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Effects of thermal treatment on organic-inorganic hybrid perovskite films and luminous efficiency of light-emitting diodes

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ABSTRACT

To improve the electroluminescence efficiency of organic-inorganic hybrid perovskite (OIP) films, we need to consider several different types of post-treatments after film formation such as thermal annealing and solvent annealing. Here, we only applied thermal treatment on the film excluding all the other treatments. Then, we analyzed the effects of annealing time t_{ann} on crystallinity of methylammonium lead bromide ($CH_3NH_3PbBr_3$) films and on luminous efficiency of $CH_3NH_3PbBr_3$-based perovskite light-emitting diodes (PrLEDs). When thermal annealing of $CH_3NH_3PbBr_3$ films was conducted at 90 °C, $t_{ann} \leq 10$ min increased its crystallinity by eliminating residual solvent and completing the conversion of precursor to crystal, but $t_{ann} > 10$ min reduced crystallinity and caused slight sublimation of CH_3NH_3Br. This was consistent with trend of the luminous efficiency of our PrLEDs that showed the optimum performance at $t_{ann} = 10$ min. These results demonstrate that optimizing t_{ann} of $CH_3NH_3PbBr_3$ films is a simple way to improve the luminous efficiency of PrLEDs by controlling their crystallinity.

Organic/inorganic hybrid perovskite (OIP) materials can attain power conversion efficiency> 20% due to their unique properties such as small exciton binding energy (<50 meV), long exciton diffusion length (>100 nm) and high absorption coefficient so that they have possible applications in the light-absorption layers of solar cells [1–6].

OIPs also have potential applications as emitters in light-emitting diodes (LEDs) because the emitting materials are inexpensive, processing can be done at low cost, and the emitting spectrum is very narrow (full width at half maximum (FWHM)≤ 20 nm) [7,8]. Also, their easy band-gap tunability by simple atom substitutions of organic cations [9,10], inorganic anions [11] and metal cations [12], and independence of color purity on crystal size [13,14] make them feasible in alternative emitters that do not have the disadvantages of conventional organic emitters (e.g. low color-purity, complex synthesis and high cost), and inorganic quantum-dot (QD) emitters (e.g. color purity easily affected by crystal size, high cost and finely controlled synthesis) [15,16]. Although excitons in OIP films can be easily dissociated by thermal ionization, OIP films can be converted to bright emitters by controlling charge injection barrier and exciton quenching at the interface between OIP and adjacent hole/electron injection layer [17-20]. However, controlling several factors in forming the OIP layer that are strongly related to the photoluminescence quantum efficiency (PLQE) of OIPs and luminous efficiencies of OIP based LEDs should be done carefully.

Electroluminescence (EL) of OIPs can be affected by the imperfect crystallization caused by residual solvent, and by incomplete conversion of precursor to crystal in the OIP film [21,22]. To make better poly-crystal films for devices, several different types of post-treatments such as thermal annealing and solvent annealing can be applied [22,23]. When OIP is not thermally annealed or annealed too short, the film has low crystallinity which can decrease its PLQE by reducing radiative recombination and increasing non-radiative recombination [24]. Thus, to increase the EL and PLQE of the OIPs, thermal treatment after film formation must be used to increase the crystallinity by reducing residual solvent and converting remaining precursors to crystal (Fig. 1). However, thermal treatment for too long induces sublimation of organic ammonium from the perovskite film and reduces the crystallinity [25]. Thus, to increase the luminous efficiencies of perovskite-based LEDs (PrLEDs),

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the OIP needs to have perfect crystallinity without residual solvent, and the precursor need to be completely converted to crystal, in addition, sublimation of organic ammonium by thermal treatment must be avoided by adjusting annealing duration t_{ann}.

Here, we used X-ray diffraction (XRD) measurements and X-ray photoelectron spectroscopy (XPS) measurements to analyze how thermal annealing affects perovskite films and the luminous efficiencies of PrLEDs that use them without any other chemical treatments such as solvent annealing process and nano-crystal pinning process [8]. We chose $CH_3NH_3PbBr_3$ as an emitting layer (EML) because it has higher exciton binding energy (76–150 meV), shorter exciton diffusion length (~100 nm) at room temperature (RT) and more stable cubic phase [17,26] than do other perovskite materials (e.g. 2–50 meV, ~50 nm and distorted cubic phase for exciton binding energy, exciton diffusion length and crystal structure respectively of $CH_3NH_3PbI_3$ at RT) [27,28]. We used the self-organized buffer hole injection layer (Buf-HIL) composed of poly(3,4-ethylenedioxythiphene):poly(styrene sulfonate) (PEDOT:PSS) and perfluorinated polymeric acid, tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid copolymer (PFI) to facilitate the hole injection to the OIP EML and prevent the exciton quenching at the interface [17,29-31].

1. Experimental details

To synthesize CH_3NH_3Br, we reacted 50 ml hydrobromic acid (Sigma-Aldrich Inc.) (45 wt% in water) and 30 ml methylamine (Junsei Chemical Co. Ltd) (40 wt% in methanol) in a 250-ml round-bottom flask for 2 h under vigorous stirring at 0 °C. After the reaction was finished, we evaporated all solvents by heating the solution at 50 °C for 1 h in vacuum. We collected the residual precipitates and purified them by dissolving in ethanol, recrystallizing from diethyl ether, and drying at RT in a vacuum oven for 24 h.

To fabricate the PrLEDs, we sonicated the ITO-patterned glass in acetone and in 2-isopropanol for 15 min, respectively, and then boiled the clean glass in 2-isopropanol for 30 min. Then, we UV-ozone treated the cleaned ITO glass for 10 min to remove residual organic molecules, and to make the surface hydrophilic. On the cleaned glass, Buf-HIL solution composed of PEDOT:PSS mixed with PFI solution (1:1 w:w) was filtered through a 0.45-μm polyvinylidene difluoride (PVDF) syringe filter, then spin coated at 4500 rpm for 90 s to give a 40-nm thickness. The resulting Buf-HIL was annealed at 150 °C for 30 min in air to remove residual solvents. The sample was transferred to N_2 atmosphere in a glove box. $CH_3NH_3PbBr_3$ solution was prepared by mixing CH_3NH_3Br and $PbBr_2$ (Sigma-Aldrich Inc.) (1:1 mol:mol) in *N*,*N*-dimethylformamide (DMF) (40% by wt), then spin-coated on the Buf-HIL at 3000 rpm for 90 s. The $CH_3NH_3PbBr_3$ layer has both scattered large particles (>1 μm) and thin uniform film (~100 nm). Then glass/ITO/Buf-HIL/$CH_3NH_3PbBr_3$ samples were annealed by baking at 90 °C for $t_{ann} = 0, 2, 5, 10, 20, 30$, or 60 min. After annealing, each sample were transferred to a thermal evaporator, then 1,3,5-Tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene (TPBI) (50 nm), LiF (1 nm) and Al (100 nm) were deposited in sequence at 1 Å/s, 0.1 Å/s and 3 Å/s, respectively, under high vacuum ($<10^{-7}$ Torr). The pixel area of PrLEDs is 6 mm^2. The fabricated devices were encapsulated to maintain the N_2 condition, and current-voltage-luminance characteristics were measured using a Keithley 236 source measurement unit and a Minolta CS200 spectroradiometer.

2. Results and discussion

2.1. XRD analysis

We compared the XRD patterns of $CH_3NH_3PbBr_3$ layer annealed at 90 °C for different t_{ann} to quantify how t_{ann} affected the crystallinity of films. XRD patterns of all samples showed sharp diffraction peaks at ~15.04° for (100), ~21.38° for (110), ~33.96° for (210), ~37.34° for (211), ~43.34° for (220) and ~46.12° for (300) [32]. The XRD pattern about 10 min annealing is taken from our previous paper for comparison [17]. These peaks are consistent with previous reports and indicate that well-crystallized $CH_3NH_3PbBr_3$ layers with the α-axis self-assembly was fabricated (Fig. 2a) [33]. However, most XRD peak intensities tended to increase over $0 \le t_{ann} \le 20$ min (Fig. 2b–f). The remaining solvent in film after direct spin-coating induced imperfect conversion from $CH_3NH_3PbBr_3$ precursors to crystal, and yielded $CH_3NH_3PbBr_3$ layers with poor crystallinity [21,22]; annealing for $10 \le t_{ann} \le 20$ min increased this crystallinity by evaporating residual solvent (DMF).

The crystallite sizes L were calculated using the Scherrer equation ($L = \frac{K\lambda}{B\cos\theta}$, where $K = 0.94$ [dimensionless] is the Scherrer constant, $\lambda = 0.154$ [nm] is the X-ray wavelength, B is FWHM [radian] of an XRD peak and θ [radian] is X-ray angle). All L were similar to 25.7 nm ± 0.4 nm, which is smaller than the grain size (>1 μm) [34]; the difference indicates that the perovskite films are consisted of many crystalline domains. Thus, thermal annealing of OIP films can increase the PLQE and crystallinity by not only removing residual solvents and completing the conversion of precursor to crystals but also increasing the orientation uniformity of the perovskite crystalline domains.

However, XRD peak intensities decreased at $t_{ann} > 20$ min, possibly due to sublimation of CH_3NH_3Br or decomposition to CH_3NH_2 and HBr from the crystal of $CH_3NH_3PbBr_3$ film during extended annealing. The sublimation or decomposition of CH_3NH_3Br makes the non-stoichiometric molar ratio of CH_3NH_3Br to $PbBr_2$ in $CH_3NH_3PbBr_3$, so this sublimation or decomposition can degrade the cubic phase crystal structure and reduce the XRD peak intensity. This result comes from the fact that when methylammonium halide (CH_3NH_3X; X is Cl or Br or I) and PbX_2 formed the perovskite structure ($CH_3NH_3PbX_3$), CH_3NH_3X can be released

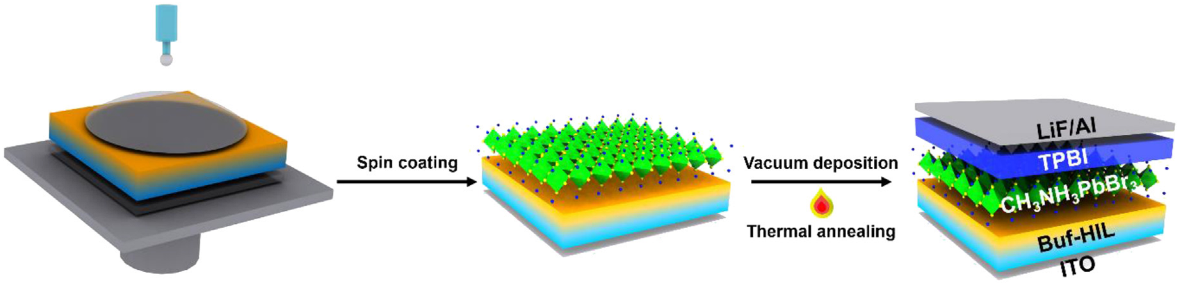

Fig. 1. Schematic illustrations of device fabrication.