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Surface and grain boundary carbon heterogeneity in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites and its impact on optoelectronic properties

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Abstract

Rivaling state-of-art crystalline silicon, organic-inorganic hybrid perovskites have been intensively studied in recent years. Surface and interfacial engineering have been a focus for performance improvement, yet the structure-property relationship, particularly at the surface, is still unresolved. Using soft x-ray photoemission electron microscopy (X-PEEM) and grazing incidence hard x-ray diffraction (GIXD) we investigated the surface of perovskites. We found that the nature of the surfaces was dictated by the local chemistry that varied due to mass flow during the development of the microstructure. A more homogenous chemistry, along with reduced strain and grain boundary energies, yielded more defect-tolerant films. Grain boundaries were more favorable for screening carriers than those in the control film. Our findings underscore the importance of the uniformity in the surface for developing a structure-property relationship in perovskite materials.

Introduction

Organic-inorganic hybrid perovskites have been regarded as the next generation solar technology with over 25% efficiencies being achieved with single-layer perovskite solar cells (PSCs) in the laboratory^[1]. PSCs benefit from a combination of desirable properties, including high absorption coefficients^[2], low exciton binding energies^[3, 4], low carrier recombination velocities^[5, 6], and ambipolar long-distance charge transport.^[7, 8] For a typical PSC, the nature of the surface of the perovskite absorber layer is of critical importance for affecting efficient charge transport and achieving high PSC efficiency. As a consequence of the polycrystallinity, the surfaces of perovskite films are generally populated with a high density of defects, including under-coordinated atoms^[9], halide vacancies^[10] and chemical impurities.^[11] Numerous efforts have focused on minimizing the energy loss from nonradiative recombination concentrated at the interface through interfacial engineering of the active layers.^[12-16] The surface properties are also dictated by the strain and grain boundary energies.^[17-21] Further improvements in device efficiency and in expansion into other energy-related applications require a quantitative understanding of the surface properties and their influence on the local and overall charge carrier behavior.

Within the surface region, grain boundaries (GBs) have been given much attention, though there is disagreement as to how they impact photophysical processes.^[22] For example, some studies reported that GBs do not impede photogenerated carrier transport^[23-26], while other studies demonstrated the detrimental impact of GBs on charge carrier dynamics under simulated working conditions.^[15, 27, 28] Due to surface-to-volume (GB to crystal volume) ratio, it is generally believed that larger crystal dimensions lead to better performance, since GBs are discontinuities in the crystal structure. The chemical and physical characteristics intrinsically rely on the formation of adjacent grains, giving rising to heterogeneities in perovskite films. By manipulating the surroundings of GBs, which can be done by surface modification, it is possible to critically address the role of GBs.

In this report we focus on surface properties of perovskite films by modifying their microstructure using solvent annealing (SA), which has been shown to be an effective way to improve the film quality, both for organic and perovskite systems.^[29, 30] Methylammonium (MA) lead triiodide perovskite films were imaged by X-PEEM and GIXD at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL). As a powerful and highly sensitive spectromicroscopy, X-PEEM, with a spatial resolution of ~30 nm, was used to probe the surface. By using an energy analyzer, chemically selective images were obtained with topographic and chemical contrast. The local chemistry was found to depend on the preparation conditions, e.g. the GBs of the SA sample were rich in carbon, while the thermally annealed sample (the control) had GBs with carbon-related contaminants. Using static and *in-situ* GIXD, the formation of a liquid-like intermediate phase during SA was found that influenced the homogeneity of the local chemistry. The homogeneity of the chemistry eliminated surface states, improving the local and overall photophysical responses.

Figure 1. X-PEEM working mechanism and images with topographic contrast. (a) Three physical processes occur during X-PEEM measurements: (1) excitation of a core electron into an empty valence state by resonant absorption of an x-ray photon, leaving a core hole, (2) The decay of the core hole through emission of an Auger electron, (3) generation of secondary electrons through inelastic scattering of Auger and photo-electrons; (b)-(e) X-PEEM images

with topographic contrast mechanism obtained by exciting the SA sample with x-rays of selected energies. The field of view (FOV) of the images is 10 μm , B.E. is the binding energy; (f) and (g) are the x-ray absorption spectra for the SA and control samples respectively, obtained by integrating the intensity of X-PEEM images taken around the carbon *K* edge. Both are fit with three chemical states, labeled as C1, C2 and C3, respectively.

The observation of local chemistry variation. We used X-PEEM to resolve detailed real space information on perovskite surfaces. Figure 1a shows a schematic of X-PEEM where electrons from core levels are excited into unoccupied states after absorbing x-ray photons with energies characteristic of the elements present in the sample, leaving empty core states (process 1). These core holes predominantly decay through Auger electron emission (process 2), generating a cascade of low-energy secondary electrons (SEs) through inelastic scattering of Auger electrons and photo electrons (process 3). Some of the SEs with energies above the work function of the material from the topmost layers can escape into the vacuum without being captured and are detected by the X-PEEM optics. Consequently a spatial map of the absorption in the near-surface region of the sample is obtained, with a probing depth of at most a few nm.^[31]

Here, we focus on the strong absorption at C *K*-edge of MAPbI₃ films and obtained images with topographic and chemical contrast. The detailed experimental method is included in Materials and Methods in Supplementary Information (SI). Fig. 1b-e show the topography images of the SA samples acquired at 284.7 eV, 285.7 eV, 287.2 eV and 289.2 eV, respectively. These energies were chosen based on absorption resonances shown in Fig. 1f and 1g, which were acquired by integrating the intensity of images taken at discrete energies around the C absorption edge. It is seen that the free surface of perovskite films has mainly three chemical states (labeled as C1, C2 and C3), located at 285.5 (285.6) eV, 287.2 (287.2) eV, and 288.8 (289.1) eV for SA (control) sample, respectively. These peaks are consistent with reported C 1s spectrum obtained by x-ray photoelectron spectroscopy (XPS), where C1 is attributed to intrinsic carbon species in perovskites, and C2 and C3 are related to the methyl and carbonyl groups of residual *N,N*-dimethylformamide (DMF) molecules, which may retard charge transfer at the interface by the introduction of non-radiative recombination sites.^[32-34] This carbon contamination was verified by

comparing with the spectrum of the control, where the intensity ratios of both C2 and C3 to C1 were greatly increased. The grains and boundaries from the topographic images shown in Fig. 1b-e are easily resolved, indicating sufficient resolution of X-PEEM to image spatial heterogeneities. Two phases (the grain and GB regions) are shown in all images with the boundary area being brighter, consistent with the dominant topographic contrast.^[35] Some grains show additional contrast, indicating an inhomogeneity in the crystal grains.^[28] The similar contrast below and above the C *K*-edge indicates that there is no significant carbon segregation when comparing GB and grain interior (GI) regions. Unfortunately, we could not obtain distinguishable topographic contrast for the control, shown in Figure S1 and S2, due to surface charging, indicating a number of defect states were located at the sample surfaces, especially at the GBs, since they appear brighter. The blurry images are consistent with the increased signals from carbon-related impurities.

Figure 2. X-PEEM images with a FOV of 10 μm obtained using a chemical contrast mechanism at the three states resolved in Fig. 1f. (a-c) The images were obtained at C1, C2 and C3 states,

respectively; (d-f) Corresponding line profiles of aa' (black) and bb' (red) labeled in (a-c). The arrows in (d) indicate the locations of grain boundaries.

To obtain contrast of chemical origin, the images above the C *K*-edge (Fig. 1c-e) were normalized to that below the edge (Fig. 1b). Figure 2a-c show these images with chemical contrast, and Fig. 2d-f are the corresponding line profiles. It is evident that C1 state concentrates at the boundaries. This observation is quite surprising, since the GBs are the discontinuities between crystal grains, where high concentrations of imperfections, disorder and chemical contamination would be expected. This should lead to a depletion of intrinsic elemental/chemical species. For example, inhomogeneities in the concentrations of Pb and I were previously found due to the topography.^[36] The observed strong C-rich nature suggests an integrity and functionality of methylammonium (MA) molecules at the GBs, which would assist in healing deep states and screening carriers.^[37-39] On the other hand, the C2 and C3 impurity states were also located in the two regions, in keeping with the above. Combining the distribution of the three detectable states, it is reasonable to argue that the GBs in the SA sample would not impede charge transfer, as previously reported^[23-26], while those defective ones in the control originated from the chemical contamination and inhomogeneity of the chemistry.^[36] The observation of GBs with C-rich nature and defective GBs is in keeping with the arguments suggesting a non-uniformity of local chemistry at film surfaces.

The origin of local chemistry variation. The X-PEEM images indicate that the SA process changes the local chemistry. This post-annealing process is associated with structural evolution, indicating that the variations in surface chemistries arise from grain growth dynamics. To confirm this, scanning electron microscopy (SEM) and GIXD measurements were performed. As shown in the SEM images (Figure 3a,b), the SA film had larger grains (~400 nm) in comparison to the control (~200 nm), consistent with previous reports claiming that polar solvent vapor leads to a recrystallization process by wetting the surface layer, facilitating grain growth and coalescence.^[30, 40] Interestingly, the textured grain surfaces (the striations), which balance the strain energy in the film^[41], significantly decreased after SA, indicating a surface relaxation. The smoothing of grain surfaces implies a lateral diffusion of material on the surface which will

modify the local chemistry. The atomic force microscopy (AFM) images, shown in Figure S3, also verified the variation of surface textures.

Figure 3. Microstructural characterizations for perovskite films with and without SA treatment. (a) and (b) are the top-view SEM image for the control and SA samples, respectively. Scale bar, is 1 μm; (c) and (d) are the azimuthal angle dependent intensities at $q=1 \text{ \AA}^{-1}$ retrieved from incident angle dependent GIXD measurements for the control and SA samples, respectively. Incident angle varies from 0.2 to 0.6°, corresponding to a penetration depth from 70 nm to 209 nm; (e) Incident angle dependent orientation parameters (O.P.) derived from (c) and (d); (f) Incident angle dependent microstrain derived from the GIXD patterns; (g) Representative images from *in-situ* GIXD measurements showing an intermediate phase was formed after 10 min of SA

process that are entirely transformed after SA for another 20 min. The scattering at $q \sim 0.4 \text{ \AA}^{-1}$ is from an aluminum cap that was used to maintain the solvent vapor environment.

Figure S4 shows GIXD patterns of the perovskite thin films (thickness $\sim 370 \text{ nm}$) under different preparation conditions at different angles of incidence (penetration depths). From the 1D diffraction profiles, a tetragonal perovskite phase was evident for both films. The stronger and sharper diffraction peaks of the SA film indicate enhanced crystallinity and crystal size of the polycrystal grains (Figure S5). The redistribution of crystal orientation was confirmed by the azimuthal dependent intensity at $q = 1 \text{ \AA}^{-1}$, the (100) plane. As the incidence angle was increased to 0.3° , corresponding to a hard x-ray absorption depth of $\sim 105 \text{ nm}$, the peak at $\phi = 90^\circ$ for SA samples emerged. Increasing the penetration depth led to no further changes in the orientation distribution (Fig. 3d). These changes are clearly indicative of a depth dependent orientation of the crystals. The control sample, on the other hand, was laterally more homogenous, regardless of the depth (Fig. 3c).

The preferential orientation normal to the substrate is associated with the crystal formation starting from the bottom of the film during thermal annealing. The normal grain growth agrees with the grainy matrix of small units. When using solvent vapor, the surface is wetted and liquid-like, so that growth into larger units with a random orientation of grains occurs readily. To quantify the crystal orientation, orientation parameters (O.P.) were calculated as shown in Fig. 3e. The O.P. of the control film was nearly constant at 0.28, while the SA film had a value of 0.32 in the surface region ($\sim 70 \text{ nm}$) and 0.30 in the bulk. According to the definition of O.P. (see Materials and Methods in SI), a value of 0.33 indicates no preferential orientation. The variation of the O.P. indicates that the orientation decreases with penetration depth after SA treatment.

Lattice strain can be qualified by using a modified Williamson-Hall plot of the diffraction peak broadening, as shown in Fig. 3f. The reduction of microstrain was generally determined from the depth of the SA sample compared with the control while it was more pronounced (about 15% reduction from 5.5% to 4.7%) in the near-surface region. The strain gradient is consistent with recent observations.^[42] The stress relief confirmed the existence of the quasi-liquid surface

described above. As reported^[17], strain increases with the elimination of boundaries during grain growth. Thus, the lattice strain cannot be relaxed if the solvent molecules only act as binders between adjacent grains. A liquid-like phase must be formed at the surface to allow mass flow so as to release the lattice strain^[21] and eventually change the chemical nature of the GBs. The existence of a liquid-like phase was further verified by *in-situ* GIXD measurements during the post SA process where an intermediate non-perovskite phase was observed (SA for 10 min, Fig. 3g). The static and *in-situ* GIXD results confirmed the relationship between structural and chemical evolution during the post-annealing process and that the observed variation of the surface chemistry resulted from a liquid-like surface allowing diffusion from the surface to the boundaries and stress relief, leading to a reduction of chemical contamination.^[17]

Figure 4. (a) Light intensity dependent average CPD values on the SA and control films; (b) The difference in CPD values (Δ CPD) of the studied films in (a); (c) and (d) are the zoom-in topographic images for the SA and control film, respectively; (e) and (f) show the line profiles of height (red) and light intensity dependent CPD values labeled in (c) and (d), respectively. Among them, the orange line is in dark condition, the blue one under 11 mW/cm^2 , the pink is under 60 mW/cm^2 , and the cyan is one under 106 mW/cm^2 . The numbers of Δ CPD between a GB and adjacent grain are marked in (e) and (f).

The impact from local chemistry variation. Since a variation in the local chemistry was found, we probed the impact on the physical behavior of the perovskites. The X-PEEM results already show that the C-rich nature of the surface prevented surface charging, indicating surface defect states can be significantly suppressed. This was confirmed by performing photoluminescence (PL) measurements on different sides of the sample to elucidate any contribution from defect traps that induce intraband energy levels.^[16] Figure S6 shows steady-state PL results by irradiating the sample from both the front (free surface) and back (ITO substrate) sides for SA and control samples, respectively. The excitation wavelength was 450 nm, with a penetration depth of $\sim 50 \text{ nm}$. The PL emission from front excitation was redshifted in comparison to the back excitation (781 nm vs. 777 nm). While for the SA sample, PL spectra were nearly identical for both excitations with an emission at 782 nm. Relative intensity of PL emission was enhanced when solvent vapor annealing was adopted. These PL measurements indicate that the SA sample was more defect-tolerant in comparison to the control that had considerable surface states.

To gain further insight on reduced surface states, Kelvin probe force microscopy (KPFM) measurements were performed using different intensities of light illumination. Shown in Figure S7 (a)-(f) are the corresponding contact potential differences (CPD) at different light intensities. The changes in the average CPD values for the two samples are shown in Figure 4a. The surface potential continuously increased with incident light intensity and tended to be saturated up to an illumination of 20 mW/cm^2 , suggesting that the predominant surface states, if any, should act as electron traps which resulted into free hole accumulation at the surface. Compared with the control, the average CPD in the dark was significantly increased in the SA sample ($>150 \text{ mV}$),

meaning that the surface electron traps had been markedly eliminated, resulting into less hole accumulation due to surface-states-induced band bending, consistent with the PL studies. As shown in Fig. 4b, the difference of CPD between the two films (ΔCPD) increased with increasing light intensity. The difference between the CPD under illumination and in the dark was magnified for the SA sample, indicating photogenerated charge separation, rather than a surface-states-related mechanism, dominated the signal after SA treatment. It also implies that the SA sample had a stronger photovoltaic effect which could help produce devices of a larger open-circle voltage.

Based on above results, we can conclude that the homogeneous distribution of local chemistry is responsible for the suppression of trap-mediated processes, resulting in enhanced PL and CPD values. As the carbon primarily originates from the MA molecules in the perovskites, the benefit from the liquid-like orientation of the organic cations can be anticipated. It has been widely recognized that the existence of MA rotation is responsible for many advantages of perovskites, such as healing deep trap states^[37], contributing to efficient charge carrier screening and strikingly large dielectric constant.^[43, 44] Given our results, it is expected that photogenerated charge separation could more readily occur around the GBs of C-rich nature compared with the defective ones. This hypothesis was confirmed by the line profiles from KPFM images. Fig. 4c and 4d are zoomed-in topographic images where the lines are labeled for the SA and control samples, respectively. Fig. 4e and 4f show the corresponding line profiles. The CPD difference between grains and GBs became smaller with incident light (from ~ 0.09 V to ~ 0.05 V) for SA sample, meaning the boundary area gained more photocarriers and contributed to the increase in CPD, while the local difference became slightly larger. The local potential differences demonstrate that C-rich GBs can intrinsically act as channels to efficiently separate and accumulate carriers rather than nonradiative recombination centers.

It can be concluded that surface chemical engineering critically affects structural and physical properties. From the structural and optical characterizations, it is known that there are depth dependent microstrains and bandgaps.^[42] The mismatch of associated bandgaps between the surface region and the bulk is detrimental, since it could facilitate surface/interfacial nonradiative

recombination when the surface has a narrower bandgap and form unfavorable band alignment at charge-selective interfaces. Conversely, the more homogenous the surface chemistry, the more uniform the energetic level within the perovskite absorber, which is more favorable for charge carrier transport and better performance. By fabricating complete devices, we can see the enhanced performance of devices with SA (Figure S8). All PV parameters show a noticeable improvement, verifying the benefit of both charge carrier separation and extraction.

In summary, GB regions were found to be C-rich by X-PEEM by using a post-annealing treatment. The film formation was altered by generating an intermediate liquid-like surface that enabled mass flow. The homogeneity of the surface chemistry was associated with a significant release of the lattice strain in the film. The local dielectric response was enhanced, the films more defect-tolerant, and energetic bandgaps became more uniform along the film thickness, suppressing the carrier recombination within the absorber and at the interface. This study described the correlation between the chemical nature and resulting performance, and provided an explanation of the photophysical performance within the boundary area. This study underscores the critical importance to engineer local chemistry towards high-performance and stable devices.

Conflicts of Interest

There are no conflicts of interest to declare.

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