Efficient Flexible Inorganic Perovskite Light-Emitting Diodes Fabricated with CsPbBr$_3$ Emitters Prepared via Low-Temperature in Situ Dynamic Thermal Crystallization

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ABSTRACT: The present study systematically investigates the morphology and crystallization process of inorganic CsPbBr$_3$ perovskite layer films fabricated by thermal coevaporation in conjunction with continuous low-temperature thermal annealing to promote in situ dynamic thermal crystallization. The results confirm for the first time that both the crystal grain size and the compactness of the CsPbBr$_3$ films can be tuned during the thermal coevaporation fabrication process via in situ dynamic thermal crystallization. The performance of the PeLEDs employing the CsPbBr$_3$ films as the emitter layer is investigated in detail with respect to the substrate temperature and deposition rate employed during deposition of the CsPbBr$_3$ film. This study provides guidelines for developing suitable film production processes and highlights future challenges that must be addressed to facilitate the commercial development of large-area, uniform, and flexible perovskite-based optoelectronic devices.

KEYWORDS: In situ dynamic thermal crystallization, Low-temperature preparation process, Large-area, Flexible Perovskite light-emitting devices

Metal-halide perovskites have attracted increasing attention in the past decade due to their exceptional electrical and optical properties that make them ideal for use in optoelectronic applications. As a result, these materials have been employed in a wide variety of optoelectronic devices such as solar cells, light-emitting diodes (LEDs), photodetectors, and lasers. Among these applications, solution-processed hybrid inorganic–organic perovskite solar cells have obtained certified power-conversion efficiencies up to 25.2%, which is comparable to solar cells employing widely used inorganic semiconductors such as Si and GaAs.

Whereas hybrid inorganic–organic perovskites have been extensively developed, a group of inorganic CsPbX$_3$ (X = Cl, Br, I) perovskites has recently been investigated for their potential optoelectronic applications. These materials exhibit high photoluminescence quantum yields (PLQYs) >90% for nanocrystals in solution, high luminance, narrow optical emission bands with full width at half-maxima (fwhm) <20 nm, solution processability, and exceptional thermal stability compared with hybrid organic–inorganic perovskites. These properties make CsPbX$_3$ materials particularly promising for use as the emitting layers in perovskite-based LEDs (PeLEDs). Currently, the most widely studied PeLEDs have been based on CsPbBr$_3$ fabricated via the synthesis of colloidal nanocrystals. However, the central emission wavelength and fwhm of these nanocrystal emitter materials are typically limited by quantum-size effects. In addition, the electroluminescence (EL) peaks of CsPbBr$_3$ nanocrystals have been demonstrated to shift significantly with increasing nanocrystal size and increasing temperature. Furthermore, the photoluminescence (PL) of CsPbBr$_3$ nanocrystal films has been observed to exhibit a red shift relative to that of CsPbBr$_3$ nanocrystals in solution, which is closely related to energy transfer from smaller to larger sized nanocrystals in the films.

The use of colloidal nanocrystals for the development of CsPbBr$_3$ films introduces additional challenges. Several different methods have been developed for fabricating dense CsPbBr$_3$ perovskite films with uniform thickness, such as solution-processing methods, including one-step spin-coating, two-step spin-coating, spray-coating method, and inkjet printing. However, rapid solvent evaporation during
solution processing tends to produce nonuniform film morphologies, whereas low CsBr solubility in organic solvents severely limits the practical application of PeLEDs. Therefore, the development of CsPbBr₃ perovskite film preparation methods that can overcome these limitations is urgently needed to manufacture efficient and reliable PeLEDs. Thermal vacuum evaporation has been extensively used in the field of organic LEDs. This method has demonstrated superior controlled codeposition of organic semiconductor materials compared with solution processing methods and is particularly advantageous for ensuring optimum temperature conditions and deposition rate stability. However, whereas thermal evaporation has been applied to fabricate perovskite films, the films exhibit low crystallinity, which limits the

Figure 1. (a) Schematic diagram of the CsPbBr₃ layer thermal vacuum coevaporation deposition process in conjunction with in situ dynamic thermal crystallization. (b) Structure and band-gap energy of each functional layer. (c) Colorized cross-sectional scanning electron microscopy (SEM) image of a representative PeLED. (d–f) Representative top-view SEM images of 100 nm thick CsPbBr₃ films prepared at 30, 60, and 80 °C, respectively, under a standard deposition rate of 1.0 Å/s, where the insets present their corresponding grain size distributions and average grain sizes. (g) Relative work function over the surfaces of CsPbBr₃ films prepared at different temperatures.
EL performance of PeLEDs with emitter layers fabricated by this method.18

The present study addresses these issues by developing a film deposition strategy that combines the thermal coevaporation of inorganic CsPbBr3 perovskite precursors with continuous thermal annealing to promote in situ dynamic thermal crystallization. The morphology and crystallization process of the as-prepared inorganic CsPbBr3 perovskite layers are systematically investigated with respect to the substrate temperature and the deposition rate, and the results confirm for the first time that both the crystal size and the compactness of CsPbBr3 films can be tuned during the thermal coevaporation fabrication process via in situ dynamic thermal crystallization. The performance of the flexible large-area PeLEDs employing CsPbBr3 films as the emitter layer is investigated in detail. The optimum PeLED exhibits an exceptionally high luminance of ∼17 350 cd/m2 at 6.5 V. Moreover, this PeLED demonstrates a maximum current efficiency of ∼10.3 cd/A. In addition, the PeLED device exhibits excellent stability with a half-lifetime exceeding 400 min for an initial luminance of 500 cd/m2, which is among the best reported in the literature.18

Results and Discussion

Shown in Figure 1a is a schematic diagram of the CsPbBr3 layer thermal vacuum coevaporation deposition process in conjunction with in situ dynamic thermal crystallization. The in situ thermal dynamics have a precision on the order of ±1 °C. The individual material layers of the fabricated PeLEDs are illustrated in Figure 1b. Accordingly, the PeLEDs consist of substrate/ITO/HAT-CN (5 nm)/TAPC (45 nm)/CsPbBr3 (100 nm)/PO-T2T (30 nm)/Liq (1 nm)/Al (100 nm) layers. The details of all of the materials and the process are shown in the Experimental Section of the Supporting Information. An energy-band diagram corresponding to the PeLED layered structure is also given in Figure 1b. The colorized cross-sectional scanning electron microscope (SEM) image given in Figure 1c clearly shows a uniform CsPbBr3 perovskite emitting layer sandwiched between the TAPC and PO-T2T charge-transporting layers. The light-emitting area of the PeLEDs (3 × 3 mm2) is defined by shadow masks.

Figure 1d−f presents top-view SEM images of CsPbBr3 perovskite films deposited at different temperatures, and their corresponding grain size distributions and average grain sizes are presented as insets in the figures. The results demonstrate that the average CsPbBr3 perovskite grain size increases with increasing substrate temperature. A complete report of the average crystal grain sizes and degrees of coverage observed for CsPbBr3 perovskite films prepared at different temperatures with different rates is given in Table S1.

Kelvin probe force microscopy (KPFM) was used to measure the relative work function over the surfaces of the CsPbBr3 films grown at different temperatures, and the results are presented in Figure 1g. The data indicate that the relative surface work function of the CsPbBr3 film fabricated with a substrate temperature of 60 °C was more uniform than that of the other films, and the standard deviation was only 0.0051 eV. This can be attributed to the more uniform grain size of the CsPbBr3 film fabricated at this temperature. Moreover, the average work function values shifted upward by nearly 1 eV for the films fabricated with substrate temperatures of 60 and 80 °C. This phenomenon can be attributed to the modification of local work function values induced by clusters of CsPbBr3 grain vacancies in the film fabricated with a substrate temperature of 80 °C, which is highlighted by the red circles in Figure 1c. According to the work of Shi et al.,16 clusters of grain vacancies will strongly affect charge-carrier transport and recombination at the grain−boundary interfaces of a device.

Figure 2. Analyses of 100 nm thick CsPbBr3 films prepared at 30 and 60 °C of 1.0 Å/s: (a) X-ray diffraction (XRD) spectra. (b) Steady-state photoluminescence (PL) spectra (inset) (prepared on the ITO/TAPC) and time-resolved PL (TRPL). (c,d) Cross-sectional SEM images.
Moreover, a low grain-boundary density has been theoretically shown to decrease the extent of nonradiative recombination under conditions of comparable film coverage.30

Figure 2a presents the X-ray diffraction (XRD) spectra of the CsPbBr3 films grown on glass substrates at 30 and 60 °C. The results indicate that the in situ growth temperature does not alter the cubic phase of CsPbBr3. However, the magnitude and height variation of the diffraction peaks indicate that the growth temperature does affect both the degree of crystallinity and the crystal orientation of the layers. Here a highly crystalline perovskite layer is grown along the (100) and (200) crystal orientations for film deposition conducted at 60 °C. The absorption spectra of the CsPbBr3 films prepared at different temperatures in Figure S2 further prove the superior crystallinity of the film prepared at 60 °C. Moreover, this positively affects the uniformity of the crystal grain sizes of the

Figure 3. Atomic force microscopy (AFM) images of 100 nm thick CsPbBr3 films prepared on glass substrates at 60 °C with different deposition rates of (a) 0.5, (b) 1.0, and (c) 1.5 Å/s, respectively. (d) Schematic illustrating CsPbBr3 film growth under different deposition rates from 0.5 to 1.5 Å/s.
Figure 4. (a) Electroluminescence (EL) spectra of PeLED devices with CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates. CsPbBr₃ film emitter layers were prepared at 60 °C and 1.0 Å/s. (b) Photograph of a representative large-scale (70 mm × 20 mm) flexible PeLED. Characteristics of PeLED devices with CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates with respect to applied bias voltage: (c) current density and luminance and (d) current efficiency and external quantum efficiency (EQE).

perovskite films, as indicated by the top-view SEM images in Figure 1d,e.

In addition to the degree of crystallinity and crystal orientation of the CsPbBr₃ films grown, the nature of defects in the film is also a critical feature that affects the properties of the photogenerated carriers and the PeLED performance.⁷ Therefore, the trap states of the CsPbBr₃ films were investigated by evaluating their steady-state PL spectra and their time-resolved photoluminescence (TRPL), which are presented in Figure 2b. The steady-state PL spectra shown in the inset of Figure 2b demonstrate that the CsPbBr₃ film prepared at 60 °C provides a significantly enhanced steady-state PL intensity relative to the film prepared at 30 °C.

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\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}
\]

Table S2 summarizes the carrier lifetimes of the CsPbBr₃ films prepared at different substrate temperatures. For the latter, τ₁ increased from 11.89 to 13.60 ns and τ₂ increased from 33.54 to 47.54 ns. The increase in τ₁ indicates that defect states on the surface of the CsPbBr₃ film are reduced, resulting in less nonradiation recombination. On the contrary, the increase in τ₂ demonstrates a longer carrier lifetime and indicates the improved quality of the CsPbBr₃ film.⁶,¹⁹,⁴⁰,⁴¹ Overall, the CsPbBr₃ film fabricated at 30 °C exhibited a shorter average lifetime due to increased trap-assisted recombination at the grain boundaries.

The results of the TRPL analysis can be confirmed by the cross-sectional SEM images of the CsPbBr₃ perovskite films given in Figure 2c,d. Here the defects in crystal grain growth occurring at 30 °C along the vertical direction of the film during the thermal coevaporation process are marked with a red circle in Figure 2c. In contrast, the film prepared at 60 °C exhibits compact and homogeneous crystal grains. These data indicate that the enhancement in the PL intensity of the CsPbBr₃ film prepared at higher temperature can be attributed to a lower number of trap states originating from grain boundaries lying perpendicular to the direction of the substrate, which reduces the surface recombinations rates of the photoexcited charge carriers.²²,⁴³

Variations in the surface roughness of 100 nm thick CsPbBr₃ films grown at 60 °C with different deposition rates were evaluated by atomic force microscopy (AFM), and the results are presented in Figure 3a–c, along with the calculated root-mean-square (RMS) surface roughness values of the films. We note that the respective RMS roughness values of the CsPbBr₃ films decrease from 12.89 ± 0.23 to 8.87 ± 0.12 nm when increasing the deposition rate from 0.5 to 1.0 Å/s and increase to 11.96 ± 0.16 nm at a deposition rate of 1.5 Å/s. We can conclude that CsPbBr₃ films with smoother surfaces are obtained when employing a deposition rate of 1.0 Å/s. These findings can be understood according to the schematics given in Figure 3d illustrating film growth under the three different deposition rates. Accordingly, we propose the following mechanisms for perovskite film growth. For a low evaporation rate, island-like structures are formed, and according to the Volmer–Weber model, this is due to the lower kinetic energy of the CsBr molecules relative to that of the PbBr₂ molecules, which results in a more pronounced adhesion of CsBr molecules to the surface. As the film grows, the island-like CsPbBr₃ regions begin overlapping, and the film preferentially grows along with the optimal crystal orientation (200) of the CsPbBr₃ compound. This process would form a smooth CsPbBr₃ film. However, the direction of the crystal orientation may change when the island-like structures merge, which
would lead to defects in the films grown along a specific crystal direction. With an increasing deposition rate, the CsBr molecules exhibit higher kinetic energy than the PbBr₂ molecules, and this limits their homogeneous adhesion to the substrate, which results in the formation of a uniform layer at a deposition rate of 1.0 Å/s. Finally, the low binding energy of the films prepared by the vacuum evaporation results in the generation of voids in the film grown at the highest rate of 1.5 Å/s owing to collisions between the larger molecular weight PbBr₂ molecules or collisions with the developing film.

The effects of substrate temperature and deposition rate on the characteristics of the CsPbBr₃ films can be further analyzed by considering the performance of PeLED devices fabricated with CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates. Figure 4a presents the EL performance of PeLED devices containing CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates. We note that all EL spectra present equivalent emission peak positions at 520 nm, which corresponds to the CIE color coordinates (0.1, 0.78). We also note that the EL peak positions of the PeLEDs exhibited negligible dependence on the applied voltage, suggesting that superior color stability was obtained. Figure 4b presents a photograph of a representative large-area PeLED fabricated with a CsPbBr₃ film emitter layer prepared at 60 ± 1 °C with a deposition rate of 1.0 Å/s.

Figure 4c presents the current efficiency and external quantum efficiency (EQE) as a function of the applied bias voltage for PeLED devices fabricated with CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates, and Figure 4d presents the current density and luminance as functions of the applied bias voltage for PeLEDs fabricated with CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates. The primary characteristics of the PeLEDs fabricated with CsPbBr₃ film emitter layers prepared at different substrate temperatures and deposition rates in the present study are shown in Table S2. Compared with the EL performances of PeLEDs prepared at other temperatures (shown in the Figures S3—S5), these results demonstrate that the devices presented in the present work generally exhibit lower turn-on voltages, higher luminance, and overall better performance than previously reported PeLEDs fabricated with emitter layers prepared via conventional thermal evaporation.

The EL lifetimes of the PeLED devices were evaluated under ambient conditions (25 ± 2 °C). The half-life time of the device with the CsPbBr₃ film prepared at 60 °C was 418 min (shown in Figure S6), which is among the longest half-life times reported in the literature. At the same time, Figure S7 shows that after the long-term storage process, the performance of the device can still be maintained. The excellent half-life time and the stable luminance intensity of this device can be attributed to its large grain size and degree of coverage (Table S1) in addition to a low density of crystal grain vacancy clusters.

**CONCLUSIONS**

This study systematically investigated the morphology and crystallization process of inorganic CsPbBr₃ perovskite single-layer films fabricated by thermal coevaporation in conjunction with continuous low-temperature thermal annealing to promote in situ thermal dynamic crystallization. The results confirmed for the first time that both the crystal grain size and the compactness of the CsPbBr₃ films can be tuned during the thermal coevaporation fabrication process via in situ thermal dynamic crystallization. Moreover, the optimized fabrication procedure was employed to fabricate flexible large-area (1400 mm²) PeLEDs without damaging the substrate and adjacent functional layers, which is a common consequence of other deposition methods due to the use of high temperatures or solvents. Compared with other standard film deposition processes, such as screen printing and inkjet printing, the proposed coevaporation process is more suitable for the current industrial production. Although the current efficiencies of the PeLEDs prepared according to the proposed methodology remain relatively low, this issue can be addressed in the future by introducing a broader range of perovskite materials and designing new device structures. Therefore, vacuum evaporation technology may provide a good solution to the present problem of preparing large-area, flexible, and highly efficient perovskite-based LED displays.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c01550.

Details of experimental methods and materials. Figures showing AFM surface-relief-line images of CsPbBr₃ films, ultraviolet—visible (UV—vis) absorption spectra, characteristics of PeLED devices with different CsPbBr₃ film emitter layers, and the lifetime test data. Tables showing the average crystal grain size and the degree of coverage of CsPbBr₃ films, the carrier lifetime obtained based on the TRPL curves, and the CsPbBr₃-based PeLED characteristics of this study and published data by other groups.

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Author Contributions
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