Cryogenic spatial–temporal imaging of surface photocarrier
dynamics in MAPbI3 films at the single grain level

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Recommended Citation
Liu, Zhiyan; Park, Joong Mok; Luo, Liang; Cheng, Di; Huang, Chuankun; Kim, Richard H. J.; Vaswani, Chirag; Song, Zhaoning; Yan, Yanfa; Yao, Yongxin; Ho, Kai-Ming; and Wang, Jigang, "Cryogenic spatial–temporal imaging of surface photocarrier dynamics in MAPbI3 films at the single grain level" (2020). Ames Laboratory Accepted Manuscripts. 802.
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Abstract
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ABSTRACT
We use cryogenic spatial–temporal photoluminescence (PL) imaging measurements down to 10 K and with short-wavelength, 405 nm laser excitation to study surface charge generation, trapping, and recombination at single bright and dark grains as well as their boundaries in model methylammonium lead iodide (MAPbI$_3$) polycrystalline thin films. These salient conditions are shown to be critical for identifying both the detrimental and cooperative roles of grain microstructures where the dark grains serve as the PL quenching center, while the grain boundaries are largely benign and may promote electron–hole separation.

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The extraordinary performance of perovskites arises from their excellent optoelectronic properties such as high absorption coefficient,$^1$ small exciton binding energy,$^{1,2}$ robust vibronic coherence,$^3$ long carrier lifetime$^4$ (μs vs ns in inorganic semiconductors), and long carrier diffusion lengths$^5$ (100 nm–1000 nm vs sub-10 nm in organic semiconductors$^6$). Understanding charge dynamics and defect physics in these materials has been a major focus in the past few years.$^{12-15}$ Particularly, the surface photocarriers have been separated from the bulk ones and are shown to limit charge lifetimes in MAPbI$_3$ polycrystalline films.$^6$ However, these studies are performed in ensemble-averaged states, thereby providing no insight on surface heterogeneity at the single grain interior (GI) and grain boundary (GB) level, which is also critically needed for the optimization of power conversion efficiency.$^1$ For example, one of the outstanding issues is to resolve the correlation between the photoluminescence (PL) lifetime and GI/GB microstructures. Previous PL studies$^{17,18}$ have shown that higher defect density at the GB produces a much-reduced lifetime and emission intensity. However, recent confocal fluorescence-lifetime imaging$^{19,20}$ and transient reflectivity microscopy show enhanced charge transfer by the built-in potential and even longer lifetime.

Several important factors are required to better address the surface photocarrier responses at the single grain level: first, laser excitation near the UV region is needed for the carrier dynamics, as this minimizes the contribution of bulk states due to the significantly reduced penetration depth. For excitation photons at 405 nm, the optical penetration depth is ∼80 nm.$^{21}$ Second, pumping to the vacuum condition is desired since it allows the removal of surface passivation elements such as water and oxygen,$^{22,23}$ which creates an ideal environment to probe intrinsic surface states. Third, temperature tuning$^{15,24}$ is also a key since surface state responses will be more dominant over the bulk counterpart at cryogenic temperatures due in part to its enhanced absorption. Temperature tuning can further disentangle intertwined dynamics from various decay channels from the GI vs GB contributions. Although the carrier dynamics and PL imaging of perovskites have been extensively studied under ambient conditions and provide valuable information,$^{18-20}$ cryogenic spatial–temporal imaging in high vacuum is still extremely scarce.
In this Letter, we investigate sub-μm surface heterogeneity and photocarrier dynamics with time-resolved confocal microscopy down to 10 K induced by 405 nm laser excitation. Our results reveal the influence of grain microstructures on carrier dynamics both at the single grain level and at the surface in MAPbI$_3$ polycrystalline thin films. Above ~100 K, the surface recombination channels, both radiative and non-radiative, are shown to limit the carrier lifetimes. Below ~100 K, the combined decay processes from the surface and exciton recombination channels determine the PL decay time. Interestingly, the photocarrier lifetimes and densities at GBs are similar to those of bright GIs, in contrast to the dark GIs that exhibit much shorter lifetimes and lower densities, especially in the orthorhombic phase. These results indicate that GBs are intrinsically benign to photocarriers.

Optical fluorescence and lifetime measurements were performed using a custom-built time-correlated single-photon counting, confocal scanning microscope with a 50× long working distance objective [numerical aperture (NA) = 0.5]. The sample was put in an imaging microcryostat for vacuum and at low temperature down to 10 K. For each PL image, the monochromator was set to be the peak position of the PL spectrum and the PL signal was detected by using a microchannel plate-photomultiplier tube. The spatial resolution and response time of our spatial–temporal imaging system were 0.4 μm and ~0.5 ns, respectively. The high-quality MAPbI$_3$ polycrystalline thin films (thickness around 200 nm) were solution-processed following Ref. 25. The samples were well stored in a nitrogen glove box before the experiment for about a week and quickly loaded to the vacuum cryostat for the imaging experiment.

Figure 1(a) represents a confocal scanning PL image of the MAPbI$_3$ polycrystalline thin film that uniformly covers a glass substrate with an average grain size of ~1 μm. A magnified PL image plotted in Fig. 1(b), with a scale bar of 1 μm, clearly shows the dark GI (P. #4) and bright GIs (P. #1 and P. #3). In between the bright GIs, a 0.3 μm–0.4 μm GB region (P. #2) can be resolved with a 20%–30% reduction of PL intensity. The corresponding room temperature PL decay curves are shown in Fig. 1(c) (on a semi-log scale). The PL decay curves in bright GIs (P. #1 and P. #3) show a combination of monomolecular and bimolecular recombination from defect and radiative decay channels, respectively. The long-lived PL decay curves shown in the bright GIs are consistent with prior reports under similar measurement conditions, indicating good sample quality. In contrast, the PL decay curve in the dark GI (P. #4) exhibits a much faster initial, few-ns decay component possibly due to the higher trapping density [indicated by the black dashed line in Fig. 1(c)] followed by a final decay component with a shorter lifetime than bright GIs (P. #1 and P. #3). At the GB region (P. #2), the PL decay curve exhibits a faster initial decay component similar to the dark GI (P. #4) and has comparable long decay components as the bright GIs (P. #1 and P. #3). The peak amplitude of the PL time-resolved decay curve indicates the generated photocarrier density established right after the excitation pulse (~0.5 ns). It is critical to note that the peak amplitude of time-resolved PL decay curves is the same for all regions, as shown in Fig. 1(c). This salient feature, seen from time-resolved signals, cannot be seen in the confocal PL image, Fig. 1(b), that arises from time-integrated PL signals. The PL dynamics at the room temperature of the single GB and GI provide two compelling messages: (1) The GB has a similar PL peak amplitude (photocarrier density) right after the excitation pulse and lifetime as the bright GIs and (2) the GB may contain non-radiative trapping centers and/or a built-in electric potential that gives rise to similar fast initial decay channel as the dark GI but benign enough not to deplete photocarriers.

The inset of Fig. 1(c) compared the room temperature PL decay curves in different environments but in the same bright GI. The measured PL lifetime is significantly shorter in vacuum when compared to that in air. Note that the long and short PL lifetimes are reversible when switching the environment from air to vacuum and then back to air (blue to red to aqua). When breaking the vacuum by purging in air, we observe that the PL lifetime of the MAPbI$_3$ polycrystalline thin film becomes significantly longer again. This rules out any permanent sample change. Such a reversible process has been repeated within several lab hours. We attribute the shorter PL lifetime in vacuum to the activation and dominance of surface states over bulk states due to the removal of water and oxygen, i.e., surface contamination elements. Our assignment of the important roles of oxygen and water on surface passivation in perovskite thin films is fully consistent with the recent literature. Therefore, the vacuum condition, in addition to UV laser excitation, is needed to probe the influence of surface states in MAPbI$_3$ fully. The change in photocarrier dynamics observed highlights the difference between surface and bulk states, which will be further corroborated below by the temperature-dependent data.

To reveal the surface behaviors at the single grain level and low temperature, the photocarrier dynamics at 50 K are shown in Fig. 2. Figure 2(a) plots the confocal PL image of the MAPbI$_3$ thin film with two bright GIs (red and pink, #1 and #3), the GB region (blue, #2)
sandwiched by the two adjacent bright GIs, and one dark GI (cyan, #4) marked. The corresponding time-resolved PL decay curves are shown in Fig. 2(b). Intriguingly, the dynamics behave very differently from those at room temperature, as described in Fig. 1. In Fig. 2(b), comparable PL peak amplitude and lifetime are shown at the GB (blue, #2) and bright GIs (red and pink, #1 and #3). Recall that at room temperature, the PL peak amplitude is the same for all regions. In contrast, at 50 K, the PL peak amplitude is two times smaller in the dark GI (cyan, #4) than at the GB region (blue, #2) with a much reduced lifetime. These results clearly show that the PL quenching centers, such as dark GIs, behave very differently from GB regions, which are largely benign. It is critical to note that the measured PL dynamics at the GB region are distinct, which cannot be decomposed into a mixture of dark and bright GI dynamics. Specifically, the GB region (blue, #2) has the shorter initial PL decay than the bright GIs (red and pink, #1 and #3); the GB region (blue, #2) has a much larger PL peak amplitude and longer lifetime than the dark GI (cyan, #4). The difference in initial PL decay dynamics between the GB region and bright GI indicates the existence of either residual shallow surface trapping states or the built-in potential at the GB region. The latter can actually promote charge separation and increase the carrier lifetime. These will facilitate local photocurrent collection that is indicated by slightly faster initial dynamics at the GB region. The latter can actually promote charge separation and increase the carrier lifetime. These will facilitate local photocurrent collection that is indicated by slightly faster initial dynamics at the GB region.

Figure 2(c) shows the excitation fluence-dependence on normalized PL decay curves for bright GIs (red, #1) at three fluences 0.5 μJ/cm², 1 μJ/cm², and 2.1 μJ/cm². These fluences are comparable to the lowest excitation used in the literature. The PL decay curves can be well-fitted by a triple-exponential function \( I(t) = \sum a_i e^{-t/\tau_i}, i = 1, 2, 3 \). A slow component \( \tau_2 \) and a fast component \( \tau_3 \) correspond to the surface non-radiative trap-assisted recombination and radiative electron–hole recombination, respectively. The non-linear decay process, such as Auger recombination, is negligible in our experiment due to the small photo-excited carrier density (~10¹⁷ cm⁻³). Therefore, the sub-ns \( \tau_3 \) is not related to the non-linear decay process. Instead, later, we will show that it is related to the intrinsic radiative decay time of excitons²⁶,²⁷ existing in the orthorhombic phase. From the quantitative fittings, as the excitation fluence increases in this range, \( \tau_1 \) and \( \tau_2 \) change slightly from 21 ns to 12.6 ns and from 5.6 ns to 2.9 ns, respectively. The change in \( \tau_2 \) is negligible.

Figure 3 represents the extensive temperature-dependent measurements of surface state photocarrier properties at the single grain level: confocal PL image (a), PL spectra (b), and PL decay curves of the bright and dark GIs, marked in (a), for the long, hundreds of ns [(c)–(f)] and initial, few ns [(g)–(j)] temporal regimes in the MAPbI₃ polycrystalline thin film from 200 K to 10 K. We point out three observations. First, the PL spectra at different temperatures in Fig. 3(b) show a clear phase transition from a high-temperature tetragonal phase to a low-temperature orthorhombic phase with a transition temperature of ~170 K. This manifests as an “S”-shape spectral shift consistent with the prior literature. Second, comparing Figs. 3(c)–3(f), the integrated PL counts increase from high to low temperatures, indicating an ~3.5 times enhancement of internal PL quantum efficiency at 10 K vs 200 K, consistent with Ref. 28. Third, the dark GIs show faster initial decays and shorter lifetime than the bright GIs from 200 K down to 10 K. This corroborates the existence of higher surface defect density in dark GIs.

Most intriguingly, the PL lifetimes and the peak amplitudes show very distinct temperature dependence. On the one hand, the...
PL lifetimes of both bright and dark GIs become much shorter at low temperatures, especially deep into the orthorhombic phase, as shown in Figs. 3(c) and 3(f) when compared to the tetragonal phase, Fig. 3(c). A minority carrier lifetime at 10 K is 20 times shorter than that at 200 K, as shown in Fig. 3(f) vs Fig. 3(c). The larger lifetime reduction in the orthorhombic phase indicates the emergence of a new decay channel. We know that the reported exciton binding energy for MAPbI\textsubscript{3} perovskite is 13.5 meV–30 meV.\textsuperscript{23,29} The exciton formation only appears in the orthorhombic phase,\textsuperscript{1} and the exciton population increases as thermal ionization goes down at low temperatures.\textsuperscript{29,30} Therefore, we attribute the new decay channel to the radiative exciton recombination. On the other hand, the PL peak amplitudes of dark and bright GIs show a distinctly different temperature variation. As shown in Figs. 3(g)–3(j), we plot the PL decay curves of dark and bright GIs for the first 5 ns on a linear scale from 200 K to 10 K. In the high-temperature tetragonal phase, Fig. 3(g), the peak amplitudes of PL decay curves show a comparable size between the dark and bright GIs. The difference becomes more pronounced in the orthorhombic phase, as shown in Fig. 3(j) at 10 K, where the PL peak amplitude of the bright GI is >2 times larger than that of the dark GI. Since the PL peak amplitudes measure the transient population right after the laser excitations, the difference in photocarrier density right after the pulse excitation between dark and bright GIs at low temperature is probably due to the additional defects in the orthorhombic phase\textsuperscript{32} in the dark GIs. The non-radiative recombination due to the additional surface defect is faster than our pulse duration, causing depopulation during the pulse.

To quantify the above physical pictures of population decay processes at various microstructures and phases, we perform the PL decay fittings of bright and dark GIs from 10 K to 200 K. The detailed fitting parameters are summarized in Table I. We also provide weighted PL decay time by taking into account the weight of different decay processes, i.e., \( \tau = \sum_{i=1}^{3} \tau_{i} \), for a more straightforward comparison. Unlike the small changes in PL lifetime caused by different excitation fluences, the PL lifetimes decrease significantly when the temperature changes from 200 K to 10 K. The \( \tau \) of bright and dark GIs decrease notably from 41.9 ns to 0.4 ns and from 21.8 ns to 0.1 ns, respectively. Moreover, for the tetragonal phase, the PL decay curves for both bright and dark GIs can be well fitted by a double exponential function. The slow decay component \( \tau_{1} \) and the fast component \( \tau_{2} \) can account for the lifetime of surface non-radiative trap-assisted recombination and radiative electron–hole recombination. For the low-temperature PL decay curves, they can only be well fitted by a triple-exponential function. As previously discussed, below 100 K, the exciton population will dominate free charge carriers, thereby giving rise to the additional sub-ns\textsuperscript{26,27} radiative exciton decay channel, \( \tau_{3} \), which is limited by the instrument response time in our measurement. From the fitting, at temperatures below 50 K, the radiative exciton recombination surpasses the electron–hole recombination channel and becomes the leading factor determining the PL decay lifetimes. Finally, when the temperature goes down to 10 K, the PL lifetime is completely dominated by exciton recombination for both dark and bright GIs, resulting in an extremely short \( \tau \) in both dark (0.1 ns) and bright (0.4 ns) GIs even with very low excitation fluence. The intrinsic exciton recombination is not the dominant channel for the PL decay at higher temperatures, such as 100 K, which can be largely explained by the polaron formation by the screening of electron (hole) charge (reducing the transition matrix elements)\textsuperscript{35,36} and/or electron–hole charge separation due to surface band bending. Note that the temperature at which the fitted \( \tau_{1} \) begins to appear is higher in the dark GI (100 K) than in the bright GI (50 K), indicating the higher trap density in the dark GI.\textsuperscript{26}

In summary, we perform cryogenic confocal laser scanning microscope measurements of photocarrier dynamics in MAPbI\textsubscript{3} polycrystalline thin films with the new vacuum and temperature tuning knobs at the single grain and grain boundary level. They can be extended to characterize, understand, and optimize the surface, in addition to bulk, local microstructures to overcome the limitations of the materials’ inhomogeneity and facilitate charge delocalizations in perovskite photovoltaic devices. Our results also warrant further investigation of grain microstructures through other advanced spectroscopy/microscopy, such as terahertz (THz) conductivity,\textsuperscript{22,34} nonlinear emission,\textsuperscript{23,25} and magneto-optical techniques.\textsuperscript{37}

This work was supported by the Ames Laboratory, the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division under Contract No. DE-AC02-07CH11358 (laser scanning microscopy/spectroscopy and time-correlated single-photon counting). Sample development at The University of Toledo was supported by the National Science Foundation under Grant No. DMR 1400432.

| Temperature (K) | \( \frac{\tau_{1}}{\sum_{i=1}^{3} \tau_{i}} \) (a.u.) | \( \tau_{1} \) (ns) | \( \frac{\tau_{2}}{\sum_{i=1}^{3} \tau_{i}} \) (a.u.) | \( \tau_{2} \) (ns) | \( \frac{\tau_{3}}{\sum_{i=1}^{3} \tau_{i}} \) (a.u.) | \( \tau_{3} \) (ns) | \( \tau \) (ns) |
|----------------|----------------------------------|-----------------|----------------------------------|-----------------|----------------------------------|-----------------|----------------|
Y. Yao, K. M. Ho, and J. Wang, "Light-driven Raman coherence as a nonthermal route to ultrafast topology switching in a Dirac semimetal," Phys. Rev. X 10, 021013 (2020).

X. Yang, L. Luo, C. Vaswani, X. Zhao, Y. Yao, D. Cheng, Z. Liu, R. H. J. Kim, X. Liu, M. D. Furdyna, J. K. Furdyna, I. E. Perakis, C. Wang, K. Ho, and J. Wang, "Light control of surface-bulk coupling by terahertz vibrational coherence in a topological insulator," npj Quantum Mater. 5, 13 (2020).

A. Patz, T. Li, X. Liu, J. K. Furdyna, I. E. Perakis, and J. Wang, "Ultrafast probes of nonequilibrium hole spin relaxation in the ferromagnetic semiconductor GaMnAs," Phys. Rev. B 91, 155108 (2015).