Low-temperature Processed Color-tunable Hybrid Perovskites for Light Emitting Diodes

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ABSTRACT

Hybrid perovskites can be alternative to the conventional organic and inorganic (quantum dot) light emitting materials. Here we show the low-temperature processing of hybrid perovskites used for the light emitting diodes. The proposed process takes advantages of better controlling of the ultrathin layer morphology and high degree of freedom in device structure designing, when compared with the widely used solution process.

INTRODUCTION

Organic-inorganic halide perovskites have attracted tremendous interest due to their unique and promising properties and their application as one of the most successful material in the high efficiency solar cells. Indeed, this type of materials also show strong photoluminescent properties, making them more attractive as potential candidate for used in the light emitting and lasering devices. In the light emitting diode, the light emitting layer should be kept thin to assure low parasitic loss and high performance. However, conventional solution process has drawbacks in term of full surface coverage and good uniformity, most because of the dewetting process and self-assembling properties of these hybrid perovskite materials.

Here we show low-temperature processing of the hybrid perovskite and its application in the light emitting diode. We demonstrate the proposed close space sublimation process has the advantage of better controlling of the ultrathin film morphology, and, furthermore, high degree of freedom considering the device structure, for example, a multilayer structure could be used to realize the white light emitting diodes.

EXPERIMENTAL

Close space sublimation designed for the fabrication of the perovskite materials is illustrated in Figure 1. It consists of two heating blocks, one used for the organic source and the other for the substrate. The two heating blocks are heated respectively, and separated by 1.5 mm. The spacing betweem the source and substrate was kept at low value to enable a high material usage and fast depostion rate. Type K thermocouples embedded in heating blocks are used to allow precise temperature monitoring and feedback for the PID temperature controllers. The entire assembly is enclosed in a mechanical-pumped vacuum chamber capable of base pressures of ~ 0.1 mbar. The organic source is placed in a flat boat in the form of a pressed tablet. The flat boat sited on top of the bottom heater. The substrate pre-coated with metal halide is clamped on the top heater with the film side facing down. The closed chamber is first pumped to 1 mbar, then the chamber is vented with Nitrogen to the process pressure and maintained at this pressure with mechanical pump. If not specified, the process pressure is 2.5 mbar in our case. Once heated, the organic sublimated. The temperature of the substrate 10 °C is ahead of the source temperature during the ramping time. The typical process temperature of substrate and source are 150 °C and 160 °C, respectively. After 1-5 min process time, the two heaters are cooled down. The closed chamber is then vented to atmosphere with N2 and then the samples can be removed from the chamber.

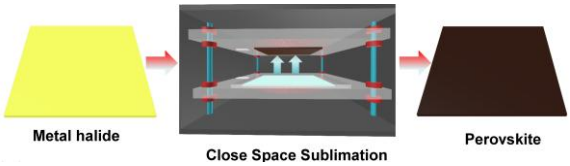

Figure 1. Schematic of close space sublimation of perovskites

RESULTS and DISCUSSIONS

1. Color-tunable hybrid perovskites

Halide perovskite is a special family of the perovskite materials, with the general formula of AMX_3, where A is small, monovalent or divalent organic cation, X is halide anion (Cl, Br or I), and B is divalent metal cation. When substituting X with different halide anions, the energy bandgap can be easily turned from 1.55 eV to 3.18 eV, corresponding to the wavelength of 800 nm to 390 nm, which is shown in Table I. The full visible spectrum can be obtained by mixing different halides. A relationship between the mixture ratio and the emission wavelength is shown in Figure 2. When using multilayers with different emission wavelength, white color perovskite light emitting diodes can therefore be easily achieved.

Table I. energy bandgap and emission wavelength of the perovskites with different halogens.

CH3NH3PbX3	X=I	X=Br	X=Cl
Eg(eV)	1.56	2.2	3.18
wavelength (nm)	800 nm	560 nm	390 nm

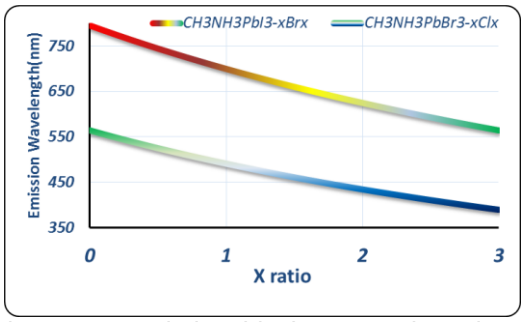

Figure 2. A relationship between the mixture ratio and the emission wavelength.

2. Close space sublimation of perovskites

The fabrication of the perovskite active layer use a two-step process. As shown in Figure 3, in the case of the single layer structure, metal halide was first deposited on the hole transporting layer (HTL) by the thermal evaporation, then the substrate was transferred to a low pressure chamber, under the vapor of the CH_3NH_3X (X can be Cl, Br, or I), the metal halide will be reconstructed to be 3-D perovskite with the form of $CH_3NH_3PbX_3$ ($MAPbX_3$). In order to fabricate the multilayer, metal halide multilayer was firstly deposited sequentially, and then it was converted into multilayer perovskite.

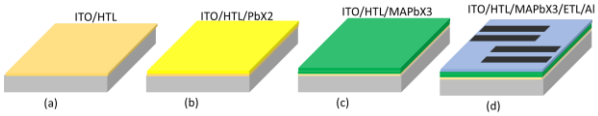

Figure 3. (a) ITO substrate coated with HTL; (b) PbX_2 is firstly deposited on the substrate by thermal evaporation; (c) the substrate is transferred to a low-pressure chamber to form the perovskite light emitting layer; (d) the device is finished by deposition of the ETL and metal contact.

The SEM image of the perovskite films using the solution process and the proposed process are shown in Figure 4. Film from the solution process has porous and rough surface morphology; on the other hand, film form the proposed process is relatively smooth and dense. When this is used in the light emitting diode which has the active layer of around 30-50 nm, the shunt problem will be effectively avoid by using the film with 100% surface coverage. Therefore, the device performance and long term stability will be improved.

The Tauc plot is used to estimate the energy band gap of the perovskites. As shown in Figure 5. The Eg of MAPbI3 and MAPBBr3 are1.58 eV and 2.15 eV, respectively, corresponding to the emitting wavelength of 760 nm and 520 nm. Varying the composition of I and Br in the resulting film will change the Eg and therefore the emitting wavelength.

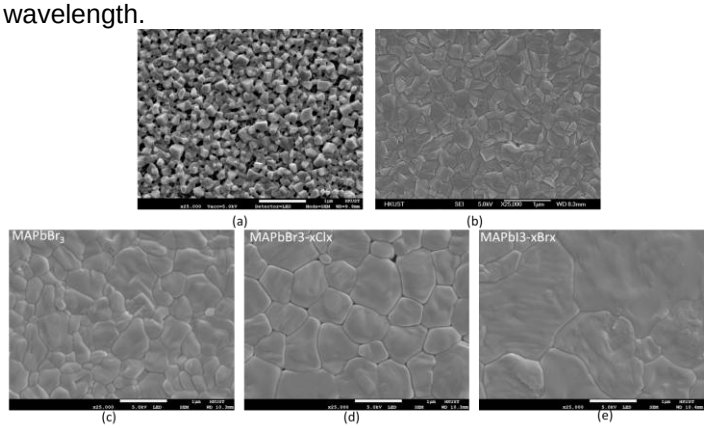

Figure 4. Sample SEM images of (a) solution processed MAPbI3, (b) css processed MAPbI3, (c) css processed MAPbBr3, (d) css processed MAPbBr3-xClx, (e) css processed MAPbI3-xBrx.

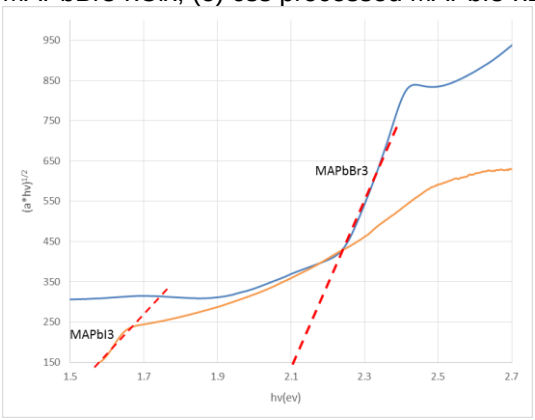

Figure 5. Tauc plot of MAPbI3 and MAPbBr3

3. Perovskite light emitting diodes

The structure of the perovskite light emitting diodes are shown in Figure 6. The substrate is ITO, PEDOT:PSS and TFB are used as the hole transporting layer and hole injecting layers, ZnO is used as the electron injecting layers. The diode can be made with a single layer perovskite layer to emit single wavelength light, for example, using the CH3NH3PbBr3 to emit the green light; the diode can also be made with multilayer to emitting white light, which is the combination of the red, green and blue light. The multilayer device will benefit from the proposed process with is suitable for sequential deposition of the metal halide layers, which is difficult for the solution process.

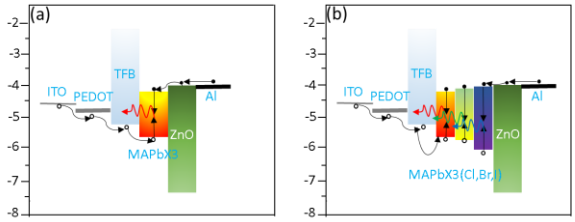

Figure 6. perovskite light emitting diode structure of (a) single layer, (b) multilayers.

CONCLUSION

We have shown the low temperature close sublimation of perovskite compounds. The proposed process has better controlling of the ultrathin layer morphology and high degree of freedom in device structure designing, when compared with the widely used solution process.

References

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2. Guijun Li, Jacob Y L Ho, Kwong Lung Ching, Yibin Jiang, Man Wong, and Hoi-Sing Kwok, submitted