Tailoring Perovskite Thin Films to Rival Single Crystals

Brandon R. Sutherland¹,*

High temperature epitaxial growth has been a long-standing requirement for forming semiconductor thin films with exceptional optoelectronic properties. In this issue of Joule, Brenes and coworkers have demonstrated that atmospheric and photoinduced post-treatments of solution-processed polycrystalline metal halide perovskites can improve the diffusion length, carrier lifetime, and surface recombination velocity to values previously only achievable by single crystal materials.

Metal halide perovskite materials have invigorated the field of solution-processed optoelectronic devices. They have been predominantly studied as the active layer in third-generation thin film solar cells—a burgeoning area of research with an aim to augment or replace commercial silicon solar panels with inexpensive, lightweight, and scalable materials. Perovskites have seen extensive progress in this application with certified power conversion efficiencies advancing from 14.1% in 2013¹ to now 22.1%.² The latter result cements perovskites as a leading competitor in beyond-silicon photovoltaics.

One of the performance-critical physical parameters for the active material in a conventional solar cell is the carrier diffusion length. This parameter is a measure of how far a charge carrier can travel through a semiconductor medium due to a concentration gradient before recombining. It limits the thickness of the absorbing layer in solar cells and is overall a strong measure of the electronic quality of a semiconductor. In early 2015, two research groups near simultaneously demonstrated that perovskites can be grown into large-dimension single crystals and reported diffusion lengths in the 10 to >100 µm range.³,⁴ Despite having physical dimensions ill-suited for solar energy harvesting, this was a key result for the perovskite community as it was one of the first reports of solution-processed semiconductors possessing diffusion lengths comparable to their epitaxial counterparts (such as silicon). Researchers have since developed methods to scale down the wider-bandgap bromide perovskite to solar-relevant thicknesses.⁵ However, it remains challenging to control the growth of high-quality iodide perovskite single crystals, which possess a bandgap required for efficient single junction photovoltaics. Additionally, single crystal growth is substrate-seeded and is not directly compatible with most mass-manufacturable printing techniques. This new study by Brenes and coworkers published in the inaugural issue of Joule has shown, for the first time, that thin film perovskites can be tailored to have key semiconductor material properties—including diffusion lengths—comparable to those of single crystal materials.⁶

Perovskite materials are well known to be incredibly sensitive to both light and humidity.⁷ Fully fabricated devices generally prefer exposure to as little of each as possible. However, there has been considerable progress in improving both fronts of device stability through compositional control, electrode engineering, and encapsulation.⁸ What is interesting is that perovskite films during

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¹Joule, Cell Press, 50 Hampshire Street, 5th Floor, Cambridge, MA 02139, USA
*Correspondence: bsutherland@cell.com
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In this work, Brenes and colleagues have systematically developed a methy lammonium lead triiodide (MAPbI$_3$) perovskite treatment process that uses light and humidity to enhance the optoelectronic properties. The method is wonderfully uncomplicated, consisting of exposure to white light at near air mass 1.5 solar irradiance (1000 W/m$^2$) for 20–30 min in a 40%–50% relative humidity environment. This procedure is shown to benefit MAPbI$_3$ thin films formed via two conventional one-step deposition precursors: (1) 1:1.06 MAI to PbI$_2$ in an acetonitrile + methylamine solvent, and (2) 1:3 molar ratio of lead acetate trihydrate to MAI in a dimethylformamide solvent with a small amount of hypophosphorus acid additive.

After treatment, spatial photoluminescence mapping shows an overall enhancement in emission intensity, as well as a reduction in grain-to-grain emission variability (Figure 1). The resulting internal quantum photoluminescence efficiency approaches 89%, compared to 1% prior to treatment. Using time-resolved microwave conductivity (TRMC) measurements, the authors report long-lived effective carrier lifetimes in treated films of up to 32 µs for holes. The thickness of the film over the full lifetime yields a hole surface recombination velocity of 0.4 cm/s. From the lifetime and the inferred TRMC mobility, a hole diffusion length of 77 µm is calculated. These values are among the best-ever reported for a polycrystalline thin film and are comparable with monocristalline perovskites and electronics-grade silicon. These impressive values come with two caveats to consider: (1) the TRMC method may underestimate the effect of grain boundaries on charge transport and (2) photon recycling through successive emission and reabsorption events are included in the lifetime.

The exact mechanism leading to this improvement is still under investigation. The authors show experimental and theoretical evidence that it may be attributed to the combination of atmospheric oxygen diffusion and light-induced superoxide O$_2$ formation passivating iodide vacancies. This has the effect of reducing the shallow state density in the film, thereby suppressing nonradiative recombination and inhibiting ion migration.

The researchers applied the light and humidity exposure method to the bottom half of a perovskite solar cell and then subsequently deposited the hole transporting and electrode layers atop the treated film. These devices demonstrated a stabilized power conversion efficiency of 18.4% and a near-instantaneous rise to this value upon illumination. This is in comparison to 17.4% for the untreated devices, which show a slow rise to the saturated value. While still unoptimized for devices, the initial proof-of-concept performance is encouraging for the pure MAPbI$_3$ phase perovskite. Importantly—and unlike many previous attempts to optically enhance perovskite properties and device performance—the effects are long-lived.

With an active material possessing an effective diffusion length significantly larger than the extraction length, as well as long carrier recombination lifetimes—suggesting promise for a minimal open circuit voltage deficit—what are the remaining factors inhibiting perovskite solar cells from reaching efficiencies beyond 23%? Even with a perfect active material, interfacial recombination can pin both voltage and current, thereby constraining performance. Grain boundaries still play an important role in transport, and more work is needed to definitively elucidate their effects on limiting efficiency.

It would be interesting to see the method applied to new materials. The entire study focuses on the pure phase of MAPbI$_3$ perovskites fabricated using various one-step methods. It is known that even different fabrication processes of the same material can alter the light and humidity dependence. Does the same process benefit perovskites formed via sequential deposition or thermal co-evaporation? Many of the latest efficiency and, importantly, stability breakthroughs in perovskite solar cells have relied on compositional tuning of the A-site cation, such as MA.
blending with formamidinium$^2$ and/or cesium,$^{10}$ as well as the X-site halide (mixed iodide/bromide).$^{2,10}$ Applying systematic environmental control as a processing step on these films and studying its impact on simulated solar cell performance and stability is a natural follow-up investigation on this work.

Brenes and coworkers have fabricated a solution-processed thin film semiconductor with an electronic landscape comparable to monocrystalline semiconductors. This is a significant achievement for polycrystalline materials broadly and suggests promise for a future of large-area high-performance optoelectronic devices formed using inexpensive and scalable solution-cast materials.

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