The role of grain boundaries in perovskite solar cells

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ABSTRACT

With a certified power conversion efficiency (PCE) exceeding 22%, the hunt is now on clues to further improve the PCE and stability of perovskite (PVSK) solar cells toward commercialization. Polycrystalline PVSK films are grown by low temperature solution processes that results in the formation of sub-micron scale grains and consequent grain boundaries. The large discrepancy observed between optoelectronic properties of the polycrystalline films and single crystals of PVSK implies that grain boundaries may largely influence the optoelectronic properties of the PVSK thin film. In this article, important studies on the roles of the grain boundaries on optoelectronic properties and stability of the PVSK are reviewed.

1. Introduction

The consistent efforts to find a silicon alternative for solar cells brought about a game changer in 2009 with the perovskite (PVSK) light absorber [1,2]. With an important milestone in 2012 by introducing the solid-state version of PVSK solar cells, great attention has been focused on PVSK solar cells [3,4] yielding a certified power conversion efficiency (PCE) of 22.1% by 2016 [5]. Benefitting from low temperature and scalable solution processes, the PVSK solar cell is now one of the most promising candidates to replace the silicon solar cells [6–8].

The unprecedented rapid progress in PCE of PVSK solar cells has been attributed to its superb optoelectronic properties. The PVSK materials have a high absorption coefficient, long-range balanced electron and hole diffusion lengths and high defect tolerance, enabling efficient charge collection with comparable open-circuit voltage (VOC) deficit with single crystal GaAs solar cells [9–13]. With the consideration of photon recycling effect, PCE of 31% was suggested to be achievable for the PVSK solar cells [14].

Accompanied with remarkable progresses in film formation and compositional engineering [15–21], researches have started looking into the microscopic properties of the films to find the room for further improvement [22–24]. As the PVSK thin films are grown by low temperature solution processes, the formation of polycrystalline films with grain boundaries (GBs) is inevitable. As a result, the structural disorders at GBs potentially can form defect states, which possibly degrade the optoelectronic quality of the PVSK films. Indeed, the charge carrier diffusion lengths measured from polycrystalline thin film and single crystal PVSK show large discrepancy [10,12,25,26], which implying clues for further enhancement of PCE possibly lays on the microstructure.

Recent studies on local proprieties on PVSK have revealed that the GBs and defects associated them have important roles in both photovoltaic performance and stability of the PVSK solar cells [23,27–30]. In this article, we introduce the studies on microstructure using a variety of analytical tools including computation, photo-physical characterization and atomic force microscope (AFM). In particular, from crystallization and formation of GBs in PVSK films, to their influences on optoelectronic and photovoltaic properties will be addressed. Finally, important progresses to passivate the GBs will be reviewed.

2. The roles of GBs in PVSK solar cells

2.1. Phase formation and crystal growth of the PVSK

The PVSK materials used for photovoltaic applications employ the ABX3 crystal structure, in which A cations in cubo-octahedral site make bonding with BX6 octahedra. According to the tolerance factor which provides the geometrical guideline of formability for the PVSK structure, various components are available to sustain the...
PVSK structure [31]. The relative sizes of the A cation and the BX6 octahedra determine the dimensionality of the PVSK materials. The PVSK material can remain three-dimensional (3D) with relatively small ‘A’ cations while incorporation of larger cations result in two-dimensional (2D) or even one-dimensional (1D) chain materials with formulas A2BX4 and A2BX3 [32]. For photovoltaics, the most representative components for each site are methylammonium ion (CH3NH3+ MA) and formamidinium ion (CH3NN2, FA+) for ‘A’ site, Pb2+ and Sn2+ for ‘B’ site, Br-, and I- for ‘X’ site. Among several combinations of the components, the most common halide PVSK is MAPbI3. In most of cases, the reaction for phase formation follows combinations of the components, the most common halide PVSK is MAPbI3 because of its smaller Eg and guarantees the longer carrier lifetime while its instability of Sn2+ mainly originated from metal cation [37,38]. However, due to the tendency of antisolvent. Speciﬁcally, the amount of antisolvent helps to control the point where supersaturation initiates [46,47].

The optoelectronic properties change depending on the crystallinity of the PVSK materials because the crystallinity determines the defect density of materials. The grain boundaries (GBs) play the role of crystal defects, which changes the material properties. In this section, we deal with the methods to grow single crystal and polycrystalline PVSKs and their associated differences in properties.

Properties of the single crystal can provide a guideline for the design of materials and devices. For the single crystal halide PVSK, various growth techniques have been introduced including a top-seeded solution growth (TSSG), a hot-solution cooling-down growth, the inverse temperature method, and an anti-solvent vapor-assisted crystallization [Fig. 1] [12,25,42,43]. Regardless of the method, they all follow the same principles where the key steps are nucleation and crystal growth. Controlling the nucleation sites and understanding the growth kinetics are the most important fundamental knowledge. In addition, since all methods are based on the solution process, the growth and dissolution happen at the same time. In this case, controlling the growth rate is critical. For example, when the growth rate is too fast, the quality of the single crystal is not good enough because of the lower activation energy induces more nucleation sites, whereas dissolution disturbs the growth of single crystal halide PVSKs when the growth rate is too slow, resulting in poor crystal quality. The TSSG method utilizes a small temperature gradient between the top and the bottom of the solution and the temperature gradient induces convection to convey the materials to the seed to enlarge the crystal [25]. With the beginning of MAPbI3, MAPbBr3, and MAPbCl3, even mixed halide single crystals were also demonstrated [44]. The cooling down method utilized the control of the amount of saturated precursors using Pb(CH3COOH)2·3H2O in hydroiodic acid (HI) to mix with MAI [12]. However, the growth rate is quite low in this case because the halide PVSK has inverse tendency of solubility according to the temperature. That is, it has lower solubility in the solvent at higher temperature unlike the common case. Due to this reason, the inverse temperature method has been introduced to use the inverse tendency of solubility [45]. In this case, the growth rate becomes much faster. Because the antisolvent can work as another source to control the chemical potential, the single crystal is grown by controlling the antisolvent. Specifically, the amount of antisolvent helps to control the point where supersaturation initiates [46,47].

The optoelectronic properties of single crystal halide PVSKs vary depending on the characterization and growth methods. However, in general, the single crystal PVSKs do not have GBs and have fewer defects, which leads to reduced recombination. Also, the absorption edge and external quantum efficiency extends up to 850 nm

Table 1
Crystalllographic information of various halide PVSK materials. Reprinted with permission from Ref. [41].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Volume (Å³)</th>
</tr>
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<td>6.3115</td>
<td>6.3161</td>
<td>251.6</td>
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<tr>
<td>MAPbI3</td>
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<td>12.642</td>
<td>990</td>
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<tr>
<td>MAPbI3</td>
<td>γ</td>
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<td>5.628</td>
<td>11.182</td>
<td>959.6</td>
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<tr>
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<td>11.182</td>
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<tr>
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<tr>
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<td>8.9554</td>
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<td>1959.2</td>
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whereas those from polycrystalline films are only around 800 nm. Thereby, Voc and fill factor (FF) can increase. Thus, more than 25% performance enhancement can be expected with other developments for the devices of single crystals [46,47]. However, although it has benefits in terms of carrier movement, the current single crystals only have bulky shape. In other words, it cannot be used for thin film electronics like solar cells and light emitting diodes. Thus, another approach is required to use it as a material in thin film electronics.

PVSK solar cells utilize polycrystalline thin films grown by solution process. As a result, the effects of grain size and morphology on photovoltaic performance have been investigated. There are two representative ways to make polycrystalline halide PVSKs; one-step and two-step methods [18,48]. The two-step method consists of two sequential deposition steps. The first step is to deposit PbI2 film and a second step is reacting the deposited PbI2 with MAI either by vapor evaporation, spin coating or dipping to convert it into MAPbI3 [17,49,50]. According to the thermodynamic regulation, the grain size (Y) of the resulting PVSK film fabricated by the two-step method can be determined by following relationship,

\[
\ln Y = \frac{32\sigma_{41}}{3kT \left( \frac{1}{\gamma_A} - \ln X - \ln C_0(T) \right)^3}
\]
$\sigma_{1}$ is the average surface tension, $k$ is Boltzmann constant, $T$ is temperature of the reaction, $X$ is the MAI concentration, $C_0$ is equilibrium concentration of MAI [51]. As a result, the grain size ($Y$) of the MAPbI$_3$ can be controlled by changing the reaction temperature or concentration of MAI (Fig. 2) [51,52]. The photovoltaic performance of the PVSX solar cells were found to be strongly affected by the grain size of the film, which indicates the importance of GBs in PVSX solar cells. Furthermore, in the two-step method, the film quality including morphology and optoelectrical properties is strongly affected by the quality of the PbI$_2$ layer [51–53]. Due to the hygroscopic nature of PbI$_2$, the control of the humidity and temperature during the deposition of PbI$_2$ is critical to produce the superb device performance [8]. Q. Chen et al. demonstrated a vapor-assisted two-step process [50]. The vapor-assisted solution process uses the phase transformation from vapor to solid phase at a second step. Unlike the PbI$_2$, the sublimation temperature of organic components, such as MAI and FAI, is relatively low. Accordingly, PbI$_2$ dissolved in solvent is firstly deposited via spin coating and later the vaporized MAI or FAI components are deposited on the top of the PbI$_2$ layer. They reported reliable device performance with large grain size. However, the phase transformation of vapor to solid phase accompanies the slow kinetics and, thus, the deposition rate of vaporized materials is much lower than solution process as usual.

In the one-step method, all the precursors for PVSX are dissolved in a single solution. The one-step method has shown poor film quality due to the difficulty in controlling the reaction kinetic and, thus it produced poor device performance [48]. In this regard, the anti-solvent method was introduced to control the reaction kinetics. As an anti-solvent, toluene is widely used because it does not dissolve the precursor MAI and PbI$_2$ [20,54]. Instead, the toluene was involved into the reaction kinetics to induce the fast nucleation and crystallization of the film by controlling chemical potential. M. Xiao et al. tested 12 solvents working as the antisolvent, and chlorobenzene was found to be the best in terms of the device performance [55]. Another approach is to utilize the intermediate phase. Lewis acid–base adduct approach has been introduced by Park et al. [15,16] Lewis acid PbI$_2$ was reported to form adduct by reacting with oxygen, nitrogen, and sulfur bearing lone pair electrons. Dimethylsulfoxide and thiourea has been used to form the adducts with PbI$_2$, MAI and FAI [15]. The formation of intermediate adducts enables control of crystallization kinetics to form highly uniform and crystalline PVSX films. While the coverage and grain size can be controlled in some extent, the formation of GB is inevitable, which motivated researchers to study the roles of the GB.

2.2. Photo-physical and computational works on GBs

As the PVSX solar cells have demonstrated unprecedentedly rapid enhancement of PCE, the optoelectronic properties have been studied using photo-physical characterization tools to find the origin of the superior photovoltaic performance. Charge carrier lifetime and diffusion length have been investigated using microscopic photoluminescence (PL) measurements with aid of transient absorption spectroscopy, in which both electron and hole diffusion lengths were determined to be ~100 nm for MAPbI$_3$ and ~1 μm for MAPbI$_3$·xCl$_x$, which is much longer than typical solution processed organic materials (~10 nm) [10,26]. The superior charge transporting ability was regarded as one of the main advantages of organometal halide PVSX to show superb photovoltaic performance. While the polycrystalline thin films were characterized in their initial stages, researchers have started to characterize the optoelectronic properties of single crystal PVSX materials to explore intrinsic properties of PVSX materials [12,25]. Dong et al. synthesized the 3 mm thick single crystal using supersaturated MAPbI$_3$ solution [25]. Notably, the MAPbI$_3$ single crystal demonstrated much longer diffusion length than polycrystalline thin film.
in which the diffusion length was determined to be exceed 3 mm under weak light (0.003 mW/cm$^2$) and 175 μm under 1 sun (100 mW/cm$^2$) illumination, respectively. Shi et al. also characterized the MAPbI$_3$ single crystals, in which diffusion length was measured to be ~8 μm [12]. The measured diffusion length of the single crystal is more than one order of magnitude longer than polycrystalline MAPbI$_3$ film, which implies characteristic GBs in polycrystalline thin film comparing with single crystal counter parts probably have significant influence on charge transporting mechanism.

To understand the origin of superior charge carrier transporting ability of the PVSK materials, first principle density-functional theory (DFT) calculations have been done to investigate the dominant intrinsic defects in the PVSK materials [11]. It was found that the dominant point defects in MAPbI$_3$ PVSK are p-type $V_{\text{PI}}$ and n-type $\text{MA}$, and both defects with low formation energies create only shallow states due to strong Pb lone-pair s orbital and I p orbital antibonding coupling and high iconicity of MAPbI$_3$. The low transition energy level of the dominant defects with low formation energy can be a possible origin of the superior intrinsic charge carrier transporting properties of PVSK materials since the shallow defect states do not contribute to Shockley–Read–Hall (SRH) non-radiative recombination loss, which is generally originated from deep gap states with higher transition energy [11,28,56].

The similar atomistic defects at GBs can induce the additional structural disorder such as a dangle bond and uncharacteristic wrong bond like cation–cation and anion–anion bonds. Yin et al. investigated impact of such structural disorders at GBs on electronic quality of PVSK materials [12]. Fig. 3 shows calculated density of state (DOS) with different structural models at GBs. $\Sigma 3(111)$ and $\Sigma 5(310)$ GBs were considered for MAPbI$_3$ while $\Sigma 3(111)$ and $\Sigma 5(310)$ GB, respectively) compared to ionic radius of Pb$^{2+}$ (1.33 Å). On the other hand, both cations and anions induced wrong bonds in CdTe (Fig. 3c and f) forms deep subgap states in CdTe, which strongly contribute to the non-radiative SRH recombination. The results explain why the solution processed polycrystalline PVSK film can have such an excellent charge transporting properties and resulting high open-circuit voltage ($V_{oc}$) comparable to single-crystal GaAs thin film. However, although the wrong bonds in GBs of PVSK do not form deep trap states, they are still found to form shallow defect states. As can be seen in Fig. 3b and e, the I–I wrong bond in $\Sigma 5(310)$ GB forms shallow defects states close to valance band maximum (VBM). Although this shallow state is not as critical as deep levels as in CdTe, it possibly increase the effective mass of holes or trap the holes to decrease the hole mobility or induce non-radiative SRH recombination [12]. Long et al. also observed accelerated non-radiative recombination at GBs through time domain atomistic simulation via nonadiabatic (NA) molecular dynamics combined with time-domain density functional theory [57]. While GBs were confirmed to not forms deep gap states, they concluded that GBs reduce the $E_g$ and enhance the electron phonon coupling to accelerate the non-radiative charge recombination loss.

With expected detrimental effects of GBs on photovoltaic performance suggested from computational works, the presence of such defect states have confirmed from experimental observation. Duan et al. observed presence of the defect states ~0.16 eV above the valance band using admittance spectroscopy [58]. The defect trapping and resulting non-radiative recombination have been observed from microscopic PL measurement with much shorter decay time constant (<10 ns) than radiative recombination at bulk PVSK (>100 ns) [59]. However, the microscopic characterization tools could not specify the origin of the defect states and resulting non-radiative recombination. Confocal fluorescence microscopy
measurement was suggested as a powerful tool to investigate spatially resolved charge carrier recombination dynamics. de Quilettes et al. first incorporates the confocal PL to study local PL decay dynamic of the polycrystalline PVSK thin film [22]. Regardless of long microscopic PL lifetime exceeding 1 μs, the steady-state PL intensity showed significant heterogeneity across the PVSK film. More importantly, closer inspection of local PL unraveled that steady-state PL intensity at GBs was lower than that of grain interiors, which was found to be due to much shorter charge carrier lifetime at GBs. Considering the local PL intensity and lifetime, it was concluded that the non-radiative trap-assisted recombination due to defects is more severe at GBs, which is correlated with computational works mentioned above. More recently, Ham et al. also observed accelerated charge carrier recombination at GBs of MAPbI$_3$ PVSK films prepared from both stoichiometric and non-stoichiometric precursor solutions (Fig. 4) [60]. Statistical distribution of average charge PL lifetime ($\tau_{\text{avg}}$) clearly indicates that the $\tau_{\text{avg}}$ is relatively longer at grain interiors compared to GBs regardless of the composition of the precursor solution. The shorter PL lifetime was found to be due to contribution of trap-assisted non-radiative recombination, which is more dominant at GBs of MAPbI$_3$ compared to grain interiors.

However, there are still contradictory reports regarding impact of GBs on charge carrier lifetime. Yang et al. performed confocal fluorescence-lifetime imaging of MAPbI$_3$ grown from non-stoichiometric precursor solution [61]. They observed comparable PL lifetime at grains interiors and GBs although the intensity of PL is weaker at GBs compared to grain interiors. They observed that the recombination in these film primarily occur in non-GB regions such as grain surface or grain interiors. A recent study using a transient reflection spectroscopy by same group also pointed out that the charge carrier lifetime is mainly limited by surface recombination [62]. However, considering the PVSK films used for the characterization were prepared from non-stoichiometric solution (MAI excess), the chemical environment at GBs probably changed, which will affect the electronic state and resulting charge carrier behavior. Further systematic photo-physical and computational studies on GBs with different chemical environments might be necessary to fully understand the role of GBs in PVSK solar cells.

2.3. AFM and KPFM studies on GBs

In analogous to the local PL measurement, the Kelvin probe force microscopy (KPFM) and atomic force microscopy (AFM) are efficient tools to investigate the local properties of the halide PVSK (Fig. 5a and b). The main function of KPFM is to measure the contact potential difference from the vacuum level and the surface photovoltage. The KPFM is taken at a noncontact mode. In noncontact mode, a conducting cantilever is scanned over the surface of samples. The cantilever keeps a constant height to measure the contact potential difference between samples and the cantilever which is regarded as a reference electrode. Thus, work function of the samples can be characterized. On the other hand, local photocurrent of the halide PVSK materials can be measured using conducting AFM (c-AFM) mode. Whereas AFM is utilized to measure the topography of the surface, the c-AFM can be used to measure the electric current flow between a conducting cantilever and samples. The c-AFM is operated in contact mode. The cantilever is scanned under a constant voltage to get current information.

Structural defects at GBs can induce change in electronic band structure. For example, GBs in polycrystalline Si thin film creates deep energy states between the conduction band and the valence band, which works as a recombination site [63,64]. Whereas, GBs in chalcogenide compounds such as CZTS, CZTSSe, CIGS, have

![Confocal photoluminescence images of PVSK films prepared from (a) stoichiometric (st) solution and (b) non-stoichiometric (nonst) solution (MAI:PbI$_2$ = 1.06:1.0). Scale bar is 500 nm. (c,d) Two-dimensional scatter plots of PL intensity and average lifetime for (c) st-PVSK and (d) nonst-PVSK MAPbI$_3$ films. (e,f) Representative time-resolved PL decay curves at grain (red circle; ◊) and GB (yellow triangle; △) in st-PVSK films are shown in (e). PL decay curves at grain (blue square; □) and GB (green diamond; ♦) in nonst-PVSK film are shown in (f). Reprinted with permission from Ref. [60]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)}
beneficial effects in terms of minority carrier collections [65]. It is reported that GBs in the compounds do not produce deep states within the E_g. Instead, the GBs are electrically charged and induce built-in potential. As a result, photo-generated electrons and hole near the GBs can be easily separated by the built-in potential, which enhances photocurrent. In the same manner, Yun et al. found out that the GBs in PVSK can help the charge separation and collection by observing the KPFM and AFM results in PVSK films [23]. They claimed that the potential barrier along the GB was observed under dark conditions whereas higher photovoltage was obtained along the GB compared with the grain interior under the illumination (Fig. 5c). Thus, the higher current collection near GBs is observed in their work, which supports the beneficial role of GBs in terms of charge collection. Q. Chen et al. also studied contact potential difference between near and at GBs [66]. They employed scanning kelvin probe microscopy (SKPM) to examine the surface and GBs and concluded that there is band bending near the GBs. Releasing the organic species to form PbI_2 changes the grain to GB bend bending from downward to upward, preventing the charge recombination at the interface between PVSK and the charge transporting material. Son et al. reported that the self-formed GB healing layer using 6 mol% excess CH_3NH_3I [29]. More efficient current flow through the GBs was confirmed by c-AFM, which can be further enhanced by the 6 mol% excess CH_3NH_3I (Fig. 5d). Recently, the heterogeneity of halide PVSK materials was reported by Leblebici et al. using c-AFM [24]. Local characterization by the c-AFM allowed them to investigate the microscopic and nanoscopic photovoltaic performance of the PVSK layers. The heterogeneity is not only presented between the intra-grain and GBs but also even within the intra-grain. They insist that difference in defect density with different crystal facet contributes to the heterogeneity in local photovoltaic performance, which eventually influences the macroscale solar cell performance.

2.4. Hysteresis and ion migration

While characterizing photovoltaic performance of PVSK solar cells, researchers had observed the irregular current–voltage (I–V) characteristics (i.e. the I–V curve of PVSK solar cells varies depending on the scan direction and the scan speed) at the early stage, which was defined as I–V hysteresis. Three possible mechanisms of the hysteresis phenomenon have been proposed: 1) trapping and detrapping effect on charge carriers, 2) polarization due to the ferroelectric properties, 3) ion migration [67,68]. Supported by many direct and indirect evidences, such as the active energy of ion movements and the response time scale of the hysteresis, it has been believed that ion migration plays a crucial role in the hysteresis behavior of PVSK solar cells [29,68–71].

Under external electric field, ions are driven to the specific direction and accumulate at the interfaces between the PVSK and the charge transporting layers to form the doped regions (as illustrated at Fig. 6) [69]. The accumulated ions can induce an internal electric field near the interface (space charge), screening the applied voltage, which induce the I–V hysteresis [29,68–70]. The evidence of ion migration in the PVSK device has been distinctly reported through the observation of the field-switchable photovoltaic effect, in which the photocurrent direction can be switched repeatedly by applying a small electric field [69].

The existence of defects in the condensed materials provides the medium for ion migration. The possibility of ion migration highly depends on their activation energy (E_a). There are several factors contributing to the activation energy, such as crystal structure, ion radius and valence state of ions. The ion migration rate r_m can be estimated by Arrhenius relation: $r_m \approx \exp\left(-\frac{E_a}{k_BT}\right)$, where $k_BT$ is the thermal energy with $k_B$ for the Boltzmann constant and $T$ for absolute temperature. A series of experimental studies combined with the first principles calculations has clearly revealed the
possible mobile ion species and migration paths in PVSK compounds [29,72–76]. Taking MAPbI3 PVSK as an example, the most likely mobile ion is considered to be iodide ions. Eames and his coworkers identified the ionic transport mechanisms involving vacancy hoping between neighboring positions (as shown in Fig. 7), in which Pb\(^{2+}\) ions move along the diagonal <110> direction, I\(^-\) ions migrate through the octahedron edge, and MA\(^{+}\) ions jump into the nearest vacant cages [72]. Based on the density functional theory methods, they found the facial vacancy-assisted migration of I\(^-\) ions with activation energy of 0.58 eV that is lower than the one of MA\(^{+}\) (0.84 eV) and Pb\(^{2+}\) (2.31 eV). By the comparison with the result of the temperature- and time-dependent kinetic

![Figure 6](image1)

**Fig. 6.** Illustration of induced ion drift within PVSK device by (a) positive and (b) negative poling. The p- and n-doped regions arise from the ion accumulation at interface. (c,d) Three ionic transport mechanisms in MAPbI\(_3\) PVSKs. (c) Pb and I vacancies. (d) MA vacancy. Reprinted with permission from Refs. [69,72].

![Figure 7](image2)

**Fig. 7.** The illustration of the ion migration induced by different mechanisms. (a) Schottky defects, (b) Frenkel defects, (c) Lattice distortion by accumulated charges and (d) dissolved impurities, (e) soften lattice by lamination, (f) GBs and (g) strain induced defect. Reprinted with permission from Ref. [29].
measurements, their calculated activation energy for iodide ions migration fits well for the formation of hysteresis (0.60–0.68 eV) [72]. Another theoretical computations performed by Azpiroz et al. also shows the identical tendency with regard to the activation energy of ion migration via vacancy hopping in the similar migration paths. Conversely, they suggest that MA⁺ ions migration with $E_A$ of 0.5 eV is responsible for the slow response in PVSK solar cells. According to their prediction, the iodide ion migration with the small $E_A$ (0.08 eV) can only occur within a very short time (<1 μs) that is too fast to explain the slow response of hysteresis effect in PVSK (usually in the order between few seconds to minutes) [73].

Besides through the bulk point defects (i.e. Schottky and Frankel defects) inside the grain interior, ions can also migrate along the GBs preserving high density of defects. With more open space and lack of chemical bonding at GBs, the activation energy of ion migration is expected to become lower than the one in the grain interior. In addition to point defects and GBs, softener lattice and lattice distortion can also be the causes of ion migration. The possible pathways for the ion migration are illustrated in Fig. 7 [29].

Recently, several experimental observations have indicated that GBs might play a critical role as well as an ion migration channel. In Xiao et al.’s work, the grain size dependence of the switchable photovoltaic effect in symmetrical lateral PVSK devices was investigated. They found that it is easier to polarize the films with more GBs, and attribute it to the profound vacancy concentration [69]. In addition, Shao et al. also observed the grain size dependent ion migration by analyzing the measurement of conductive-AFM, SEM and EDS. They revealed that ion migration in polycrystalline PVSKs is governed by GBs evidenced by distinct element redistribution along GBs after electrical poling [30]. By using KPFM and AFM, Yun et al. confirmed that GBs can act as shortcuts for ionic migration [77]. The ions move faster at the GBs compared to the grain interior owing to higher ionic diffusivity and higher segregation of ions at the GBs. The result was correlated with the report by Xing et al.; a single crystal PVSK possess at least two-fold higher activation energy for ion movement than the one in the polycrystalline thin film, which probably due to absence of GBs [78].

The GBs were found to have important role in stability of the PVSK solar cells [79–81]. Redistribution of the ions under operation possibly causes the degradation of device performance. Domanski et al. reported the loss of the performance by migration of cations in PVSK layer although it is observed to be reversible upon storage under dark [81]. Furthermore, the ingestion of moisture occur preferentially from GBs, and as a results, the films with more GBs demonstrated poor moisture stability, which also observed in terms of device stability [79,80]. Therefore, the growth of perovskite films with larger grain is thought to be better to improve the stability of the device.

2.5. Passivation of GBs

It has been widely shown that varying the stoichiometry of the precursor solutions and subsequent solid-state films can affect the optoelectronic properties of PVSK thin films. For the one-step precursor deposition technique, this is achieved in a controlled manner by intentionally altering the molar ratio off a one-to-one stoichiometry by adding additional methylammonium halide (MAX/FAX) or lead halide (PbX₂) to add excess organic or lead content, respectively. For two-step deposition techniques, it is more difficult to precisely control stoichiometry, where typically excess PbI₂ is formed at GBs during prolonged annealing due to thermal decomposition of species. The effect of thermally induced PbI₂ on photovoltaic performance was first reported by Chen et al. [66] Their results demonstrated that thermally induced PbI₂ formed at GBs could provide beneficial passivation effects by suppressing recombination between the selective contacts and PVSK, thus improving the photovoltaic performance as shown in Fig. 8.

Excess MAI has also been shown to lead to improved carrier lifetimes and performances in PVSK thin films [29,66]. It was found that excess MAI was able to provide beneficial passivating effects on GBs to achieve higher carrier lifetimes and photoluminescence intensities as was evidenced through spatially and temporally resolved photoluminescence measurements, ultimately resulting in higher device performances [60]. The improvements were attributed to a smaller initial decay component resulting from passivation effects near GBs through excess iodine that served to suppress non-radiative recombination as well as improve the quality of the individual grains in terms of morphology and Schottky disorder. Moreover, excess MAI at GBs has shown to provide a ‘conductive pathway’ due to their formation and passivating effects at GBs, as shown through conducting atomic force microscopy (c-AFM).

**Fig. 8.** Schematics showing proposed mechanisms for PbI₂ passivation in PVSK solar cells. Reprinted with permission from Ref. [66].

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measurements in previous section (Fig. 5d). Ultimately, these devices were able to achieve efficiencies exceeding 20% [29].

In terms of halide substitution, small amounts of chlorine incorporation have been widely shown to improve performances and carrier lifetimes of PVSK thin films. Yin et al. found through computational studies that Cl and O can spontaneously segregate within GBs and passivate defect/trap states [12], thus explaining how such small amounts of Cl incorporation can have significant effects on carrier lifetime and performance. In addition, chlorine inclusion has shown to assist in film formation effects, thus improving the grain quality and mitigating defect-induced non-radiative recombination at GBs. Bromine has been another halide that has been used to partially substitute for iodine to improve performances [82,83]. Bromine partial substitution has shown to have effects on GB passivation and surface defect reduction. For instance, Yang and company used a MABr surface treatment to convert MAPbI3 thin films to higher qualities through an Ostwald-ripening process with a 1–Br anion exchange [83]. This led to not only higher performances but devices with higher stability as well. Ultimately, varying halide species can result in enhanced crystallinity by changing the nature of the film growth, due to changes in solubility of precursors, changing reaction pathways, etc, and also provide passivation effects at GBs when in excess. Therefore, off-stoichiometry presents one viable technique to improve the optoelectronic properties of PVSK films towards higher performances.

Aside from adjusting the stoichiometry of the PVSK precursor components, additives have been used as GB engineering techniques to provide further control over the nucleation and growth processes of PVSK thin films, and serve as passivating species to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a small amount of guanidinium halides has shown to improve optoelectronic properties. Incorporation of a s In addition, a three-fold increase in photo luminescence intensity and order of magnitude increase in carrier lifetime was observed for PVSK films with the guanidinium additives (Fig. 9c and d). This led to higher device efficiency with a V_{oc} over 1.1 V for planar two-step devices. The improvements were attributed to reduced defect densities and GB passivation effects via the guanidinium-based additives [84]. Lead thiocyanate has also been used as an additive to improve the properties of the PVSK films, where HSCN and CH3NH3 gases were shown to evolve from reactions during film formation that resulted in the formation of excess PbI2 at GBs, providing passivating effects [85]. Hypophosphorous acid (HA) as an additive has shown to improve grain quality and performance, which the authors attribute to reducing the defect density at GBs and surfaces during film growth [40]. KPFM measurements showed a reduction in surface potential of 210 mV that changes the band bending, the magnitude of which indicates the density of surface trap states, while fluorescence microscopy analysis showed enhanced fluorescence and lifetimes due to HA addition.

Since PVSKs are ionic compounds, the constitute ions can form chemical interactions with added chemicals. For example, under-coordinated Pb2+ ions at GBs and surface of grain can be passivated by interacting with lone pair electrons in pyridine [86]. Furthermore, polymer-templated growth of PVSK films has recently been demonstrated by Bi et al., where GBs grew perpendicular to the substrate under the influence of the PMMA additive, which effectively reduced the surface area of the boundaries [87]. This controlled growth using PMMA led to long photoluminescence lifetimes and a certified power conversion efficiency over 21%. The commonality behind additive-based GB engineering is that additives can be used to control crystallization processes and enhance film quality, while also providing passivating effects via remnant species within the film. Additives are becoming more widely studied in more detail and represents a powerful technique to enhance optoelectronic quality of PVSK thin films.
3. Conclusion

Investigation of underlying microscopic properties of the PVSKs becomes more important to understand the origin of their bulk properties. Although it is still unclear whether the GBs are beneficial or detrimental on photovoltaic performance and stability of the PVSK solar cells, they undoubtedly play important roles in optoelectronic and physical processes in the PVSK solar cells. Further works will be required to fully understand the role of GBs. We expect the understanding of microscopic properties will provide the important insight to improve the performance and stability of the PVSK solar cell towards commercialization.

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