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ABSTRACT

Polycrystalline CsPbBr₃ thin films are deposited by vacuum co-evaporation of cesium halide and lead halide precursors, leading to uniform pinhole-free morphology and precise control over the film thickness and precursor stoichiometry. By utilizing the organic hole and electron transport layers, all-vacuum-deposited perovskite LEDs are fabricated. The resulting devices exhibit a maximum luminance of 1800 cd/m², a 531 nm emission wavelength peak with a spectral linewidth of 21 nm, and an external quantum efficiency of 1.1%.

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INTRODUCTION

In recent years, organic–inorganic hybrid perovskites have emerged as an exciting class of semiconducting materials for thin-film optoelectronics. These semiconductors possess unique electro-optical properties, such as long carrier diffusion length, high absorption coefficients, and low levels of defect states. When used as photoactive films, perovskite solar cells with >20% power conversion efficiency have been demonstrated. As light emitters, perovskite materials exhibit narrow emission bandwidth, wavelength tunability across the visible spectrum, and high photoluminescence quantum yields (PLQYs), reaching 90% in solution for perovskite nanocrystals. Perovskite thin films have been adopted as the luminescent layer in light-emitting diodes (LEDs), with Friend et al. demonstrating the first room-temperature electroluminescence in organic–inorganic hybrid perovskite devices. While the external quantum efficiency (EQE) of these initial perovskite LEDs was low (<1%), the EQE has since improved to over 20% with the control of the film crystallization process and/or utilization of anion-exchanged perovskite nanocrystals.

Compared to organic–inorganic hybrid perovskites, all-inorganic CsPbX₃ (where X = Cl, Br, and I) perovskites exhibit superior thermal and chemical stability, while maintaining saturated color emission, making them an ideal candidate for perovskite LEDs. Currently, most studies of CsPbX₃ perovskite thin film fabrication focus on solution processing techniques using spin-coating deposition. However, low solubility limits of cesium halide salt hinder the spin-coating fabrication of a dense, compact CsPbX₃ crystalline film with complete area coverage. Incomplete coverage of the emitting layer can lead to substantial leakage current in a device, limiting the efficiency of the previously reported perovskite LEDs based on pristine CsPbX₃ perovskites.

One scalable alternative to solution processing for depositing high quality perovskite thin films is vacuum-based deposition, which has proven to be an effective technique for fabricating optoelectronic devices with multilayer stacks such as organic light-emitting diodes (OLEDs). Vacuum-based thermal evaporation can potentially deliver reproducible uniform perovskite thin films, and offer precise control over the precursor stoichiometry and thickness. Liu et al. demonstrated an efficient perovskite solar cell with planar heterojunction by evaporating methylammonium iodide and lead iodide precursor materials simultaneously to produce the CH₃NH₃PbI₃ absorber layer. While others have reported difficulties with evaporating the organic methylammonium halide precursor at a stable deposition rate under a high vacuum level due to its high vapor pressure, this problem can be resolved by replacing organic halides with inorganic cesium halide salt precursors, allowing controlled thermal evaporation.

In the present study, we report a systematic approach to preparing uniform and crystalline CsPbBr₃ perovskite thin films with
complete surface coverage via vapor co-evaporation of CsBr and PbBr₂ precursors. The ratio between the two precursors was found to play a critical role in enhancing the photoluminescence efficiency of the deposited perovskite thin films. An all-vacuum-deposited device architecture is developed, exploiting small-molecule organic charge transport layers together with the evaporated polycrystalline CsPbBr₃ thin film as the light emitter. The resulting green perovskite LED achieved a luminance of 1800 cd/m² and an EQE up to 1.1%.

RESULT AND DISCUSSION

Compact thin films of CsPbBr₃ were prepared using vacuum deposition (see detailed description in the section titled Experimental Methods). Figure 1(a) displays schematics of the deposition process where CsBr and PbBr₂ precursors were simultaneously thermally evaporated onto the rotating substrates placed at the top of the thermal evaporator under a high vacuum condition. Five perovskite samples with different molar ratios of CsBr and PbBr₂ (1:1, 2:1, 3:1, 4:1, and 5:1) were fabricated to further study the thin film characteristics. The crystal structures of the vapor-deposited perovskite films were analyzed by x-ray diffraction (XRD) measurements. Figure 1(b) shows the XRD spectra of CsPbBr₃ films deposited on glass substrates with varying molar ratios. All samples exhibit diffraction peaks at 15.2°, 21.6°, 30.6°, 34.4°, and 38.0°, matching with the orthorhombic (Pnma) crystal structure of CsPbBr₃, corresponding to the (101), (121), (202), (141), and (321) crystal planes. The lattice parameter is consistent with a number of previous reports. 20–22,30–32 CsBr and PbBr₂ characteristic peaks are absent, suggesting a complete transformation of the vapor-deposited CsPbBr₃ film. Furthermore, the change in film stoichiometry has a very little effect on the crystal structure of the deposited films, as evidenced by the stability in peak positions. The morphology of the
perovskite films is investigated by conducting top section SEM, as shown in Fig. 1(c). The films are uniform and pinhole-free with clear crystal domains. The coverage of these films is much improved compared to those fabricated by solution-processed techniques. We note that the grain size of the perovskite films becomes smaller as we increase the molar ratio. This could be due to the hindered crystal growth when an excess of CsBr is added. The exact cause requires further investigation.

To study the optical properties of the deposited perovskite films, we measured their absorption and photoluminescence (PL) spectra. Figure 2(a) plots the absorption spectra of CsPbBr$_3$ films with the molar ratio of CsBr to PbBr$_2$ varied from 1:1 to 5:1, showing sharp absorption peaks at wavelengths between $\lambda = 516$ nm and $\lambda = 518$ nm. All of the films also exhibit a saturated green PL emission [Fig. 2(b)] with peaks between $\lambda = 525$ nm to $\lambda = 531$ nm and a full-width-at-half-maximum (FWHM) as low as 20 nm. The small spectral shift between the absorption edges and PL peaks suggests that the PL emission of these perovskite films originates from the direct recombination across the band edge. We find that the molar composition of precursor materials plays an important role in the emission efficiency of the as-deposited perovskite films. As shown by the inset in Fig. 2(b), the films with 1:1 and 2:1 molar ratios have a relatively low PLQY with barely observable emission when those films are exposed to UV light. The film PLQY improves by a factor of 25 from 0.2% to 5.1% as the molar ratio is increased from 1:1 to 5:1. The correlation between the film composition and the PLQY has previously been noted in both spin-coated and vapor-deposited perovskite films. For instance, this PL enhancement has been ascribed to the reduced grain size that results in stronger exciton confinement, thereby enhancing radiative recombination. This agrees with the present study, which shows that the grain size of the deposited film clearly reduces when excess CsBr is introduced, according to the SEM results [Fig. 1(c)]. Other studies have attributed the gain in the PLQY to the improved surface passivation of CsPbBr$_3$ domains that could help mitigate the trap states, acting as non-radiative recombination centers.

Using the highest PLQY CsPbBr$_3$ thin films as the light emitting layer, we then demonstrate all-vapor-deposited perovskite LEDs. The device architecture of the perovskite LED is sketched in Fig. 3(a). Small-molecule organics Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (30 nm thick) and 1, 3, 5-tris (N-phenylbenzimiazole-2-yl) benzene (TPBi) (40 nm) are selected as...
hole- and electron-transport layers, respectively to ensure efficient charge injection into the perovskite layer. Thin films of indium-tin-oxide (ITO) (150 nm), Al (100 nm), MoO$_3$ (5 nm), and LiF (1 nm) serve as anode, cathode, hole-injection layer, and electron-injection layer, respectively. The energy band diagram of all layers is shown in Fig. 3(b). The entire device fabrication is performed at room temperature under vacuum conditions, ensuring an ultra-clean environment.

To evaluate the LED performance, current density–voltage–luminance (J–V–L), EQE-voltage characteristics, and external quantum efficiency spectra are recorded and shown in Fig. 4. The J–V characteristics [Fig. 4(a)] of devices show an electrical turn-on at $\sim$2.2 V, as evidenced by a sharp rise in the current density. We observe progressive improvement in EQE [Fig. 4(b)] with an increase in CsBr content, consistent with the enhancement in the perovskite film PLQY. The most efficient devices containing a 150 nm thick CsPbBr$_3$ emitting layer with a 5:1 precursor ratio have a peak EQE of 1.1% at 5.8 V, which is to our knowledge among the best for perovskite LEDs based on fully evaporated CsPbBr$_3$. The internal quantum efficiency (IQE) of 5.5% can be estimated by dividing the peak EQEs with an estimated out-coupling factor ($\sim$0.2). This IQE value suggests a near perfect charge injection and charge recombination efficiency with the current device architecture, and the EQE is dominantly limited by the perovskite film PLQY. As shown in Fig. 4(a), the 5:1 device’s luminance rises sharply as the bias is increased beyond 3 V, reaching a maximum luminance of 1800 cd/m$^2$ at an applied bias of 6.3 V. The turn-on voltage is 4.4 V (evaluated at a luminance of 1 cd/m$^2$). The device performance of all perovskite LEDs and the corresponding thin film PLQYs is summarized in Table I. Statistics of the peak device efficiency is also included in Fig. 4(c), which shows excellent device reproducibility within the range of 1:1 to 5:1 CsBr:PbBr$_2$ ratios. Figure 4(d) presents the external quantum efficiency spectrum of the perovskite LED under an applied bias of 5.5 V. The spectrum peaks at $\lambda = 531$ nm with a FWHM of 21 nm, and no parasitic emission from the adjacent organic layers is observed, indicating efficient carrier recombination solely within the perovskite emitting layer. Under ambient light, a uniform and stable electroluminescence (EL) is visible to the naked eye, as shown in the inset of Fig. 4(d).

In summary, we demonstrate all-vapor-deposited perovskite LEDs based on inorganic CsPbBr$_3$ emitters. Fabrication of CsPbBr$_3$ polycrystalline thin films by vapor co-evaporation of precursor materials CsBr and PbBr$_2$ enables uniform pinhole-free morphology and precise control over the film thickness and
stoichiometry. Our best performing device exhibits a peak EQE of 1.1% with the luminance reaching as high as 1800 cd/m² and EL peak emission at $\lambda = 531$ nm with a FWHM of 21 nm. With this and other recent demonstrations of LEDs containing vapor-deposited inorganic cesium halide perovskites, it is clear that evaporative deposition is a viable method for controlling the fabrication of high quality perovskite films, as needed for the LED and possibly future displays and lighting applications.

**EXPERIMENTAL METHODS**

**Materials**

PbBr$_2$ (99.999%) and CsBr (99.999%) were purchased from Sigma-Aldrich and used without further purifications. LiF (Lumtec, >99.9%), MoO$_3$ (Alfa Aesar, 99.995%), Tris(4-carboxyl-9-ylphenyl)amine (TCTA; Lumtec, >99.5%), 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi; Lumtec, >99.5%), and Al (Alfa Aesar, 99.999%) were used as received.

**Deposition of perovskite thin film**

The perovskite emissive layer (CsPbBr$_3$) is deposited by dual source thermal evaporation from the two precursor materials PbBr$_2$ and CsBr. Two crucible boats loaded with precursor materials are located at the bottom of the evaporator chamber. A quartz crystal monitor is installed above each evaporation source to monitor the film thickness and the rate of evaporation. The tooling factors of two sources are first calibrated individually before the co-evaporation.

The correct tooling factor is then determined by $T_f/T_m$, where $T_m$ is the actual film thickness measured by the quartz crystal monitor and $T_f$ is the film thickness measured using ellipsometry. We placed the device samples in a substrate holder above the sources with the film side facing downward. The substrate holder is constantly rotated to make sure uniform deposition throughout the process. As the pressure in the chamber reaches $10^{-6}$ Torr, we start to heat up the source boats and let the materials evaporate for 5–10 min to remove possible volatile impurities. Once the desired deposition rates are reached, the substrate shutter that separates the source boats and substrate holder is opened to commence deposition. The molar composition of CsBr to PbBr$_2$ is varied from 1:1 to 5:1. The molar ratios of the precursors can be calculated from the known film thicknesses, molecular weights, and density of the precursors. We can thus tune the molar ratios simply by changing the deposition rates of the two precursor materials. The rates are typically fluctuated by less than ±0.2 Å/s and ±0.1 Å/s for CsBr and PbBr$_2$, respectively. The as-deposited film is annealed on a hotplate at 100 °C for 30 min in a nitrogen-filled glovebox before deposition of subsequent layers.

**Perovskite LED fabrication**

Prior to device fabrication, pre-patterned indium-tin-oxide (ITO) substrates (obtained from Thin Film Devices, Inc.) are cleaned by sonication in detergent, de-ionized (DI) water, and acetone (5 min each), followed by boiling in isopropanol twice for 5 min. Oxygen plasma is subsequently used to treat the substrate for 10 min. The substrates are then loaded into a thermal evaporator for subsequent material depositions. MoO$_3$ (5 nm), TCTA (30 nm), CsPbBr$_3$ (150 nm), TPBi (40 nm), LiF (1 nm), and Al (100 nm) are thermally evaporated through a shadow mask at a base pressure of $10^{-6}$ Torr. The LED active area of 1.21 mm$^2$ is determined by the overlap of ITO and Al electrodes. The deposition rates are controlled at 1 Å/s for TCTA and TPBi, 0.5 Å/s for MoO$_3$ and LiF, and 3 Å/s for Al.

**Characterization and testing**

Steady-state PL spectra are obtained by exciting the perovskite film with a $\lambda = 405$ nm laser and collecting the emission spectra using a Si charge-coupled detector array (Princeton Instruments, Inc. Pixis). A Cary 5000 UV–vis spectrophotometer is used to take the optical absorbance data with a 1 nm wavelength step. The absolute PL quantum yield (PLQY) at room temperature is measured using an integrated sphere in air. Samples are excited with $\lambda = 405$ laser light nm at an intensity of 1 mW/cm$^2$. X-ray diffraction (XRD) patterns (20 scans) are obtained using a Buerk D8 diffra- tometer system with a Cu Kα radiation source. Scanning electron microscopy (SEM) is performed with a Zeiss FESEM Ultra Plus. The film thickness is measured using a Woollam variable-angle spectroscopic ellipsometer.

Perovskite LED device characterization is undertaken inside a nitrogen-filled glovebox. The electroluminescence (EL) spectrum is measured using an Ocean Optics SD2000 fiber-coupled spectrometer. Current density–voltage (J–V) characteristics are recorded using a computer-controlled Keithley 2636A source meter. A calibrated Newport 818-UV silicon photodiode is used to measure the optical power output. Luminance and EQE are then calculated by assuming the Lambertian emission profile and accounting for the wavelength dependence (weighted by the device’s EL spectrum) of the photodiode’s responsivity.

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