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Strategic heating for growing perovskite single crystals

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The development of perovskite-based high-performance optoelectronic devices requires the growth and fabrication of perovskite single-crystal thin films (PeSCTFs). Recently, scientists at the Southern University of Science and Technology demonstrated a new crystal growth strategy that achieved PeSCTFs on transport layers with a high area-to-thickness ratio by using gradient heating nucleation and room temperature growth. The resulting formamidinium lead bromide PeSCTFs exhibit a record low trap density and high carrier mobility. This method can be potentially applied to PeSCTFs of various compositions on different transport layers, making it a versatile technology for developing high-performance perovskite optoelectronics.

Perovskite materials have demonstrated excellent optoelectronic properties, such as high carrier mobility, long carrier lifetime, and tunable bandgap.[1] However, the performance of perovskite optoelectronics is limited by the perovskite film quality fabricated by solution growth or physical evaporation. These methods often result in polycrystalline films with grain boundaries and defects that trap charge carriers and reduce device efficiency.[2] PeSCTFs have fewer defects and thus higher carrier mobility and longer carrier lifetime than polycrystalline films.[3–5] A typical method is to fabricate PeSCTFs to transfer it from initially grown substrates to target transport layers, which usually causes poor interfacial contacts and mechanical damages. To solve this problem, *in situ* growth of PeSCTFs on transport layers is developed to avoid any additional post-processing.[6] However, *in situ* grown PeSCTFs typically have an area less than 1 cm^2, which is not ideal for device integration, and have a thickness greater than tens of micrometers, which is not suitable for carrier transport.[6] The *in situ* growth of PeSCTFs on transport layers with a high area-to-thickness ratio remains a challenge.

Wang et al. demonstrated a new crystal growth strategy that overcomes this challenge by using gradient heating nucleation and room-temperature growth (GHN-RTG) (Figure 1A).[7] The authors were able to grow formamidinium lead bromide ($FAPbBr_3$) PeSCTFs with a record low trap density of 3.76×10^8 cm^{-3}, a high carrier mobility of up to 185 $cm^2V^{-1}s^{-1}$, and an area-to-thickness ratio of 1.84×10^5 mm.[7]

To understand the mechanism of crystal nucleation and growth, the authors designed three control experiments using the high-temperature growth (HTG) method, the gradient heating nucleation and high-temperature growth (GHN-HTG) method, and the GHN-RTG method. In all methods, the precursor solution was dropped on the substrate and capped by another superstrate coated with different transport layers to form a sandwich structure.[8] To measure the solubility of $FAPbBr_3$ crystals, the authors added extra solvents to the solution until excess solute was completely dissolved. As the name suggests, HTG anneals the sandwiched precursor solution at a high temperature (Figure 1B, from A1 to B1, C1, and then D1), while GHN-HTG involves annealing the solution at a slowly increasing temperature and then maintaining it at a high temperature (Figure 1B, from A2 to B2, C2, D2, E2, F2, G2, H2, I2, J2, K2, L2, and M2), and GHN-RTG involves slowly heating the solution to a high temperature and cooling it down to room temperature (Figure 1B, from A2 to B2, C2, D2, E2, F2, G2, H2, I2, J2, K2, L2, and then M3). Among the three methods, the GHN-RTG method gives the best crystal quality, as evidenced by X-ray diffraction (XRD) measurements.

When the temperature is gradually heated up (from A2 to B2, C2, D2, E2, F2, G2, H2, I2, J2, K2, and then L2), inverse temperature growth promotes the formation of multiple nuclei with the c-axis perpendicular to the substrate surface.[7,9] Lots of nuclei and clusters would form with different in-plane orientations and the crystal quality would be compromised. However, in GHN-RTG, after a small number of nuclei form at a slightly oversaturated zone, the temperature is decreased immediately to M3 so that fewer nuclei will form and the crystal will grow slowly. A slow growth rate suppresses the formation of defects. Additionally, the reduced growth temperature decreases the precursor oversaturation and thus dissolves the small crystals, leaving behind only the big crystals because of Oswald ripening.

The authors investigated the effect of transport layers on the crystal growth and electronic properties of $FAPbBr_3$

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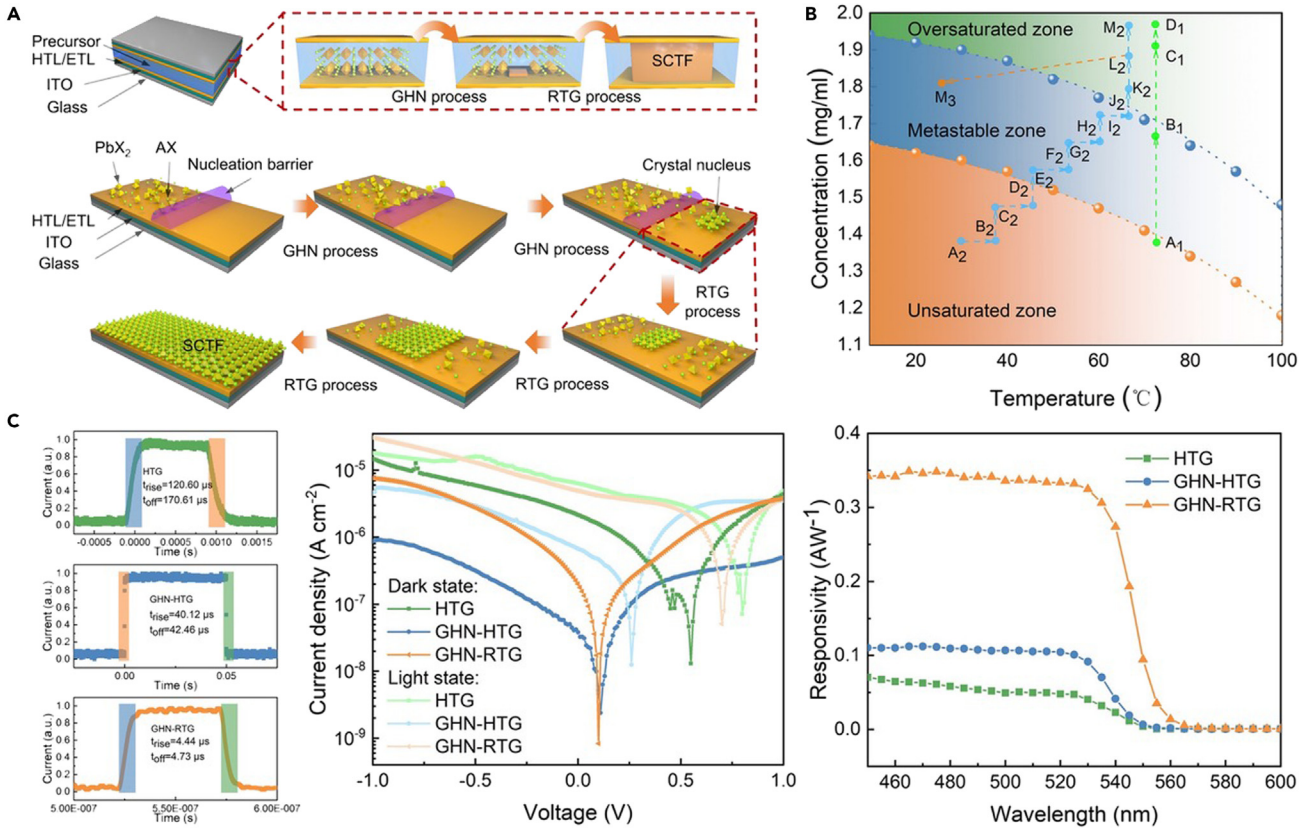

Figure 1. Growth process and device performance of $FAPbBr_3$ PeSCTFs

(A) Schematic of the nucleation and growth process of the $FAPbBr_3$ PeSCTFs on a tin-doped indium oxide (ITO)/ hole transport layer (HTL) or electron transport layer (ETL) substrate by GHN-RTG.

(B) The GHN-RTG process in the solubility map of $FAPbBr_3$.

(C) The response time (left), dark/light current density (middle), and responsivity (right) of photodiodes based on crystals grown by HTG, GHN-HTG, and GHN-RTG.

(A)–(C) are reproduced and adapted from the paper by Wang et al.

PeSCTFs. They found that poly[bis (4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) layers promoted the best crystal quality and highest carrier mobility due to its low surface energy and strong hydrogen bonds at the PTAA/perovskite interface. The low surface energy decreases the nucleation rate and minimizes the number of nuclei, leading to enhanced crystal quality.[6] The strong hydrogen bond between the PTAA substrate and $FAPbBr_3$ PeSCTFs enables efficient separation and extraction of carriers, leading to high-performance photodetectors.

The authors also investigated the stability of $FAPbBr_3$ PeSCTFs under ambient conditions by storing them in air at room temperature for up to 30 days. $FAPbBr_3$ PeSCTFs grown by the GHN-RTG method had enhanced stability because of the presence of few grain boundaries and thus a lack of channels for water and oxygen molecules to diffuse and attack the grain boundaries. Photoluminescence measurements under different humidity also showed that they had a slower signal decay compared to those grown by the GHN-HTG and HTG methods.

The authors fabricated photodiodes and measured their performance based on the $FAPbBr_3$ PeSCTFs (Figure 1C). The devices exhibit a fast response time of 4.44 μs, a low dark current density of 8.0×10^{-10} A/cm^2 at −0.10 V bias voltage, and a high responsivity of up to 0.35 A/W. These properties are among the best reported for PeSCTF-based photodiodes, which demonstrates the potential of this crystal growth strategy for high-performance optoelectronic devices.

This strategy can be applied to grow perovskite materials of other compositions such as $MAPbI_3$, PEA_2PbI_4, and $Cs_{0.05}FA_{0.9}MA_{0.05}PbI_{2.7}Br_{0.3}$, as well as on other transport layers. This method is compatible with large-area deposition techniques such as slot-die coating and spray-coating. By using

large-area substrates, this method has the potential to be scaled up for industrial production.

Despite the promising results, there are still several challenges to be addressed in future studies. One challenge is to improve the reproducibility and yield of this method by optimizing the growth conditions. Another challenge is to investigate the stability and degradation mechanisms of whole PeSCTF devices, instead of bare thin films, under various environmental conditions such as humidity, temperature, and light exposure.[10] Integrating the thin film into devices will introduce many complicated factors that will influence the stability of the whole devices. Finally, the proposed method requires a long growth time of 30 days, which limits its throughput and practical uses. Future studies could explore ways to shorten the growth time while maintaining the quality of the PeSCTFs. Nevertheless, this work has the potential to revolutionize the field of perovskite optoelectronics by enabling the mass production of high-quality PeSCTFs.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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All-thermally evaporated perovskite LEDs toward high-resolution active-matrix displays

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Perovskite LEDs (PeLEDs) have shown great promise for next-generation displays. However, the performance of evaporated PeLEDs has been hindered by perovskite films with a high density of defects. In a recent study published in *Nature Photonics*, Tang et al. developed a tri-source co-evaporation strategy that effectively confines charge carriers and passivates surface defects, resulting in the fabrication of efficient all-thermally evaporated PeLEDs, which is promising for high-resolution active-matrix displays.

The emergence of an information society has spurred the development of next-generation Rec. 2100 display technology, which is capable of rendering information more clearly and vividly on a variety of devices, including smartphones, computers, and televisions.[1] Light-emitting diodes (LEDs) fabricated using emitters hold great promise for next-generation full-color display and solid-state lighting technologies. Of all the electroluminescent (EL) emitters, traditional III-V group GaN-based LEDs have been highly developed, exhibiting high brightness, high efficiency, and outstanding stability. However, their preparation requires

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