Measuring Diffusion Length in Single Crystal Halide Perovskites

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In recent years, the research devoted to halide perovskites has yielded exciting advances in the field of photovoltaics. Of particular interest are bulk single crystal devices, in which the absence of grain boundaries promotes good charge transport properties. Here, we synthesize and characterize spatially-confined $MAPbI_3$ single crystals conformally grown on pre-patterned electrodes. We measure charge carrier diffusion lengths on the order of 90 μm at low temperatures (80 K), which is about three times greater than the high-temperature diffusion lengths. We attribute this primarily to a temperature-induced phase transition around 160 K. These results can be used to better understand the fundamental properties of halide perovskites, an essential step in the development of inexpensive, efficient perovskite solar cells.

I. INTRODUCTION

Lead halide perovskites show promising potential in the fields of photovoltaics, light emission, and photodetection. Having emerged very recently, perovskite's good charge transport properties make them a strong contender to replace the more expensive silicon solar cells in use today. They also exhibit excellent solar spectrum absorption and an easily tunable bandgap. These hybrid organic-inorganic materials ($CH_3NH_3X_3$, X=Cl, Br, I) have already reached efficiencies exceeding 20% in their polycrystalline form; however, the presence of grain boundaries in a polycrystal leads to more defects (such as states between bands where excited charge carriers may become trapped) and hindered mobilities. For this reason there is great interest in studying the properties of single crystal (SC) perovskite.

This work focuses on the synthesis and characterization of thin, smooth SC $MAPbI_3$ microplates. Restricting the thickness to 2.5 μm allows us to apply a gate voltage and change the crystal's conductivity. Due to the large number of charge carriers that can respond an applied field, even very high gate voltages produce an electric field that dies off quickly within the sample, so field-effect measurements must be performed on a thin device. Using a gate voltage to change the perovskite's conductivity could help illuminate how we might integrate perovskites into traditional semiconductor devices such as field-effect transistors (FET). Additionally, smooth surfaces ensure that optical measurements don't result in an excess of scattered light. Here, we study the charge carrier diffusion length L_d over a range of temperatures (300 K to 80 K) with different applied bias voltages V_b. L_d is the average distance charge carriers can move through a material before they recombine. It is an important parameter in photovoltaics, with longer diffusion lengths generally leading to more efficient solar cells.

II. TECHNICAL BACKGROUND

To grow the SC we utilize a technique called Inverse Temperature Crystallization (ITC), first discovered by Saidaminov, et al. [1] This method allows for simple, inexpensive fabrication that takes very little time: we usually see millimeter-scale SC after 8-9 hours. An illustration of ITC is
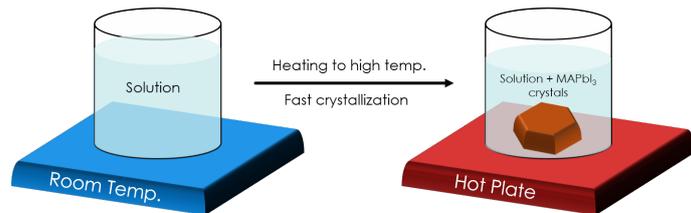

FIG. 1: A schematic representation of the Inverse Temperature Crystallization (ITC) method. When heated to about 100 °C, the $MAPbI_3$ solution begins to precipitate and form crystals.

shown in Fig. 1. This rather counter-intuitive growth procedure works for only a small group of substances, for reasons beyond the scope of this paper; however, Saidaminov, et al. note that the individual precursors PbX_2 and MAX do not exhibit any inverse temperature solubility behavior, indicating that the phenomenon is tied to the perovskite structure. ITC allows us to fabricate samples directly on pre-patterned electrodes. Nominally, this creates a good metal-semiconductor contact to allow for high quality bottom-gate-bottom-contact devices. It is worth mentioning here that we do see more nucleations on the Au electrodes than on the oxide substrate, indicating that the presence of a metal can affect the perovskite growth.

Another advantage of ITC is that the crystal dimensions can be easily controlled by varying growth conditions. Closely following the work of Amassian, et al., we construct an apparatus that allows for uninhibited growth in the x-y plane while confining growth in the z-direction (i.e., the thickness) [2]. A schematic of the sandwich-making process is seen in Fig. 2. The substrate of our z-confinement device (a.k.a. "sandwich") is 500 μm of Si with a 300 nm insulating layer of SiO_2 on top. Pre-patterned gold electrodes (not shown in the figure), ranging from 30 nm to 100 nm, are deposited on the oxide layer. The superstrate is a thin glass microscope slide, joined to the substrate via two strips of melted PET film that provide the 2.5 μm spacing. We explain this process in more detail in the Methods section.

Aside from ensuring thin samples, another advantage of using the sandwich growth technique is the ability to control surface roughness. The conformal growth tends to produce smooth crystal surfaces as the perovskite is pressed against
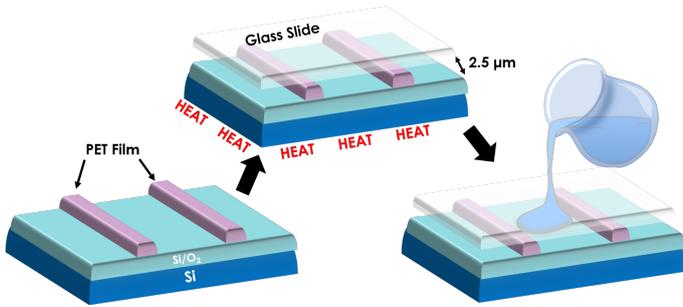
FIG. 2: Schematic representation of height confinement structure used to produce thin SC.
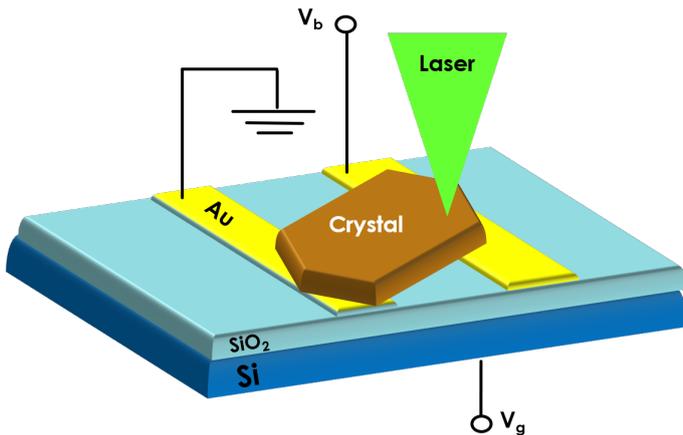

FIG. 3: A schematic of our SPCM setup after the glass and PET have been removed. The green laser is raster-scanned over the SC surface, and the resulting photocurrent is measured.

the substrate and superstrate. Our main method of characterization is Scanning Photocurrent Microscopy (SPCM), which relies on a laser for charge carrier injection; surfaces free of defects reduce photon scattering. In SPCM (Fig. 3), a laser is raster-scanned over the planar surface of a crystal and the resultant photocurrent is measured as a function of the laser's position [3]. This unique measurement technique gives us a spatial photocurrent mapping that allows for easy extraction of important parameters like L_d.

We perform SPCM through a range of temperatures, from about 300 K down to 80 K, to see how L_d changes. Namely, we aim to explore how charge carrier diffusion lengths change with decreasing temperature. An interesting factor to consider is the first-order phase transition at approximately 160 K, at which point the perovskite's lattice structure transitions from the tetragonal phase (high temperature) to the orthorhombic phase (low temperature).

III. RESULTS AND DISCUSSION

Atomic force microscopy (AFM) measurements show that the confinement method does indeed have the ability to yield smooth surfaces, with a measured rms surface roughness of
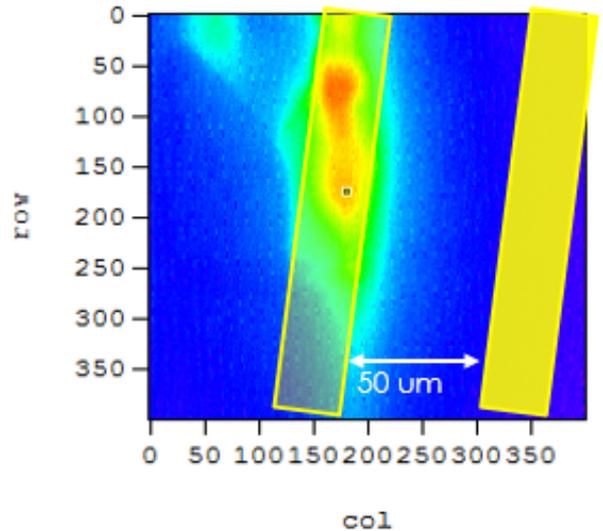

FIG. 4: SPCM raw data with Au electrodes (yellow bars) overlaid. The left electrode is made transparent to show the data underneath. The red is high photocurrent while the blue is low photocurrent.

<5 nm. As we discuss later in this section, problems with surface smoothness arose when removing the glass superstrate. These AFM measurements were performed on the smoothest samples, where there was no peeling, and they match the surface roughness of the glass slide. An AFM scan of the sample edge shows that the SC is $\approx 2.5 \pm 0.2$ μm thick, which indicates that the crystal is growing up to its superstrate limit.

SPCM measurements done at room temperature (above the phase change) and at 8 0K (below the phase change) are presented here. Cooling down, we notice a sharp difference in diffusion length immediately after the phase transition, and then the trend continues gradually until 80 K. Figure 4 shows the photocurrent map of a sample with gold electrodes overlaid for reference. These data are taken at 300 K with an applied bias voltage between the electrodes of 5 V.

Figure 5 shows photocurrent scan lines for V_b = 5 V, 7 V, and 10 V. By altering the potential difference across the electrodes we are changing the electric field strength between them. In general, a curve with a steeper slope indicates a sharper fall-off in photocurrent, meaning a shorter L_d. We fit the curves and extract a L_d of about 30 μm for each, which seems to indicate that the drift component (i.e., how much charge carriers are affected by the electric field) is negligible compared to the diffusion component of their movement.

We use liquid nitrogen to lower the temperature to 80 K, which is below the phase change. As is clear from Fig. 6, there is diffusion length extension at low temperature. L_d pulled from our fits is 90 ± 7 μm, a factor of three greater than the high-temperature measurement for the same bias voltage. We attribute this extension primarily to the phase change. In the orthorhombic phase there are fewer scattering mechanisms to cause recombination, which can be understood partly by the reduced motion of ions at low temperatures [4]. Thus in the
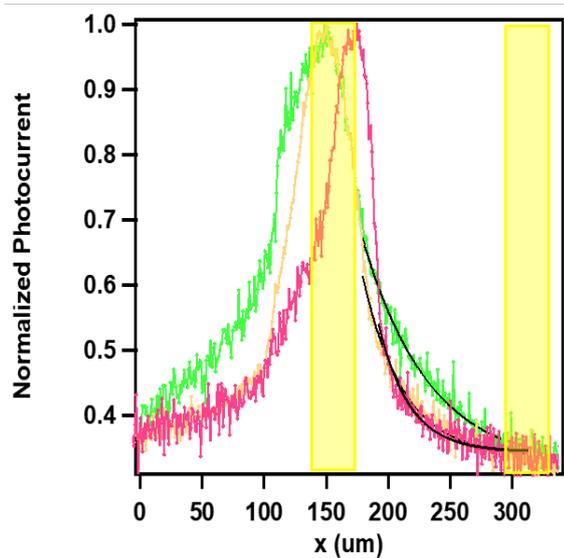
FIG. 5: Photocurrent line scan for three different values of V_b: 5 V (orange), 7 V (green), and 10 V (red). The black lines are the curve fits, and the yellow bars are the gold contacts. The diffusion length remains comparable for each.
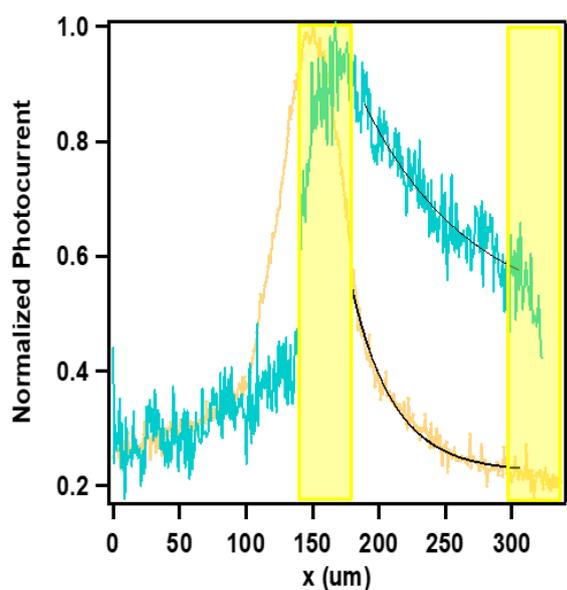

FIG. 6: Photocurrent line scans for two different temperatures: 300 K (orange) and 80 K (green). The black lines are the curve fits, and the yellow bars are the gold contacts. The low temperature scan shows a diffusion length of around 90 μm while the high temperature scan yields about 30 μm.
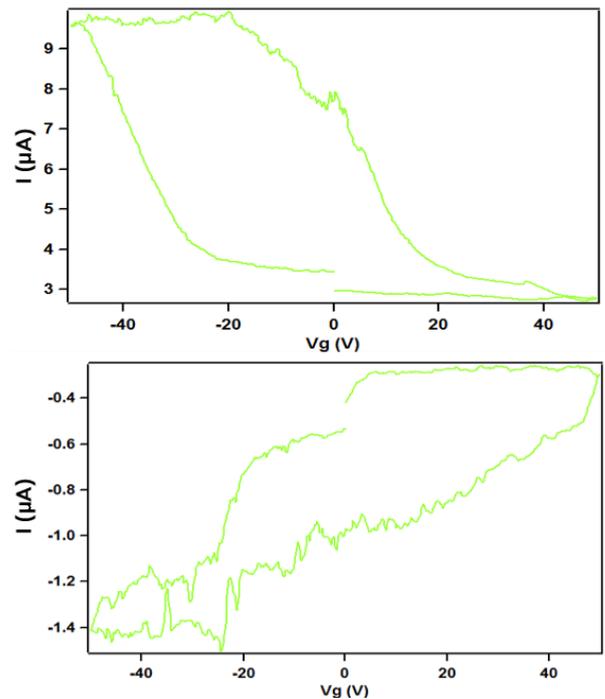

FIG. 7: Current vs gate voltage scans (80K in the dark) for V_b>0 (top) and V_b<0 (bottom). These results indicate our samples are p-type.

orthorhombic phase charge carriers are allowed to diffuse further through the material before recombining.

Lastly, we sweep through a range of gate voltage (V_g) values and measure the resultant current. Fig. 7 shows I vs. V_g plots for a positive constant V_b (top) and a negative constant V_b (bottom). Since a positive V_g injects electrons, a decrease in current for $V_g > 0$ indicates that our sample is dominated by *positive* charge carriers; or, in other words, it is p-type. This observation is supported by both the top and bottom gate scan plots.

While informative, the extremely small data set means these results are far from conclusive. Our main obstacle was in the synthesis of these SC devices: after a crystal had grown on the electrode-patterned substrate, we needed to remove the glass superstrate to make electrical contact. However, in most cases the crystal preferred the glass and the electrode-perovskite contact was largely (or entirely) compromised. This can be seen from Fig. 4, in which the highest photocurrent is located at a single point rather than uniformly along the electrode. In the few cases that the sample remained on the substrate, the surface was usually peeled and roughened. Many variations on the fabrication method were attempted, including treating the superstrate with Silane to reduce "stickiness" and plasma-etching the substrate to promote adhesion. Neither of these yielded drastic improvements in crystal quality.

We have demonstrated that, using a height confinement method, it is possible to produce large, thin perovskite crystals grown directly on gold electrodes. Moreover, the growth process is an order of magnitude faster than previous experiments cited. The SC nature of our samples makes for fewer interfacial defects, trap states, and grain boundaries than normally seen in a polycrystalline film, as evidenced by order of magnitude longer diffusion lengths. [5] While previous work has produced single crystals of these dimensions via ITC, our

unique experiments using SPCM allow us to easily determine diffusion lengths as a function of temperature. In the future, we would like to continue to optimize the growth procedure so that we can produce clean, large SC that make good contact with the electrodes. This may involve trying other substrate treatments such as UV-O_3 to encourage the perovskite to stick better. Additionally, we would like to do x-ray diffraction on our samples to confirm their chemical makeup.

IV.   METHODS

A.   Materials

We use the powder precursors lead iodide (PbI_2) and Methylammonium (CH_3NH_3) as well as the solvent gamma-Butyrolactane (GBL). These chemicals were purchased from Sigma-Aldrich.

B.   Synthesis

First, a substrate (Si/SiO_2, overlaid with prepatterned gold electrodes) and a glass slide superstrate are cleaned with Acetone and Isopropyl Alcohol, and then dried with nitrogen gas. Two thin strips of 2.5 μm polyethylene terephthalate (PET) film are placed on the substrate with a gap of about a millimeter between them. The glass is placed on top and the entire device is heated to 240 °C to melt the substrate and superstrate together. We then prepare a one-molar solution of the chemicals listed above, heating on a hot plate at 60 °C for an hour to allow for complete dissolution. The solution is filtered through a 2 μm filter and approximately 5 μl of the filtrate is placed into the z-confinement device. This is achieved by simply placing the drop on the sandwich edge and allowing capillary forces to draw it into the gap. Lastly, the filled device is put on a hot plate at 100 °C for 8-9 hours.

C.   Characterization

The glass is removed to allow for electrical contact to be made via wire bonding. I-V measurements are performed under different microscope light settings to determine if the device is functional and photoresponsive. SPCM measurements are done over a range of bias voltages, gate voltages, laser intensities, and temperatures. The SC are measured as grown, on the pre-patterned substrate.

[1] Saidaminov, M. I. et al., "High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization", *Nat. Commun.* **6**, 7586 (2015).

[2] Amassian, A. et al., "Single crystal hybrid perovskite field-effect transistors", *Nat. Commun.* **9**, 5354 (2018).

[3] Yu, D. et al., "Photocurrent mapping in single-crystal methylammonium lead iodide perovskite nanostructures", *Nano Lett.* **16**, 7710 (2016).

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[5] Adhyaksa, G. et al, "Carrier Diffusion Lengths in Hybrid Perovskites: Processing, Composition, Aging and Surface Passivation Effects", *Chem. Mater.* **28**, 5263 (2016).