Post Annealing Effects of Perovskite (CH$_3$NH$_3$PbI$_3$) Thin Films for Solar Cell Applications

Ipsita Mohanty$^1$, S. Mangal$^{1,a)}$, S. Jana$^1$ and Udai P. Singh$^2$

$^1$School of Applied Sciences, Kalinga Institute of Industrial Technology (KIIT), Bhubaneswar, India.
$^2$School of Electronics Engineering, Kalinga Institute of Industrial Technology (KIIT), Bhubaneswar, India

$^a)$Corresponding author: sutanufpy@kiit.ac.in

Abstract. In this work, methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$) thin films were deposited using spin-coating method. The thin films were investigated as a function of different thermal annealing temperatures with time being constant and as a function of time with constant temperature. The compositional and structural analyses have been studied by EDXRF and XRD respectively. The optical and chemical properties were also studied using UV-Vis spectrophotometer and FTIR spectroscopy. The characterization result shows the change in its properties with increase in temperature and time. From the XRD data, it can be observed that with an increase in temperature, the CH$_3$NH$_3$PbI$_3$ decomposes to PbI$_2$, and with an increase in annealing time, the CH$_3$NH$_3$PbI$_3$ peaks show degradation. A basic comparison has been made in order to study the effect of annealing on the CH$_3$NH$_3$PbI$_3$ thin films.

INTRODUCTION

A new platform for research and development for inexpensive and efficient solar cells have been evolved based on halide perovskite materials. Methyl ammonium lead iodide perovskites has piles of extraordinary properties like low exciton energy, high optical absorption coefficient, long free diffusion length, and low temperature solution processed synthesis. All these properties become ineffectual because of its moisture instability. Although perovskite solar cells technology has an excellent commercialization potential, it is still in the early stages as there are many concerns that remain to be addressed. The major issues include degradation of perovskite materials in presence of moisture and instability.

In perovskite materials, the method of synthesis plays a vital role in the physical and chemical properties. The route of synthesis strongly affects the physical properties like morphology, grain size-dispersion, surface area, phase purity, crystallinity, homogeneity, and composition [1]. There are many methods of synthesis like solid-state reactions, thermal evaporation, solvothermal process, but the most general route of synthesis is by chemical route [2], since it is cost effective as well as less time consuming. Along with the mode of synthesis, heating effect also introduces some change in the structural, optical, morphological and transport properties [3].

In this work, methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$) thin films were deposited using spin-coating method. The thin films were investigated as a function of different thermal annealing temperatures with time being constant. Another investigation includes variation of time with constant temperature. A basic comparison has been made in order to study the effect of annealing on the CH$_3$NH$_3$PbI$_3$ thin films.

EXPERIMENTAL SECTION

In this study, methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) was synthesised using lead (II) acetate trihydrate, aqueous concentrated HI (57% by wt.), and methylamine (40% solution in water). Using this wet chemical synthesis procedure, CH$_3$NH$_3$PbI$_3$ was obtained as a black precipitate. The precipitate was then dried to obtain CH$_3$NH$_3$PbI$_3$ powder [2]. A fine paste of CH$_3$NH$_3$PbI$_3$ has been made on addition of ethanol. CH$_3$NH$_3$PbI$_3$ thin films were then deposited by spin-coating process at 3000 rpm for 20 s. Two layer depositions at same conditions were done in order
to achieve a thin film with uniform thickness. Thermal annealing of the CH$_3$NH$_3$PbI$_3$ thin films in RTP furnace have been done categorizing it in two groups: Group A varying temperature with constant time, and Group B varying time with constant temperature. The details of the samples are expressed in tabular form in Table 1.

**TABLE 1.** Details of the Samples

<table>
<thead>
<tr>
<th>GROUP</th>
<th>TEMPERATURE (°C)</th>
<th>TIME (min)</th>
<th>SAMPLE NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A</td>
<td>80</td>
<td>5</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5</td>
<td>A2</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>5</td>
<td>A3</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>5</td>
<td>A4</td>
</tr>
<tr>
<td>Group B</td>
<td>100</td>
<td>10</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15</td>
<td>B3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>20</td>
<td>B4</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Compositional Analysis**

The compositional analysis of all the annealed perovskite thin films was studied using ED-XRF. In Table 2, the analysis of the annealed samples at different temperatures with constant time (Group A), and the annealed samples at different time duration with constant temperature (Group B) has been summarized. From the table, it can be observed that, in Group A, the atomic percentage of iodine is decreasing, along with an increase in the concentration of lead. A gradual decrease in the I:Pb ratio with the rise in temperature has been noted. But a different pattern has been observed in the Group B samples. In Group B samples, the exact opposite of Group A has been noted. With increase in time duration, the iodine concentration increases, with a decrease in lead concentration, and eventually increase in I:Pb ratio. The I:Pb ratio is observed to be higher than the theoretical values (i.e. 3:1) in both the groups. According to reports, the decrease in the ratio marks the formation of PbI$_2$ and increase in the ratio marks the formation of hydrates [4]. However, Yang et.al. confirmed that the hydrate, so formed, is unstable in room temperature which results in reforming back to CH$_3$NH$_3$PbI$_3$ [5]. Thus, it can be noted that with increase in annealing temperature, the I:Pb ratio is getting close to the theoretical value (i.e. 3:1). But with increase in time duration of annealing, the ratio increases, thus marking formation of hydrates.

**TABLE 2.** Compositional Analysis of Perovskite Samples

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>I (atom %)</th>
<th>Pb (atom %)</th>
<th>I:Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>79.76</td>
<td>20.24</td>
<td>3.94:1</td>
</tr>
<tr>
<td>A2</td>
<td>79.45</td>
<td>20.55</td>
<td>3.86:1</td>
</tr>
<tr>
<td>A3</td>
<td>79.17</td>
<td>20.74</td>
<td>3.81:1</td>
</tr>
<tr>
<td>A4</td>
<td>79.13</td>
<td>20.86</td>
<td>3.79:1</td>
</tr>
<tr>
<td>B1</td>
<td>79.45</td>
<td>20.55</td>
<td>3.86:1</td>
</tr>
<tr>
<td>B2</td>
<td>80.18</td>
<td>19.82</td>
<td>4.04:1</td>
</tr>
<tr>
<td>B3</td>
<td>80.96</td>
<td>19.04</td>
<td>4.25:1</td>
</tr>
<tr>
<td>B4</td>
<td>81.33</td>
<td>18.67</td>
<td>4.35:1</td>
</tr>
</tbody>
</table>
Optical Properties

The absorption spectra of the CH$_3$NH$_3$PbI$_3$ thin films treated under different annealing temperatures and different time duration is shown in figure 1(a and b), ranging from 400 nm to 900 nm. As shown in figure 1(a), the absorption of the CH$_3$NH$_3$PbI$_3$ thin films with low annealing temperatures i.e. 80 and 100 °C, is relatively low, as compared to that of high annealing temperatures i.e. 120 and 140 °C. But the A3 and A4 samples have double absorption peak, which may indicate the formation of some new compound. Similarly, in figure 1 (b), the absorption of B1 and B2 samples are higher than that of the samples with higher time duration. The absorption spectra of B3 and B4 samples are almost the same, indicating double absorption peak. Chen et.al. [6] reported that, the CH$_3$NH$_3$PbI$_3$ perovskite films need a thermal annealing process to drive the interdiffusion between the precursors. The optical band gaps of all the samples were determined using Tauc equation:

$$(\alpha h \nu)^n = A(h \nu - E_g)$$

where $\alpha$= Absorption co-efficient, $h$= Planck’s constant, $\nu$= frequency, $n$= photon frequency, $A$=constant, and $E_g$= Band gap energy. The plots for $(\alpha h \nu)^2$ $vs$ $h \nu$ for all the samples of the two groups (A and B) are shown in the figure 2 (a and b). The optical band gaps are obtained by drawing the respective tangents to x-axis at $y=0$. As shown in the figure 2 (a), the band gap has been calculated to be around 1.5 eV for all the samples. However, a very small increment in band gap is observed with increase in annealing temperature. The increment in band gap maybe due to the change in the chemical composition of the samples, as already reported in the compositional analysis. Also, the increased values of $E_g$ are associated with the phase transition of perovskite crystals [3]. In figure 2(b), it can be...
observed that, there is no change in the band gap of the samples. But double band gap characteristics have been found on both B3 and B4 thin films. The reason for double band gap characteristics may be the change in the composition or formation of a new compound.

**Structural Analysis**

To characterize the change in the crystal structure of the CH$_3$NH$_3$PbI$_3$ thin films after heat treatment, XRD analysis have been performed. The XRD spectra of both groups are plotted in figure 3 (a and b). From both the graphs, it can be noted that the main peaks are found to be around 14°, 28.5° and 31°. However, small shift in the peaks has also been observed. This may be due to change in the microstructure parameters i.e. crystallite size and lattice strain. All the structural parameters have been summarized in table 3. The crystallite size and lattice strain have been calculated using Scherrer equation:

\[
D = \frac{K\lambda}{\beta \cos \theta}, \quad \epsilon = \frac{\beta \cos \theta}{4}
\]

where, \(D\) - Average crystallite size (nm), \(K\) - Scherrer constant, \(\lambda\) - X-ray wavelength, \(\beta\) - FWHM (Full Width at Half Maximum) of XRD peak, \(\theta\) - XRD peak position, and \(\epsilon\) - lattice strain.

From the table, it can be seen that the two groups are yielding totally different features. In Group A, the main peak is shifting to left from 13.74° (A1) to 13.72° (A4), whereas in Group B, the main peak is shifting to right from 13.73° (B1) to 13.94° (B4). This shift in the peak reveals the change in structural parameters like crystallite size and lattice strain. As calculated in Group A, with increase in temperature, FWHM increases, crystallite size decreases, lattice increases and crystallinity decreases. However, in Group B, with increase in annealing time, FWHM decreases, crystallite size increases, lattice strain decreases and crystallinity decreases. The crystallinity of the absorber layer plays a vital role in the stability of the device. Thus, when annealing temperature and time both increases, the crystallinity decreases, thus resulting in the stability degradation of both the CH$_3$NH$_3$PbI$_3$ layer and the solar cell [7].

As shown in figure 3 (a), the A3 and A4 samples show decomposition of CH$_3$NH$_3$PbI$_3$ to PbI$_2$, which is in accordance with the EDXRF data, which depicts that decrease in I:Pb ratio results in formation of PbI$_2$ [4]. However, as observed in the EDXRF data of group B, there is an increase in I:Pb ratio, which marks the formation of hydrate. But in the XRD spectra of Group B, as shown in figure 3 (b), no presence of hydrate compound is observed. This is basically due to the reforming back property of the obtained hydrate. However, the graphs of group B seem to be distorted with peaks being sharp but with low intensity. Thus, it can be commented that with an increase in temperature, the CH$_3$NH$_3$PbI$_3$ decomposes to PbI$_2$, and with an increase in annealing time, the CH$_3$NH$_3$PbI$_3$ peaks show degradation. As reported, the annealing time should be appropriate in order to eliminate the extra solvent, and it should not be long or short enough to result in degradation [8].

**FIGURE 3.** XRD spectra of the Perovskite samples of (a) Group A, and (b) Group B
TABLE 3. Structural Parameters of CH$_3$NH$_3$PbI$_3$ Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Angle (2θ) (°)</th>
<th>FWHM (β) (°)</th>
<th>Crystallite Size (D) (nm)</th>
<th>Interplanar Spacing (d) (Å)</th>
<th>Crystallinity (%)</th>
<th>Lattice Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>13.74</td>
<td>0.43</td>
<td>19.45</td>
<td>6.44</td>
<td>84.96</td>
<td>0.40</td>
</tr>
<tr>
<td>A2</td>
<td>13.73</td>
<td>0.51</td>
<td>16.40</td>
<td>6.44</td>
<td>82.59</td>
<td>0.63</td>
</tr>
<tr>
<td>A3</td>
<td>13.72</td>
<td>0.51</td>
<td>16.40</td>
<td>6.45</td>
<td>71.77</td>
<td>0.79</td>
</tr>
<tr>
<td>A4</td>
<td>13.72</td>
<td>0.62</td>
<td>13.49</td>
<td>6.45</td>
<td>67.33</td>
<td>1.34</td>
</tr>
<tr>
<td>B1</td>
<td>13.73</td>
<td>0.51</td>
<td>16.40</td>
<td>6.44</td>
<td>82.59</td>
<td>0.63</td>
</tr>
<tr>
<td>B2</td>
<td>13.85</td>
<td>0.51</td>
<td>16.40</td>
<td>6.40</td>
<td>82.58</td>
<td>0.57</td>
</tr>
<tr>
<td>B3</td>
<td>13.92</td>
<td>0.46</td>
<td>18.19</td>
<td>6.36</td>
<td>81.43</td>
<td>0.52</td>
</tr>
<tr>
<td>B4</td>
<td>13.94</td>
<td>0.45</td>
<td>18.59</td>
<td>6.34</td>
<td>77.60</td>
<td>0.26</td>
</tr>
</tbody>
</table>

FTIR Analysis

In order to analyse the chemical structure of the CH$_3$NH$_3$PbI$_3$ thin films, FTIR analysis have been done. Figure 4 (a and b) shows the respective FTIR spectra of Group A and B. From the figure, it can be observed that the peaks get smaller with increase in temperature as well as time. The Pb-I bonds are not observed in the IR region, but the bonds related to organic groups are observed in FTIR spectra. The C-H rock, C-H bend, and the stretching bonds O-H, N-H, C-H are observed in almost all samples. A small shift has been noted with change in parameters, which is summarized in table 3. It can be observed that in group A, the wavenumber of C-H rock and O-H stretch decreases with increase in temperature, whereas, C-H and N-H stretch shows a gradual increase. This shifting of the bonds to higher wavenumber is due to molecular vibrational energy [3]. It is also noteworthy that the C-H bend disappears in samples at temperatures 100 °C and 120 °C. However, a different pattern of shift is observed in Group B. As shown in figure 4 (b), the number of peaks get lesser and the peaks also get smaller with increase in annealing time. It can be observed that there is a gradual decrease in C-H bending and stretching, with an increase in N-H and O-H stretching. It has been reported that, the N-H stretch vibrations are known for their sensitivity to the strength of interaction between Methylammonium (MA) and iodine (I). The hydrogen bonds between N-H and I are affected by O-H oscillations of water molecule [9]. Thus, increase in O-H stretch bonds with increase in annealing time, reveals the formation of a hydrate compound, which is in accordance with the EDXRF data.

TABLE 4. Summary of Various Bonds Observed in Ftir Spectra

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>C-H Rock (cm$^{-1}$)</th>
<th>C-H Bend (cm$^{-1}$)</th>
<th>C-H Stretch (cm$^{-1}$)</th>
<th>N-H Stretch (cm$^{-1}$)</th>
<th>O-H Stretch (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>705</td>
<td>1450</td>
<td>2931</td>
<td>3020</td>
<td>3679</td>
</tr>
<tr>
<td>A2</td>
<td>696</td>
<td>-</td>
<td>2931</td>
<td>3026</td>
<td>3673</td>
</tr>
<tr>
<td>A3</td>
<td>690</td>
<td>-</td>
<td>2934</td>
<td>3032</td>
<td>3667</td>
</tr>
<tr>
<td>A4</td>
<td>687</td>
<td>1465</td>
<td>2942</td>
<td>3044</td>
<td>3649</td>
</tr>
<tr>
<td>B1</td>
<td>696</td>
<td>-</td>
<td>2931</td>
<td>3026</td>
<td>3673</td>
</tr>
<tr>
<td>B2</td>
<td>697</td>
<td>1487</td>
<td>2919</td>
<td>3021</td>
<td>-</td>
</tr>
<tr>
<td>B3</td>
<td>697</td>
<td>1488</td>
<td>2909</td>
<td>3034</td>
<td>3789</td>
</tr>
<tr>
<td>B4</td>
<td>698</td>
<td>1453</td>
<td>2909</td>
<td>3032</td>
<td>3810</td>
</tr>
</tbody>
</table>
CONCLUSION

In the present study, it has been observed that the I:Pb ratio decreases with increase in temperature, marking the formation of PbI$_2$, which is confirmed by the XRD spectra of higher temperature annealed CH$_3$NH$_3$PbI$_3$ thin films. The decomposition of CH$_3$NH$_3$PbI$_3$ to PbI$_2$ has been observed in the samples annealed at 120 °C and 140 °C. The I:Pb ratio increases with increase in the annealing time duration, marking the formation of hydrate. This has been confirmed in the FTIR analysis by the increase in the O-H stretching bonds in the samples annealed for 10, 15 and 20 minutes. The band gaps of the samples are found to be around 1.5 eV. But a double band gap characteristic is observed in the samples annealed for 15 and 20 minutes. Therefore, it can be concluded that, the annealing temperature and time should be appropriately selected in order to remove the extra solvent in the film along with avoiding degradation. The sample with annealing temperature 100 °C and annealing time 5 minutes holds the maximum potential for device applications.

REFERENCES


