Solution-Processed Epitaxial Growth of MAPbI$_3$ Single-Crystal Films for Highly Stable Photodetectors

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Recent years, organic-inorganic hybrid perovskites (OIHPS) have been widely used in applications, such as solar cells, lasers, light-emission diodes, and photodetectors due to their outstanding optoelectronic properties. Nowadays photodetectors based on perovskite films (PFs) suffer from surface and interface traps, which result from low crystalline quality of perovskite films and lattice mismatch between perovskite films and substrates. Herein, we fabricate MAPbI$_3$-(MA = CH$_3$NH$_3$) single-crystal films (SCFs) on MAPbBr$_3$ single crystal substrates in MAPbI$_3$ precursor solution during crystallization process via solution-processed epitaxy. Benefit from the good lattice matching, epitaxial MAPbI$_3$ SCFs with high crystallinity and smooth morphology are of comparable quality to MAPbI$_3$ PSCs and are of better quality than MAPbI$_3$ polycrystalline films. Here we report that epitaxial MAPbI$_3$ SCFs have a low trap density of $5.64 \times 10^{11} \text{cm}^{-3}$ and a long carrier lifetime of 11.86 µs. In this work, photodetector based on epitaxial MAPbI$_3$ single-crystal film (SCF) exhibits an excellent stability of a long-term stable response after 120 days, a fast response time of 2.21 µs, a high responsivity of 1.2 A W$^{-1}$ and a high detectivity of $3.07 \times 10^{12}$ jones.

Keywords: perovskite, epitaxial growth, photodetector, solution-processed, single-crystal film

INTRODUCTION

Organic-inorganic hybrid perovskites (OIHPS) have attracted worldwide numerous attention in recent years due to their remarkable properties in optoelectronic applications, such as solar cells, lasers, light-emission diodes and photodetectors (Shao et al., 2014; Tan et al., 2014; Wang et al., 2014, 2019a; Cho et al., 2015; Stranks and Snaith, 2015; Ling et al., 2016). As a new generation of promising semiconductor materials, solution-processable OIHPS are low-cost and have high absorption coefficient, tunable bandgap and long carrier lifetime and diffusion length (Xing et al., 2014; Fang et al., 2015; Wei et al., 2017). Up to now, not only devices based on perovskite single crystals (PSCs) have been widely used but also perovskite films (PFS)-based devices have shown great potential for high-performance photodetectors for visible light, near-infrared light...
and high energy ray (Shao et al., 2014; Kim et al., 2017; Wang et al., 2018, 2020). For example, Kim et al. (2017) used MAPbI$_3$ films for large-area, low-dose X-ray imaging, Ji et al. (2018) reported OIHPS films-based photodetectors with high-performance and Hou et al. (2020) reported narrowband photodetectors based on mixed halide PFs. The critical factors of PFs-based devices are high crystallinity, smooth morphology of films and good lattice matching between layers to form high-quality epitaxial films on substrates, which result in low trap density, long carrier lifetimes, and long diffusion lengths (Shi et al., 2015; Ji et al., 2018; Tang et al., 2019; Chen et al., 2020). Although many epitaxy approaches, such as spin-coating method, vapor-phase epitaxy as well as van der Waals epitaxy have been used to grow PFs used for optoelectronic devices (Wang et al., 2015, 2021; Yang et al., 2015; Long et al., 2018; Kelso et al., 2019; Chen et al., 2020), it is also a challenge to overcome the lattice mismatching between epitaxial PFs and substrates and to obtain high-crystallinity PFs with smooth morphology and good stability. Furthermore, the high trap density, short carrier lifetimes and short diffusion length of epitaxial PFs have restricted the development of photodetectors based on PFs (Wang et al., 2014; Chen et al., 2015; Tong et al., 2017; Yang et al., 2017; Abdi-Jalebi et al., 2018).

Methylammonium lead halide perovskites (MAPbX$_3$, where X = Cl, Br, I) have been the most widely studied OIHPS (Wei et al., 2017; Jiang et al., 2019) and the lattice parameters of MAPbI$_3$ and MAPbBr$_3$ are calculated as 6.23 and 5.93 Å, respectively. The lattice mismatching rate is calculated to be only 4.81% at room temperature so that MAPbI$_3$ single-crystal films (SCFs) are able to be epitaxially grown on MAPbBr$_3$ single crystal substrate (Wang et al., 2020; Xu et al., 2020). Here in this work, different from reported solution-processed epitaxy, such as spin-coating method, our work directly put MAPbBr$_3$ substrates into MAPbI$_3$ precursor solution. Benefit from good lattice matching, MAPbI$_3$ layers can directly grow on the surface of MAPbBr$_3$ substrates in MAPbI$_3$ precursor solution at optimal growth temperature during crystallization process. This method in our work can easily get high-quality epitaxial layers with high crystallinity, good morphology and thickness of micro level for stable photodetectors. The epitaxial MAPbI$_3$ SCFs are of comparable quality to MAPbI$_3$ PSCs and are of better quality than MAPbI$_3$ polycrystalline films. Furthermore, epitaxial MAPbI$_3$ SCFs with dense structure have much better stability than polycrystalline films. X-ray diffraction (XRD) is used to compare the crystallinity of epitaxial MAPbI$_3$ SCFs and scanning electron microscopy (SEM) is used to characterize the surface morphology and the thickness of epitaxial MAPbI$_3$ SCFs. Additionally, this work fabricate a high performance stable photodetector based on high-quality epitaxial MAPbI$_3$ SCFs on MAPbBr$_3$ single crystal substrate as well as a photodetector based on MAPbI$_3$ PSCs for comparison. Moreover, the trap density is characterized by space-charge-limited-current (SCLC) and the stability is exhibited by long-term dark currents and photocurrents. The high-crystallinity film has low trap density of $5.64 \times 10^{12}$ cm$^{-3}$ and long carrier lifetime of 11.86 μs. Briefly, this photodetector has outstanding optoelectronic performance with a good stability, a fast response speed of 2.21 μs, a responsivity of 1.2 A W$^{-1}$ and a high detectivity of $3.07 \times 10^{12}$ jones.

### MATERIALS AND METHODS

#### Preparation of CH$_3$NH$_3$I Powder and CH$_3$NH$_3$Br Powder

To get CH$_3$NH$_3$I powder, Hydroiodic Acid (40 wt% in water, Macklin) reacted with Methylamine (30–33 wt% in ethanol, Macklin) in a 50 ml bottle at 0°C for 2 h with stirring. After fully reaction, the mixed solution was heated to 100°C on a hot plate with magnetic stirring then the precipitate of CH$_3$NH$_3$I gradually appeared. The precipitate of CH$_3$NH$_3$I was washed in ether solution twice and was re-dissolved in absolute ethanol. The CH$_3$NH$_3$I powder was collected after dried at 75°C in a vacuum dryer (China) for 12 h. To get MAPbBr$_3$ powder, Hydrobromic Acid (55 wt% in water, Macklin) was mixed with Methylamine (30–33 wt% in ethanol, Macklin) and other steps are the same as the synthesis of CH$_3$NH$_3$I powder.

#### Preparation of Precursor Solution

To get MAPbI$_3$ precursor solution, as-prepared CH$_3$NH$_3$I and Lead iodide (PbI$_2$, 99%, Sigma Aldrich) with a ratio of 1:1 were dissolved in anhydrous γ-butyrolactone (GBL, 99%, Aladdin). The final concentrations were 0.1 M Lead iodide and 0.1 M CH$_3$NH$_3$I mixed in 100 ml GBL solution. And MAPbBr$_3$ precursor solution was a N, N-Dimethylformamide (DMF, 99.5%, SCR) solution which dissolves as-prepared CH$_3$NH$_3$Br and lead bromine (PbBr$_2$, 98%, Sigma Aldrich) with a ratio of 1:1.

#### Device Fabrication

To grow high-quality MAPbBr$_3$ PSCs as substrate, the MAPbBr$_3$ precursor solution was heated in crystallizing dish in air from 55 to 80°C at a rate of 0.3°C h$^{-1}$. Then the MAPbBr$_3$ PSCs was put into MAPbI$_3$ precursor solution to grow epitaxial MAPbI$_3$ SCFs at 110°C. The absolute dichloromethane solution was used to wash off the remains of the precursor solution from the crystal surface. The programmable heating control system was realized on IKA-RET control-visc. The final device was cut by diamond wire (Φ0.35 mm) and polished by Glycerin and diamond powder (Φ0.5 μm) mixed solution. The cutting and polishing system (STX-202A, UNIPOL-802) was pursued from KEJING company (Shenyang, China). And the toluene solution was used to wash the mixed solution remaining on the surface of single crystal. The gold electrodes were deposited on the surface of MAPbI$_3$ single-crystal film by a metal shadow mask with 500 μm channel by thermal evaporation in vacuum.

#### Characterization

Scanning electron microscopy (SEM) images were taken with a Quanta 200 FEI (United States). Atomic force microscope (AFM) was obtained by Mlyumode-8-AM. X-ray diffraction (XRD) patterns were obtained by XTRA (Switzerland). Photoluminescence (PL) spectra was measured by UV–vis spectroscopy (Lab Tech Bluestar, United States).
Device Performance Measurements
All measurements were performed on the probe station. Keithley 2410 was used as the voltage source to measure current-voltage curve (I-V) with 0.6 V/s voltage sweep rate. A 355 nm pulsed Nd:YAG laser with 6 ns pulse width at 20 Hz was used as the illumination source and response time was measured using an Agilent oscilloscope (DSO-X4054A) of KEYSIGHT. The 670 nm light source was obtained from L10762 of Hamamatsu. Agilent 81110A was use to power the light-emitting diode (LED). The working voltage and current of XRD copper target ray tube is 40 KeV and 40 mA, respectively. And the emission laser of 450 nm is obtained from NBET-LASER.

RESULTS AND DISCUSSION
As illustrated in Figure 1A, a solution-processed epitaxy is employed to fabricate MAPbI₃ SCF on MAPbBr₃ single
crystal substrate. Firstly, a high-quality MAPbBr\(_3\) single crystal is put into the precursor solution of MAPbI\(_3\) heated to 110°C at which the MAPbI\(_3\) SCFs can be densely and rapidly grown on the whole surface of the substrate. Then, after cutting and polishing, a MAPbI\(_3\) SCF is deposited on MAPbBr\(_3\) (200) single crystal substrate. SEM images of the epitaxial MAPbI\(_3\) SCF and the cross section of the epitaxial MAPbI\(_3\) SCF on MAPbBr\(_3\) demonstrate the morphology and thicknesses of epitaxial MAPbI\(_3\) SCFs. As shown in Figure 1B, epitaxial MAPbI\(_3\) SCF with smooth surface are grown densely on the MAPbBr\(_3\) single crystal substrate. Moreover, the thickness of epitaxial films is about 37.1 µm which are two orders of magnitude thicker than films deposited by spin-coating method (Wang et al., 2014; Fei et al., 2017; Ji et al., 2018), as clearly shown in Figure 1C. And the small picture in Figure 1C shows the interface of the epitaxial layer and substrate. Epitaxial MAPbI\(_3\) SCF with smooth morphology and controllable thickness can be directly grown on MAPbBr\(_3\) single crystal substrate due to good lattice matching (Li et al., 2020; Pan et al., 2020; Xu et al., 2020). As shown in Figures 1D,E, Atomic force microscope (AFM, Mulyimode-8-AM) was performed to further characterize the surface of MAPbI\(_3\) film and the roughness is approximately 14.9 nm.

XRD and PL characterization are performed to determine the quality and crystallinity of the epitaxial MAPbI\(_3\) SCFs. For comparison, the XRD spectra of the epitaxial MAPbI\(_3\) on MAPbBr\(_3\) (orange line), MAPbBr\(_3\) PSC (green line) and MAPbI\(_3\) PSC (blue line) are shown, respectively, in Figure 2A.

Different from MAPbI\(_3\) single crystal of hexagonal structure, the epitaxial MAPbI\(_3\) film changes to cubic structure because of the cubic MAPbBr\(_3\) substrate (Wang et al., 2019b). Additionally, Figure 2B shows a clear MAPbI\(_3\) (200) peak at a Bragg angle of 2θ = 28.22° and a MAPbBr\(_3\) (200) peak at 2θ = 28.47°. Furthermore, MAPbI\(_3\) (200) peak with a full width at half-maximum (FWHM) of 0.0925 in Figure 2B, which is comparable to MAPbI\(_3\) single crystal (200) peak with a FWHM of 0.1121, indicates the high crystallinity of epitaxial MAPbI\(_3\) SCFs (Liu et al., 1991, 2016). Figure 2C demonstrates the steady-state PL spectra at room temperature with a strong emission peak at 791 nm under the 450 nm excitation with a FWHM of 32.3 nm, which is smaller than 60 nm of MAPbI\(_3\) single crystal and 55 nm of MAPbI\(_3\) polycrystalline film (Han et al., 2018), confirming the high quality of epitaxial film.

Moreover, Figure 2D illustrates that the absorption onset of epitaxial MAPbI\(_3\) SCF is 840 nm, which are comparable to the 850 nm absorption onset of MAPbI\(_3\) single crystal (Dong et al., 2015). And the redshift is obvious compared to the 780 nm absorption onset of polycrystalline MAPbI\(_3\) film (Zhang et al., 2016). As shown in Figure 2E, double exponential fitting is performed to evaluate the carrier lifetime (τ) of epitaxial MAPbI\(_3\) SCF. The short lifetime of 0.874 ± 0.002 µs indicates surface recombination while long lifetime of 11.86 ± 0.14 µs suggests bulk recombination (Shi et al., 2015). The carrier lifetime of epitaxial MAPbI\(_3\) SCF is much longer than the carrier lifetime of polycrystalline film of nanosecond scale (Tong et al., 2017). In addition, space-charge-limited current (SCLC)
technique is used to estimate the trap density of epitaxial MAPbI$_3$ SCF (Rose, 1955). The formula is $n_{traps} = \frac{2eV_{TFL}}{qL}$, where $\varepsilon$ is relative dielectric constant, $V_{TFL}$ is the trap-filled limit voltage, $q$ is the electronic charge. As to the horizontal device architecture in this work, $L$ is the channel length between two gold electrodes, which were deposited on the surface of MAPbI$_3$ films by a shadow mask. As shown in Figure 2F, there is a linear current-voltage curve ($n = 1$) obeying Ohm’s law since the injected charge carriers at low applied voltage is too weak to completely fill trap center. As the applied voltage gradually increases, the injected carrier concentration is greater than the thermally excited carrier concentration and the conduction law changes from the ohmic mode to the SCLC mode. When the applied voltage further increases, all injected charge carriers are used to fill deep traps and all traps will be filled at $V_{TFL}$ (Quah and Cheong, 2013a,b). Figure 2F exhibits the current-voltage curve for the epitaxial MAPbI$_3$ based structure. The $L$ is 500 $\mu$m with 1% error and $V_{TFL}$ is 50 V so that the low trap density is calculated as $5.64(\pm0.12) \times 10^{11}$ cm$^{-3}$, which is much lower than polycrystalline films (Dong et al., 2015; Li et al., 2018). The high quality and crystallinity of epitaxial MAPbI$_3$ SCF benefit the wider absorption range, longer carrier lifetime and lower trap density than polycrystalline films.

To further validate the quality of the epitaxial MAPbI$_3$ SCF, a horizontal architecture photodetector with two golden electrodes deposited on the surface of epitaxial MAPbI$_3$ SCF is fabricated as shown in Figure 3A. A light-emitting diode at 670 nm is used as light source for characterization of optoelectronic performance. Figures 3B,C plot the typical I-V curve under various light illumination intensities and the temporal response at different voltage bias of our photodetector, respectively. The dark current is very low of 7.1 nA at 0.2 V, which benefits the high photocurrent to dark current ratio ($I_{ON}/I_{OFF}$) of 331.7 with 2.5 mW cm$^{-2}$ light illumination. Additionally, responsivity ($R = \frac{P_{light} - P_{dark}}{J_{dark}}$) and detectivity ($D = \frac{\sqrt{P_{light}}}{\sqrt{P_{dark} J_{dark}}}$) are calculated to evaluate the performance of this photodetector (Gong et al., 2009; Zhang et al., 2018). As shown in Figure 3D, R is as high as 1.38 A W$^{-1}$ and the maximum D is $3.07 \times 10^{12}$ Jones at 20 V bias with 90 $\mu$W cm$^{-2}$ illumination at 670 nm, which are higher than polycrystalline films-based devices, reflecting the efficiency and ability of this photodetector responds to weak optical signal (Jiao et al., 2017; Wang et al., 2019c). Additionally, responsivities as a function of wavelength from 400 to 900 nm are illustrated in Figure 3E. And the normalized EQE of MAPbBr$_3$ single crystal in Figure 3E indicates that photodetectors based on epitaxial films can widen the absorption range of substrate. As shown in Figure 3F, a 6 ns pulsed laser is used to measure the response speed and it takes only 2.21 $\mu$s for current decay to 63% at 20 V bias, which is much faster than devices based on polycrystalline films, owing to the high quality of epitaxial MAPbI$_3$ SCF (Horvath et al., 2014; Mi et al., 2017; Wu et al., 2020).
To further indicate the high quality of epitaxial MAPbI$_3$ SCF, variable temperature crystallization (VTC) method (Wang et al., 2017) is employed for synthesis of MAPbI$_3$ PSC and a photodetector based on MAPbI$_3$ PSC is fabricated and tested under same test environment for comparison in this work. Figures 4A,B illustrate the dark current and the photocurrent with 90 $\mu$W cm$^{-2}$ illumination at 670 nm of epitaxial film-based device and PSC-based photodetector. Epitaxial film-based device has lower dark currents at voltages from 0.2 to 10.4 V bias and higher photocurrents than PSC-based photodetector. As shown in Figure 4C, the $I_{ON}/I_{OFF}$ ratios of epitaxial film-based device are about 10 times higher than those of PSC-based photodetector. Figure 4D shows the dark current densities at 20 V bias after various days, which of 25.3 $\mu$A cm$^{-2}$ on day 0 and of 33.11 $\mu$A cm$^{-2}$ on day 120. In addition, Figure 4E shows the long-term stable response of our device on day 120 at 20 V bias. The increasing rate formula is $\text{Rate} = \left( \frac{(J_m - J_n)}{(m - n)} \right) \times J_n$, where $J_m$ and $J_n$ are the dark current densities on day m and day n. The calculated rate of change in dark current density is about 0.255% per day. The good morphology and crystallinity of epitaxial films benefit better stability than polycrystalline films (Salim et al., 2015; Tailor et al., 2020). The comparison of photoelectric performance between different MAPbI$_3$-based devices is shown in Table 1. The excellent performance actually validates the high-quality of the epitaxial MAPbI$_3$ SCFs.

### FIGURE 4
(A) Dark current of our photodetector and MAPbI$_3$ PSC-based photodetector under different voltage bias. (B) Photocurrent of our photodetector and MAPbI$_3$ PSC-based photodetector at 670 nm under 90 $\mu$W cm$^{-2}$ light illumination intensity. (C) $I_{ON}/I_{OFF}$ current ratios of our photodetector and MAPbI$_3$ PSC-based photodetector at 20 V bias under various light illumination intensity from 90 $\mu$W cm$^{-2}$ to 3.2 mW cm$^{-2}$. (D) Long-term dark current density test at 20 V bias. (E) Long-term response of devices after 120 days with a 0.5 Hz LED at 670 nm of 90 $\mu$W cm$^{-2}$ as light source.

### TABLE 1
| Material (structure) | Detectivity (Jones) | Responsivity (A W$^{-1}$) | $I_{ON}/I_{OFF}$ Ratio | References |
|----------------------|---------------------|---------------------------|------------------------|------------|
| MAPbI$_3$ single-crystal film | $3.07 \times 10^{12}$ | 1.2 | $10^2$ | This work |
| MAPbI$_3$ single crystal (lateral) | $10^{10}$–$10^{12}$ | 0.15 | $10^1$ | Sun et al., 2017 |
| MAPbI$_3$/TiO$_2$ film | $2.5 \times 10^{10}$ | 2.4 mA W$^{-1}$ | $10^1$ | Jiao et al., 2017 |
| MAPbI$_3$ film | $1.22 \times 10^{13}$ | 0.418 | – | Zhang et al., 2018 |
| MAPbI$_3$/P3HT films | $1.5 \times 10^{10}$ | 0.053 | – | Yakunin et al., 2016 |
| MAPbI$_3$ network PD arrays | $1.02 \times 10^{12}$ | 0.12 | – | Li et al., 2015 |
| MAPbI$_3$ film (lateral-MSM) | $1.3 \times 10^{11}$ | 0.11 | – | Wang et al., 2016 |
| MAPbI$_3$ nanofilms | – | 60 mA W$^{-1}$ | $10^2$ | Qin et al., 2016 |
| MAPbI$_3$ nanowires | $2.5 \times 10^{12}$ | 1.32 | – | Tang et al., 2016 |
| ZnO/MAPbI$_3$ nanowires (lateral) | $1.74 \times 10^9$ | 4 | – | Qiao et al., 2016 |
CONCLUSION

In summary, this work demonstrates the epitaxial growth of high-quality MAPbI₃ single-crystal film on MAPbBr₃ substrate with good lattice matching. XRD, AFM, and SEM characterizations are performed to confirm the high crystalline and smooth morphology, which result in the low trap density of 5.64 × 10¹¹ cm⁻² and long carrier lifetime of 11.86 μs. Additionally, we fabricate a high-performance photodetector based on epitaxial MAPbI₃ SCF with responsivity of 1.2 A W⁻¹, detectivity of 3.07 × 10¹² jones, response time of 2.21 μs and excellent stability for 120 days. Therefore, this epitaxial growth method provides a new path for high-stability perovskite film-based devices.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation, to any qualified researcher.

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AUTHOR CONTRIBUTIONS

XY, JZ, and YL grew the perovskite single crystals. XY and JZ did the epitaxial experiments. XY, YP, and JZ did the measurements. XW and YX analyzed these results. YX wrote the manuscript. All authors made comments on this manuscript.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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