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STRUCTURE AND OPTICAL CHARACTERIZATION OF ORGANIC-INORGANIC METHYL AMMONIUM LEAD BROMIDE FILM FOR SOLAR CELLS

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Abstract

Structure and optical characterization of organic-inorganic methyl ammonium lead bromide film was fabricated by using spin coating and dipping two-step deposition method. The humidity and temperature effect were characterized to improve the morphology of the perovskite film. To verify the thickness of the film and properties, the spin coating rate, dipping solution concentration and annealing temperature were varied. The consistency with mesoporous structure and the color changes of the film at different stages were initialized. The structure of organic- inorganic lead bromide film was analyzed by using XRD characterization. The nano-range grain size and morphology of the perovskite film were characterized by measuring scanning electron microscopy (SEM). The UV measurement was performed to determine the band-gap of the film to justify the parameter of the photovoltaic performance of the solar cell. Finally, the properties of methyl ammonium lead bromide perovskite film and TiO2 film were optimized by varying the thickness of the TiO2 film for high efficiency solar cell performance.

Keywords: Methyl ammonium leads bromide, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Ultraviolet- Visible (UV- VIS).

Introduction

Photovoltaic devices which convert solar energy to electricity are one of the most important technologies for renewable energy. As a photo absorber and carrier transporter, photovoltaic cells using perovskite. Since perovskite based solar cells not only have high power conversion efficiency but also can be fabricated by a solution processed using cheap materials. Organic-inorganic hybrid solar cells with perovskite-type pigments have been widely fabricated and rapidly studied. Solution-processed hybrid organolead trihalide perovskite solar cells (PSCs) have now achieved 21% certified power

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conversion efficiencies . One of the most important properties of the organic-inorganic perovskite for their use in photovoltaic cells is the possibility to tune their optical properties (e.g band gap). The band gap of CH3NH3PbI2Br perovskite is 1.5 eV and it is used as the light- absorbing material in bilayer solar cells architecture. These perovskite-type materials often have nanostructure in the solar cell devices and it is useful for structure analysis on the perovskite-type crystal. One of the most popular methods is the spin-coating technique for applying thin films onto flat surface. In photovoltaic research, it is used frequently due to its ease of use and relatively low cost. By using SEM characterization and UV measurement, methyl ammonium lead bromide film is analyzed. These are powerful tools for surface morphology and energy band gap of perovskite-type solar cells.

Materials and Methods

Preparation of TiO_2 powder

Starting materials TTIP (Titanium tetra isopropoxide), Ethanol and distilled water were used for TiO_2 powder preparation process. Firstly, 50 ml Ethanol and 50 ml distilled water were mixed and stirred at 60 ºC for 30 mins. And then 15 ml TTIP was added to this solution and stirred at 50 ºC for 10 hrs. As soon as adding process, TTIP becomes small pieces. After 10 minutes later, the solution turned to dark milk color solution. Then, this solution was dried at 60ºC for 2 days and pulverized to get TiO_2 powder. Finally, fine and dry nanostructure TiO_2 powder was successfully prepared. The phase formation of the raw and cleaned TiO_2 powder was identified by XRD diffractometer.

Preparation of TiO_2 solution and Film

Titanium dioxide 1g and ethanol 2 g were mixed and stirred by magnetic stirred at room temperature for one hour. After that this solution was pasted on the glass substrates at 2500 rpm for 30 s by using spin coating method. This solution process was performed two times. After the two-circles layer coating process, the substrate was annealed at 80 ºC for 15 mins.

Methyl Ammonium Iodide (MAI) Solution for Dip Coating

Methyl ammonium iodide was formed by doing several steps. CH3NH3I was synthesized by reacting methylamine (33wt% in ethanol) and hydroiodic acid (57wt% in water). Firstly, 7 ml of methylamine was put into the beaker. Then the temperature 3 was adjusted to stabilize at 0 ºC. Then 7.5 ml of hydroiodic acid (HI) was drop wised into the methylamine solution at 0 ºC for 10 min. The solution was slightly changed to light yellow while the dropping time. That solution was stirred at 0ºC for 2 hrs. After stirring 30 mins, the solution was changed to dark yellow color. When the stirring time was finished, the precipitate was collected by removing the solvents at 60 ºC for 2 hrs. The solution was changed to dark brown color after heating 30 mins. When the evaporation time was nearly finished, the solution was getting boiled and changes from solution to semi MAI solid. Then the obtained precipitate was filtered and washed diethyl ether for several times to remove any impurities. The light brown MAI was resulted and called methyl ammonium iodide. Then CH3NH3I was put into the vacuum oven at 100 ºC about one day to get the MAI powder. Lead II bromide (PbBr2) and dimethylformamide (DMF) solution pasted on the three glass substrates and MAI with isopropanol have been used for dipping. Firstly, 3 substrates were heated at 70 ºC for 30 mins. Then these three samples were dipped in the MAI solution for an hour. As soon as dipping, the glass substrate are turned to light brown. Due to humidity, the color of the substrates were changed when they were heated at 70 ºC for 30 min. Finally, CH3NH3PbI2Br perovskite coated layer were completely fabricated.

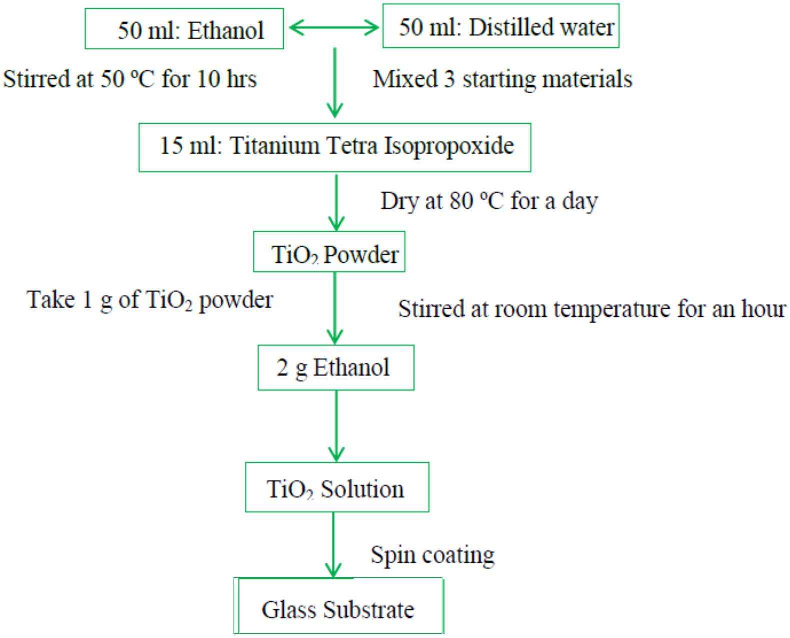

Figure1: Preparation of TiO_2 electron collection layer

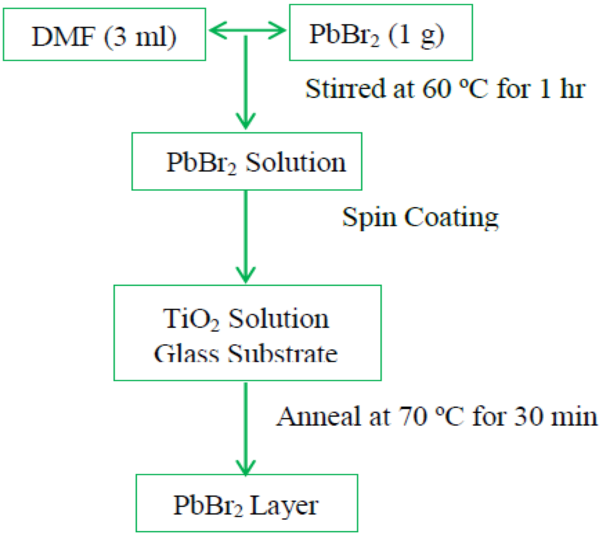

Figure 2: Preparation of spin coating for $PbBr_2$ layer

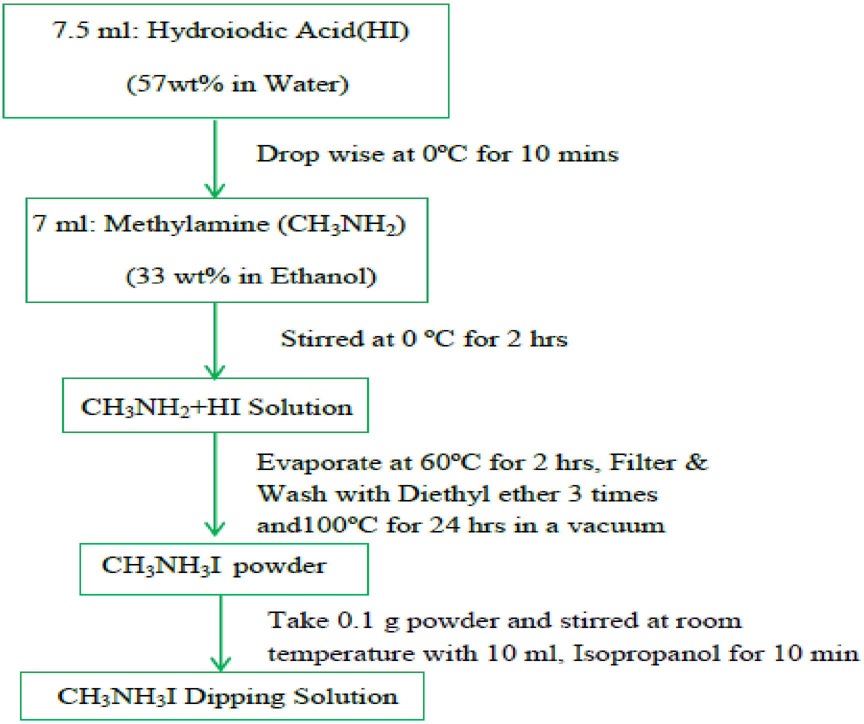

Figure 3: Preparation of methyl ammonium iodide CH_3NH_3I solutions for dipping process

Results and Discussion

XRD Method

For determining the crystal structure of materials, X-Ray Diffraction methods are the most effective methods. By Bragg’s law, the relationship is satisfied.

$$n\lambda = 2d\sin\theta$$

λ = the wavelength of the incident X-ray beam

The path difference depends on the incident angle and the spacing between the parallel crystal planes (d). The plane spacing of cubic crystal relates to the lattice parameter (a) by the following equation

$$d = \frac{a}{h^2+k^2+l^2}$$

The crystallite size can be estimated using the Scherrer equation

$$D = \frac{ky}{B\cos\theta}$$

Table 1: The crystallite size of electrons collection layers for TiO_2 at 2500 rpm

No	2-Theta	(hkl)	FWHM	Crystallite size
1	25.9413	(1 0 1)	1.6111	48 nm
2	37.9255	(1 0 3)	1.6111	48 nm
3	39.5673	(1 1 2)	1.6111	48 nm
Average				48 nm

Table 2: XRD parameters of $PbBr_2$ crystallite size at different spinning rate

No	Spinning rate	2-Theta	(hkl)	FWHM	Crystallite size
1	3000 rpm	14.4243	(0 1 1)	0.2054	38.3 nm
2	3500 rpm	14.3831	(0 1 1)	0.2208	35.5 nm
3	4000 rpm	30.1803	(0 1 3)	0.5759	34.3 nm
Average					36.03 nm

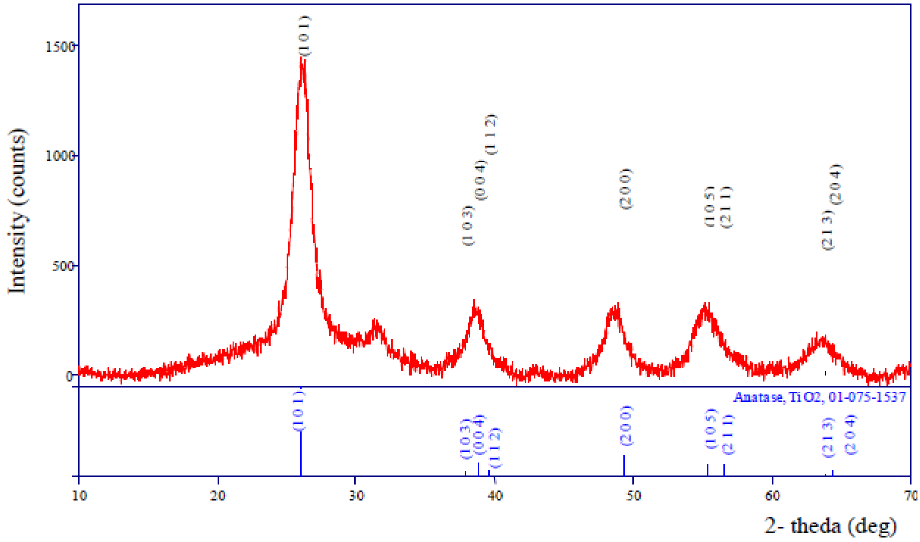

Figure 4: XRD spectrum of TiO_2 powder at spinning rate 2500 rpm

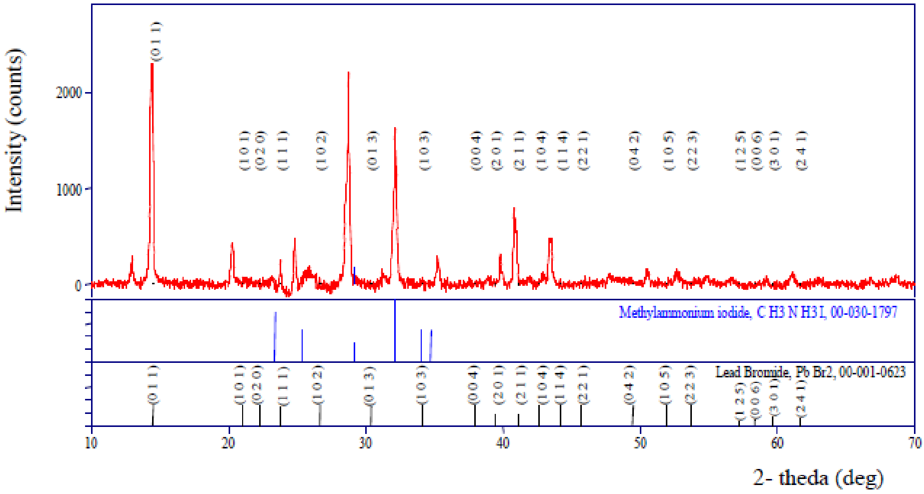

Figure 5: XRD spectrum of $CH_3NH_3PbI_2Br$ perovskite layer at spinning rate 3000 rpm

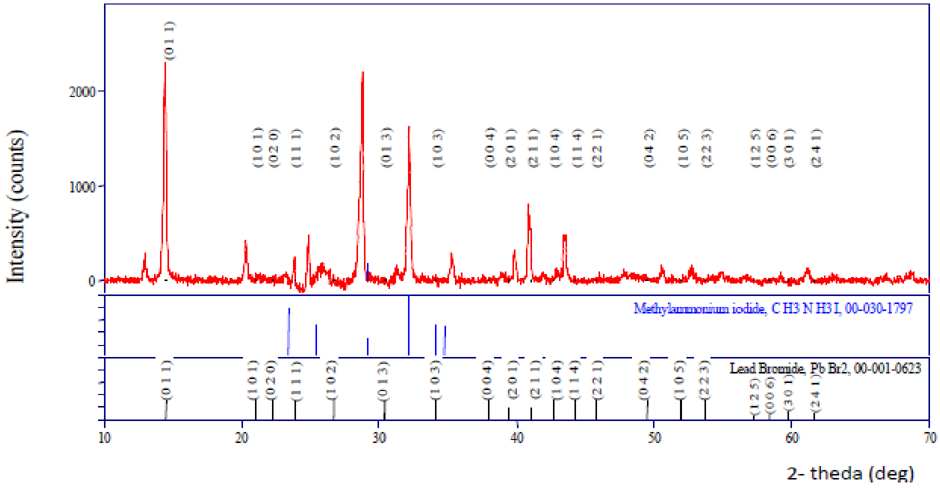

Figure 6: XRD spectrum of CH3NH3PbI2Br perovskite layer at spinning rate 3500 rpm

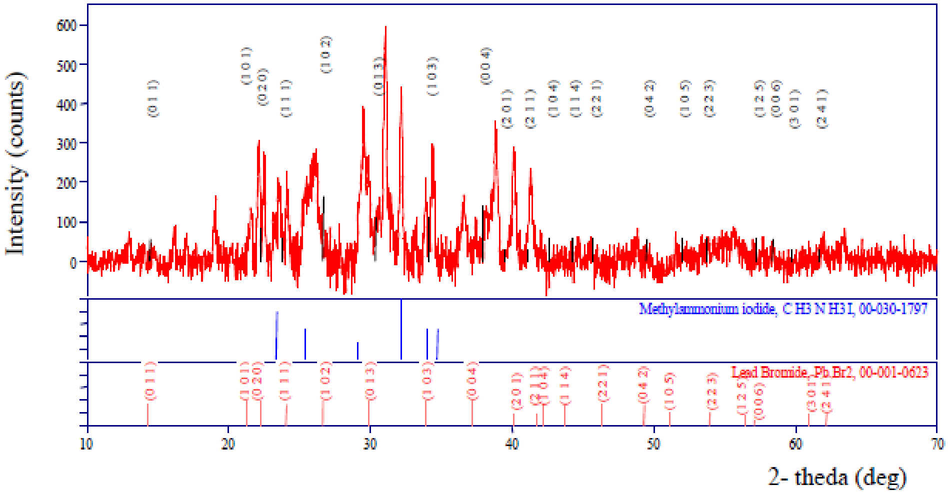

Figure 7: XRD spectrum of CH3NH3PbI2Br perovskite layer at spinning rate 4000 rpm

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a type of electrons microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain characteristic information of the samples surface topography, morphology and chemical composition. The electron beam is scanned in a raster scan pattern and the beam position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum chamber. The most common SEM mode is detection of secondary electrons emitted by atoms excited by electrons beam. The number of secondary electrons that can be detected depends on the specimen topography. By scanning the sample and collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created. The micrographs of thin films were obtained using JEOL Scanning Electron Microscope model JSM – 5610 LV.

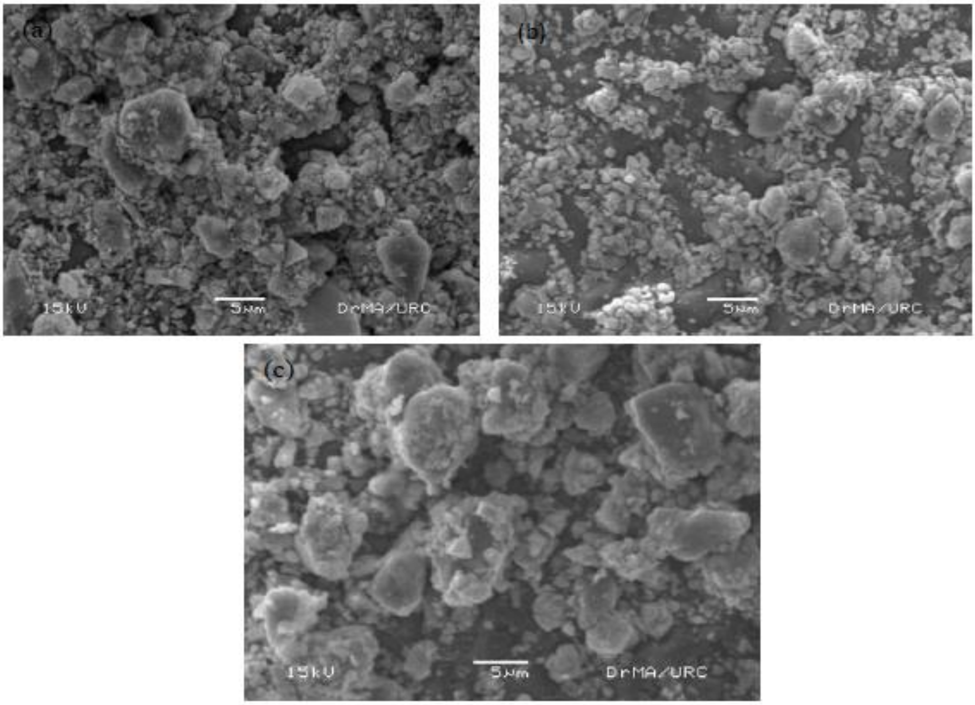

Figure 8: SEM images of PbBr2 perovskite layer spinning rate (a) at 3000 rpm (b) at 3500 rpm and (c) at 4000 rpm

Ultraviolet- Visible (UV- VIS)

UV – VIS refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet visible spectral region. It uses in the light visible and adjacent range. The absorption or reflectance in the visible range directly affects the color of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state while the absorption measures transitions from ground state to the excited state.

For the optical characterization of CH3NH3PbI2Br perovskite, optical absorption spectra of the perovskite layers were investigated with SHIMADZU UV- 1800 Spectrophotometer in the wavelength range of 300 nm to 900 nm. The optical energy band gap, Eg of the perovskite was measured from the absorption spectrum. The band gap is important to enhance the efficiency of photovoltaic cells as it determines the absorbing portion of the solar spectrum.

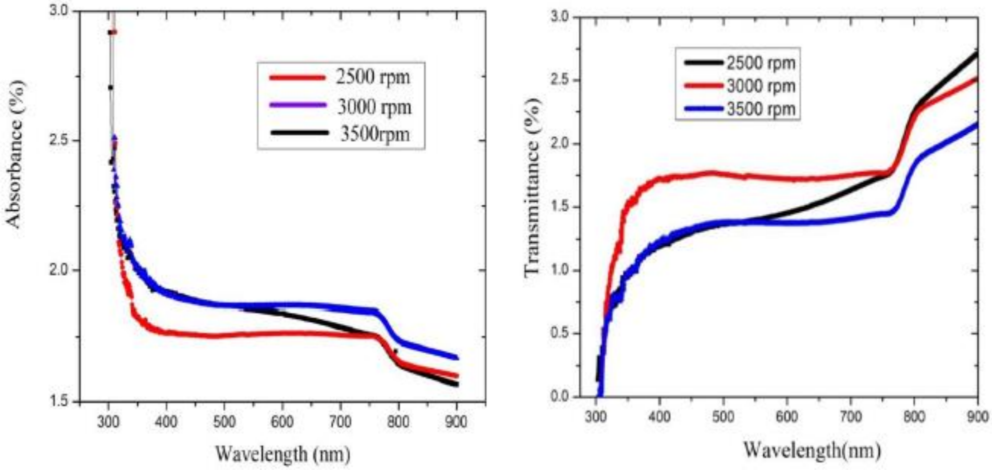

Figure 9: Comparison of UV- Vis spectra at different spin coating rates of PbBr2

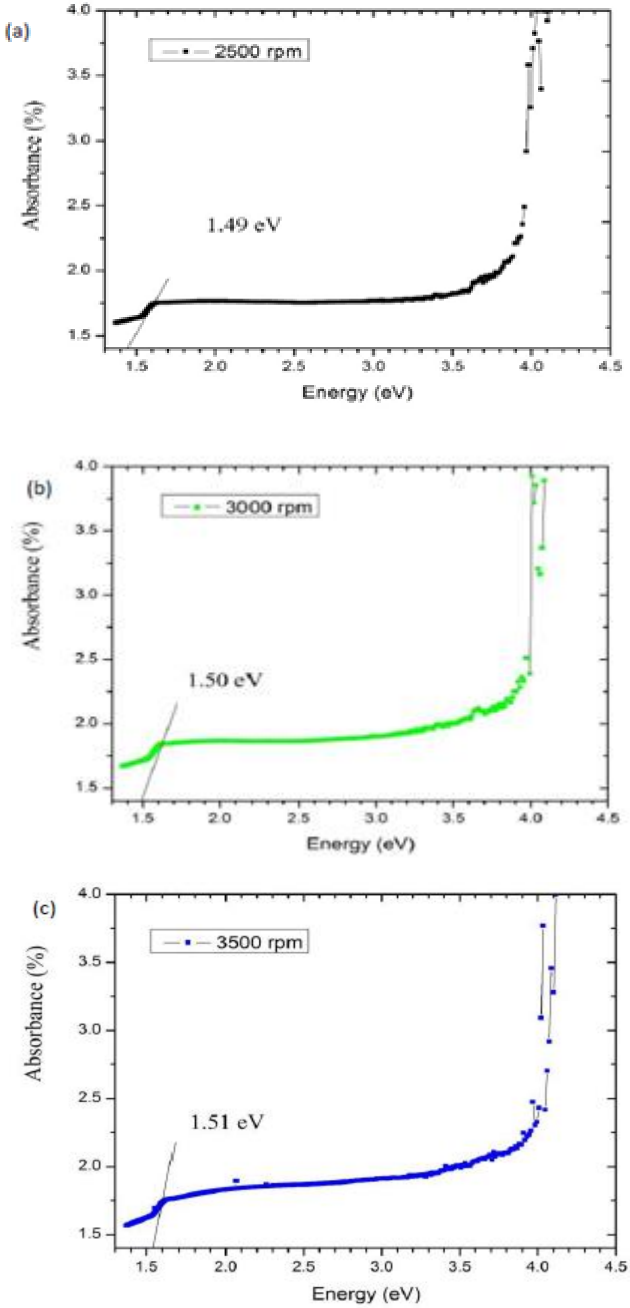

Figure 10: Energy band gap of $CH_3NH_3PbI_2Br$ perovskite layer (a) at 2500 rpm $PbBr_2$ (b) at 3000 rpm $PbBr_2$ (c) at 3500 rpm $PbBr_2$

Structure and optical characterization of organic- inorganic methyl ammonium lead bromide film was prepared by using spin coating and dipping two-step deposition method. Table 1 shows the XRD patterns of TiO_2 powder at spinning rate 2500 rpm for 30 s, the powder was performed at pure anatase phase of tetragonal structure. For XRD characterization, both TiO_2 and $CH_3NH_3PbI_2Br$ are coated by using spin coating and dipping technique as two- step deposition method on glass substrate. The spin coating rates were increased for three samples and the dipping rate was fixed at 1 hr. The spin coating rate is increased, the smaller crystallite size has been characterized from XRD pattern of $CH_3NH_3PbI_2Br$ layer. $CH_3NH_3PbI_2Br$ perovskite coating process, the color rapidly changes from light yellow to light brown color. This effect mentions sensitive to humidity of $CH_3NH_3PbI_2Br$ organometal halide material.

SEM images of perovskite solar cells are shown in figure 8.The surface morphology of perovskite are imaged by using scanning electron microscopy. The average grain sizes of the $CH_3NH_3PbI_2Br$ layer are 1.74 μm at 3000 rpm, 2.12 μm at 3500 rpm and 1.77 μm at 4000 rpm. The bigger grain size is observed in $PbBr_2$ spinning rate at 3500 rpm. The best surface morphology of perovskite layer is 1.74 μm at 3000 rpm. This is one of the important properties of perovskite layer to fabricate perovskite solar cell. To check the variation of the optical properties in the hybrid perovskite, the UV absorption spectra are measured as shown in figure 9. The energy band gap and absorption peaks are characterized from these absorption spectra. The absorbance spectra are shifted from 817.55 nm to 828.53 nm. So the wavelength tuning is observed by varying the spin coating rates. This is the good results for the actual applications. Figure 10 shows the energy band gap of perovskite layers. The results of the energy band gap are 1.49 eV at 2500 rpm, 1.50 eV at 3000 rpm and 1.51 eV at 3500 rpm for perovskite layers. The band gaps of $CH_3NH_3PbI_2Br$ perovskite are reliable range compare with the band gap of typical perovskite film 1.5 eV in all spinning rates.

Conclusion

Structure and optical characterization of organic- inorganic methyl ammonium lead bromide film was fabricated by using spin coating and dipping two-step deposition method. Methyl ammonium lead bromide perovskite layer was fabricated on TiO_2 electron collection layer and glass substrate. The dipping time and annealing temperature are fixed and the variation of spinning rate was characterized. The 12 crystallite size of TiO_2 layer was characterized 48 nm. From the first step spin coating and second step dipping $CH_3NH_3PbI_2Br$ layer, the crystallite size was characterized 38.3 nm, 35.5 nm and 34.3 nm for three samples. The better spinning rate was configured at 4000 rpm for perovskite layer. The dependence of crystallite size of perovskite on spinning rate and influence of humidity was characterized. The average grain sizes of the $CH_3NH_3PbI_2Br$ perovskite are slightly changed and the best surface morphology of the perovskite layer is 1.74 μm at 3000 rpm. The results of the energy band gap are 1.49 eV at 2500 rpm, 1.50 eV at 3000 rpm and 1.51 eV at 3500 rpm for perovskite layers. The band gaps of $CH_3NH_3PbI_2Br$ perovskite are reliable range compare with the band gap of typical perovskite film 1.5 eV in all spinning rates.

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