.4 eV. As the concentration of the CsI dopant increases to 15%, resulting in the peak shifts toward higher binding energy - from 726.4 eV to 726.8 eV. The difference in binding energies of Cs 3d core levels in these samples indicates a substantial chemical reaction between CsI and Alq₃, additional positive charges surrounding the Cs atom, resulting in positively charged Cs⁺ species. The excess electrons are therefore transferred to the Alq₃ matrix. Thus, doping CsI into the Alq₃ increases the carrier concentration for current conduction [5].

The absorption spectra of Alq₃:CsI film with various CsI doping concentration are shown in Fig. 3 Compared with an absorption spectrum of undoped Alq₃, peaks around 450 nm of the CsI-doped Alq₃ drastically decreased, which implies a reaction between CsI compounds and Alq₃, forming radical anions of Alq₃, or CT complexes between CsI and Alq₃. A similar reaction between Alq₃ and Ca was already confirmed by Choong *et al.* for Ca and Alq₃[6]. Experimental results also indicate that excess Cs cations may either exist at the Alq₃/Alq₃:CsI interface or even migrate into and react with the Alq₃ EML. Alq₃ is a chelate metal complex. The diffusion of Cs cations into the Alq₃ EML results in an unsaturated metal ion, as explained by our work on copper (Cu) liberation in OLEDs with an Alq₃ EML.[7] Metal doping heavily quenches light-emitting excitons in an EML.

4. Conclusions

OLEDs were successfully fabricated with an ITO/NPB/Alq₃/CsI-doped Alq₃/Al structure. The characteristics of the OLEDs were studied by adjusting the doping concentration of CsI in an Alq₃:CsI ETL. Experimental results reveal that metal compound doping is an effective way to promote the electron injection from the cathode into the EML and further enhance the luminous efficiency.XPS and UV-vis absorption spectra of CsI-doped Alq₃ films suggest that Alq₃ radical anions are formed by charge transfer from CsI, enhancing the electron conductivity in the CsI-doped Alq₃ ETL. Excess Cs cations may exist at the Alq₃/Alq₃:CsI interface or even migrate into and react with the EML, which worsens the optoelectronic characteristics of the OLEDs.

Acknowledgement

The authors would like to thank the National Science Council of the Republic of China, for financiallysupporting this research under Contract No. NSC98-2218-E-214-001 and 98-2221-E-214-003-MY3. The authors would also like to thank the MANALAB at ISU, Taiwan.

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Table I. Optoelectronic characteristics of the OLEDs with an Alq₃: x% CsI transporting layer driven at 20 mA/cm²

Device Alq ₃ :x% CsI	Voltage (V)	Luminance (cd/m2)	Efficiency (cd/A)
0%	13	499	2.41
5%	9.9	1180	5.27
10%	9.61	1002	5.04
15%	8.42	948	4.27



Fig. 1 Current density-voltage characteristics of the OLEDs with an Alq₃: x% CsI transporting layer. The inset shows the device structure.







Fig. 3 UV–Vis absorption spectra of Alq₃:CsI films with various concentration of CsI.