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Characterization of Sequential Physical Vapor Deposited Methylammonium Lead Tri-Iodide Perovskite Thin Films

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Abstract

Methylammonium lead tri-iodide perovskite (MAPbI\textsubscript{3}) thin film for solar cells, chemical formula \(\text{CH}_3\text{NH}_3\text{PbI}_3\), is synthesized in situ via sequential thermal vapor deposition of lead (II)iodide (PbI\textsubscript{2}) and methylammonium iodide (MAI) single layers. The structural, morphological, optical, and electrical attributes are highly dependent on annealing time and MAI thickness. X-ray diffractograms confirmed the tetragonal crystal structure of MAPbI\textsubscript{3} with I\textsubscript{4}/mcm space group, good crystallinity which increases with the thickness of MAI and transformation of PbI\textsubscript{2}-deficient MAPbI\textsubscript{3} to PbI\textsubscript{2}-rich MAPbI\textsubscript{3} upon increasing annealing time. UV-Vis optical spectra reveal a redshift in the onset of absorption from 750 to 780 nm as the MAI thickness increases and a slight blueshift as the annealing time increases. Field emission scanning electron microscopy micrographs show densely packed polycrystalline grains with negligible pinholes and full coverage. The current density-voltage (J-V) characteristics under illumination reveals that the photogenerated current decreases with an increase in annealing time. Space charge limited current analysis of dark current J-V curves shows that PbI\textsubscript{2}-deficient MAPbI\textsubscript{3} has higher mobility than PbI\textsubscript{2}-rich MAPbI\textsubscript{3} and trap density increases with annealing time.

Keywords: Methylammonium lead tri-iodide, sequential physical vapor deposition, thickness assessment, annealing time, perovskite solar cell.

1 Introduction

The fastest emerging third-generation solar cell technology is based on halide perovskites (HPs). They have desirable optoelectronic properties and versatile low-cost preparation options. Their outstanding
characteristics including extensive diffusion length [1], large carrier mobility [2], self-doping [3], low defect density [4], low phonon energy [5], ambipolar charge transport [6], broad absorption spectra [6], and tunable bandgap [7] are the driving forces behind the swift rise in performance of perovskite solar cells (PSCs). Just over a decade of intensive research, the power conversion efficiency (PCE) of PSCs has improved from 3.8 [8] to 24.2 % [9], which exceeds values for commercial multi-crystalline silicon (22.3 %) and copper indium gallium selenide (22.9 %) solar cells [10]. In addition to the upsurge in PCE, PSCs have flexible preparation methods that are fast and economical. These synthesis techniques comprise doctor blade [11], spin coating [12–14], physical vapour deposition [15], spray coating [16], inkjet printing [17], meniscus printing [18], pulsed laser deposition [19], atomic layer deposition [20], meniscus-assisted solution printing [21] and dip coating [22]. Most solution-based methods are lab-scale, not suitable to implement in the fabrication of multi-junction tandem solar cells and produce low-quality films [23]. Physical vapour deposition (PVD), widely used in industry for thin film deposition is scalable, environmentally friendly and results in high-quality films [23]. Despite the surge in performance and low-cost processing methods, inherent instability, reproducibility, and scalability are major hindrances towards the commercialization of PSC technology. Factors affecting the stability of PSCs include moisture [24], high temperatures [25], UV-radiation [26], crystalline structure and stoichiometry [27]. These factors limit the lifetime of the devices to 3000 hours, which is very short compared to the lifespan of commercial silicon photovoltaics (25 years) [28]. The fundamental strategies being employed to improve the stability of perovskites solar cells include developing resilient halide perovskite and protecting the vulnerable absorbers with coatings [29]. Efforts to improve the stability of perovskites absorber are geared towards improving film quality [30] and developing stable stoichiometry [31]. Film quality can be improved by reducing grain boundaries (growing large grains), minimizing micro-strain density and producing densely packed grains to minimize leakage currents. Yang and co-workers [32] improved stability by passivating and minimizing grain boundaries. Zhao and co-workers [33] showed that the rate of degradation can be decreased by reducing residual strain. Likewise, Zhang and co-workers [30] showed that high quality films with large densely packed grains result in stable and high-performance PSCs.

Methylammonium lead tri-iodide (MAPbI$_3$), chemical formula CH$_3$NH$_3$PbI$_3$, is the best efficient and extensively investigated HP for solar cells. However, its preparation by PVD, which may improve its stability
and scalability, has rarely been exploited. Bonomi and co-workers [15] used RF-magnetron sputtering to prepare MAPbI$_3$ from single source containing methylammonium iodide (MAI)/lead(II)iodide (PbI$_2$). They achieved high purity films with full coverage within a large thickness range less than 200 nm to greater than 3 μm. Momblona and co-workers [34] synthesized MAPbI$_3$ films by co-evaporation PbI$_2$ and MAI from two separate crucibles. They obtained a homogenous morphology of smooth thin films resulting in PCEs of 15 %. The co-evaporation and single source approaches involve checking that rate of deposition. However, reproducibility is a problem since the deposition rates of powdered organic precursors are difficult to monitor because they are unsteady. The fluctuating rates are as a result of the small molecular weights of the precursors leading to random diffusion of the vapor molecules inside the enclosure [35]. Also, the rate of deposition may differ for various MAI precursors due to the presence of variable concentrations of methylammonium dihydrogen phosphide (MAH$_2$PO$_3$) and methylammonium hypophosphite (MAH$_2$PO$_2$) impurities [36]. On the contrary, the sequential physical vapor deposition (SPVD) approach is thickness regulated. Thickness monitoring using a quartz crystal monitor is more reproducible than the rate of deposition. One of the pioneering studies on SPVD involved the preparation of cesium lead tri-iodide (CsPbI$_3$) by alternate layer-by-layer deposition of CsI and PbI$_2$ [37]. This approach, though reproducible, is time-consuming as time is wasted during to alternate between several layers. There are a few reports on the growth of MAPbI$_3$ by SPVD. Miguel and co-workers [38] prepared MAPbI$_3$ using a system that automatically controls the source temperature and rate of deposition, and achieved phase pure films upon annealing at 140°C. The method still involves rate monitoring, which fluctuates for MAI and PbI$_2$ [35], hence difficult to reproduce. Patel and co-workers [39] slowed down the formation of MAPbI$_3$ during the SPVD of MAI on PbI$_2$ by lowering the substrate temperature to 0°C, which prevented inter-diffusion. By in-situ monitoring the absorption spectrum during the deposition process, they saw that nascent MAPbI$_3$ was formed as the substrate temperature was gradually increased due to the intermixing of MAI and PbI$_2$. However, ambient air was needed for the complete crystallization of MAPbI$_3$ and removal of excess MAI. Also, it is not clear what amounts (thicknesses) of MAI and PbI$_2$ where used in their experiment.

In this study, we prepared 3D MAPbI$_3$ thin films by SPVD of single layers of PbI$_2$ and MAI and optimized their structural, optical, morphological and electrical by varying the thickness of MAI and post-annealing
time. FTO/MAPbI₃/Au devices were fabricated and their J-V characteristics under dark measured. The characteristics were used to calculate the carrier mobility and trap density by the space charge limited current (SCLC) theory. This method is simplified, scalable, reproducible and paves the way for the preparation of stable thin MAPbI₃ films for solar cells.

2 Experimental details

Fig. 1 illustrates the set up for the preparation of MAPbI₃ thin films by SPVD of PbI₂ and MAI single layers using a resistive thermal evaporator. Microscopic glass substrates were trimmed into 15 x 20 mm and cleaned in acetone, isopropanol and deionized water respectively using an ultrasonic bath for 10 mins, to remove oils grease, and particle contaminations. Thereafter, they were dried by blowing with nitrogen gas remove moisture. PbI₂ (99.9 %) and MAI (0.42 M in 2-propanol) were obtained from Sigma Aldrich. The PbI₂ was used as received whereas the MAI solution was evaporated using a rotary evaporator to obtain a powder.

Before deposition, the chamber was cleaned using a solution of extran diluted with deionized water (volume ratio 1:4) and high-pressure cleaner, to remove the effects of residual contaminants. The substrates were seated on to a holder and installed in the chamber. PbI₂ and MAI powder were inserted into separate cylindrical boron nitride boats, B₁ and B₂. The chamber was evacuated to a vacuum pressure of 2.0 x 10⁻⁵ mbar. The sequential deposition of the precursors was controlled by the switches, S1 and S2. The PbI₂ film was first deposited while switch S1 was closed and S2 opened, next MAI film was deposited while S2 and S1 are potentially interchanged, forming a layer of MAI on PbI₂. The thickness of PbI₂ was fixed at 100 nm while that of MAI was varied from 300 to 500 nm in steps of 100 nm. An inbuilt quartz crystal monitor, placed at the same level as the substrate inside the chamber, was used to monitor the thickness of thin film during the deposition process. The crystal monitor was calibrated for PbI₂ thickness measurement by setting the density to 6.16 g cm⁻³ and Z-factor to 1.10. Also, MAI film thickness was monitored by setting the density to 1.20 g cm⁻³ and Z-factor to 2.70. The crystallization of MAPbI₃ was accomplished by annealing the compound film at 100°C for 10 mins in an air-heated oven. The films grown using PbI₂ (99.9 %) and MAI (0.42 M in 2-propanol) are called SPL1. Finally, the experiment was repeated using PbI₂ (99.9 %) and MAI (98%) with MAI thickness maintained at 500 nm while annealing time was varied from 0 to 60 mins. The samples formed from PbI₂ (99.9 %) and MAI (98%) are called SPL2.
The XRD spectra of the thin films were measured by a Bruker D2-Phaser X-ray diffractometer using Cu Kα radiation with a wavelength of 0.15405 nm. The angle between the incident and diffracted rays, 2θ, was varied from 10 to 50° in steps of 0.05. The measured spectra were used to determine the structure, crystallinity, crystallite size, micro-strain, and dislocation density of the films. The morphological properties were revealed by field emission scanning electron microscope (FE-SEM Zeiss Crossbeam 540), with an accelerating voltage of 2.0 kV. Grain size analyses were performed from the FE-SEM images following the American Standard for Testing Materials (ASTM) using the Image J software. The optical absorption spectra of the films were measured by CARY 100 BIO UV-Vis spectrometer with the wavelength of incident light in the 400-800 nm range. J-V measurements under illumination were performed using a Model 91150V Solar Simulator with solar output conditions of 100 mW cm² at 25°C and Air-Mass 1.5 Global (AM 1.5 G) reference spectrum.
3 Results and discussion

3.1 Structural properties

3.1.1 Structural properties of MAPbI$_3$ for various MAI thickness

Fig. 2 (a) displays the diffractograms of the synthesized SPL1 thin films for peculiar thicknesses of MAI. The patterns show fine peaks saying good crystallinity and the crystal structure was then indexed to the tetragonal crystal system of MAPbI$_3$, with I$4/mcm$ space group [14,41–43]. Notably, Frohna and co-workers [44] demonstrated from first principle calculations that tetragonal MAPbI$_3$ is centrosymmetric at room temperature with I$4/mcm$ space group. The intensity of the extra (001) diffraction peak is indexed to the PbI$_2$ residue according to JCPDS card number 07-0235. Additionally, it is seen to decrease with increase in the thickness of MAI. This shows that the phase-purity of MAPbI$_3$ increases as MAI thickness is increased. Fig. S1 (supporting information) has spectra for 50 nm PbI$_2$:350 nm MAI and 300 PbI$_2$:100 nm MAI. Particularly, the characteristic (110) and (220) peaks showing the formation MAPbI$_3$ were absent. However, when the thickness of PbI$_2$ is kept at 100 nm and that of MAI increased from 300 to 500 nm, the peaks for MAPbI$_3$ appeared. The intensities of (110) and (220) diffraction planes increase with MAI thickness as shown in Fig. 2 (a), indicating an increase in crystallinity of MAPbI$_3$. This is because increasing the thickness of MAI may increase the amount of carbon, hydrogen and iodine atoms that are needed at Wyckoff positions in the crystal lattice, bringing about high structure factor. The increase in peak intensity may also arise from a rise in the number of reflection planes, which increases the multiplicity factor and hence the intensity. This is because each added layer of atoms contributes to the resultant intensity of the diffraction peaks because of coherent scattering. It is worth noting that the thickness ratio of PbI$_2$ to MAI that gave SPL1 is different from that obtained by Miguel and co-workers [38] using an automated SPVD method. The difference may come from the deposition parameters and conditions used.
The crystallite size and micro-strain were calculated from the Williamson-Hall (W-H) plot. The W-H plot is applied when the simultaneous contributions of crystallite size and micro-strain to X-ray line broadening is required [45]. The W-H relation is given by Equation 1,

\[ \beta \cos \theta = \frac{K \lambda}{D} + 4 \varepsilon \sin \theta \]

where \( D \) is the crystallite, \( \beta \) is the full width at half maximum, \( \lambda \) is the wavelength, \( \theta \) is the Bragg’s diffraction angle, \( \varepsilon \) is the micro-strain, \( K \) is the Scherrer constant which is determined by the crystallite shape and is considered as 0.94 for spherical crystallites with cubic symmetry. Fig. S2a shows the W-H plot for various MAI thicknesses. The micro-strains are obtained from the slopes while the crystallite sizes are calculated from the intercepts. The slopes are negative and decrease in magnitude as the thickness of MAI is increased, which indicates that the strains are compressive and decrease with MAI thickness as shown in Fig. 2 (c). Zhao and co-workers [33] showed that decrease in the micro-strain enhance hole extraction at the perovskites/hole transport layer interface by flattening the valence band. Furthermore, they pointed out that carrier mobility increases when micro-strains are removed. Jones and co-workers [46] showed that micro-strain promotes defect concentration in MAPbI\textsubscript{3} films and enhances non-radiative recombination. Therefore, the decrease in micro-strain is expected to reduce defect density and non-radiative recombination. The calculated average crystallite sizes increase with the thickness of MAI as shown in Fig. 2 (b), and the increase may be due to a decrease in micro-strain which is expected to cause a decrease in band gap.

The lattice constants are computed using Bragg’s law (Equation 2) and the relationship between the interplanar spacing, \( d \), and the Miller indices of a tetragonal crystal structure is given by Equation 3,

\[ n \lambda = 2d \sin \theta \]

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{c^2} \]

where \( n = 1 \).
where \( a \) and \( c \) are the lattice constants and \( (hkl) \) are the miller indices. A least-square fitting procedure is used to extract the lattice constants of the MAPbI\(_3\) for various MAI thicknesses and presented in Table 1. The results show that the unit cells increase continuously on the \( c \)-axis but contracts and then elongates as the thickness of MAI is increased from 300 to 500 nm. For the PbI\(_2\)-rich MAPbI\(_3\) thin film having 100 nm PbI\(_2\) and 300 nm MAI, the lattice constants are \( a = 8.881 \) and \( c = 12.479 \). Increasing the thickness of MAI from 300 to 400 nm causes the tetragonal structure to contract on the \( a \)-axis and elongates on the \( c \)-axis. As the thickness of MAI is increased beyond 400 nm, the unit cell elongates along both axes. The change in unit volume as thickness is increased correlates with changes in the micro-train which includes the peaks of PbI\(_2\) shown in Fig. S3. The decrease in unit cell volume as the thickness of MAI is increased from 400 to 500 nm can be due to change of the micro-strain shown in Fig. S3 from tensile to compressive. The increase in volume as thickness is increased from 400 to 500 nm may be due to reduces in the size of the compressive micro-strain.

Table 1 Variation of lattice constants and unit cell volume of the SPL1 thin film with thickness of MAI.

<table>
<thead>
<tr>
<th>Thickness of MAI (nm)</th>
<th>Lattice constant, ( a ) (Å)</th>
<th>Lattice constant, ( b ) (Å)</th>
<th>Lattice constant, ( c ) (Å)</th>
<th>Unit cell volume, ( V ) (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>8.881</td>
<td>8.881</td>
<td>12.479</td>
<td>984.246</td>
</tr>
<tr>
<td>400</td>
<td>8.860</td>
<td>8.860</td>
<td>12.508</td>
<td>981.873</td>
</tr>
<tr>
<td>500</td>
<td>8.902</td>
<td>8.902</td>
<td>12.542</td>
<td>993.898</td>
</tr>
</tbody>
</table>

The dislocation density \( \rho \), representing imperfections in the crystal, was calculated using the Williamson and Smallman formula given by Equation 4 [47].
\[ \rho = \frac{n}{D^2} \]

where \( D \) is the crystallite size and \( n = 1 \) for minimum \( \rho \). The dislocation density is seen to decrease continuously with increase in MAI thickness, when the peaks corresponding to PbI\(_2\) are excluded in the calculation, as shown in Fig. 2 (d). Including the PbI\(_2\) peaks reduces the \( \rho \) from \( 3.825 \times 10^{11} \text{ cm}^{-2} \) to \( 2.947 \times 10^{11} \text{ cm}^{-2} \) for the 300 nm MAI thick film. As the MAI film thickness is increased, there is a first increase in \( \rho \) and a later decrease. PbI\(_2\)-rich films have lower dislocation densities than PbI\(_2\)-deficient (MAPbI\(_3\)-pure) films as shown in Figure S3. Dislocations have been shown to reduce the performance of perovskites solar cells. Haque and co-workers [48] calculated the \( \rho \) of solution-processed caesium lead tri-iodide (CsPbI\(_3\)) solar cells and observed that cells with lowest \( \rho \) had the best PCE. Furthermore, the presence of defects generally lead to decrease in performance for HPs solar cells [49]. Therefore, the film having 500 nm thick MAI, with lowest \( \rho \), may result in high performing solar cells.
Fig. 2. (a) Diffractograms of the SPL1 thin films for peculiar thicknesses of MAI; (b) Micro-strain of the SPL1 thin film against MAI thickness; (c) Crystallite size of the SPL1 thin film against MAI thickness; (d) Dislocation density of SPL1 thin film against MAI thickness.

3.1.2 Structural properties of MAPbI$_3$ thin films for various annealing times

Fig. 3 shows the structural analysis of SPL2 thin films for various annealing times. The diffractograms show sharp peaks indicating good crystallinity and a strong dependence on annealing time as shown in Fig. 3 (a). In comparison, the crystal structures are tetragonal with I4/mcm space, like the results for SPL1 thin films, vide infra. The spectrum of the as-deposited film reveals a pure tetragonal MAPbI$_3$ phase, showing that crystallization of the SPL2 thin film starts during the deposition. This could be possible because the temperature of the substrate (95°C) was within the range of annealing temperatures for MAPbI$_3$, thus MAI could diffuse into the voids in the PbI$_6$ octahedra framework and recrystallize to form MAPbI$_3$. The annealing temperature for the crystallization of MAPbI$_3$ is within a 90–105°C range [50]. It is known that inter-diffusion of MAI and PbI$_2$ during vapor deposition is determined by the substrate temperature. Patel and co-workers [39] showed that inter-diffusion and reaction during vapor deposition can be prevented by lowering the temperature of the substrate to 0°C before the deposition of MAI on the PbI$_2$. They added that PbI$_2$ and MAI
are transformed to MAPbI$_3$ under vacuum at room temperature, but the reaction is incomplete as MAI residue stays in the film. The MAI residue is completely converted to MAPbI$_3$ when the film is exposed to humid air at 21°C, because moisture exposure makes the MAI more mobile. Also, they saw that longer annealing times improved the crystallinity and absorbance continuously. During the first 20 mins of annealing our films, no noticeable change in the phase purity is seen on the diffractograms. However, after 40 mins, a very intense PbI$_2$ peak is seen, showing that annealing for a long time causes a transformation MAPbI$_3$ to PbI$_2$, consistent with previous results [51]. As annealing continues from 40 to 60 mins, the intensity of the PbI$_2$ peak decreases as the time, showing a possible retransformation of PbI$_2$ to MAPbI$_3$. The formation of PbI$_2$ during annealing has also been seen by other authors. Chen and co-workers [51] showed that increasing the annealing time beyond that needed to just complete the formation of MAPbI$_3$ leads to the release of PbI$_2$, which passivates the grain boundaries, thus improving electrical properties and performance. Park and co-workers [52] demonstrated that the formation of PbI$_2$ residues occurs during the annealing step of the reaction rather than at the initial stages.

Fig. 3 (b) shows how the average crystallite size of SPL2 thin films vary with annealing time. The crystallite size decreases slightly during the first 20 mins, then increase greatly after 40 mins before decreasing to a value close to that seen after 20 mins. In comparison, the change in crystallite size follows the same trend as the changing intensity of the PbI$_2$ peak. Thus, the fluctuations of the average crystallite size with increase in annealing time may be due to the reversible phase transformations occurring in the sample. Interestingly, we realized that the crystallite size is highest after 40 mins, when the PbI$_2$ peak is most intense. Therefore, we think that the presence of PbI$_2$ residue in MAPbI$_3$ thin films increases the average crystallite size.

Fig. 3 (c) shows how the micro-strain of SPL2 thin films vary with annealing time. The as deposited films show a large negative (compressive) micro-strain that decreased (relaxes) slightly as time is increased from 0 to 20 mins. Beyond 40 mins, the micro-strain changes again from tensile to compressive. The dependence also shows a strong correlation with the changing intensity of the PbI$_2$ peaks. The tensile nature of the micro-strain may have caused the large crystallite size in the presence of a large proportion of PbI$_2$ from the transformation of MAPbI$_3$. 
Fig. 3 (d) shows that the dislocation density increases slightly during the first 20 mins of post-annealing, then decreases drastically between 20 and 40 mins before increasing again. The fluctuations in dislocation is also due to the continuous transformation between PbI$_2$ and MAPbI$_3$ phases as the annealing time is increased. In particular, the smallest dislocation density is seen after 40 mins of annealing when the (100) peak corresponding to PbI$_2$ is most intense. This points out that the dislocation density is lower for the PbI$_2$-rich MAPbI$_3$ films than for the PbI$_2$ deficient films. The presence of unreacted PbI$_2$ in MAPbI$_3$ thin film has previously been shown to have both positive and negative effects on the performance of solar cells. Jacobsson and co-workers [53] showed that PbI$_2$-deficient MAPbI$_3$ thin films have high crystalline quality and result in solar cells with high $V_{oc}$, however, their PCE is low due to MAI at grain boundaries which offer barriers to charge transport. Conversely, the solar cells having PbI$_2$-rich films showed the highest performance. Kwon and co-workers [54], on the other hand, demonstrated that pure MAPbI$_3$ (without PbI$_2$ residue) has high photon absorption and long carrier lifetimes which leads to more photogenerated current and high PCE.
Structural analysis of SPL2 thin film having 400 nm thick MAI for various annealing times; (a) XRD diffractograms of SPL2 thin film against annealing times; (b) Average crystallite size of SPL2 thin films against annealing time; (c) Micro-strain of SPL2 thin film against annealing time; (d) Dislocation density of SPL2 thin films against annealing time.

Table 2 shows the lattice constants, unit cell volumes and grain sizes, depending on the annealing time, with non-linear relationships. The non-linear change in unit cell volume (V) with annealing time can be related to the effects of thermal expansion [55] and the phase transformations from MAPbI₃ to PbI₂, depicted by Fig. 3 (a), consistent with previous reports by Chen and co-workers [51]. As can be seen in Figure 3a and Table 2, the as deposited film is deficient of PbI₂ with lattice constants a and c equals 8.905 and 12.526 Å respectively. The lattice constants increase after 20 mins of annealing, leading to an increase in V of the unit cell, which may be due to thermal expansion during annealing. However, increasing the annealing time from 20 to 40 mins leads to a decrease in V and the sudden appearance of the very intense PbI₂ peak. This may be because the effect of phase transformation from MAPbI₃ to PbI₂ dominates that of thermal expansion and leads to a decrease in the decrease in V. Increasing the time to 60 mins reduces the intensity of the PbI₂ peak and there is a slight increase in V possibly due to thermal expansion.

Table 2 Variation of lattice constants, unit cell volume and grain size of SPL2 thin film for various annealing times.

<table>
<thead>
<tr>
<th>Annealing time (mins)</th>
<th>Lattice constant, a (Å)</th>
<th>Lattice constant, b (Å)</th>
<th>Lattice constant, c (Å)</th>
<th>Unit cell volume, V (Å³)</th>
<th>Average grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.905</td>
<td>8.905</td>
<td>12.526</td>
<td>993.230</td>
<td>501.56±36.47</td>
</tr>
<tr>
<td>20</td>
<td>8.924</td>
<td>8.924</td>
<td>12.553</td>
<td>999.693</td>
<td>413.07±57.12</td>
</tr>
<tr>
<td>40</td>
<td>8.897</td>
<td>8.897</td>
<td>12.556</td>
<td>993.890</td>
<td>264.31±32.78</td>
</tr>
<tr>
<td>60</td>
<td>8.907</td>
<td>8.907</td>
<td>12.549</td>
<td>995.571</td>
<td>206.46±20.85</td>
</tr>
</tbody>
</table>
3.2 Morphological properties

3.2.1 Surface morphology analysis of MAPbI₃ for various MAI thicknesses

Fig. 4 presents the surface morphology of the synthesized SPL1 thin films for various MAI thicknesses. The films shown in Fig. 4 (a, b) were formed by deposition of 300 and 400 nm of MAI, respectively. Densely packed and randomly oriented grains were seen. The dense morphology is good for solar cells since photo-current leakage is presumably be minimized [56]. Furthermore, the grains have variable sizes and orientations. The variable orientations show that films are polycrystalline in nature. In addition, there was full coverage of substrate with negligible pinhole defects which may presumably reduce leakage current, increase open-circuit voltage and fill factor [57]. Likewise, the grain size increased from 150 to 180 nm corresponding to increased thickness from 300 to 400 nm of MAI. The grain size was not calculated for the sample with 500 nm MAI thickness films because the grains were not visible as observed in Fig. 4 (c). This could be a result of excess MAI, presumed covering the grains. The results showed that the average grain size is proportional to MAI thickness for all the samples. The increase in grain size will inevitably result in the fewer grain boundaries leading to reduced electron scattering and trap density [58]. Liu and co-workers [59] showed that reduction in trap density by passivating with polyhedral oligomeric silsesquioxane; which contains an amino group, improved device efficiency, open-circuit voltage and stability. We, therefore, deduce that the decrease in grain boundaries will lead to an increase in the stability.

![Fig. 4](image_url) The FE-SEM images of SPL1 thin film for various thickness of MAI; (a) Having 100 nm PbI₂ and 300 nm MAI thickness ratio; (b) Having 100 nm PbI₂ and 400 nm MAI thickness ratio; (c) Having 100 nm PbI₂ and 500 nm MAI thickness ratio.
3.2.2 Surface morphology analysis of MAPbI$_3$ for increasing annealing time

Fig. 5 is the SEM micrographs of SPL2 annealed in air at 100°C for different times. All the films show densely packed randomly oriented pin-hole-free grains. Note that the difference in the average grain sizes of SPL2 (Fig. 5) and SPL1 (Fig. 4) may be based on the difference in purity of the MAI used in the deposition. The MAI powder precursor used for the preparation of the SPL1 is obtained by the evaporation of 2-propanol from 0.42 M solution of MAI while that for SPL2 is of 98% purity and used as received. The average grain size decreases with an increase in annealing time as shown in Table 2. In particular, the average grain size for the as deposited is two times larger than that of film annealed after 40 mins. According to the XRD spectra, the as deposited film is PbI$_2$ deficient while the film annealed for 40 mins is rich in PbI$_2$. The decrease in average grain size maybe because of the transformation from MAPbI$_3$ to PbI$_2$. This agrees with Meerholz and co-workers [60] who showed that the effect of excess PbI$_2$ in precursor solution includes the accumulation of excess crystalline PbI$_2$ at grain boundaries and the surface, and the reduction in average grain size.
Fig. 5. FE-SEM micrographs of SPL2 thin films for various annealing times; (a) Micrograph of as deposited sample; (b) Micrograph of SPL2 thin film annealed for 20 mins; (c) Micrograph of SPL2 thin film annealed for 40 mins; (d) Micrograph of SPL2 thin film annealed for 60 mins.

3.3 Optical properties

3.3.1 UV-Vis absorption of MAPbI$_3$ for various MAI thickness

Fig. 6 (a) depicts the UV-Vis absorption spectra of SPL1 thin films for peculiar MAI thicknesses. Each spectrum shows a wide absorption band between 500 and 400 nm wavelengths, which agrees with the literature [61]. The absorption onset experiences a redshift as MAI thickness increases, which results in a decrease in direct and indirect bandgaps from 1.66 to 1.60 eV and 1.65 to 1.59 eV respectively, as shown in Fig. 6 (d). The decrease in bandgap may be due to the increase in crystallite size and tensile strain [62]. M. Oztas [62] observed that the energy bandgap of indium phosphide (InP) thin film is inversely related to the grain size and strain. Similarly, Innocenzo and co-workers [63] studied the relationship between morphology and luminescence properties of HPs and showed that optical bandgap decreased as crystallite size increased leading to longer carrier lifetimes. Furthermore, narrowing the bandgap is desirable to improve the PCE of the single-junction perovskite solar cells according to Shockley-Queisser theory [64]. Sha and co-workers [65] reported that the maximum PCE of 31 % is attained at the Shockley-Queiser optimum bandgap of 1.40 eV for single-junction PSCs. Therefore, better performing solar cells may be achieved when the bandgap approaches 1.40 eV. Likewise, bandgap reduction reduces the chances of creating deep level traps (recombination centers) in MAPbI$_3$ which may decrease carrier lifetimes [66].

The bandgap was computed using the Mott and Davis equation. Mott and Davis developed Tauc’s idea of determining the bandgap of semiconductors. They proved that the optical absorption strength was proportional to the difference between photon energy and bandgap according to Equation 5 [67],

$$\frac{1}{(\alpha h\nu)^n} = A(h\nu - E_g)$$

where $E_g$ is bandgap and $A$ is a proportionality constant, $\alpha$ is the absorption coefficient, $h$ is the Planck’s constant, $\nu$ is the frequency, $n$ is a numerical constant and its value determines nature of the transition; $n$
equals $\frac{1}{2}$, 2, 3/2, and 3 for direct allowed transitions, indirect allowed transitions, direct forbidden transitions and indirect forbidden transitions respectively. Fig. 6 (b, c) show the direct and indirect bandgaps from respective Tauc-plots, close to the absorption edge. In both cases, perfect fits are seen, indicating that the MAPbI$_3$ naturally exhibits both direct and indirect bandgap character, known as Rashba effect [68]. Etienne and co-workers [69] proved that the Rashba effect in HPs originates from splitting and shifting of the conduction band minimum in the $k$-space due to spin-orbit coupling. Rashba spin-orbit coupling has also been shown to enhance charge carrier lifetime in HPs [70].

![Fig. 6.](image)

Fig. 6. (a) UV-Vis absorption spectra of SPL1 thin films for peculiar MAI thicknesses; (b) Direct bandgap Tauc-plot of SPL1 thin films for peculiar thicknesses; (c) Indirect bandgap Tauc-plot of SPL1 thin films for peculiar thicknesses; (d) Bandgap of SPL1 thin films against MAI thickness.
3.3.2 UV-Vis absorption of MAPbI$_3$ for varying annealing time

Fig. 7 (a, b) show the UV-Vis absorption spectra and direct bandgap Tauc-plot of the sequential physical vapour deposited thin SPL2 films respectively, for peculiar annealing times. The spectra of the films show an absorption edge close to 780 nm, which confirms the formation of MAPbI$_3$. However, the direct bandgap from Tauc-plot reveals a uniform increase with annealing time as shown in Fig. 7 (c). The increase in bandgap can be linked to the decrease in grain size as shown in Fig. 7 (d), consistent with the literature [71]. The increase in bandgap with annealing time may also be due to the presence of PbI$_2$, with absorption onset at 515 nm (large bandgap), [72,73], from the transformation of MAPbI$_3$ as the annealing time was increased.

Increase in annealing time affects the absorbance differently in various regions of the visible spectrum. The absorbance of the as deposited thin film, which is deficient in PbI$_2$, is highest in the 500-800 nm range, while the absorbance of the film annealed after 40 mins is lowest in the same range. This indicates that the PbI$_2$-deficient MAPbI$_3$ thin-films absorb more in the 500-800 nm range (visible range) than PbI$_2$-rich thin-films, and this is consistent with previous reports by [54,73]. Kwon and co-workers proved that MAPbI$_3$ with excess PbI$_2$ has a lower absorbance than that of pure MAPbI$_3$ [54]. Similarly, Abdelmageed and co-workers showed that the intensity of visible light absorption decreased as more PbI$_2$ was produced from the degradation of MAPbI$_3$ [73]. Fig. 7 (b) shows that the square of the product of absorption coefficient and energy decreases as annealing time increase. This implies that the absorption coefficient decreases with increase in annealing time and could be due to the presence of more PbI$_2$ in the thin SPL2 film, from the transformation of MAPbI$_3$ as the annealing time is increased.
Fig. 7. (a) UV-Vis absorption spectra of thin SPL2 films for different annealing times; (b) Direct bandgap Tauc-plot of SPL2 for different annealing times; (c) Bandgap of thin SPL2 films vs. annealing time; (d) Bandgap of thin SPL2 films vs. average grain size.

3.4 Electrical properties

Fig. 8 shows the semi-logarithmic current density-voltage ($J-V$) characteristics under dark and light conditions for various FTO/SPL2/Au devices, where SPL2 the thin films are annealed at different times. The dark semi-log $J-V$ plots are to verify the nature of the contacts and the possibility of using the space charge limited current (SCLC) theory to calculate the carrier mobility and trap density. All the curves are symmetric showing small barrier to charge carrier injection from the electrodes (ohmic contacts) and validating the
possible application of SCLC theory, in accordance with the literatures [13,74]. The quality of the ohmic contacts were determined by calculating the specific contact resistivity [75], \( \rho_c \), which is the reciprocal of the gradient of the \( J-V \) curve as \( V \) turns to zero. The values of \( \rho_c \) are inversely related to the doping concentrations [76] and are displayed in Table 3. The small values of \( \rho_c \) reveal good ohmic contact [75], implying that SPL2 may be p-type materials, since p-type semiconductors make ohmic contacts with high work function metals like gold. The \( J-V \) measurements under illumination conditions were performed, with the devices exposed to solar simulated light of 1000 W m\(^{-2}\) intensity. The \( J-V \) measurements show that the current density for any given voltage under illumination conditions is higher in all the devices than the dark current density. This means that the SVP deposited MAPbI\(_3\) HPs can generate charge carriers when exposed to sunlight, however, the amount of photogenerated charge carriers decreases with increase in PbI\(_2\) produced during thermal annealing time. The as deposited SPL2 film generated the highest number of carriers when in forward bias. This is consistent with the UV-Vis spectrum of the sample which has the highest absorbance in the 500-800 nm visible range. The differences between the current densities under light and dark conditions are small. This narrow difference could be because the electric field at the p-n junction is weak such that the charge separation is ineffective.

![Current density plots](image1.png)

![Current density plots](image2.png)

![Current density plots](image3.png)

![Current density plots](image4.png)
Fig. 8. Semi-log $J$-$V$ characteristics of FTO/SPL2/Au devices under dark and illumination, where the SPL2 thin films are annealed at different times; (a) $J$-$V$ curves of FTO/SPL2/Au devices having as deposited SPL2 thin film; (b) $J$-$V$ curves of FTO/SPL2/Au devices having SPL2 thin film annealed for 20 mins; (c) $J$-$V$ curves of FTO/SPL2/Au devices having SPL2 thin film annealed for 40 mins; (d) $J$-$V$ curves of FTO/SPL2/Au devices having SPL2 thin film annealed for 60 mins.

The non-linear dark forward $J$-$V$ characteristics suggest a power law dependence of $J$ on $V$ given by

$$J \alpha V^m$$

where $m$ is an exponent corresponding to the slope of the double-log $J$-$V$ plot and reveals the bulk charge transport mechanism. Ohmic conduction is said to dominate when $m \sim 1$, trap-free space charge limited current (SCLC) conduction dominates when $m = 2$ and trap limited SCLC conduction in the presence of traps exist when $m > 2$ [40]. During ohmic conduction, the current is driven by mobile charge carriers in the material. Thus, the carrier density needs to be known to calculate the mobility. Conversely, for SCLC conduction, the current is dominated by injected carriers from the contacts and it is solely dependent upon the mobility of the charge carriers that can be determined from a simple double-log $J$-$V$ plot.
Fig. 9 is the double-log $J$-$V$ characteristic of the FTO/SPL2/Au for different annealing times. The device containing as deposited SPL2 reveals ohmic transport and trap limited SCLC conduction as shown in Fig. 9 (a). The devices containing annealed SPL2 reveal ohmic transport and trap free SCLC conduction regions shown in Fig. 9 (b-d). As the biasing voltage is increased, charges are injected into the bulk of the MAPbI$_3$ leading to traps being filled continuously until the trap-filled limit ($V_{TFL}$) is reached, when all the traps are filled. The $V_{TFL}$ is seen to increase with increase in annealing time as shown in Fig. 9. $V_{TFL}$ is linked to the trap density $N_t$ according to Equation 7,

$$V_{TFL} = qN_t \frac{d^2}{2\varepsilon_o \varepsilon_r}$$

where $d$ is the film thickness, $q$ is the electronic charge, $\varepsilon_o$ is the permittivity of free space and $\varepsilon_r$ is the dielectric constant of the MAPbI$_3$ which is equal to 32 according to previous reports by Makhsud I Saidaminov and co-workers [77]. Since the $V_{TFL}$ is directly proportional to $N_t$, it implies the $N_t$ also increases with increase in annealing time. The calculated values for $N_t$ increase as the annealing time increases and range from 3.25-4.55 $\times$ 10$^{16}$ cm$^{-3}$ as shown in Table 3. This can be because longer annealing times cause more trap charge carriers to gain enough energy to be released from localized states. The relationship between the current density and carrier mobility beyond the trap-filled limit is given by Equation 8,

$$J = \frac{9}{8} \varepsilon_o \varepsilon_r \theta \mu_p \frac{V^2}{d^3}$$

where $J$ is the current density, $V$ is the voltage at the onset of space charge limited region and $\theta$ is the trap factor, which is the ratio of free carriers to the sum of free and trapped carriers. $\theta$ is calculated by dividing the current at the onset of the space charge region by the current at the end [13,40,74] and results represented in Table 3. It increases with increase in annealing time and is consistent with the effect of annealing time on trap density. On the other hand, $\mu_p$ initially decreased after annealing for twenty mins, and then increased steadily with annealing time. This first decrease in $\mu_p$ may be because of the increase in $N_t$ for the same MAPbI$_3$.
phase. As heating continues beyond 20 mins, there is a transformation from MAPbI$_3$ to PbI$_2$ that may cause the mobility to increase slightly, even though the trap density increases. It can be deduced that PbI$_2$ deficient MAPbI$_3$ has a higher mobility than PbI$_2$-rich MAPbI$_3$.

Table 3 Variation of trap density, charge carrier mobility, trap factor and specific contact resistivity of SPL2 thin films with annealing time.

<table>
<thead>
<tr>
<th>Annealing time (mins)</th>
<th>Trap density (cm$^{-3}$)</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Trap factor</th>
<th>Specific resistivity (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$3.25 \times 10^{16}$</td>
<td>1.29</td>
<td>0.235</td>
<td>0.067</td>
</tr>
<tr>
<td>20</td>
<td>$4.22 \times 10^{16}$</td>
<td>0.43</td>
<td>0.420</td>
<td>0.073</td>
</tr>
<tr>
<td>40</td>
<td>$4.51 \times 10^{16}$</td>
<td>0.49</td>
<td>0.495</td>
<td>0.071</td>
</tr>
<tr>
<td>60</td>
<td>$4.55 \times 10^{16}$</td>
<td>0.56</td>
<td>0.496</td>
<td>0.054</td>
</tr>
</tbody>
</table>
Fig. 9. Double-log $J-V$ characteristics of FTO/SPL2/Au devices for which the SPL2 is annealed for different times; (a) Double-log $J-V$ curves of FTO/SPL2/Au devices having as deposited SPL2; (b) Double-log $J-V$ curve of FTO/SPL2/Au devices having SPL2 annealed for 20 mins; (c) Double log $J-V$ curves of FTO/SPL2/Au devices having SPL2 annealed for 40 mins; (d) Double log $J-V$ curves of FTO/SPL2/Au devices having SPL2 annealed for 60 mins.

4 Conclusions

We have demonstrated the preparation of thin MAPbI$_3$ films by SPVD of PbI$_2$ and MAI single layers. The structural, optical, morphological, and electrical properties were optimized by controlling the MAI film thickness and post-deposition annealing time. All the XRD diffractograms showed the tetragonal MAPbI$_3$ phase having the I4/mcm space group. The crystallinity was observed to increase with increase in MAI film thickness while prolonging the post-deposition annealing time resulted in the transformation of MAPbI$_3$ to PbI$_2$. Importantly, the unannealed films showed the pure MAPbI$_3$ phase, indicating crystallization started in situ during the deposition of MAI on PbI$_2$ at a substrate temperature of 95$^\circ$C. The micro-strain and crystallite size increased, and dislocation density decreased with increase in MAI thickness while the changes of these properties with annealing time showed no regular pattern. FE-SEM results showed compact grains of variable sizes and orientations and with average grain size that increases with the thickness MAI but decreased with increased in post-annealing time. The reason for the decrease in average grain size with increasing post-annealing time, however, needs further investigation. Direct and indirect Tauc-plots of the UV-Vis absorption spectra showed a small Rashba effect, with optimum direct and indirect bandgaps of 1.60 and 1.59 eV, respectively. Also, the bandgap increased, and absorption intensity decreased with increase in annealing time. We observed that films containing PbI$_2$ produced during post-annealing showed lower absorption intensity. The trap density was observed to decrease with increase in annealing time and the maximum charge carrier mobility of 1.29 cm$^2$ V$^{-1}$ s$^{-1}$ was obtained for the unannealed film. The $J-V$ characteristics under illumination
also revealed that the unannealed film had the highest photogenerated current. Based on our findings, we recommend the optimal thickness of 100 nm PbI₂ and 500 nm MAI and no post-annealing for low trap density, high charge carrier mobility, and pure thin MAPbI₃ films by SVPD.

Supporting Information

Three supporting figures: XRD spectra showing films with a ratio of PbI₂ to MAI greater than one and films with a ratio of PbI₂ to MAI less than one, W-H plots of MAPbI₃ for various thicknesses of MAI and various annealing times, average crystallite size, micro-strain, the dislocation density of MAPbI₃ for various MAI thickness with the effect extra PbI₂ peaks included.

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Highlights

➢ Simplified growth of MAPbI$_3$ by sequential physical vapor deposition of PbI$_2$ and MAI single layers.

➢ Prolong annealing of MAPbI$_3$ causes reversible phase transformation between MAPbI$_3$ and PbI$_2$.

➢ Optimization of the stoichiometry of MAPbI$_3$ by precise thickness regulation.

➢ Trap density and carrier mobility of MAPbI$_3$ thin films by space charge limited current theory.
All authors declare no conflict of interest.