J. Myanmar Acad. Arts Sci. 2019 **Vol. XVII. No.2A**

CHARACTERIZATION OF METHYL AMMONIUM LEAD IODIDE PEROVSKITE FILM BY TWO-STEP DEPOSITION METHOD

Aye Aye Kay Kyi[1], Soe Soe Han[2], May Myint Si[3]

Abstract

Methyl ammonium lead iodide perovskite films were fabricated by using two-step deposition method. PbI_2 film was coated by using spin coating method. Making a high quality PbI_2 film was easier and better to fabricate a good perovskite film.The spin coating rate, the concentration of the solution and the dipping time was varied to analyze the properties of the perovskite films. The structure of the methyl ammonium lead iodide perovskite films was analyzed by using XRD characterization. The color change of the films at different stages and the mesoporous structure of the film in two-step deposition method were evaluated. The morphology of the perovskite film was characterized by scanning electron microscopy (SEM). The band-gap of the film was analyzed to determine the parameter of the photovoltaic performance of the solar cell by using UV measurement. Finally, the combination of light harvesting layer methyl ammonium lead iodide perovskite film and electron transporting layer TiO_2 film was summarized for perovskite solar cell performance.

Keywords: Methyl ammonium lead iodide, X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-VIS

Introduction

Organic-inorganic lead halide-based hybrid perovskites have recently emerged as a promising photo-absorber material for efficient and low-cost solar cells. Solar cells with a perovskite structure have high conversion efficiencies and stability as the organic solar cells. The first perovskite solar cell was demonstrated by Miyasaka et al., in 2009. The perovskite solar cells were based on the structure of the solid state dye sensitized solar cell by using perovskite instead of dye as light absorber. Perovskites are absorber materials that have the ABX_3 crystal structure. The most commonly studied perovskite absorber is methyl ammonium lead trihalide ($CH_3NH_3PbX_3$, where X is a halogen atom such as iodine, bromine or chlorine), with an optical bandgap

1. Assistant Lecturer, Department of Physics, Dagon University

2. Dr, Lecturer, Department of Physics, University of Yangon

3. Dr, Professor and Head, Department of Physics, Dagon University

between 1.5 and 2.3 eV. The PCE for perovskite solar cells have increased from 3.8% in 2009 to 22.1% in early 2016. The photovoltaic properties of these solar cells are strongly dependent on the crystal structure of the perovskite compound, the fabrication process, the hole transport layer, the electron transport layer, the nanoporous layer and interfacial microstructure. Especially, the crystal structures of the perovskite-type compounds, strongly affect the electronic structures such as energy band gaps and carrier transport, and a detailed analysis of them is mandatory. In this paper, solar cell was investigated by using nanoparticles of TiO_2 and light absorbing perovskite material. Several preparation steps are needed to make perovskite material such as spin coating of TiO_2, deposition the perovskite by spin coating, thermal evaporation and dip coating. The crystal structures of perovskite type compounds $CH_3NH_3PbI_3$ was analyzed by using X-ray diffraction (XRD). Surface morphology and energy band gaps of the perovskite layer were investigated using scanning electron microscopy (SEM) and UV measurements.

Experimental Procedure

Perovskite solar cell was manufactured by going through several processes such as cutting, washing, stirring, spinning, dipping and annealing of under layer.

TiO_2 Film Deposition by Spin Coating

Titanium dioxide (TiO_2) was deposited on glass substrate by spin coating method. To prepare the TiO_2 pastes by mixing 1g of TiO_2, 2 g of terpineol and 2 g of ethanol. Then the mixture was stirred for 30 min to get homogeneous solution. The TiO_2 paste was deposited on glass substrates by spin coating at room temperature with a rate of 1500 rpm for 20 s, 2500 rpm for 30 s and 3500 rpm for 30 s. After each spin coating step, the films were annealed at 80˚ C for 15 min. The procedure from coating to annealing was repeated three times. The flow chat of TiO_2 deposition by spin coating is shown in Figure 1 (a).

PbI_2 Solution for Spin Coating

Prepare the PbI_2 pastes by mixing 1 g of lead (II) iodide powder and 3 ml of dimethyl formamide (DMF) solution. Then the solution was stirred at the temperature of 60˚ C about 1 hour. When the stirring time was 40 min, TiO_2 glass layers were annealed on the hot plate at 100˚ C for 15 min. After stirring the solution, the precipitate was filtered and PbI_2 solution was come out. The PbI_2 paste was spin coated on the TiO_2 glass layer at a rate of 3500 rpm for 30 s. All the pastes were come out as light yellow color. And then PbI_2 glass layers were annealed on the hot plate at 70˚ C for 30 min. After the glass layers were annealed, they changed from light yellow to bright yellow color. The flow chat of spin coating for PbI_2 layer is shown in Figure 1 (b).

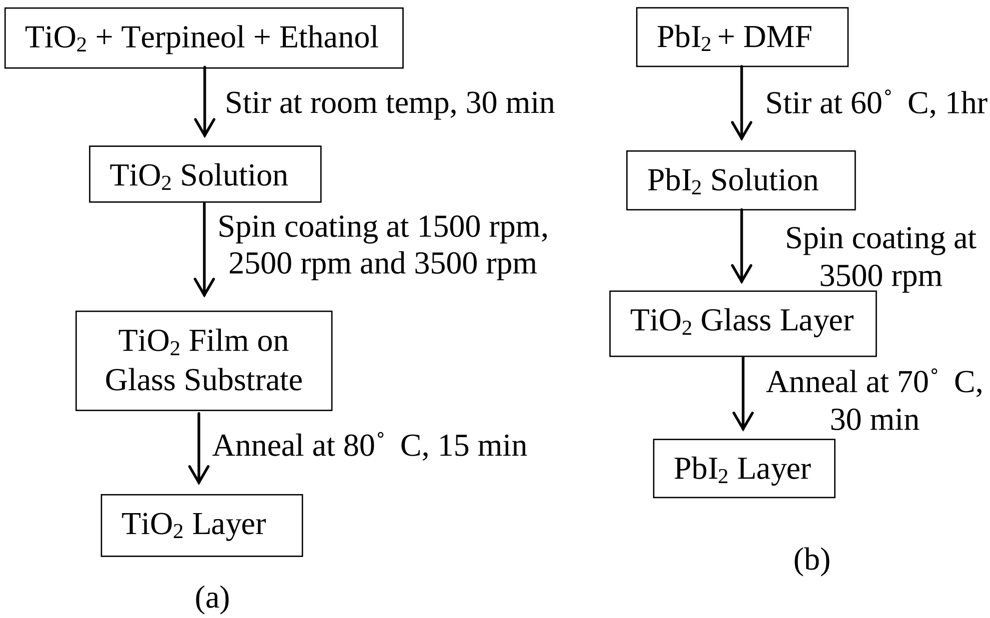


Figure 1: Spin coating for (a) TiO_2 Layer (b) PbI_2 Layer

Dip Coating Procedure

For dipping process, 0.1 g of MAI powder was dissolved in 10 ml of isopropanol and stirred at room temperature about 10 min to get the homogeneous MAI solution. The PbI_2 layers were pre annealed at 70˚ C about 30 min before dipping. All the PbI_2 layers were dipped into the MAI solution for 1 hour. While the films were dipping, the color was slightly changed to light brown. Then $CH_3NH_3PbI_3$ perovskite layers were placed on the hot plate at 70˚ C for 15 min. After annealing, the film's color was changed to dark brown. The flow chat of dip coating process is shown in Figure 2.

MAI + Isopropanol Solution

↓ Dip for 1 hr

TiO_2 + PbI_2 Film

↓ Anneal at 70˚ C, 15 min

$CH_3NH_3PbI_3$ Layer

Figure 2: Preparation of perovskite layer by dip coating process

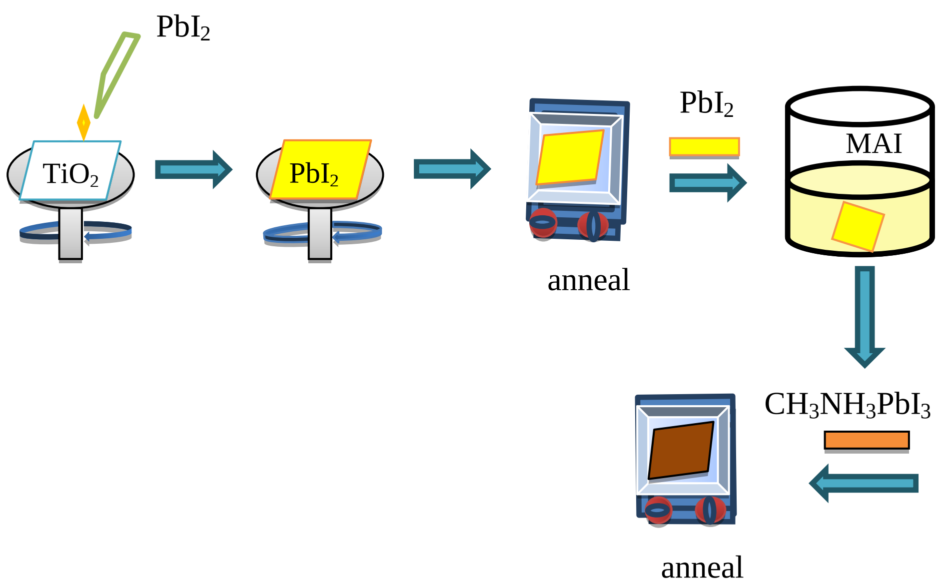


Figure 3: Preparation of methyl ammonium lead iodide layer from PbI_2 spin coating to dip coating

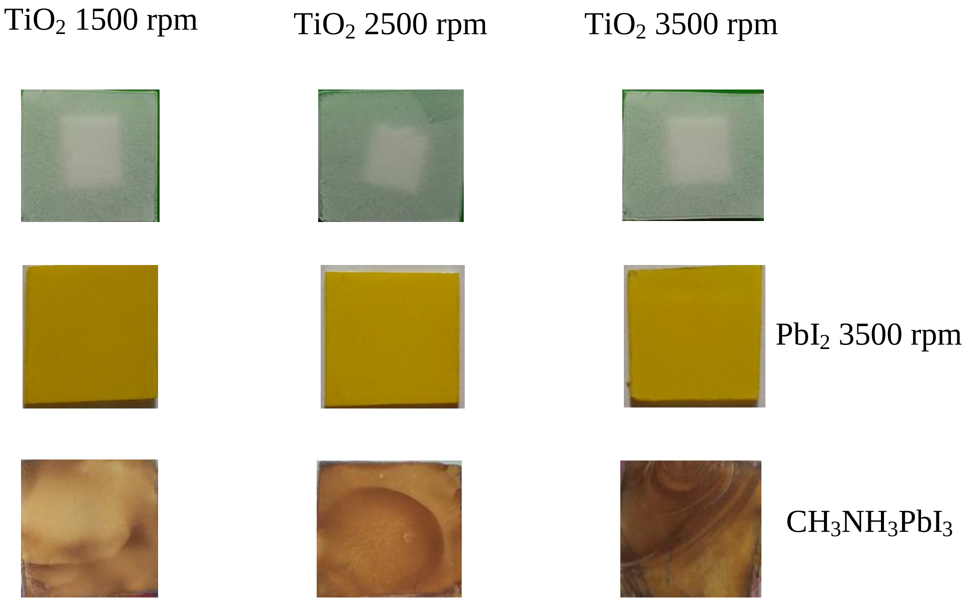


Figure 4: The color changing from TiO_2 spin coating to dip coating

Results and Discussion

XRD Analysis

The crystal structure of methyl ammonium lead iodide perovskite layers was analyzed by using X-ray diffraction technique. For TiO_2 layer coating, the spin coating rate was varied 1500 rpm, 2500 rpm and 3500 rpm for three samples (1), (2) and (3). The crystallite sizes of TiO_2 layers are 58 nm (sample-1), 54 nm (sample-2) and 17 nm (sample-3). By increasing the spin coating rate of TiO_2, the crystallite sizes were gradually decreased. The smallest crystallite size 17 nm is collected the better condition of TiO_2 to fabricate the complete perovskite solar cell. After TiO_2 layer coating, the PbI_2 layer was continued to fabricate by using spin coating rate 3500 rpm for sample 1, 2 and 3. The crystallite sizes of PbI_2 layers are 118 nm, 95 nm and 46 nm for three samples.

Finally, dip coating process of methyl ammonium iodide is continued to fabricate complete ($CH_3NH_3PbI_3$) perovskite layer. After dipping process, the crystallite sizes of PbI_2 are uniformly decreased to 85 nm, 83 nm and 81 nm. The average crystallite sizes of methyl ammonium iodide (MAI) are decreased 59 nm, 26 nm and 22 nm by varying the spinning rate. The XRD spectra of PbI_2 and MAI are illustrated in Figures 5, 6 and 7. The crystallite sizes of TiO_2, MAI and the comparative result of PbI_2 before dipping and after dipping process are shown in Table 1. The humidity and moisture sensitive properties of methyl ammonium lead iodide perovskite layers were studied by observing the changing of the color. The films color was changed from bright yellow to dark brown due to the chemical reaction.

Table 1: The average crystallite size for TiO_2, PbI_2 and MAI

TiO_2 Spin Coating Rate	Average Crystallite Size (nm)			
	Before dipping		After dipping	
	TiO_2	PbI_2	PbI_2	MAI
1500 rpm	58	118	85	59
2500 rpm	54	95	83	26
3500 rpm	17	46	81	22

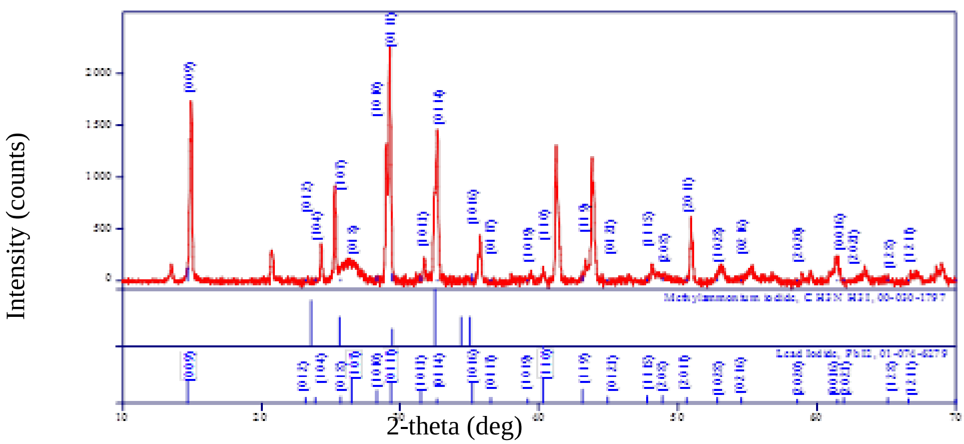


Figure 5: The XRD pattern of crystallite size for PbI_2-3500 rpm at TiO_2 -1500 rpm after dipping

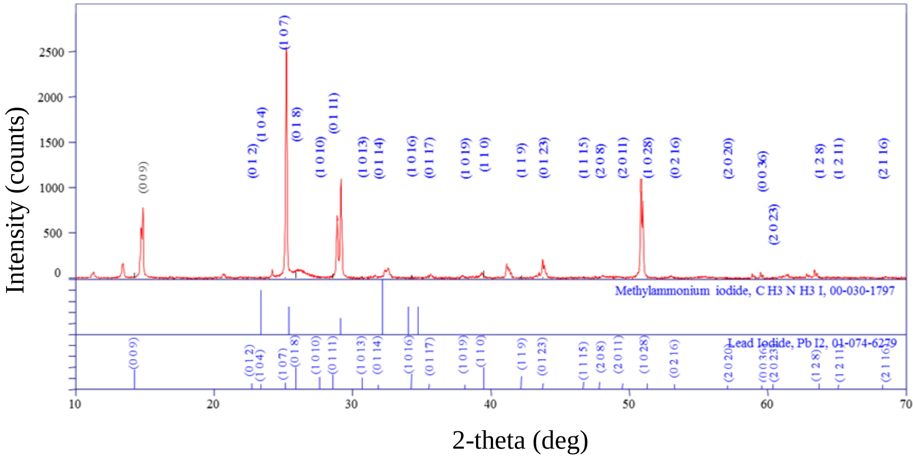


Figure 6: The XRD pattern of crystallite size for PbI_2-3500 rpm at TiO_2 -2500 rpm after dipping

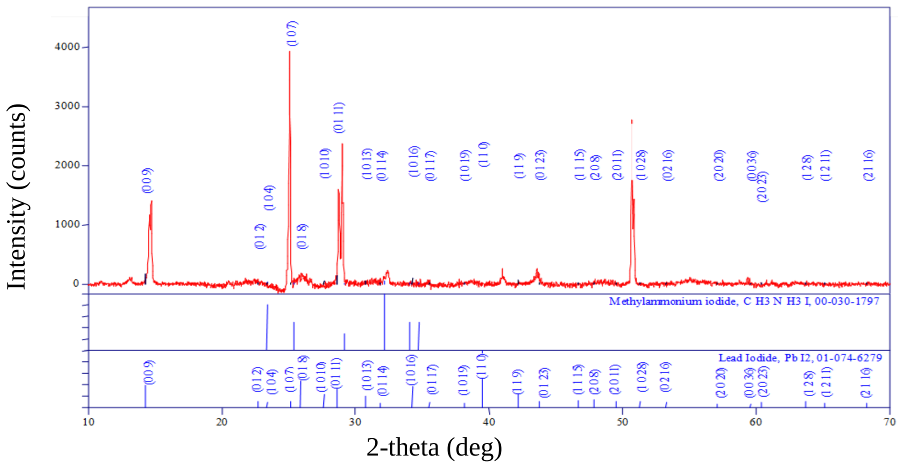
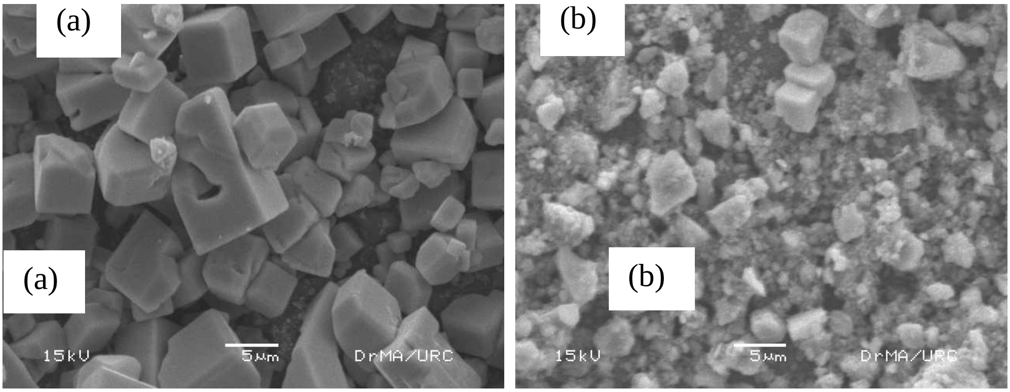


Figure 7: The XRD pattern of crystallite size for PbI_2-3500 rpm at TiO_2 -3500 rpm after dipping

SEM Analysis

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 grain size and surface morphology of the methyl ammonium lead iodide ($CH_3NH_3PbI_3$) perovskite layers were analyzed by Scanning Electron Microscope JEOL-JSM 5610 LV (SEM). The grain size was calculated by line interception technique. The average grain sizes of methyl ammonium lead iodide perovskite layers are 3.106 µm (sample-1), 2.329 µm (sample-2) and 2.299 µm (sample-3). By increasing the spin coating rate of



TiO_2, the grain sizes were gradually decreased. The decreasing of grain size is getting the better condition of surface morphology. This is the one good reason to fabricate the solar cell. The SEM images of perovskite layers are shown in Figures 8 (a), (b) and (c).

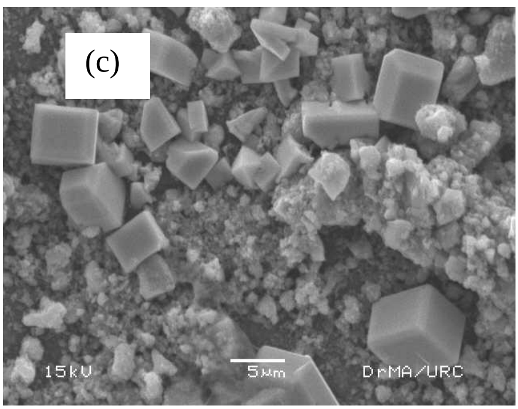
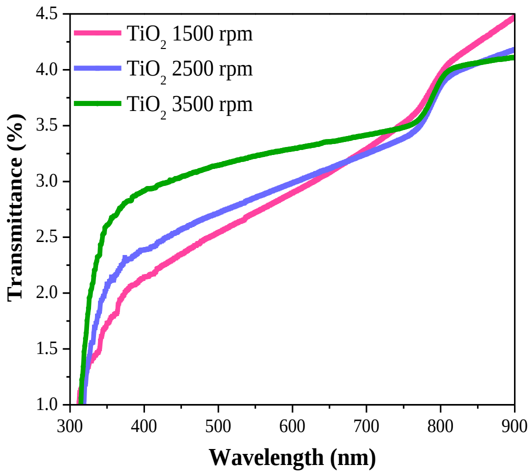


Figure 8: The SEM images of perovskite film for (a) TiO_2 1500 rpm, (b) TiO_2 2500 rpm and (c) TiO_2 3500 rpm

UV Measurement

The energy band gap of the methyl ammonium lead iodide ($CH_3NH_3PbI_3$) perovskite layers were analyzed by UV measurement. The maximum absorbance is observed for TiO_2 spin coated at 1500 rpm with the bigger grain size in the wavelength region from 300 nm to 600 nm. The wavelength is gradually tuned to the red shift from 750 nm to 810 nm. Changes of spin coating rate can tune the wavelength from lower range to higher range. The transmittance is drastically decreased around 800 nm .The transmittance is dropped and closed to 1% in the wavelength range from 400 nm to 315 nm. The highest transmission is at the spin coating rate of TiO_2 3500 rpm. The absorption and transmision spectra of UV measurements for perovskite layers are illustrated in Figures 9 (a) and (b).

The energy gaps of the methyl ammonium lead iodide perovskite layers are 1.475 eV, 1.480 eV and 1.485 eV. By increasing the grain size, the energy gap is tuned to lower range. The energy band gaps of perovskite layers are shown in Figures 10 (a), (b) and (c). The band gap of methyl ammonium lead iodide perovskite layer is typically around 1.5 eV. So the results of the band gap ranges are reliable to fabricate the perovskite solar cell.



(a) (b)

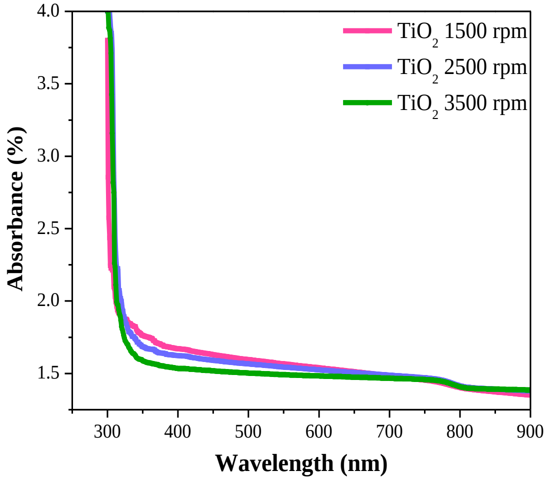
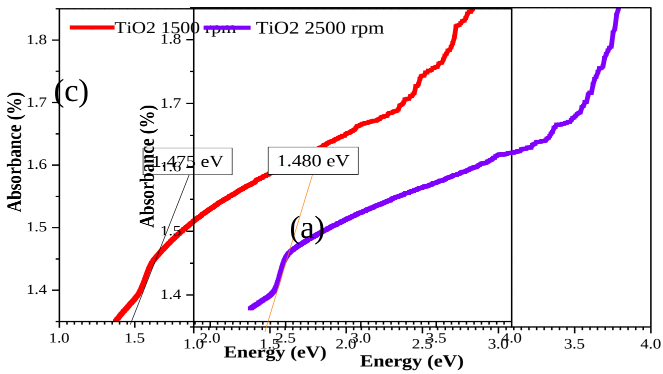


Figure 9: Comparison of UV-Vis spectra at different spin coatin g rates of TiO_2 layers (a) Absorption Vs Wavelength (b) Transmission Vs Wavelength



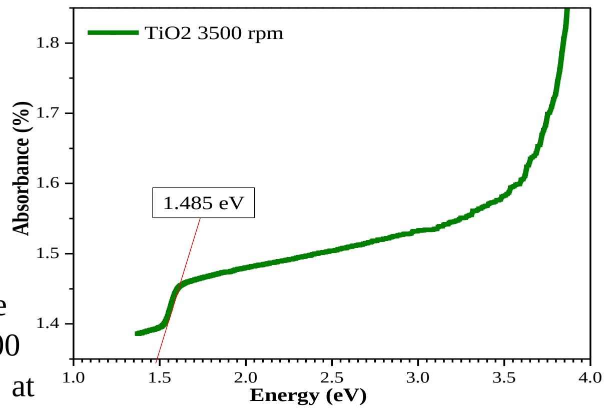


Figure 10: Energy band gap of methyl ammonium lead iodide perovskite layers (a) at TiO_2 1500 rpm, (b) at TiO_2 2500rpm, (c) at TiO_2 3500 rpm

Conclusion

The perovskite layers were prepared by using low cost spin coating method and dip coating method. The XRD studies indicate the hexagonal structure of lead (II) iodide with preferred orientation along the (0 0 9), (1 0 7), (0 1 11) after dipping. Crystallite size has been estimated by using Scherrer equation. The crystallite sizes of PbI_2 and MAI was varied by increasing the spin coating rate of TiO_2. Band gaps have been estimated by using UV measurement. It has been found that the grain sizes of perovskite layers are decreased by increasing the spin coating rate of TiO_2 layer. The average grain size is decreased from 3.106 µm to 2.299 µm. The best surface morphology is observed at spin coating rate 3500 rpm. The wavelengths have been tuned to the higher wave number from 750 nm to 810 nm. By increasing the grain size, the energy gap is shifted to lower range. The results of the energy band gap ranges are around 1.5 eV.

Acknowledgements

This research was totally done at Department of Physics, University of Yangon in Myanmar. I would like to thank Professor Dr Khin Khin Win, Head of Department of Physics, University of Yangon for her kind permission to carry out of this study. I would like to express my sincere thanks to Professor Dr Aye Aye Thant, Department of Physics, University of Yangon for her valuable suggestion and comments for this work.

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