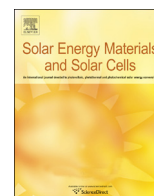




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Chemically, spatially, and temporally resolved 2D mapping study for the role of grain interiors and grain boundaries of organic-inorganic lead halide perovskites

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ABSTRACT

Grain interiors (GIs) and grain boundaries (GBs) of perovskites have been investigated using chemically, spatially, and temporally resolved measurements. Two dimensional (2D) chemical mapping measurements revealed the GBs consisted of the non-stoichiometric PbI_x or $\text{CH}_3\text{NH}_3\text{PbI}_x$, that were characterized by an absence of chloride, an enriched oxygen concentration, and a high density of iodide vacancies. In addition, steady-state 2D photoluminescence showed the bandgap broadening at the GBs while 2D lifetime mapping measurement suggested that the GBs indeed contained deep defect centers. However, it is found that defective GBs in perovskite materials do not act as high recombination sites for photo-generated charge carriers due to the bandgap broadening of non-stoichiometric PbI_x or $\text{CH}_3\text{NH}_3\text{PbI}_x$ perovskites at the GB that forms the potential barriers for photo-generated charge carriers toward the GBs. As a consequence, the photo-generated charge carriers adjacent to the GBs will be easily repelled by the GBs, resulting in a greater reduction of the recombination of photogenerated charge carriers. This is one possible reason for the high performance of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ based solar cells.

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1. Introduction

Halide perovskites have gained tremendous research interest as a new category of semiconductor materials that will revolutionize photovoltaic technologies. During the last few years, significant improvements in the performance of halide perovskite solar cells have been made, thanks to a new understanding of the materials and new device architecture designs [1–7]. Particularly, spurred world-wide research efforts have revealed the exceptional optical and electrical properties such as high electron and hole mobility, strong defect tolerance, large absorption characteristics resulting from s-p antibonding coupling and the long electron-hole diffusion lengths exceeding $1\ \mu\text{m}$ [1–7]. All of these unique characteristics of perovskites led to unprecedented energy conversion

efficiency of perovskite solar cells. However, many problems remain to be solved to unravel the underlying mechanisms that will allow for improved photovoltaic performances. The outstanding challenges to be urgently addressed include, but are not limited to, long term stability issues, light soaking, hysteresis, charge carrier dynamics, and Pb-free light absorber of perovskites [8–11]. In addition, there's been intensive interest in understanding the nature of grain boundaries (GBs) of perovskites in the solar cell community [12–19]. Since the perovskites are prone to defect formation, due to the low thermal stability of the materials, it is expected that the chemical disorders occur, particularly at the GBs. According to theoretical studies, the GBs are characterized by defects that have very shallow intrinsic levels, i.e. the GBs are completely benign [12]. On the contrary, Agiorgousis et al., also conducted a theoretical calculation and found that the deep charge-state transition levels within the bandgap were indeed possible by forming Pb dimers and I trimmers through very strong covalent bonds [13].

In addition, experimental studies also revealed controversial results. Till now, the GBs of organic-inorganic halide perovskite films were characterized by confocal fluorescence microscopy,

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conductive atomic force microscope (*c*-AFM), Kelvin probe force microscopy (KPFM), and electron beam-induced current (EBIC) [14,16–19]. Nanoscale photoluminescence (PL) and lifetime mappings [14,16] unambiguously revealed that the GBs exhibited strong non-radiative relaxation of charge carriers. This result implies that the GBs are defective and not as benign as previously suggested in Ref. [12]. In contrast, *c*-AFM measurements indicate a higher short-circuit current was observed at the GBs than at the grain interiors (GIs), indicating the photo-generated charge carriers more effectively separated at the GBs [17]. Yun et al., also conducted KPFM measurements that revealed greatly enhanced charge separation and collection at the GBs, indicating the benign characteristics of the GBs [17]. In short, the confocal microscope optical measurements [14,16] concluded that the GBs can be detrimental whereas the benign characteristics were unveiled by other measurements [17,18]. This begs the question of why defective GBs in perovskite materials do not act as high recombination sites for photogenerated charge carriers but enables perovskites solar cells to achieve their high efficiencies. To address this question, we need to clearly understand the nature of the GBs for perovskite solar cells by contrasting them with the GIs. Hence, this study is focused on probing defects at the GIs and GBs, on characterizing the discrete roles of the GIs and GBs mostly influenced by morphological, and chemical variations of perovskites through concerted combinations of chemically, spatially, and temporally resolved microscope studies at the nanoscale. To perform this investigation, we used an energy dispersive X-ray spectroscope (EDS), two-dimensional (2D) photoluminescence (PL) and lifetime to chemically, spatially, and temporally resolve the chemical variations, disorder, and PL decay dynamics across the GBs at the nanoscale.

2. Experimental details

Perovskite ($\text{PbCH}_3\text{NH}_3\text{I}_{3-x}\text{Cl}_x$) films were prepared using hot casting technique. Perovskite ($\text{CH}_3\text{NH}_3\text{I}_{3-x}\text{Cl}_x$) solution was prepared by dissolving equimolar ratios of lead iodide (PbI_2 , Sigma-Aldrich, 99%) and methylamine hydrochloride (MACl , Sigma-Aldrich) in *N,N*-dimethylformamide (DMF, Sigma-Aldrich, anhydrous, 99.8%) in 11% concentration. The solution was ready for use after heating in a hot plate at 70 °C for 24 h with magnetic stirring in a N_2 filled glove box. Glass substrates were cleaned with four times sonication (each for 10 min) in de-ionized (DI) water, methanol, acetone, and 2-propanol (IPA) respectively. Afterwards, the substrates were dried with nitrogen followed by heating in a hot plate at 120 °C for 15 min to remove the last traces of any solvent. Glass substrates were kept at different temperatures ranging from 100 to 180 °C while perovskite solution was kept at 70 °C. The solution was then immediately deposited on the hot substrate by spin coating at 4000 rpm for 15 s so that the substrate temperature is retained. During this process, the temperature was closely monitored using an IR thermal gun. For a comparison, perovskites were prepared using the hot-casting technique at different temperatures [20,21]. In this case, a lower hot-casting temperature (100 °C) resulted in smaller grain size, with typical grain size of 1–2 μm . Hot-casting temperatures higher than 100 °C produced perovskite samples with larger grains of \sim more than tens of micrometers, which was confirmed by a high-resolution scanning electron microscope (SEM). Grain sizes and morphologies of our samples are consistent with experiments reported in Refs. [20,21], which also demonstrated the correlation between energy conversion efficiencies of perovskite solar cells and large grain sizes. The PL intensity and peak-position mapping image of submicron-scale were performed using confocal micro-spectroscopy (NTEGRA spectra, NTMDT). In-plane spatial resolution of \sim 380 nm was

indicated by an objective lens with numerical aperture of 0.7 and a solid-state laser with 405 nm wavelength for the excitation. The excitation power of 0.2 $\mu\text{W}/\text{cm}^2$ was used to avoid degradation by laser. The signal collected by the objective lens was detected by a thermoelectrically cooled CCD detector. For analysis of time resolved PL (TRPL), multifunctional confocal microscopy including a time-correlated single photon counting (TCSPC) system was employed (NTEGRA, NT-MDT). For the TRPL excitation source, a 405 nm pulsed laser with a repetition rate of 50 MHz, a pulse width down to 60 ps and excitation power of 0.2 $\mu\text{W}/\text{cm}^2$ was used. A high-speed PMT detector (PMC-100, Photonic Solutions) was applied for photon counting. A field emission scanning electron microscope (FESEM, JSM7500F, JEOL) was used to investigate the surface morphology of the perovskite solar cells. The elemental compositions of the perovskite films prepared with different hot casting temperatures were carried out using energy dispersive spectroscopy (EDS) mapping in SEM mode. Samples for SEM/EDS were prepared by Pt coating with three times for preventing electron charging. In the case of EDS, analysis data excluded Pt information from original EDS data. To analyze the compositions of each component in perovskite films, EDS was calibrated with a series of standard samples including SiO_2 , KCl, PbF_2 , Cu (K_α – 8.04 keV, K_β – 8.9 keV) and others. And the measurement uncertainty was estimated to be $\pm 1\%$ by statistical analysis of a series of observation.

3. Results and discussion

To investigate the local chemical compositions of the GIs and GBs for perovskites, an EDS measurement coupled with an SEM was performed. Fig. 1 shows the two dimensional (2D) EDS mapping of a higher (180 °C) hot-casting perovskite that highlighted the chemical distributions across the GBs. Remarkably, a higher hot-casting perovskite produced pin-hole free GBs, as shown in SEM image of Fig. 1(a). Particularly, the chemical components composed of perovskites were carefully examined between the GIs and GBs in order to fully understand the role of GIs and GBs of perovskites. The chlorine signal (2.621 keV) [22] was clearly distinguished from the Pb signal (2.342 keV) as shown in Supplementarily Fig. S1. The resultant EDS mapping of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ clearly revealed that the contents of lead (Pb) and chloride (Cl) in Fig. 1(b) and (c) were significantly lower at the GBs. Note that the EDS mapping of iodide (I) was not shown, but found to be similar to that of Pb. One of the critical observations is an increase in O contents when approaching the GB, as shown in Fig. 1(d). As illustrated in Fig. S2 in the Supporting Information, the further comparison of EDS mapping of smaller and larger grain perovskites was shown. Notably, the similar chemical distributions at the GBs for both perovskites were observed, i.e. the chemical components of perovskites were concentrated at the GIs, while the GBs were characterized by the higher concentration of oxygen but the deficiency of Pb, Cl, and I.

Fig. 2 shows the quantitative analysis of the variations of the chemical components of perovskites as functions of grain sizes and the positions of perovskites. In this study, the controlled grain sizes of perovskites ranged from a few micrometers to \sim 60 μm in Fig. 2a–c. The quantitative atomic percentage of $\text{MAPbI}_{3-x}\text{Cl}_x$ for representative areas in Fig. 2(a) and (b) was analyzed and listed in Table 1. Interestingly, the density of chemical compositions (C, Pb, Cl and I) of perovskites at the GIs is gradually reduced when the grain sizes of perovskites were reduced, as shown in Fig. 2(d). Notably, a higher atomic percentage (5%) of Cl was found with enlarged grain size (60 μm) perovskites, which is contrasted with a negligible amount ($< 1\%$) of Cl for smaller grain perovskites. Note that Cl-doping is a common technique for achieving higher open

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