Processing Solvent Dependent Electronic and Structural Properties of Cesium Lead Triiodide Thin Films

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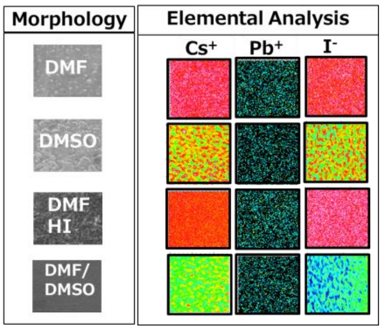
Cesium lead triiodide ($CsPbI_3$) is an attractive material for photovoltaic applications due to its appropriate band gap, strong optical absorption and high thermal stability. However, the perovskite phase suffers from moisture induced structural instability. Previous studies have utilized a range of solvent systems to establish the role of solvent choice in structural instabilities. Despite this, effects of different solvents on the electronic structure of this material have not been compared. We report substantial chemical and compositional differences in thin films of $CsPbI_3$ prepared from a range of solvent systems. We confirm via X-ray diffraction thin films formed from DMF, DMSO and a mixture of these solvent systems share the same crystal structure. However, secondary ion mass spectrometry, X-ray photoelectron spectroscopy and low energy ion scattering measurements, reveal significant differences between films processed via different solvent systems. Our findings reveal the critical impact solvents have upon compositional stoichiometry and thin-film morphology.



KEYWORDS Cesium lead triiodide, photoelectron spectroscopy, secondary ion mass spectrometry, low energy ion scattering.

Progress in the development of lead halide perovskite solar cells has been swift with device efficiencies now being reported above 20%, approximately an 18 percent growth in 6 years.[1–5] This rapid improvement and the associated swift growth of the wider research field is underpinned by the simplicity with which thin films can be fabricated from solution. The ease with which a solid thin-film of electronically active perovskite can be produced often masks the complicated nature of crystallization processes at work in solution and the difficulty of establishing or selecting particular morphologies or structures. Organic-inorganic metal halide perovskites contain cationic organic moieties, and inorganic atomic cations, such as cesium, can replace them to yield all-inorganic binary perovskite materials. Significant recent research effort has been directed towards binary inorganic perovskites for photovoltaic device applications.[6–8] Cesium lead halides, a family of binary inorganic perovskites, are an attractive alternative to organic-inorganic hybrid lead halides due to impressive thermal stabilities (>460°C for cesium lead bromide ($CsPbBr_3$) and cesium lead iodide ($CsPbI_3$)) and attractive optical band gaps for tandem perovskite solar cells.[6,7,9] Lead-halide based perovskite materials have great potential as a commercial presence when combined with existing silicon photovoltaic technologies in perovskite-on-silicon tandem devices.[10] As such, the identification of perovskite materials with suitable optical band gaps for tandem solar cells is becoming increasingly important. A concerted research effort has focused on film fabrication in perovskite active layers in an attempt to understand and control crystallization of perovskites.[11] Optimization of film fabrication processes have been fairly successful, with device efficiencies exceeding 10% for devices fabricated using $CsPbI_3$ nanocrystals and approaching 10% for mixed halide inorganic perovskites.[7,12] Despite qualitative general discussion on the influence of processing conditions on device performance and morphology, their influence upon fundamental electronic structure remains ambiguous.

Cesium lead iodide is a perovskite with a reported optical band gap of 1.73 eV and an orthorhombic crystal structure at room temperature. Its most stable "yellow phase" polymorph, when incorporated into a photovoltaic device, only achieves up to 0.09% PCE.[6,13,14] Heating to ~300°C in inert atmospheres induces a phase transition to the cubic perovskite polymorph which can be meta-stable at room temperature, and is much more effective in photovoltaic devices.

Currently only dimethylsulfoxide (DMSO) and dimethylformamide (DMF) have been identified to sufficiently solvate cesium and lead halide precursor salts to be used as processing solvents. Addition of hydroiodic acid (HI) to DMF solutions lowers the polymorphic transition temperature and when used as an additive has contributed to device efficiencies of 2.9%.[6] Despite the limited choice of solvents for thin film production, little emphasis has been placed on understanding the difference in composition and electronic structure of films processed from each solvent or with an HI additive. In this work we examine the effects of solvent choice on the electronic, structural and morphological properties of cesium lead triiodide thin films and compare solvent mixtures to additive solutions.

Thin films of cesium lead iodide were fabricated, through spin-coating, on fluorine-doped tin oxide (FTO) glass from 0.5M solutions using the following solvents: dimethylformamide (DMF), dimethylsulfoxide (DMSO), DMF with 3.3% HI and DMF:DMSO mixture in a 2:1 ratio. All films were processed using the same conditions, as reported in the experimental methods section, however the annealing temperature and timing differed for those films fabricated with HI as an additive. For these films the parameters reported by Eperon and co-workers were utilized.[6]

The structure and morphology of these films was investigated using x-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively (Figure 1).

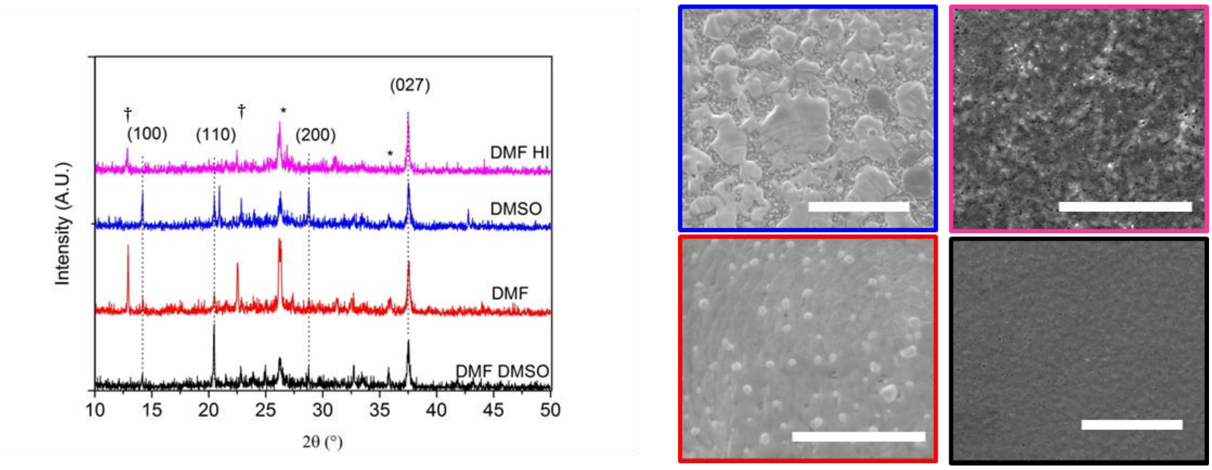


Figure 1. X-ray diffraction patterns and scanning electron micrographs (SEM) of cesium lead iodide films fabricated from DMF: DMSO (2:1) (black), DMF (red), DMSO (blue) and DMF HI (pink). Asterisks on diffractograms indicate peaks which are attributed to the FTO substrate, dagger indicates peaks which are attributed to PbI_2, scale bars on scanning electron micrographs are 5μm.

$CsPbI_3$ thin films for device applications would ideally be composed of a single polymorph, absent of crystalline impurities which could result from starting materials which have not been incorporated into the perovskite structure. X-ray diffraction measurements (Figure 1) confirm the presence of the “black phase” of cesium lead iodide in all thin films despite significant differences in morphology. DMF and DMF w/HI exhibit diffraction peaks which can be attributed to crystalline PbI_2 suggesting phase segregation of PbI_2 and $CsPbI_3$ within the thin-films. These regions make reproducible processing of films considerably more challenging since multiple crystallite types are forming simultaneously. The presence of crystalline PbI_2 is often observed in other lead-halide perovskites and has been suggested as the decomposition product of several perovskites upon exposure to air.[15] Films fabricated using DMSO do not contain crystalline PbI_2, and their corresponding XRD patterns can be explained by a combination of the $CsPbI_3$ and FTO substrate crystal structures.

SEM images of the films (Figure 1) show significant differences in morphology associated with changes in solvent, or inclusion of HI. Films formed from DMF appear continuous and are comprised of roughly circular crystallites, while the addition of HI results in films which have smaller grains and small holes in the surface of the film. DMSO as the sole solvent produces incomplete films with limited coverage of the FTO substrate whereas a DMF:DMSO solvent mixture yields uniform, continuous films with small holes similar to the DMF/HI.

The optimum perovskite thin film morphology is a continuous monolithic film devoid of bare substrate and holes. When incorporated into a solar cell, exposure of the substrate during deposition of the charge extraction layer and metal top contacts results in short-circuits and leakage current due to direct contact of the top and bottom electrodes which dramatically reduce the efficiency of a photovoltaic device. Imaging by SEM is insufficient to examine the nature of the smallest “pin holes”, since it is not possible to determine whether they penetrate to the substrate or are merely confined to the topmost layers of a film.

To probe changes in the chemical composition of the films through the entirety of their thickness, for each solvent, depth profiling time-of- flight secondary ion mass spectrometry (ToF-SIMS) was employed. In this experiment a Cs^+ ion beam was used to sputter through the $CsPbI_3$ film whilst a Bi^+ ion beam was used as the primary ion source. The positive and negative ions detected whilst sputtering through the films are reported as a function of sputtering time in Figure 2.

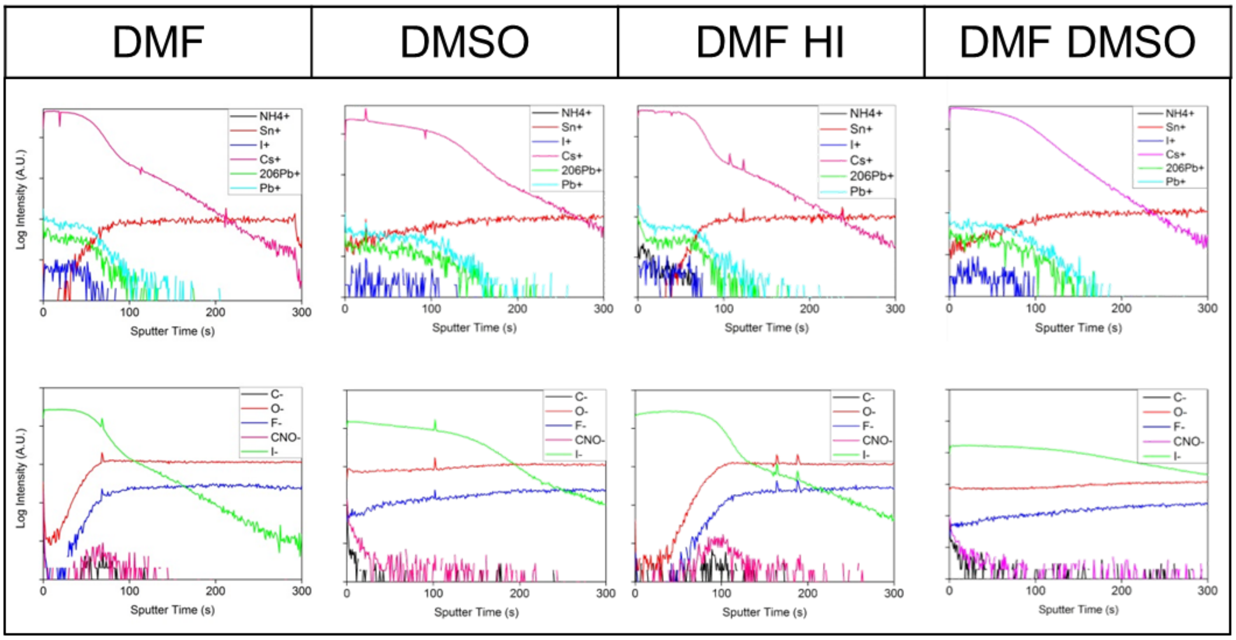


Figure 2. Secondary Ion Mass Spectrometry (SIMS) measurements of cesium lead iodide films. Traces resulting from the detection of positive ions are displayed in the first row and those from negative ions are displayed in the second row.

Positive and negative secondary ion depth profiles were measured separately, and are presented in Figure 2. Ions directly relating to $CsPbI_3$ ($^{206}Pb^+$, Pb^+ and I^-) and FTO (F^-, Sn^+, O^-) were measured. In addition ions typically observed as a result of impurities or solvents due to solution processing were also detected (CNO^- and NH^{4+}). The depth profiles measured during sputtering can be used to approximate the position of the interface between the perovskite film and the FTO electrode. The traces for ions relating to the FTO substrate (F^-, Sn^+ and O^-) plateau when sputtering deep within the FTO film. As such the position of the bottommost part of the perovskite film is determined to occur just before the plateau of traces. The simultaneous observation of I^- (from $CsPbI_3$) and O^- (from FTO) after this plateau suggests migration of ions into the FTO electrode.

SIMS traces for thin films formed in the presence of DMSO show a gradual slope for the profiles of Cs, Pb and I ions throughout the films suggesting an even distribution of the elements. Films formed from DMF and DMF w/HI show a higher proportion of Pb^+ and I^- at the surface than within the bulk of the film, and the sputter rate of these films was notably higher than that observed in the DMSO formed films. This suggests that there may be preferential sputtering occurring as a result of less-dense films being formed. A significant increase in CNO^- ions is observed prior to the plateau of associated with the FTO electrode, these ions can be attributed to DMF and suggest a significant amount of solvent incorporation. This incorporation is observed despite annealing above the boiling point of the solvent (153°C) and introduction of the samples into ultra-high vacuum (UHV) environments which often remove residual high vapour pressure solvents.

All films studied with SIMS exhibit significant migration of I^+ ions into the FTO electrode, a well-documented phenomenon within the field of organic-inorganic lead halide perovskite research.[16,17] The migration of I^- into the FTO electrode will necessarily effect the electronic structure of FTO and may modify hole or charge extraction at this interface with the perovskite and charge extraction layers.

The differences in bulk film composition observed for each solvent system may reasonably be expected to affect the chemistry of thin films. Of particular significance are differences in the chemistry of the films' surfaces as the nature of interfaces within a photovoltaic device can hugely impact performance.

To correlate composition and surface chemistry low energy ion scattering (LEIS) measurements were used to examine the topmost few layers (Figure 3) of the same samples.

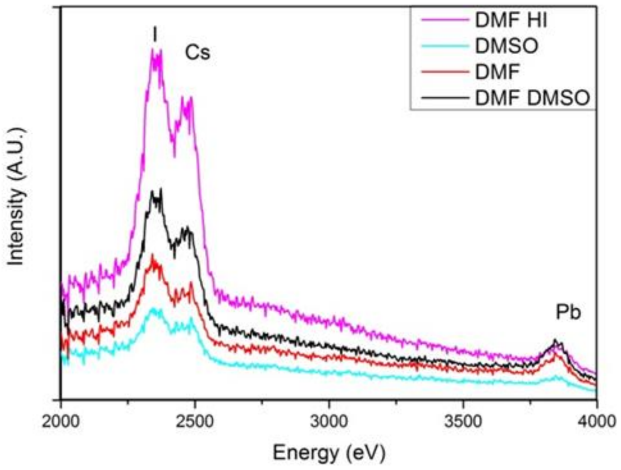


Figure 3. Low energy ion scattering (LEIS) measurements of cesium lead iodide films. Scattering was carried out using a Ne^+ ion source.

Surface chemistry differences like those presented here can affect not only influence the properties of thin films, but also the wetting and film formation of subsequent layers deposited on top. Traces presented in Figure 3 have not been offset and the significant differences in peak intensities and low/high energy tails are a direct measurement of surface chemistry differences. Encouragingly, all thin films contained Cs, Pb and I in the outermost atomic layer of the films, however, the intensities of the scattering, and therefore the stoichiometries of the elements, varied significantly for each solvent system. Table 1 shows the approximate stoichiometries which were calculated from the LEIS measurements.

<table>
<tr><td colspan="4">Approximate stoichiometry of cesium lead iodide thin film surface as determined by LEIS measurements.</td></tr>
<tr><td></td><td>Cs</td><td>Pb</td><td>I</td></tr>
<tr><td>DMF</td><td>2</td><td>1</td><td>3</td></tr>
<tr><td>DMF w/HI</td><td>4</td><td>1</td><td>7</td></tr>
<tr><td>DMSO</td><td>1</td><td>1</td><td>2</td></tr>
<tr><td>DMF:DMSO (2:1)</td><td>1</td><td>1</td><td>3</td></tr>
</table>

Table 1. Approximate stoichiometry of utmost surface of cesium lead iodide films as determined by low energy ion scattering measurements. The area of surface probed by scattering is 1mm^2.

Films fabricated from DMSO, and DMSO mixed with DMF exhibited surface stoichiometries most closely resembling the bulk chemistry of $CsPbI_3$. Films cast from DMF resulted in stoichiometries which differed significantly from the (1:1:3) ratio of Cs:Pb:I which would be expected from a stoichiometric perovskite crystal. The addition of HI resulted in a significant increase in the amount of iodine present at the surface of the films, which is perhaps not surprising. In this system the ratio of cesium (to I and Pb) was also significantly higher than that observed in the solely DMF system. Due to the significant differences in annealing temperature (for conversion) between the DMF and DMF w/HI systems it is not possible to determine if the increase in I and Cs at the surface of the DMF w/HI is a direct result of the addition of HI or a result of the lower annealing temperature. LEIS measurements involve the scattering of noble gas ions from the nucleus of atoms on a surface and the resulting energy of the detected scattered ions allows chemical identification. The nature of this scattering does not provide information about the chemical bonding environment of the surface. To investigate this, X-ray Photoelectron Spectroscopy (XPS) measurements were carried out, with the results presented in Figure 4.

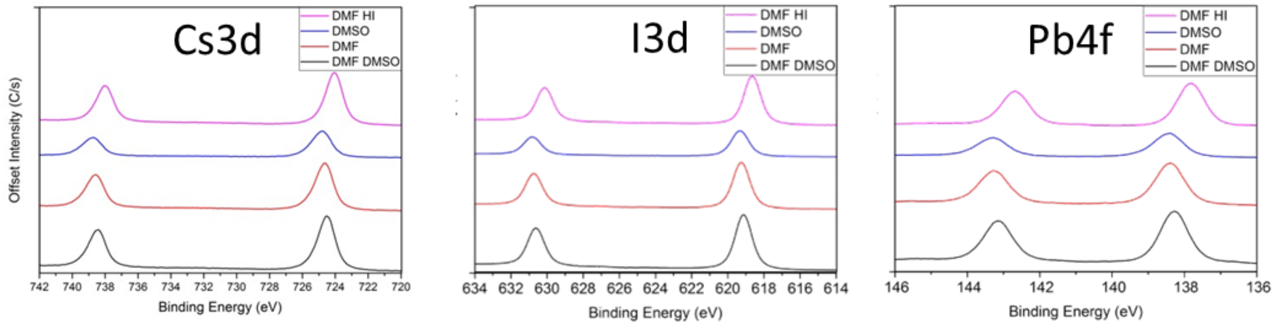


Figure 4. High resolution X-ray Photoelectron Spectroscopy (XPS) measurements of cesium lead iodide films on FTO glass.

Figure 4 shows high resolution XPS scans of the component elements (Cs, Pb, I). Core level peaks are observed for Cs at 724.7eV for DMF and DMF/DMSO formed films. Those formed from DMSO and DMF w/HI are observed at 724.9eV and 724.1eV respectively. The peaks observed at 724.7eV and 724.9eV can be attributed to CsI and the peak observed at 724.1eV can be attributed to CsOH. Peaks for I are observed at 619.2eV for all films (except DMF w/HI for which the peak is observed at 618.6eV), these can be attributed to PbI_2 and CsI respectively.[18,19] Core level peaks for Pb are observed at 138.4eV for all films (except DMF w/HI at 137.8eV). The peaks at 138.4eV can be attributed to PbI_2 and those at 137.8eV can be attributed to Pb_3O_4.[20] There is no evidence for the presence of Pb^0 (expected at 137.0eV) in any film studied here.[21] All elements have well separated spin-orbit components which are observed at higher binding energies.

When DMSO, DMF and mixtures of the two were used, the chemistry of the perovskite film surface is very similar. DMF with HI results in significant changes to the chemical composition of $CsPbI_3$. The partly aqueous HI solutions employed introduce water into the perovskite precursor solutions which is likely the source of major the differences in chemical structure in the corresponding films.

Although it is not possible to determine if these changes in chemistry are propagated throughout the bulk of the films we can be certain that there are significant differences, relating to processing solvent, at the interfaces of the films.

These measurements suggest that although both DMF and DMSO can be used to produce films of $CsPbI_3$ the resulting structure and composition of the films are not equal. Whilst DMF produces films with a uniform morphology and few pin-holes, it also results in the presence of crystalline PbI_2 within the perovskite film. Additionally SIMS measurements suggest that the films are not completely continuous across the FTO substrate and therefore undergo preferential sputtering under an ion beam. The addition of an acid to DMF to reduce the polymorphic transition temperature does not improve the formation of $CsPbI_3$ films and results in shifting of the core-levels in XPS measurements. The surface of the perovskite film has a stoichiometry that is far from ideal and also has a significant Pb_3O_4 component, which we postulate to be due to the water present in the HI.

Conversely whilst DMSO does not suffer from the incomplete film formation which plagues those formed from DMF, it does result in films with incomplete coverage. The desirable film properties which DMSO provides (complete film formation, more ideal stoichiometry, a lack of PbI_2) can be achieved with the combined mixed DMF:DMSO solvent. A mixed solvent system of DMF:DMSO has been shown to be highly beneficial to the film formation of several perovskite materials previously,[22] and is indeed the solvent system of choice for the highest efficiency reported for perovskite solar cells. Our results here for $CsPbI_3$, shed light on the fundamental impact of differing processing solvents upon the resulting structural properties of the perovskite films.

The formation of cesium lead triiodide thin films using solvent systems of solely DMF or DMSO result in films with significant differences and less than ideal characteristics. A solvent system comprised of a mixture of DMF and DMSO produces films of cesium lead iodide with ideal stoichiometries, uniform morphologies and complete film formation.

For perovskite materials to become a realistic commercial presence, a thorough understanding of the fundamental structure and composition of these materials is necessary. Fully inorganic perovskites are highly promising materials for perovskite-on-silicon-tandem applications, however this will not be realized without a thorough understanding of the chemistry of these materials.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge on the ACS Publications website at DOI:

Experimental methods, SIMS mapping and corresponding SEM images (file type, i.e., PDF)

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Notes

The authors declare no competing financial interests.

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