Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp9-10

Enhanced Electroluminescence from Organic Light-Emitting Diodes with an Organic-Inorganic Perovskite Host Layer

Toshinori Matsushima[1-3], Chuanjiang Qin[1,2], Kenichi Goushi[1-3], Fatima Bencheikh[1,2], Takeshi Komino[1,2], Matthew Leyden[1,2], Atula S. D. Sandanayaka[1,2], and Chihaya Adachi[1-3]

[1] OPERA, Kyushu Univ.
[2] JST-ERATO
[3] WPI-I^{2}CNER, Kyushu Univ.
744 Motooka, Nishi, Fukuoka 819-0395, Japan
Phone: +81-92-802-6923 E-mail: tmatusim@opera.kyushu-u.ac.jp

Abstract

In this study, we show that the organic-inorganic perovskite $CH_3NH_3PbCl_3$ ($MAPbCl_3$) can be used as a host layer for OLEDs. Vacuum-evaporated $MAPbCl_3$ films have a wide band gap of about 3 eV and very high and relatively balanced hole and electron mobilities, which are suitable for the host material. Photoluminescence and electroluminescence take place through energy transfer from $MAPbCl_3$ to an organic emitter in films. Incorporation of a $MAPbCl_3$ host layer into OLEDs leads to a reduction of driving voltage and enhancement of external quantum efficiency as compared to devices with a conventional organic host layer. Additionally, OLEDs with a $MAPbCl_3$ host layer demonstrate very good operational stability under continuous current operation.

1. Introduction

Organic light-emitting diodes (OLEDs) are highly promising for applications in next-generation displays and lighting because of their film processability, mechanical flexibility, high response speed, and emission color tunability. In the past three decades, the electron-to-photon conversion efficiency of OLEDs has increased to 100% through development of novel organic emitters. Organic emitters have generally been doped into organic host layers with wider energy gaps. Organic host materials frequently used in OLEDs are carbazole, organosilicon, and phosphine oxide derivatives. Host layers play crucial roles in transporting electrons and holes, delivering excited-state energy to emitters, and improving electroluminescence (EL) efficiency and durability. Thus, development of higher-performance host materials is important.

Organic-inorganic perovskites are currently attracting considerable attention for use in applications such as the light absorber for solar cells, the emitter or the carrier transport layer in LEDs, the semiconductor in field-effect transistors, and the gain medium for amplified spontaneous emission and lasing. In these devices, very high performances can be obtained. One reason for this is the excellent carrier transport through perovskite films. It is widely known that perovskite films have much higher carrier mobility than that of conventional amorphous organic films. In this study, by taking advantage of the excellent carrier transport of perovskite films, we employed a perovskite as the host layer in OLEDs. Among the many perovskite materials, we chose methylammonium lead trichloride $CH_3NH_3PbCl_3$ (hereafter abbreviated as $MAPbCl_3$) because this material has a wide band gap of about 3 eV, which is suitable as a host material for energy transfer to organic emitters. We fabricated OLEDs with a $MAPbCl_3$ host layer doped with the fluorescent emitter, and demonstrated better device performance compared with OLEDs with a standard organic host layer. This study contributes toward the fabrication of OLEDs with lower operation voltages, higher efficiency, and good stability, at a lower cost.

2. Results and discussion

MACl, $PbCl_2$, and coumarin 153 were simultaneously evaporated from separate tantalum boats resistively heated under vacuum to prepare 1 wt.%-coumarin-doped $MAPbCl_3$ films on substrates. In these films, energy transfer from $MAPbCl_3$ to coumarin took place because of an overlap between the $MAPbCl_3$ emission spectrum and the coumarin absorption spectrum. The green photoluminescence (PL) observed from coumarin-doped $MAPbCl_3$ films was attributable to coumarin while undoped $MAPbCl_3$ films had a deep-blue PL with the main peak at ≈ 400 nm. Most of coumarin molecules is speculated to exist at crystallite or grain boundaries in polycrystalline $MAPbCl_3$ films because of similar X-ray diffraction patterns while coumarin molecules are uniformly dispersed in amorphous 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) films used later as a reference host material for OLEDs.

To demonstrate the potential application of coumarin-doped $MAPbCl_3$ films in optoelectronic devices, we fabricated OLEDs with a structure shown in Fig. 1a. Using a $MAPbCl_3$ host layer reduced the driving voltage compared with a mCBP host layer; the driving voltages at 1 mA cm^{-2} were 5.3 ± 0.1 V for $MAPbCl_3$-based OLEDs and 6.2 ± 0.1 V for mCBP-based OLEDs (Fig. 1b). One source of the reduced voltage is efficient electron and hole transport through the host layer. Analyzing current density-voltage properties of hole- and electron-only $MAPbCl_3$ devices with a space-charge-limited current model yielded hole and electron mobilities around 3.4 and 2.1 cm^2 V^{-1} s^{-1}, respectively. These values are much higher than those of amorphous organic films used for OLEDs (< 10^{-3} cm V^{-1} s^{-1}).

These OLEDs demonstrated high luminance along with green EL originating from coumarin as shown in Fig. 1c and

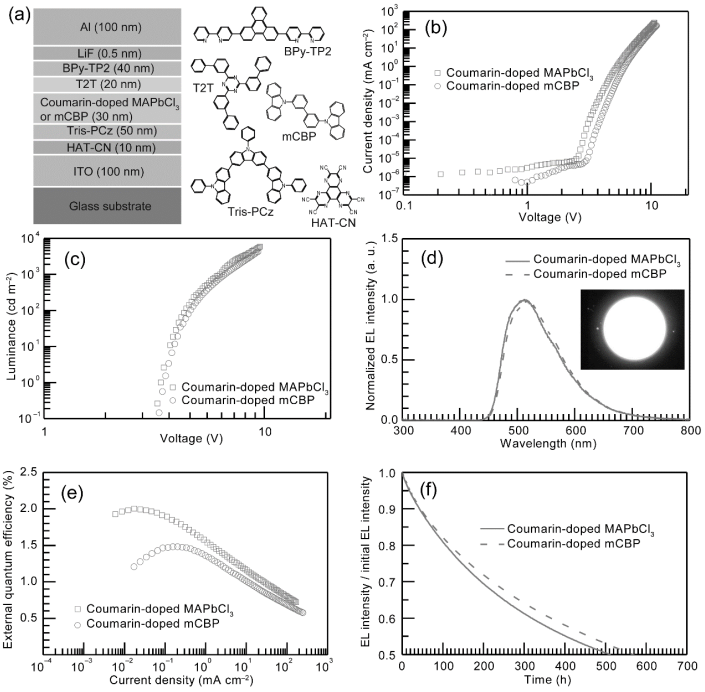

Fig. 1. (ref. 1) (a) Schematic of OLED architectures and chemical structures of HAT-CN, Tris-PCz, mCBP, T2T, and BPy-TP2. (b) Current density-voltage and (c) luminance-voltage curves, (d) EL spectra measured at 10 mA cm^{-2}, (e) external quantum efficiency-current density curves, and (f) luminance evolutions of OLEDs with $MAPbCl_3$ and mCBP host layers. The inset in (d) is the photograph of a working OLED with a $MAPbCl_3$ host layer. The luminance evolutions were measured at 50 mA cm^{-2}.

1d. The inset of Fig. 1d is the photograph of a working $MAPbCl_3$-based OLED. $MAPbCl_3$-based OLEDs (~2.02%) had higher external quantum efficiencies than mCBP-based OLEDs (~1.48%) had (Fig. 1e). Overall, better OLED performance could be obtained by utilizing $MAPbCl_3$ than mCBP as the host layer.

To gain insight into the observed EL properties, external quantum efficiency was theoretically calculated at 1.24% by multiplying carrier balance factor (100%), typical radiative singlet exciton generation efficiency (25%), measured PL quantum yield (18%), and calculated light outcoupling efficiency (27.6%). The experimental external quantum efficiency (2.02 ± 0.11%) surpassed the calculated one (1.24%) for $MAPbCl_3$-based OLEDs. As the coumarin doping concentration used in this study was very low (1 wt.%), recombination of electrons and holes traveling from electrodes could mainly occur on $MAPbCl_3$ host layers, followed by energy transfer to coumarin dopants. The high singlet exciton generation efficiency could be related to this energy transfer process. Perovskites are materials that emit light via a band-to-band transition. The energy transfer from such a band-to-band transition perovskite material to an organic molecule may lead to the generation of more singlet excitons than usual and therefore overcome the singlet exciton generation limit. It has been reported that singlet and triplet excitons exist in some perovskite materials and have similar energy levels.[2,3] Under that situation, more singlet excitons can be generated via reverse intersystem crossing from the triplet excitons as observed in thermally activated delayed fluorescence-based organic emitters, which increases the singlet exciton generation efficiency.

Perovskite emitter LEDs still have significant stability issues, where the EL intensity quickly degrades under continuous operation.[4,5] We speculate that one reason for the quick degradation is because of unstable excited states of perovskite in the presence of high electric field. In an organic-doped perovskite system like coumarin-doped $MAPbCl_3$ used in this study, the unstable excited states are immediately removed by the energy transfer to organic molecules, which might be expected to improve operational stability. In fact, our $MAPbCl_3$-based OLEDs had operational stability comparable to that of mCBP-based OLEDs (Fig. 1f). Thus, we would like to emphasize that the use of a perovskite host layer for OLEDs leads to not only the reduced voltages and the enhanced efficiencies, but also good operational stability.

3. Conclusions

In summary, we showed that it is possible to obtain PL and EL from organic molecules doped into a perovskite host film. Our perovskite layer had excellent carrier transport. Therefore, driving voltages of OLEDs with a perovskite host layer were lower than those with a conventional organic host layer. OLEDs with a perovskite host layer demonstrated enhanced EL, which may have resulted from an increased radiative singlet exciton generation efficiency by perovskite-to-organic energy transfer. The present EL efficiency is not high in our current OLEDs (about 2%). However, it may be possible to enhance efficiency by managing the defect states in films. This can be done with further research into an improved understanding of defect origins, and optimization of perovskite fabrication conditions and device architectures. Additionally, operational stability of OLEDs with a perovskite layer was found to be good and comparable to that of OLEDs with an organic host layer. By use of a perovskite host, OLED-based displays and lighting can be fabricated with low cost, low driving voltage, high efficiency, and good stability. Perovskite host layers can also potentially be used for other devices, such as current injection-type laser devices and light-emitting transistors, in which both efficient emission and high-speed carrier transport are required.

References

[1] T. Matsushima *et al.*, Adv. Funct. Mater. 29 (2019) 1807148.
[2] K. Ema *et al.*, Phys. Rev. Lett. 100 (2008) 257401.
[3] M. A. Becker *et al.*, Nature, 553 (2018) 189.
[4] N. Wang *et al.*, Nature Photonics 10 (2016) 699.
[5] Z. Xiao *et al.*, Nature Photonics 11 (2018) 108.