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We have presented a detailed analysis of phase transition kinetics and binding energy states of solution processed methylammonium lead iodide (MAPbI$_3$) thin films prepared at ambient conditions and annealed at different elevated temperatures. The processing temperature and environmental conditions predominantly control the crystal structure and surface morphology of MAPbI$_3$ thin films. The structural transformation from tetragonal to cubic occurs at 60°C for 30 minutes annealing time while 10 minutes annealed films posses tetragonal crystal structure. The transformed phase is greatly intact even at higher annealing temperature of 150°C and time of 2 hours. The charge transfer interaction between Pb 4f and I 3d oxidation state is quantified by the XPS.

1. Introduction

World’s energy consumption is moving towards the renewable energy resources, mainly the solar energy due to environmental concern related to global warming and sustainability. The challenge has always been in the conversion of solar energy into an electrical energy with efficient and cost-effective way. Though, crystalline silicon dominates the photovoltaic industry with efficiencies over 20%, it remains relatively expensive to manufacture. In silicon photovoltaics, the substantial reduction of manufacturing cost is highly required to assure the mass production and fulfill future energy consumption demand. Recently, single or multiple solution processes have been introduced to fabricate dye-sensitized quantum dot, and polymer solar cells at low temperature and the manufacturing cost of the cells are cheaper than silicon cells; however, they still suffer from long-term stability and low power conversion efficiency (PCE) as a result of fundamental energy losses occurring at heterojunction interface.

Perovskite solar cells have emerged as a leader of the photovoltaic technology and it seems to contribute large scale solar energy production due to its high PCE and compatibility with scalable processes are promising an alternative to conventional silicon solar cells. Especially, the MAPbI$_3$ perovskite light harvester having the direct band gap of about 1.45–1.6 eV, high carrier mobility, large absorption coefficients and ability to form very high quality crystals rapidly at low temperature are added advantages. The introduction of MAPbI$_3$ as a sensitizer in an electrolyte based dye-sensitized solar cells (DSCs) is marked as the beginning of perovskite-based photovoltaic technology. Consequently, the planar heterojunctions and mesoscopic metal oxide structured solar cells boot with higher concert. Since the first work published on MAPbI$_3$ perovskite, a set of prominent ideas stimulated over past few years with different feasible methodologies focused only to achieve higher efficiency, but lacks on identifying the cause of perovskite degradation when exposed to the air.

The hygroscopic nature of methylammonium (MA) cation traps the moisture from the air which increases the crystal size along with contamination. However, moisture is not the only problem for degradation, even the perovskite devices processed in inert (N$_2$) atmosphere also undergoes destabilization. Device interface may also play a crucial role in degradation mechanism. This issue has grown as a big concern to fabricate perovskite-based photovoltaic devices in large scale. It is mainly due to the lack of understanding their physical properties. In this work, we have intensely focused to investigate the phase transition kinetics and surface binding states of MAPbI$_3$ thin films prepared at ambient conditions and processed at different temperatures such as 60°C, 100°C, and 150°C and tried to understand the real issues instigated on the perovskite over the fundamental physical properties beyond the concern of photovoltaic efficiency. Here, we report the MAPbI$_3$ thin film prepared on Fluorine doped tin oxide (FTO) substrate under atmosphere. It is highly challenging task to make the uniform coverage of perovskite film on FTO by the spin coating at ambient atmosphere. Accordingly, we optimized the parameters such as concentration of both methylammonium iodide (MAI) and lead iodide (PbI$_2$), utilized different solvents based on their dielectric constant, spin speed with respect to the number of layers deposited, annealing time and temperature helped us to achieve uniform film coverage with stability. Subsequently, the samples were employed for different physical characterizations to examine the quality of film through the structural and morphological properties. The phase transition occurs at 60°C for
the films annealed for 30 minutes and the noticeable changes in the binding states according to atmospheric effects are discussed in this work.

2. Experimental

2.1 Preparation of MAPbI$_3$ thin film

The FTO substrates (7-10 Ω cm$^{-1}$, Hartford Glass Corporation) were well-cleaned sequentially in an ultrasonic bath with ethanol, acetone and deionized water for 10 minutes followed by drying under N$_2$ gas. All chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. The MAPbI$_3$ perovskite precursor was prepared by dissolving 2:1 molar ratio of MAI and PbI$_2$ in N, N-dimethylformamide (DMF) under stirring at 60 °C for overnight. The MAPbI$_3$ precursor solution was drop casted on FTO for three consecutive cycles at an optimized spin speed of 2000 rpm for 30 s. After spin coating, each set of films were annealed at 60 °C, 100 °C and 150 °C in air for 10, 30, 60 and 120 minutes.

2.2 Characterization

The phase identification of the spin-coated MAPbI$_3$ perovskite films were analysed by X-ray diffraction (XRD; Bruker D8-Advance) with Cu Kα radiation ($\lambda = 1.54054$ Å) source operated at 40 kV and 30 mA in the range 10–60°. UV-visible spectroscopy was performed by using an Optizen 3220 UV spectrophotometer in the 400-800 nm wavelength range. The morphology of the films was observed using a field-emission scanning electron microscopy (FE-SEM) (Hitachi, model S-4700) operated at 15 kV, 150W. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific (U.K) ESCALAB 250 system with monochromatic Al Kα radiation of 1486.6 eV and with an electron take off angle of 45°. The measurement was conducted without ion etching, to avoid reconfiguration of the bonds. The pressure of the chamber was kept at 10$^{-10}$ Torr during the measurement. The survey spectrum was scanned in the binding energy (BE) range 100 - 1200 eV in steps of 1 eV with spot size 500 μm. All of the obtained binding energy is compensated with the core level peak of adventitious carbon (C 1s) at 284.6 eV, fixed as a reference. We used the lowest possible number of components to fit the data satisfactorily. The uncertainty in binding energy position was within 0.05 eV for a particular component. Peak fitting and quantitative analysis were done using Casa XPS program (Casa Software Ltd) and the results were justified by average matrix relative sensitivity factor (AM-RSF) with respect to peak area and atomic sensitivity factor of the identified components. The binding energy of the identified components was assigned from NIST X-ray Photoelectron Spectroscopy Database (NIST Standard Reference Database 20, Version 4.1).

3. Results and discussion

3.1 Structural analysis

XRD analysis was carried out to understand the effect of temperature on structural properties of MAPbI$_3$ films processed in atmospheric conditions. Figure 1(a) shows the XRD for the MAPbI$_3$ films annealed at 60 °C, 100 °C and 150 °C for 10 minutes. The diffraction peaks of FTO at 26.52, 33.67, and 37.75° are assigned to (222), (314), (200) lattice planes. The MAPbI$_3$ thin films have preferential orientation with a=8.789Å and c=12.567Å axis for tetragonal perovskite structure at RT with (110), (202), (220), (310), (224), (314), (330) lattice planes corresponding to 14.10, 24.5, 28.50, 40.55, 43.17 and 44.60° (2θ) diffraction positions respectively. The indexing was performed by the relative combination of planar-spacing and Bragg’s law, which determine the unit cell parameters from the peak positions. The intensity of MAPbI$_3$ characteristic peaks gradually raised with reduced full width at half maximum when annealing temperature is increased along with few peaks disappeared and new minor peaks appear at 150 °C due to elimination of defects. The substantial changes in the MAPbI$_3$ perovskite crystal structure from tetragonal to cubic occurs at 60 °C through unit cell distortion and maintained the crystal structure even at 150 °C with increased grain size. Figure 1(b) shows XRD spectra of MAPbI$_3$ thin films annealed at 60 °C for 30 and 60 minutes. Even though, the crystal growth has been initiated at RT itself, the film structure is significantly reformed at 60 °C annealed for 30 minutes. It is observed that shifting of MAPbI$_3$ characteristic peaks occur towards the lower angles and new peaks appear at (111), (112), (004), (312), (324) lattice planes corresponding to 19.59, 20.85, 28.80, 46.24, 46.75°(2θ) positions respectively. The diffraction peak of (220) split into (004) and (220) crystal planes for the films annealed at 60 °C for 30 minutes indicates the structural transformation of MAPbI$_3$ from the tetragonal to cubic crystal structure and is shown in Figure 2. However, there is no significant change in the crystal structure is observed even when the annealing time is increased up to 120 minutes at 60 °C. The parallel results are obtained for the higher annealing temperatures of 100 °C and 150 °C.
°C as is shown in Figure 3. The phase transformation of perovskite from tetragonal to cubic is schematically represented in Figure 4. The transformed phase is highly conserved at longer annealing time of 120 minutes and higher annealing temperature of 150 °C. The phase transition of perovskite is mainly due to its low tolerance factor of 0.83 and the alteration of its bandgap upon annealing. The tetragonal crystal structure exhibited below 60 °C is distorted by the thermal vibration of lattice planes upon annealing by the rotational disorder of MA ions due to short relaxation and the atomic disordering of iodide (I) ions which may decrease or increase its symmetry in the way of expanded or contracted.  

Figure 3. XRD spectra of MAPbI thin films annealed at 100 °C and 150 °C for 60 and 120 minutes.

Figure 4. Graphical images of structural transformation of MAPbI, perovskite from tetragonal to cubic phase.

The tetragonal symmetry has been distorted only along one preferential axis which changes the unit cell dimensions and generates more diffraction lines as well as shift in its peak positions. The average grain sizes were calculated using Scherrer’s formula (Equation (A) in supplementary) and are 36.0, 39, 47.7, 59.1 nm respectively for 10, 30, 60 and 120 minutes annealed films at 60 °C.

3.2 Optical and morphological studies

UV-visible spectroscopy studies were carried out to investigate thermal effects on electronic band gap of MAPbI films. Figure 5 (a) shows the absorption spectra of MAPbI thin films annealed for 10 minutes at different temperatures. The exciton state in the inorganic layers which deliver a sharp peak even at RT. The absorption spectra exhibits a very wide spectral response over the entire visible range and the exciton peak appeared in the range of 400 - 450 nm and onset of absorption is between 700 - 800 nm. Figure 5 (b) shows the absorption spectra of films annealed at 60 °C for 10, 30, 60 and 120 minutes to further examine the variation of the band gap. The Figure 5 shows the UV-Visible spectra of MAPbI, perovskite annealed at 100 °C and 150 °C for 1 and 2 hours and shows a very little influence on absorption and band gap energy. It is observed that the absorption onset shifts towards the longer wavelength region with increased annealing temperature and time. The reduced optical bandgap energy with respect to annealing temperature and time is because of the increased grain size. The band gap of the MAPbI films were estimated from absorption spectrum fitting (ASF) method where the absorption coefficient as a function of wavelength (λ) is,

$$\alpha(\lambda) = B(\lambda c)^{-m} \left( \frac{\lambda}{\lambda_a} \right)^g$$  (1)

Here, $\lambda_a$, c, and h are wavelength corresponding to the optical bandgap, velocity of light and Planck’s constant, respectively. Using Beer-Lambert’s law in equation (1),

$$Abs(\lambda) = B_1 \left( \frac{\lambda}{\lambda_a} \right)^g + B_2$$  (2)

Here $B_1 = \left( \frac{\lambda G}{2} \right) \frac{d}{300}$ and $B_2$ are the constants

Equation 2 was used to estimate the bandgap by ASF method without the need of film thickness. The value of band gap in eV, can be calculated from the parameter $\lambda_g$ using,

$$E_{gap}^{opt} = \left( \frac{1239.83}{\lambda_g} \right)$$  (3)

The $\lambda_g$ value can be calculated from Figure 6(a-d) by extrapolating the linear region of $\left( \frac{\lambda}{\lambda_a} \right)^g$ vs $\left( \frac{1}{\lambda_a} \right)$ curve at $\left( \frac{\lambda}{\lambda_a} \right)^g = 0$.

Figure 6 shows the band gap energy for the films prepared at RT and annealed at 60 °C, 100 °C, and 150 °C for 10 minutes and are 1.73, 1.66, 1.62, and 1.56 eV respectively. Figure S1 shows the perovskite films annealed at 100 °C and 150 °C for 1 and 2 hours with minor changes in the bandgap of 1.55, 1.53, 1.52, and 1.51 eV respectively. Upon annealing, the bandgap may also reduce due to the thermal vibrations of the organic (MA) crystal ions which weakly interact with the inorganic species (Pb) through the intermolecular hydrogen bonding occurring through the NH$^+$ group which predominantly reduce the surface energy of organic-inorganic interfaces. It is also suggested that longer annealing time increases the grain size by the agglomeration of grains at the surface of the film as confirmed in XRD and morphological analysis.
The SEM images (Figure 7 (a-d)) depict the thermal effects on the surface morphology of the MAPbI$_3$ perovskite at RT and annealed at 60 °C, 100 °C and 150 °C for 10 minutes under ambient atmosphere. Instantly after spin coating, the film coverage is quite high with pinholes as shown in Figure 7(a). Upon annealing at 60 °C, the uniformity was condensed with decrease in number of pinholes and form tightly packed agglomerated grains at the surface until the crystallization is completed at the bottom layer of MAPbI$_3$. If the annealing temperature is increased to 100 °C, the size of the grains increased with voids in between due to agglomeration of small islands to become larger crystallites as is shown in Figure 7(c). The formation of still larger crystallites associated with voids in between is observed at 150 °C (Figure 7d). The change in surface morphology due to annealing is mainly caused by the excess surface energy gained from lattice which tends to increase the rate of perovskite crystallization at the organic-inorganic interfaces of MAPbI$_3$ in air.\cite{34}

The figure 7 (e-f) illustrates that the morphological transformation of MAPbI$_3$ perovskite from agglomerated crystals (Figure 7 e) to densely arranged needle like crystals. It is suggested that the change in annealing time facilitates the surface tension to upsurge the rate of perovskite crystallization by stretching the bonds at the surface of MAPbI$_3$ film.\cite{35, 36} This extended surface energy may be minimized if the atoms have enough energy and time to diffuse to a lower energy nucleation sites.\cite{37, 38} At low annealing temperature, large number of critical nucleation sites are formed that tends to form smaller crystallites and at higher annealing temperature result fewer nucleation sites roots to the formation of larger crystalline at the surface.
3.3 Surface analysis of MAPbI$_3$ Perovskites

The XPS spectra were recorded to investigate the interaction of organic-inorganic species in MAPbI$_3$ thin film and to understand the impact of annealing on elemental chemical states and relative surface elemental composition. The XPS survey spectra are shown in Figure S2. The small features at binding energies of 284.7, 401.0 and 531.0 eV corresponds to the photoelectron peaks of C 1s, N 1s, and O 1s respectively. The doublet peaks of I, Pb are located at 618, 137 eV respectively with spin orbit splitting. The elemental surface composition of the MAPbI$_3$ is depicted in Figure S2.

3.3.1 High resolution X-ray photoelectron (HRXPS) spectra of MAPbI$_3$ thin films

High resolution XPS spectra were acquired over much restricted ranges to evaluate the thermal effects on different chemical states of the same element with the atomic concentration. Typically, the atomic concentration of the element was extracted from the core-level spectra using CASA XPS software using the average matrix relative sensitivity factors (AM-RSFs) equation B given in supplementary (Figure S3). XPS data fitted with Gaussian-Lorentzian (30 % Gaussian) functions and Shirley type background. The core-level spectra of C 1s, O 1s, and N 1s for the MAPbI$_3$ perovskite at RT and annealed at 60 °C, 100 °C, and 150 °C for 10 minutes are shown in Figure 9(a-l). The deconvoluted characteristics of carbon peaks exhibited the bound state of carbon species with atmospheric oxygen, shown in Figure 8(a-d). At RT, the peak at 283.17 eV assigned to the aliphatic hydrocarbon (C-H/C-C) and the peak at 283.97 eV corresponds to hydroxyls (C-O). The next higher binding energy peak at 284.84 eV corresponds to the carbon atoms bonded with single nitrogen atoms (C-N). The carbon adjacent to (C=O) is the most electron withdrawing environment that corresponds to the peak at 285.81. This distortion causes the variation of atomic concentration of C 1s components and is given inset in Figures 8(a-d).

The hygroscopic nature of MAPbI$_3$ thin films were subjected to the surface oxidation when exposed to air. Figure 8(e-h) show the O 1s core levels spectra deconvoluted into five oxygen binding states located at 530.51, 531.17, 532.06, 532.16 and 533.22 eV come from weakly adsorbed O molecules in air, hydroxyls (C-O), carbonyls (C=O), (C=OH) and aliphatic O-C-O respectively for RT and annealed at 60 °C, 100 °C, and 150 °C. It is found that MAPbI$_3$ films drastically affected by surface oxidation resulted from the chemisorbed or dissociated oxygen species. It is clear that the variation in atomic percentage of O 1s is mainly attributed to the elimination of weakly bonded organic components at higher annealing temperature. The reduction of chemisorbed O and carbonyl (C-O) species at 150 °C lead to appear O=C=O and O=C=N species at higher binding energy range of 534.64 and 535.42 eV respectively. Figure 8(i-l) shows the XPS N 1s core levels spectra of MAPbI$_3$ films at RT and annealed at 60 °C, 100 °C, and 150 °C for 10 minutes. At RT, the N 1s deconvoluted to three spectral contributions such as single and double bounded nitrogen atoms with carbon atoms (N-C,N=C) and amide ions (-NH$_2$) located at the binding energies 398.70, 398.92, and 399.31 eV respectively. The appearance of amide group (N-C=O) is thermodynamically favourable at 100 °C and 150 °C.

The doublet orbitals of Pb (4f$_{7/2}$ and 4f$_{5/2}$) and I (3d$_{3/2}$ and 3d$_{5/2}$) are quantified with an area ratio of 3:4 and 2:3 and elemental spin orbit splitting (SOS) of 11.5 and 4.8 was fixed respectively with an equal FWHM.
Figure 9. XPS core level spectra of (a-d) I 3d and (e-f) Pb 4f doublets for MAPbI3 thin films at RT and annealed at 60 °C, 100 °C and 150 °C for 10 minutes.

The high resolution XPS spectra of I 3d (annealed at 60 °C for 30 min) is shown in Figure 11(a). Iodine exhibits very strong interaction with atmospheric oxygen since the doublets of 3d_{5/2} and 3d_{3/2} are deconvoluted into three distinguished valence states corresponding to iodide (I^-) at 629.33, 617.83 eV, triiodide (I^3-) at 619.01, 630.49 eV and iodite (IO^-) anion at 620.20, 631.81 eV respectively. The increase in annealing time increased the surface oxidation of iodine and lead to the formation of iodite (IO^-) anion and the I_2^- cation easily reduced to iodide (I^-) anion (Oxidation state of -1) in the MAPbI3 perovskite film.49

4. Conclusion

In this work, we studied the impact of temperature on structural, morphology and optical properties of MAPbI3 films with the help of complementary characterization techniques. MAPbI3 thin films are optimized for low-temperature solution process preparations at the ambient atmospheric condition.
Figure 10. Core-level spectra of a) C 1s, b) O 1s, and c) N 1s for MAPbI$_3$ thin films annealed at 60 °C for 30 minutes.

Figure 11. HRXPS core levels spectra of (a) I 3d and (b) Pb 4f for MAPbI$_3$ thin films annealed at 60 °C for 30 minutes.

Our findings are organized as follows, a) Structural transition from tetragonal to cubic of MAPbI$_3$ films occurred at 60 °C, b) The transformed cubic structure is highly preserved even when annealing temperature is elevated up to 150 °C, c) Larger aggregated grains are formed at the surface of MAPbI$_3$ films at higher annealing temperature and time, d) Changing the annealing time results in distinct morphological variance of MAPbI$_3$ films and e) The variations in binding states with atomic concentration of C 1s, N 1s, O 1s states and I 3d, and Pb 4f doublets states according to annealing temperature were clearly quantified from the XPS core-level spectra. The optimization of MAPbI$_3$ precursor concentration, solution temperature and spin speed would help to get uniform and stable perovskite film on FTO substrate at ambient atmosphere. It is suggested that annealing temperature of 60 °C for 30 minutes is superior to ensure the perovskite crystallization. We conclude that these results offer a feasible way to achieve the better uniformity of MAPbI$_3$ films under atmospheric conditions. This initial effort is to comprehend the physical properties of MAPbI$_3$ thin films and to reveal the challenges associated with the processing of MAPbI$_3$ films in atmosphere. Further devices development and characterizations are under study to get highly efficient perovskite solar cells fabricated in atmospheric conditions without organic hole conducting material to get good stability.
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Notes and references