Journal of Semiconductors
(2023) 44, 110201
doi: 10.1088/1674-4926/44/11/110201

RESEARCH HIGHLIGHTS

# Mechanical pressing method for making high-quality perovskite single crystals

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**Citation:** C L Wang, J Sun, J Z Chen, C Chen, and L M Ding, Mechanical pressing method for making high-quality perovskite single crystals[J]. *J. Semicond.*, 2023, 44(11), 110201. https://doi.org/10.1088/1674-4926/44/11/110201

Halide perovskites show excellent photovoltaic properties[1–4]. However, the preparation of high-quality perovskite crystals remains a great challenge, which limits their applications. Perovskite materials applied to photodetectors mainly include polycrystalline thin films and single crystals. Traditional solution methods are used to prepare polycrystalline thin films, and the films are full of defects such as voids and grain boundaries[5–7]. Compared to polycrystalline thin films, perovskite single crystals possess high crystallinity and low defect density[8–10]. Photodetectors based on perovskite single crystals exhibit excellent performance[11]. However, the size limitation of single crystals hinders their application in photodetectors[12].

There are several reports on perovskite quasi-single crystal wafers for photodetectors, which show low defect density and good performance[13–16]. The soft lattice of perovskite allows perovskite powder to be sufficiently deformed and densified under low pressure[17, 18]. Shrestha *et al*. used a mechanical pressing process to make polycrystalline $MAPbI_3$ wafer with millimeter thickness and high crystallinity (Fig. 1(a))[13]. They made $MAPbI_3$ wafers by applying a pressure of 0.3 GPa for 5 min to the microcrystals precipitated from solution. The wafer was then pressed onto PEDOT substrate under a pressure of 15 MPa for 2 min, thus obtaining an X-ray detector (Fig. 1(b)). The device exhibited a sensitivity of 2527 $\mu$C/($Gy_{air}$·$cm^2$) under 70 $kV_p$ X-ray exposure (Fig. 1(c)).

In addition to applying a stress field to the microcrystals/powder from perovskite precursor, a secondary coupling effect can be triggered. The direct densification of perovskite from powder to high-quality bulk crystals can be achieved in minutes under the dual action of a stress field and a thermal/electric field. Hu *et al*. prepared large $MAPbI_3$ wafers (diameter ~80 mm) from perovskite powder by heat-assisted pressing method[19]. The X-ray detector with $MAPbI_3$ wafers has an X-ray sensitivity of $1.22 \times 10^5$ $\mu$C/($Gy_{air}$·$cm^2$) at 10 V bias. Zheng *et al*. first reported an electric and mechanical field-assisted sintering technique (EM-FAST) for making perovskite wafers, which can produce high-quality bulk crystals in 5 min (Fig. 1(d))[16]. The pressure leads to better contact between the particles, thus forming a sintered neck. The small contact area at the sintered neck leads to an increase in local pressure, which triggers grain boundary diffusion and sliding. Moreover, localized thermal concentration is induced at the neck under the application of electric field, and this surface heating triggers mass transfer and grain integration. A very dense bulk crystal was obtained by using the FAST method. The optical bandgap of FAST product (1.45 eV) is close to that of the single crystal (1.51 eV) (Fig. 1(e)). The defect density of FAST product reaches $5.4 \times 10^{10}$ $cm^{-3}$, which is close to that of the single crystal (Fig. 1(f)).

The same passivation strategies applied in solution engineering can also be applied to mechanical pressing methods. Yang *et al*. introduced a bismuth oxybromide (BiOBr) heteroepitaxial passivation layer in $Cs_2AgBiBr_6$ polycrystalline wafers (Figs. 2(a) and 2(b))[14]. BiOBr initiated the epitaxial growth of $Cs_2AgBiBr_6$ grain boundaries, resulting in a grain size of 100 $\mu$m while passivating the grain boundary defects and eliminating the ion migration. The detector showed improved stability with a sensitivity of 250 $\mu$C/($Gy_{air}$·$cm^2$) (Fig. 2(c)).

Witt *et al*. investigated the factors such as pressure, pressing time and temperature during the pressing process[15]. Above 35 °C, rapid compression occurred, mainly due to two relaxation processes caused by plastic deformation and particle rearrangement. The optimal pressing conditions (100 MPa, 100 °C, 130 min) yield $MAPbI_3$ wafers with relative density >97%, high crystallinity, and an average size of 1.9 $\mu$m. Besides X-ray detectors, perovskite wafers can also be used in near-infrared detectors. Yu *et al*. made dense and smooth $MAPbI_3$ wafers from $MAPbI_3$ single crystals by hot pressing method[20]. The near-infrared detector exhibited a responsivity of 2.1 A·$W^{-1}$ (Fig. 2(d)), rise and decay time of ~239 $\mu$s and ~6.13 ms (Fig. 2(e)), and high cycling stability (Fig. 2(f)).

Most photodetectors are made from polycrystalline films or single crystals of perovskite[21–23]. All efforts focus on defect passivation[24, 25], interface modification[26, 27] and film formation control[28] of polycrystalline thin films as well as crystallization engineering of single crystals. Mechanical pressing method is an easy and fast process for preparing perovskite bulk crystals. It is also necessary to achieve high adhesion

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Received 25 SEPTEMBER 2023.

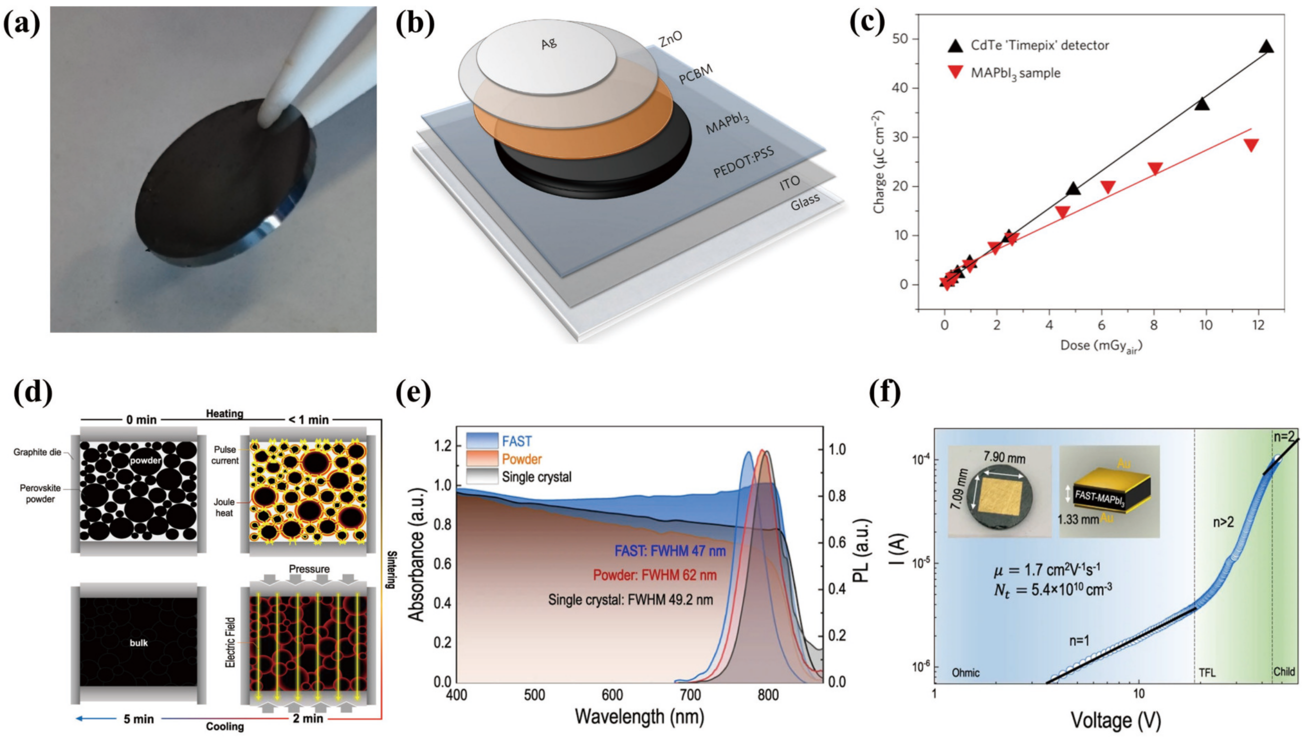

Fig. 1. (Color online) (a) The sintered $MAPbI_3$ wafer. (b) The X-ray detector with $MAPbI_3$ wafer. (c) Extracted charge at $E = 0.2$ V·$\mu$m$^{-1}$ for $MAPbI_3$-wafer-based device and CdTe reference detector. All exposures are 2-s-long pulses from an X-ray source operated at 70 kV. Reproduced with permission[13], Copyright 2017, Nature Publishing Group. (d) Densification of perovskites in graphite die. (e) UV-vis absorption and steady-state PL spectra for FAST-$MAPbI_3$ and $MAPbI_3$ powder. (f) $I$–$V$ curve for the holy-only device under dark. Reproduced with permission[16], Copyright 2016, Nature Publishing Group.

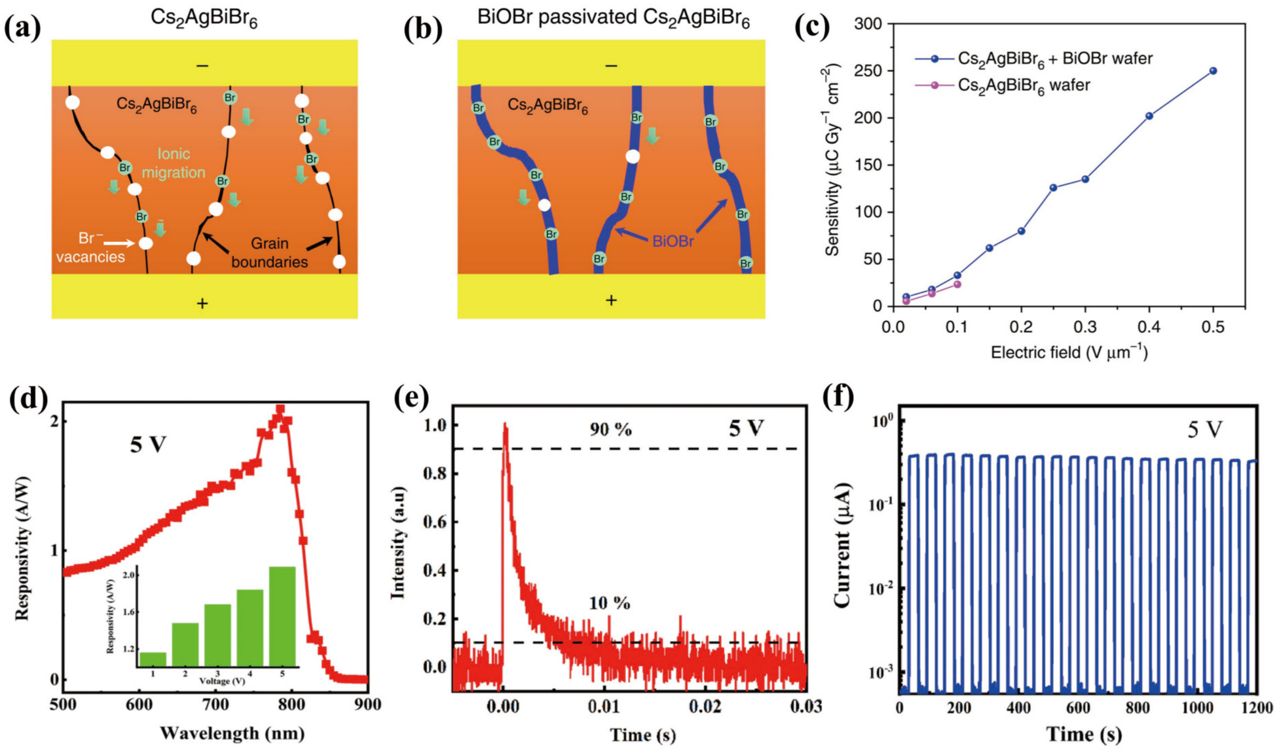

Fig. 2. (Color online) (a) Ion migration. (b) Suppressed ion migration by BiOBr passivation. (c) X-ray sensitivity under different electric fields. Reproduced with permission[14], Copyright 2019, Nature Publishing Group. (d) Photoresponse spectrum for the photodetector at 5 V. (e) Response time of the photodetector at 5 V. (f) Photocurrent of the photodetector as a function of time measured during periodical switching of 800 nm light illumination at 5 V. Reproduced with permission[20], Copyright 2023, Royal Society of Chemistry.

between perovskite wafers and the underlying substrate. We should explore the adaptability of perovskite materials with other materials (metals[29], carbon[30], 2D materials[31], etc.) to improve device performance.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (62004058 and U21A2076), Natural Science Foundation of Hebei Province (F2020202022), State Key Laboratory of Reliability and Intelligence of Electrical Equipment (EERI_PI20200005), S&T Program of Hebei (215676146H and 225676163GH), and Hebei Graduate Innovation Funding Project (CXZZBS2023037 and CXZZSS2023026). L. Ding thanks the National Key Research and Development Program of China (2022YFB3803300), the open research fund of Songshan Lake Materials Laboratory (2021SLABFK02), and the National Natural Science Foundation of China (21961160720).

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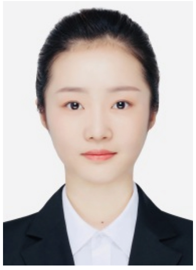

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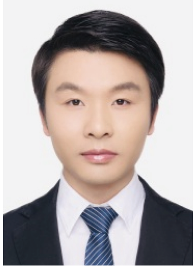

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