Synthesis and Characterization of One-Step Spin-Coated Organic Perovskite ($CH_3NH_3PbI_3$) Thin Films for Photovoltaic Applications

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Abstract. In the present work, we have synthesized methylammonium lead iodide($MAPbI_3$)films in ambient air condition using a single step spin coating technique. X-Ray Diffraction (XRD) pattern revealed the formation of perovskite films along with an average grain size of 59.44 nm. Closely packed, uneven grain sizes can be observed in the pin hole free Field Emission Scanning Electron Microscopy (FESEM) image. The calculated value of band gap for $MAPbI_3$ was estimated as 1.581 eV using Tauc's relation. The current-voltage characteristic clearly indicates the ohmic nature of the thin films. The results indicate that the films can be further used for fabrication of low-costperovskite solar cells.

INTRODUCTION

The term perovskite has been named after the Russian mineralogist L. A. Perovski and follows a common structure similar of $CaTiO_3$ (ABX_3 type). In case of the organometallic perovskites following the general chemical formula ABX_3,A represents an organic cation, B stands for divalent metal ion, and X an anion that bonds both of the above. After the pioneer work of Kojima et al. demonstrating the light harvesting properties of organic-inorganic hybrid perovskite, an intensive research has been initiated on the organometallic perovskite materials[1]. From the last decades, perovskites suchas methylammonium lead trihalide ($CH_3NH_3PbX_3$) have gained significant notice in photovoltaicapplication as a result of their low fabrication cost and high efficiency. Perovskite based photovoltaic devices have achieved efficiencies greater than 20% using solution processed fabrication techniques in ambient environment.Among all organometallic halide perovskites, methylammonium lead iodide ($MAPbI_3$) has proved its credibility owing to its direct band gap nature (~1.55eV), high absorption coefficient, ambipolar carrier transport property, large diffusion length, enhanced carrier lifetime, highly efficient charge separation along with simple low-cost fabrication technique[2]. Spin coating has been noted down as the most preferred low-cost synthesis method for preparing $MAPbI_3$ thin films. This widely used perovskite material; methylammonium lead iodide ($CH_3NH_3PbI_3$), has emerged as a game changer material for researchers with regard to the energy issues. Although it is yet not capable to compete with the key player, Silicon photovoltaics because of its stability issues, but still the rapidly increasing efficiencies of perovskite solar cell has provided a light of hope in this regard.Optical properties of thin films are of great importance because of its immense applications in various aforementioned device fabrications.

As far as photovoltaic devices are concerned, one of the technical challenge for commercialization is cost. Processing steps as well as materials are two key factors which always adds up to the cost of these devices. Mostly the vacuum based approaches adds up complexity in the fabrication and causing anincrease in the fabrication cost. Thus the solution based techniques have been widely used for the low temperature, cost-effective fabrication. But poor coverage of perovskite materials continuously deteriorates the photovoltaic performance. So it is essential to find a suitable technique for deposition of as desired smooth surface.Synthesis technique of these films have an equal dominance on the optical and electrical properties of the perovskite films, which must be optimized for best desired results.The present work contributes to the single step synthesis and characterization of optical and electrical properties of the organometallic perovskite absorber.

EXPERIMENTAL DETAILS

Chemicals and Reagents

Hydroiodic acid (HI, 57% w/w aq. solution), Methylamine (CH_5N, 40% w/w aq. solution), Ethanol (C_2H_6O, ACS grade, 94-96%), N,N–Dimethylformamide (C_3H_7NO, 99%) (DMF), Diethyl ether ($C_4H_{10}O$, HPLC grade, 99%) were purchased from Alfa Aesar Chemicals and used as received without any further purification.

Fabrication of $CH_3NH_3PbI_3$ thin films

Methylammonium iodide (MAI) powder was prepared as reported elsewhere[2].To prepare $CH_3NH_3PbI_3$ thin films a single-step deposition (SSD) process via spin-coating was followed. For this purpose, the perovskite absorber solution was synthesized by adding 2.303g of PbI_2 and 0.05g of MAI powder simultaneously in 5ml of DMF and was stirred overnight at 70 °C in ambient air conditions.The solution was filtered by a 0.25μm syringe filter following which a transparent yellow solution was obtained. Toachieve uniform perovskite films of desired thickness, the solution so prepared was spin coated on cleaned Indium Tin Oxide (ITO) coated glass substrates at 6000rpm for 30 secs. The film was dried on a hot plate at 100°C and dark films were obtained as shown in fig. 1(a).

Characterization Techniques

The structural analysis was carried out with the help of Bruker D8 Discover X-Ray diffractometer using monochromatic $CuK_{\alpha 1}$ radiation (λ= 1.5406 A°). The surface morphologies of the samples were analyzedby using ZEISS Supra 55 Field Emission Scanning Electron Microscopy (FESEM) and the elemental composition was verified by means of Energy Dispersive X-ray analysis (EDAX) provided by Oxford instruments. The absorption spectra of the nanostructured thin film were obtained using Agilent Cary 5000 UV-Vis-NIR double beam spectrophotometer. The current-voltage measurements were performed by using a Keithley 2450 source meter. Hall measurements were performed using Ecopia Hall effect measurement at Inter-University Accelerator Centre (IUAC), New Delhi, India.

RESULTS AND DISCUSSION

Structural Properties

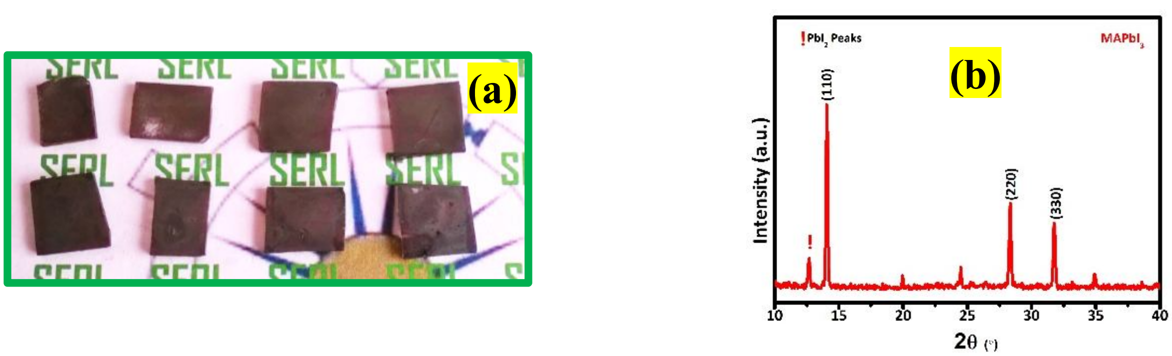

FIGURE 1.(a) Digital images of $MAPbI_3$ (b) XRD pattern of the perovskite thin film

Figure 1(b) depicts the XRD patterns of the SSD perovskite films. A strong peak at 14.06° can be clearly visualized in all the samples, which corresponds to the orthorhombic crystal structure and is in suitable agreement with the earlier reported results[3]. Along with this an additional minor peak at 12.6° can be clearly observed in the XRD pattern, which indicates that a small amount of PbI_2 has remain insoluble during preparation of absorber solution[4]. From the Debye-Scherer equation the crystallite size was calculated as 59.444 nm and the dislocation density is 0.00028299 nm^{-2}.

Morphological Properties

For fabrication of perovskite based solar cells the perovskite materials used as an absorber layer is always sandwiched between n-type and p-type materials. So a smooth, compact, non-porous film is best desirable for avoiding the shunting current between the electron and hole transport layers.Figure 2(a) represents the top view FESEM image of the one-step coated perovskite film. It can be clearly observed that large grain size of $MAPbI_3$ are formed. Besides this the obtained film is homogeneous and densely packed. Figure 2(b) depicts the EDAX image showing the presence all elements except hydrogen (as a lighter element). This also supports the formation of the desired photo absorber materials.

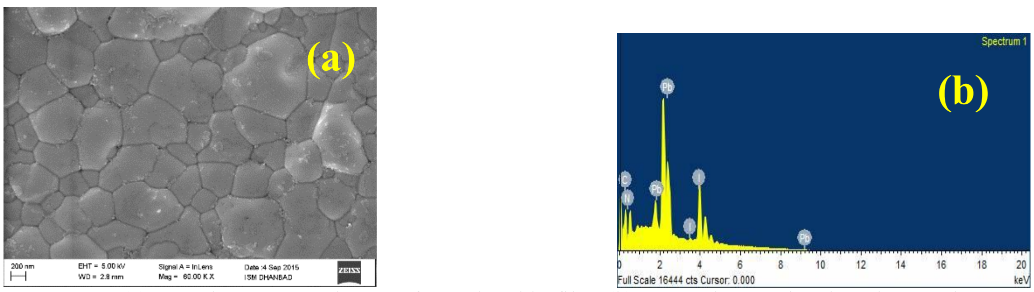

FIGURE 2.(a) Top view FESEM image of $MAPbI_3$ thin film (b) EDAX image showing elemental composition

Optical Properties

Figure 3(a) depicts the absorption spectrum for the $MAPbI_3$ films within a range from 300-800 nm. The spectrum is well contained with two dominant and distinct photo induced peaks, which confirmed the formation of perovskite materials and as reported unanimously by several other groups[4,5].

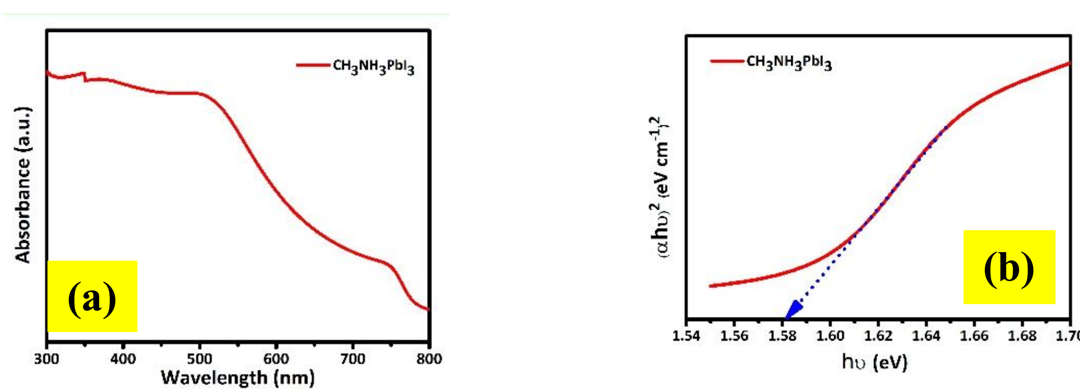

FIGURE 3. (a)Absorbance plot (b) Tauc's plot of the $CH_3NH_3PbI_3$ thin film

Figure 3(b) represents a plot of $(\alpha h\nu)^2$ versus $(h\nu)$ to elucidate the optical band gap of the perovskite materials. The linear region of the spectrum was extrapolated and the band gap of the $MAPbI_3$ layer was estimated to be 1.581 eV. The results obtained in our case are also found to be consistent with earlier reported articles[3,4]. The refractive index (n) as well as dielectric constant (ε) are two important parameters for the evaluation of optical and electrical properties of the materials.The refractive index (n) as well as static dielectric constant (ε) values were calculated as reported earlier[6]. The values so obtained were 2.8749 and 8.26505.

Electrical Properties

Figure 4 shows the I-V characteristics for the single step coated perovskite film. Ohmicbehavior of the sample can be clearly observed from the graph. The SSD $MAPbI_3$ thin films possess p-type conductivity, as confirmed from the conventional Hall based measurements. The carrier concentration was observed to be 6.7 x 10^{13} cm^{-3} along with a mobility of 232.5 $cm^2V^{-1}s^{-1}$.

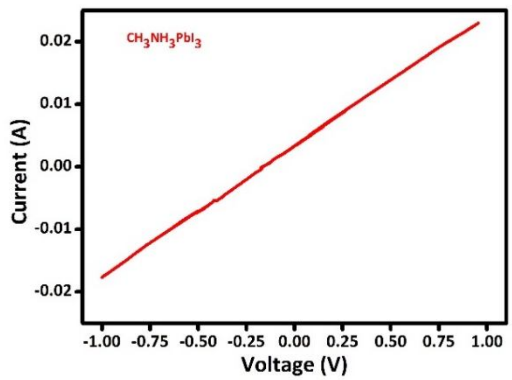

FIGURE 4. I-V characteristics of the $CH_3NH_3PbI_3$ thin film

CONCLUSION

In summary, perovskite thin films were successfully fabricated by a single-step spin-coating technique. The formation of thin films has orthorhombic phase as confirmed from XRD measurements. In the XRD patterns the additional lead iodide peaks can be removed by further optimization. Further the FESEM images clearly depicts the closely packed irregular structures of $MAPbI_3$. The strong absorption in the visible range can be conceived from the absorbance spectra. Hall measurements suggests the hole conduction properties of the materials. The ohmic nature of the thin films was observed from the I-V characteristics.These properties of thin films indicates that they can be further used for solar photovoltaic applications.

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