Microstructure engineering of organolead halide perovskites for next generation photovoltaics.

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Introduction
In the past five years, organometal trihalide perovskites have achieved outstanding device efficiencies (~20%), thereby attracting significant interest from the photovoltaics research community. However, in order to advance this material towards deployable large scale, and outdoor photovoltaics, a deeper understanding of its properties is required. Specifically, while significant progress has been made by carefully engineering deposition processes and device architectures, many unknowns remain on the relationships between structure, composition, film morphology, and the observed high power conversion efficiencies.

The goal of this project is then to study the effect of thin film morphology and texture on the photovoltaic performance of perovskites. This was done by identifying critical deposition parameters that influence thin film morphology of perovskites deposited by low pressure vapor assisted solution process.

Materials and Methods

Results
Effect of the precursor film morphology

![Figure 1: Sequential perovskite deposition via low pressure vapor assisted solution process along with a schematic of the reaction tube.](Image)

Characterization techniques

Several techniques were used to assess the structural, morphological and optical properties of the synthesized material, as well as its photovoltaic performance.

- X-ray diffraction analysis and scanning electron microscopy were used to identify the phase and quality of the grown films.
- Rietveld refinement of the XRD patterns was implemented for a quantitative microstructure and texture analysis of the samples.
- UV-Vis spectra were acquired, to measure the absorption properties of the perovskite films.
- Photoluminescence measurements were performed, to further probe the materials optical properties.
- Current-voltage characteristics of the photovoltaic devices were measured to assess the efficiencies of devices made from the grown perovskite films.

![Figure 2: XRD spectra and SEM images of PbI₂/PbCl₂ precursor films dried at different speeds. As the drying speed increased the porosity of the film decreases.](Image)

Influence of the vapor annealing atmosphere

![Figure 3: XRD spectra and SEM images of perovskite films grown from precursor films dried at different speed. No significant morphology difference is observed as expansion of the film upon conversion compensates for the porosity.](Image)

Texture and grain size control via two-step vapor annealing process

For a better grain growth control the perovskite synthesis is separated into a two temperature step process to replace the single annealing of 2 hours at 120°C (baseline process).

- A first short, high temperature step to nucleate the grains.
- A second longer step at a lower temperature for grain growth and coarsening.

The overall reaction time is kept at 2h. The reaction time is calculated using the Arrhenius law for thermally activated processes.

![Figure 5: Experimental and fitted spectrum along with the refined microstructure and texture parameters for the two studied annealing processes. The significantly larger calculated crystal sizes suggest better grain quality for the 2-step process. Additionally for this process, more grains are aligned with the (100) plane parallel to the sample surface.](Image)

Highlights and conclusion

1. Low pressure vapor assisted annealing is a reproducible and resilient process that yields high quality films with device efficiencies up to 16.8%. The process is very robust against variations of the precursor film morphology and tolerant to atmosphere contaminations.

2. Thin film morphology can be controlled by engineering the temperature profile of the low pressure annealing step. A first, high temperature step promotes growth of more textured grains while a second, low temperature step promotes grain coarsening. No differences were observed in the composition or optical properties of the materials but there were visible effects on its photovoltaic properties. Notably, the use of a two-step annealing process yields more nanoscale shunting in the films reducing the Voc, FF and overall efficiency.

- However the two-step process still yields slightly increased short circuits current suggesting improved photovoltaic properties of the grown films. This increased current potentially arises from anisotropic transport but this effect needs further investigation.

References


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