Visualizing Carrier Trapping at the Nanoscale in Hybrid Organic-Inorganic Perovskite Films

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1. Introduction

Within the last decade, hybrid organic-inorganic perovskite (HOIP) materials have received notable attention for their development and use in photovoltaic devices. Record solar cell device efficiencies have already surpassed 25% [1], comparable to established commercial silicon based devices, due to the low-cost methods for fabrication [2] and excellent optoelectronic properties [3] of HOIP. In spite of the rapid development, however, there is still much that is unknown about the nature of defects which act as recombination centers (traps) and limit the achievable device efficiency [4]. In particular, there have been reports suggesting that the traps in HOIP could be localized on a sub-micrometer size within the material [5], however this has not been fully addressed due to the limited spatial resolution of commonly used optical techniques.

In this work, we show for the first time the nanoscale extent of traps in an HOIP film using the novel microscopy technique of time-resolved photoemission electron microscopy (TR-PEEM) [6]. We find that traps are localized in nanoscale clusters on the order of 10s of nanometers in size. We show that these clusters form hole traps using photoemission spectroscopy, and further, perform time-resolved measurements where we can observe the hole trapping kinetics. Our work provides a new avenue for understanding the fundamental properties of traps in HOIP materials.

2. Experiment and Results

Experimental Setup

TR-PEEM combines a photoemission electron microscope (PEEM) with illumination from an ultrafast pulsed laser [6]. Our laser source is a high energy titanium-sapphire oscillator which drives a harmonic generation setup to produce the third (266nm, 4.65 eV) and fourth (200 nm, 6.2 eV) harmonics of the fundamental. The UV pulses are directed into the chamber of the PEEM to illuminate the sample, which creates photoelectrons that are imaged by the microscope. A portion of the laser fundamental is split off and sent to a mechanical delay stage, which is used to excite the sample in a pump-probe style configuration for time-resolved measurements. The PEEM can also work in an energy resolved mode using a hemispherical energy analyzer.

The HOIP films studied were mixed cation compositions of $Cs_{0.05}FA_{0.78}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3$ and $Cs_{0.05}FA_{0.78}MA_{0.17}PbI_3$. Samples were made through solution process and kept under nitrogen environment before loading into the ultra-high vacuum chamber of the PEEM for measurements.

Identification of Traps

Using the 4.65 eV UV probe, we photo-emit electrons from occupied states between the valence band and Fermi level in the HOIP films. The resulting PEEM images show a distribution of spots of sizes ranging from ~30 nm (instrument limit) to a few 100 nm in size. Using the spectroscopic mode of the PEEM, we show that these spots are due to occupied mid-gap states, which should then act as hole traps.

Trapping Kinetics

We then perform time-resolved using 1.55 eV (fundamental) pulses to first excite the HOIP film, then probe the resulting change in trap occupation. We see a decrease in the trap population on a 10s of picosecond time scale, showing that hole carriers are trapped at these clusters. We suggest that the trapping timescale is due to carrier diffusion to the trap cluster.

3. Conclusions

Our results show directly for the first time the nanoscale trap distribution in HOIP films. This provides a new perspective for identifying the origins of traps in HOIP, which will be crucial in designing methods to reduce or eliminate them for future devices.

References

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