Synthesis and Characterization of the Orthorhombic Cesium Lead Tri-Iodide Perovskites Thin Films by Sequential Physical Vapor Deposition for Solar Cells.

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Introduction

In this study, a sequential physical vapor deposition (SPVD) technique [1-2], was used to grow high-quality poly-crystalline yellow phase cesium lead tri-iodide (γ-$CsPbI_3$). Crystallographic parameters and the phase transitions from as-deposited orthorhombic γ-$CsPbI_3$ to tetragonal β-$CsPbI_3$ on annealing at 100°C, were determined using X-ray diffraction patterns. Computed lattice constants were a= 4.88 Å, b= 9.96 Å, and c= 16.52 Å, with average crystallite sizes increasing from 127.3nm to 243nm. Field-emission scanning electron micrographs showed uniform surface coverage with polycrystalline grains. Average grain sizes increased from 168 to 235nm as cesium iodide (CsI) thickness increased. The grains were large, pin-hole free and closely packed. Visible spectra showed a 2.05 to 2.38 eV increase in the bandgap as the thickness of CsI was increased.

Herein, we demonstrated optimized structural, morphological, and optical properties for stable and completely inorganic-$CsPbI_3$ perovskites for use in tandem solar cells.

Experimental Procedure

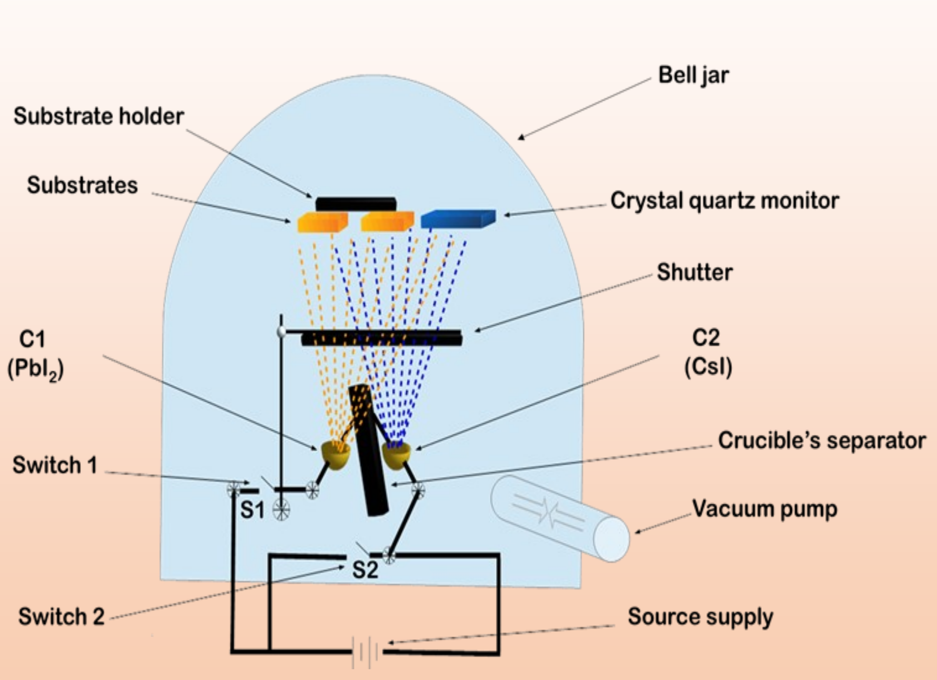


Fig. 1. SPVD of $CsPbI_3$

Materials

- Lead iodide (PbI_2) in crucible C1, cesium iodide (CsI) in crucible C2, and fluorine-doped tin oxide (FTO) on glass substrates.

Synthesis

- PbI_2 is first evaporated then followed by CsI .
- Substrates are heated 95°C for PbI_2 and 140°C for CsI, respectively during deposition.
- One of the $CsPbI_3$ films grown is left as-deposited and the other post-annealed at 100°C for 10 minutes.

Results and Discussion

Properties of Films

♦ **Surface morphology**

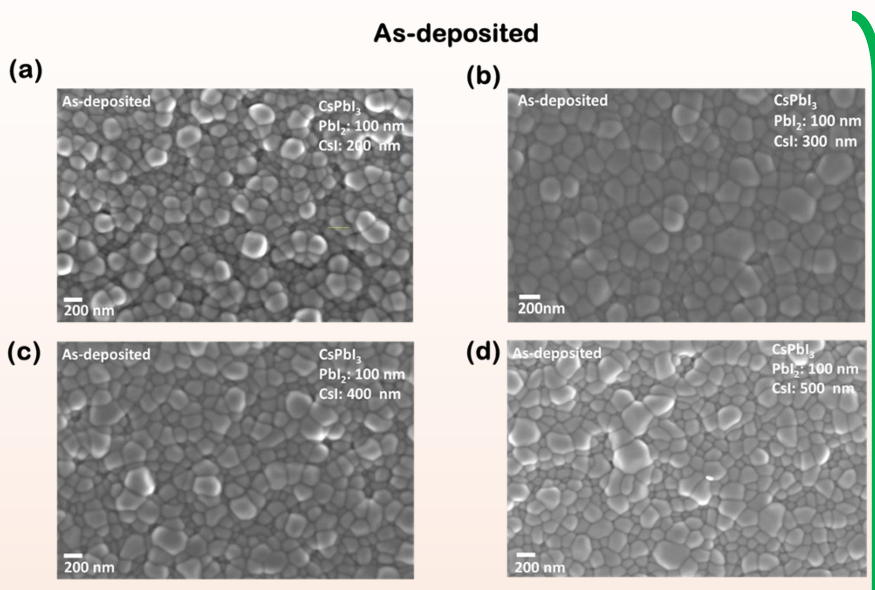


Fig. 2. Top-view field-emission scanning electron microscopy (FE-SEM) images of $CsPbI_3$ layer with varying CsI thickness (a-d) 200nm -500nm.

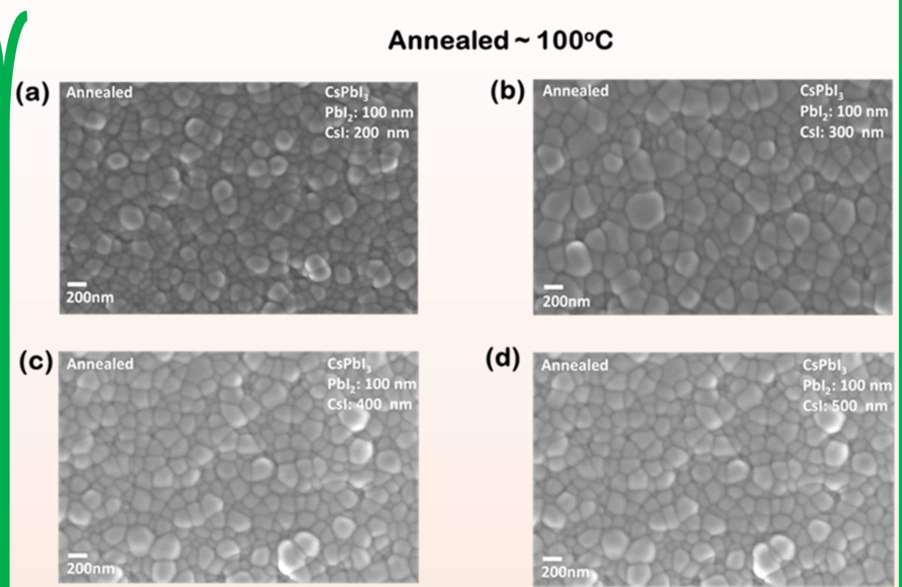


Fig. 3. Top-view FE-SEM images of $CsPbI_3$ layer with varying CsI thickness (a) 200nm, (b) 300nm, (c) 400nm, and (d) 500nm for annealed (100°C) samples.

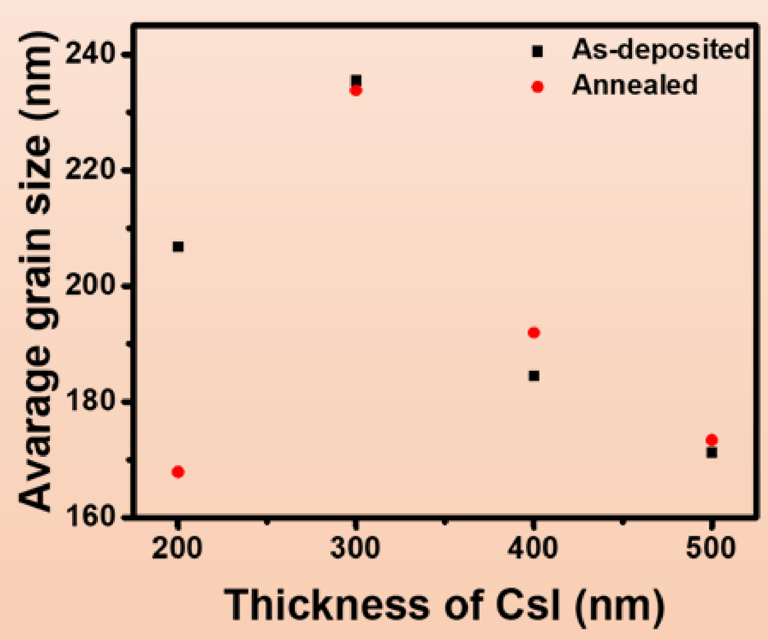


Fig. 4. Variation of $CsPbI_3$ average grain-size (nm) with varying CsI thickness.

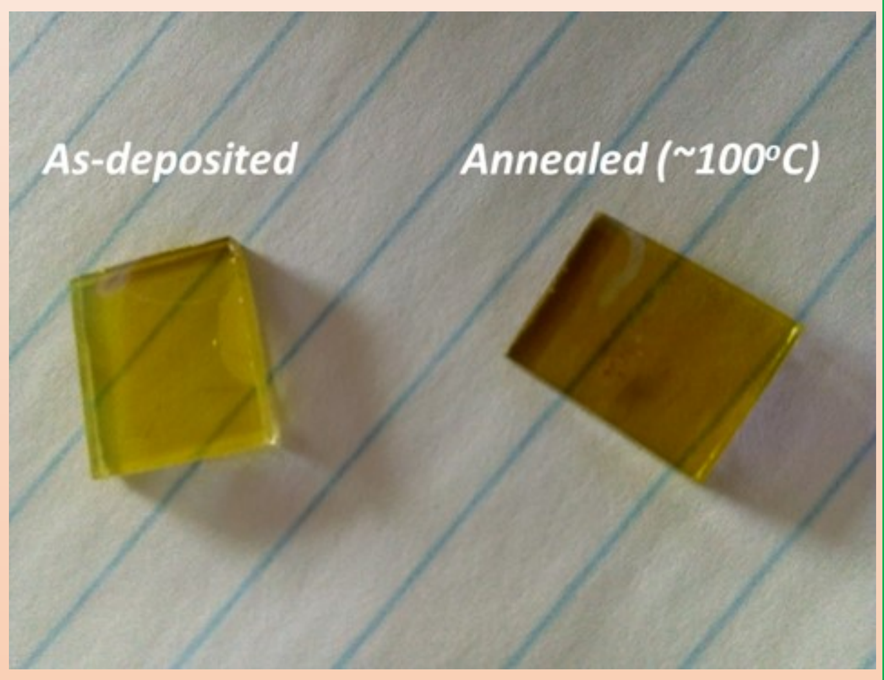


Fig. 5. Images of $CsPbI_3$ samples on Glass/FTO at 300nm CsI thickness.

♦ **Structural properties**

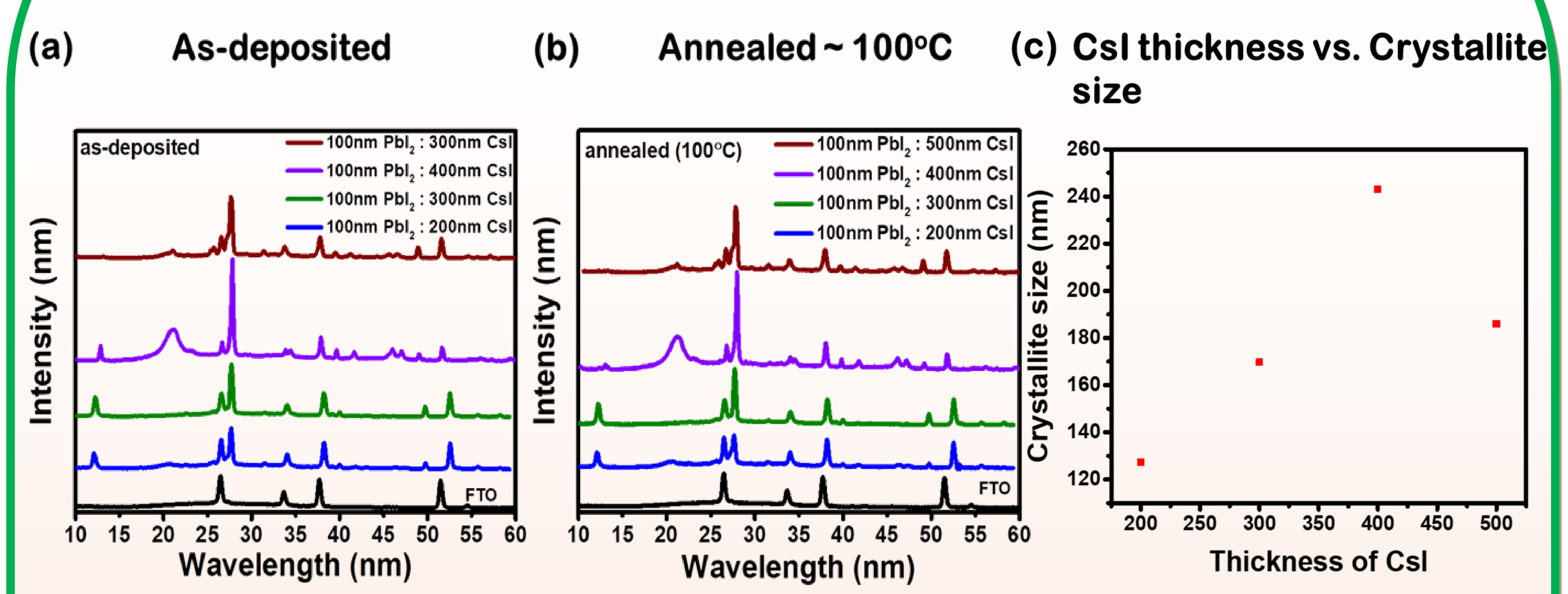
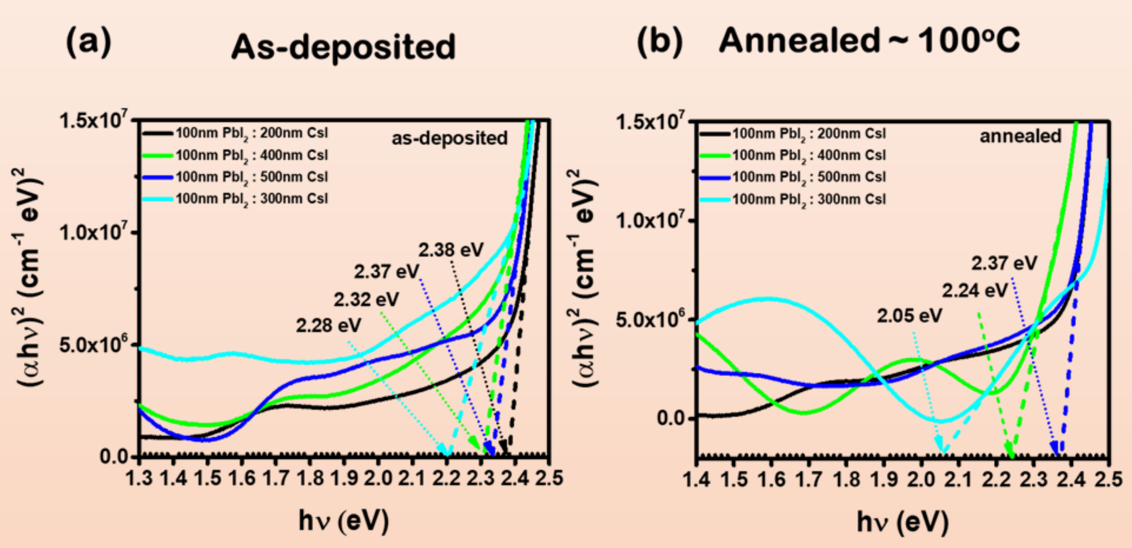
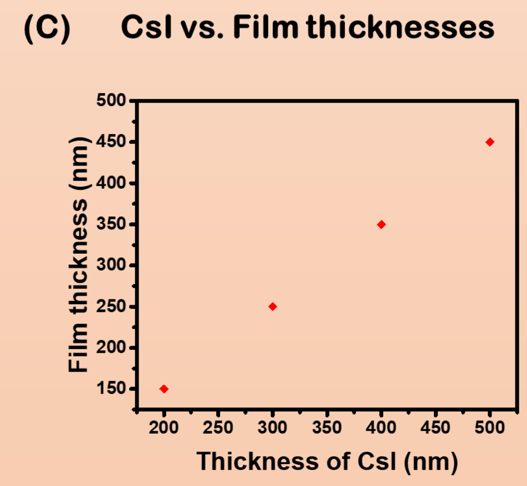


Fig. 6. XRD patterns of $CsPbI_3$, (a) as-deposited, (b) annealed at 100 °C, and (c) crystallite size (nm) vs. CsI thickness.

♦ **Optical properties**



- Estimated direct band gaps of the films ranges from 2.28 - 2.38 eV for as-deposited samples.
- Estimated direct band gaps of the films ranges from 2.05 - 2.37 eV for annealed samples



- Linearly increasing film thickness as an increase in CsI thickness.
- 100nm PbI_2: 300nm CsI sample is optimum, with least direct band gap of 2.05 eV .
- Annealed samples have reduced direct band gaps as compared to as-deposited samples.

Fig. 7. Tauc's plot for determining the bandgaps of $CsPbI_3$ layers deposited with different CsI thicknesses of (a) as-deposited, and (b) annealed 100°C, and (c) CsI vs. Film thicknesses.

Conclusions

- 3D $CsPbI_3$ thin film were prepared on FTO substrates by evaporating PbI_2 and CsI precursors using the effective sequential physical vapor deposition method.
- The structural, morphological, and optical properties of the thin films were found to depend greatly on the thickness of CsI.
- XRD diffractograms confirmed that both as-deposited and annealed $CsPbI_3$ samples are composed of the orthorhombic polycrystalline structure.
- SEM micrographs revealed:
  - large pin-hole-free grains and;
  - full surface coverage.
- Samples (100nm PbI_2: 300nm CsI) were optimum, with least direct band gap of 2.05 eV.
- This study reveals that the properties of SPVD 3D $CsPbI_3$ active layer can be enhanced by controlling the precursor's (CsI) thickness and annealing conditions.

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References

[1] Fru, J.N., N. Nombona, and M. Diale, Characterization of Thin MAPb (I Br $_x$)$_3$ Alloy Halide Perovskite Films Prepared by Sequential Physical Vapor Deposition. 2021.

[2] Fru, J.N., N. Nombona, and M. Diale, Characterization of sequential physical vapor deposited methylammonium lead tri-iodide perovskite thin films. Vacuum, 2020. 182: p. 109727.

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