The effect of the spinning speed variation on the perovskite solar cell efficiency

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Abstract
In this work, compact titanitum dioxide (c-TiO₂), amorphous titanitum dioxide (mp-TiO₂) and methylammonium lead iodide (CH₃NH₃PbI₃) films were prepared by spin coating method under different different rotational speed of the CH₃NH₃PbI₃ films. Many characterization measurements were achieved on the deposited CH₃NH₃PbI₃ films in order to study the change that resulted from different parameters. The X-ray diffraction (XRD) measurements revealed that the lattice constants of the fabricated CH₃NH₃PbI₃ films were close to the slandered values. The atomic force microscopy (AFM) measurements were conducted in order to study the morphology of the fabricated CH₃NH₃PbI₃ films at different scale, these results displayed that the grain size of the CH₃NH₃PbI₃ films in the range between about 160nm to 210 nm. The field emisioin scanning electron microscopy (FE-SEM) results of the fabricated CH₃NH₃PbI₃ films were well agreed to the AFM result especially in the grains shape and distribution. Transmittance measurements have been done to determine the variation of the energy gap and absorption coefficient the CH₃NH₃PbI₃ films. The structure form of the perovskite solar cells were FTO/c-TiO₂/mp-TiO₂/CH₃NH₃PbI₃/Au, the C-V measurements were achieved to determine the built-in potential, which found to have the highest value when using 4000 rpm during the synthesis of the perovskite layer. In addition, the I-V measurements in dark conditions have been conducted to compute the ideality factor and the saturation current, which are considered important parameters that influences the characteristics of the solar cells. The best solar cell efficiency was obtained at spinning speed of 4000 rpm.

1. Introduction
The perovskite solar cells (PSCs) that involved with organic-inorganic halide materials, have gained a great deal of attention of solar cells research society this is because an incredible devices efficiency improvement from 3.8% to 22.1% since 2009 until the writing of this thesis [1,2]. The perovskite already obtained much interest as a potential replacement of the silicon solar cells, which yet to take the main predominant position in the present-day PV markets, with recorded power conversion efficiency around 26% [3]. This kind of efficiency of solar cell that have small gap, attracted the current attention particularly from the researchers who work in the dye-sensitized solar cells or solar cells based on organic materials, because some materials can be utilized in both perovskite solar cell and organic photovoltaic. The materials of the perovskite have been observed with hugely variable band
gap (for instance, CH$_3$NH$_3$PbX$_3$ possess band gaps of values from 1.5 eV to 2.3 eV) [4], and high value of light absorption coefficient (more than 10$^4$ cm$^{-1}$) [5], which is similar to other thin film solar cell materials such as CdTe [6] and copper zinc tin sulfide (CZTS) [7]. Its low-cost and easy fabrication techniques also serve as the possible advantages compared to silicon-based devices that require complicated and costly high-vacuum deposition methods. Reports of successful cell fabrication on flexible substrates even indicated a greater possibility to the large-scale roll-to-roll manufacturing of PSCs that can be used in the industries [8]. The perovskite materials have a common formulation of ABX$_3$, where A is an organic cation (for instance methyl-ammonium CH$_3$NH$_3^+$), B referred to a metallic cation (e.g., Pb$^{2+}$) and X attributed to the halide anion (e.g., I$^-$). Miyasaka et al. [1] only less than one decade ago reported an efficiency of 3.8% based on a DSSC structure. Due to the application of liquid electrolyte in the hole-transporting material (HTM), the stability of solar cell was very weak and did not attract much attention. Similar trial was done by Park et al. [9] with the increased efficiency of 6.5% but stability was still the main problem because of the instability of HTM layer due to the liquid medium. The quick enhancement of the efficiency of PSCs make perovskite being predictable to be similar with the stable effectiveness of c-Si solar cells while all other types of non-silicon solar cells experienced great obstacles in more developments. Rendering of the theoretic calculations built on the famous Shockley-Queisser limit, the perovskite solar cells, which have the formula of (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$), might attain efficiency about 25–27% [10]. In the present study, the thin film of c-TiO$_2$, mp-TiO$_2$, and CH$_3$NH$_3$PbI$_3$ were prepared by spin coating method and investigation of the characteristics of the fabricated solar cell.

2. Experimental

2.1 FTO glass preparation

The substrates used in this work were FTO glass in size of 1.5cm × 1cm with surface resistivity of 14Ω sq$^{-1}$, these FTO glass substrates were etched by a distance of 3mm along the substrate length. The etching process was done by using zinc powder and HCl (2M). The zinc powder was placed on the edge of the substrate while the rest of the substrate was covered by insulator tape then HCl was poured on it and waiting for 1 min. then the resulting paste was removed and the FTO glass soaked in deionized water and removing any remaining paste. The processes of substrates cleaning are extremely important since even small quantity of dust or any other material present on the FTO glass will affect the quality of the fabricated film. The cleaning was done by these steps: 1- the substrate were put in mixed of solution of soap and water in 100 watt ultrasonic device for 15min. 2- Immersing the substrate in deionized water and run the ultrasonic for 15min. 3- The substrates were washed in acetone ultrasonically for a period of 15min. 4- The substrates were putting in ethanol and
ultrasonically were washed for 15 min. 5-Repeating the point number 2 for the same time. 6- Ultrasonically washing the substrates by immersing it in isopropanol for 15 min. 7-Drying the substrate by using compressed air. 8- Putting the substrate in oven at 100 °C for 15 min. 9- Applying UV light to the substrate for 30 min.

2.2 Materials preparation

Firstly we prepared a 2M of HCl from 12M HCl by using the relation M1V1=M2V2. Secondly absolute ethanol was put in two glass container each one have 5ml, then 0.635 ml of Titanium isopropoxide (TIP) was added to one container and 0.07 ml of HCl (2M) was added to the other container after that these two container were placed in an ice bath magnetic stirrer for 30 min. and then these two solution were mixed and run the ice bath magnetic stirrer for another 30min then the final solution was placed in the refrigerator. The final solution of compact TiO2 has a colorless appearance. To prepare the meso-porous TiO2, 5ml of absolute ethanol was used to solve 1g of TiO2 paste then the solution was placed on the magnetic stirrer at room temperature for 12 hours. The final solution was seemed to have a milky like appearance. The CH3NH3PbI3 solution was synthesized by dissolving PbI2 of mass 461 mg in 0.635 ml of DMF and 0.071 ml of DMSO solution and placed all these materials on magnetic stirrer at 70°C for 30 min., after leaving this solution to cool to the ambient temperature, 159 mg of MAI was added to the solution and stirred at room temperature for 30 min. Lastly we obtained a very clear yellow solution.

2.3 Device fabrication and characterization

The compact TiO2 was deposited by using spin coater when the rotational speed is (2000, 3000, 4000 rpm) and the time was sit to be 60 s. After the spin coating completed, the samples were put in the oven, at 100 °C for 30 min and then annealed at 500 °C for 1 hour and leaved to cool to the ambient temperature for about 4 hours. The deposition of the meso-porous TiO2 was done in the same condition of the compact TiO2.

After the completion of the processes, the samples were left to cool to the ambient temperature gradually. The process of deposition of CH3NH3PbI3 film was achieved by spin coating with pouring of anti-solvent (diethyl ether) in order to crystalize the perovskite material. After finishing this process the films were annealed in order to improve the crystallization. The deposition of Au was achieved by sputtering. The morphology of the films was examined using MIRA3 TESCAN scanning electron microscope (SEM). ARA AFM was used to study the topography of the films. The x-ray diffraction (XRD) patterns of substrate and perovskite films were obtained using Philips PW 1840 X-ray diffractometer of wavelength λ = 1.5406Å from Cu - Kα. A Cecile CE 7200 Spectrophotometer supplied by Aquarius company was used to record the optical transmission for the films (375-900
nm). Dark current-voltage measurements carried out by applying voltage supplied to the sample from a stabilized D.C. fine power supply, type L 30-2 Farnell of range (0.1-5)V. The current passing through the device was measured using a Keithley (2400) sourcemeter. The I-V measurements of the solar cells were done under 100mW/cm² light illumination power densities supplied by a Halogen lamp which is connected to a variable AC power supply and calibrated by Keithley 2400.

3. Results and Discussion

3.1 Structural Measurements

Fig. 1 represents three X-ray patterns of CH₃NH₃PbI₃ that fabricated in spin coating method with different rotation speed one can notice that all peaks have nearly the same diffraction planes. The standard lattice parameters (a and c) of the CH₃NH₃PbI₃ in tetragonal phase are very close to the sample prepared in rotation speed of 4000 rpm. Table. 1 shows the lattice constants and the grain size and Fig. 2 shows the variation of the lattice parameters and grain size with the rotation speed. The duration of spin coating process will affect the properties of the fabricated films due to the removal more solution from substrate that result in decreasing the film thickness, surface morphology and crystallization degree.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of the CH₃NH₃PbI₃ thin films deposited on FTO glass substrate at different speed rotation: 2000 rpm, 3000 rpm and 4000 rpm.

![Figure 2](image2.png)

A: Variation of grain size with speed of rotation; B: Variation of lattice constant (c) with speed of rotation.
Figure 2: the effect of the rotation speed of the deposited CH$_3$NH$_3$PbI$_3$ films on A: grain size, B: lattice constant c and C: lattice constant a.

Table 1: the result of XRD data of the CH$_3$NH$_3$PbI$_3$ thin films deposited on FTO glass substrate at different speed rotation.

| Rotation speed (RPM) | FWHM$^\circ$ at (110) | Grain size (nm) | a($\AA$) | c($\AA$) |
|----------------------|------------------------|-----------------|----------|----------|
| 2000                 | 0.678                  | 11.8018         | 8.852    | 12.577   |
| 3000                 | 0.658                  | 12.1675         | 8.917    | 12.563   |
| 4000                 | 0.695                  | 11.5095         | 8.783    | 12.607   |

3.2 Morphology analysis

The surface morphology of films has been investigated using AFM images, which produces images of surfaces at very high magnification. Fig. 3 displays the AFM images of samples fabricated in different spinning speed, the average diameter, of sample prepared at spinning speed of 2000 rpm, is about 210 nm, with increasing the speed of spinning the average diameter decreases and reach the values of 195 nm and 170 nm for samples fabricated at spinning speed of 3000 rpm and 4000 rpm respectively.

The surface morphology of samples fabricated with different spinning speed is shown in Fig. 4, the FE-SEM images of samples are found to have almost the same morphology which may mean the spinning speed does not affect morphology of the fabricated films, the average grain size of samples prepared with spinning speed 2000 rpm, 3000 rpm and 4000 rpm are 176 nm, 184 nm and 187 nm respectively.
Figure 3. AFM images of CH$_3$NH$_3$PbI$_3$ film prepared with different spinning speed (2000, 3000, 4000), the letters here refer to the image scale A:0.5 µm, B:1µm, C:5 µm and D:10 µm.
Figure 4. FE-SEM images of CH$_3$NH$_3$PbI$_3$ film prepared with different spinning speed (2000,3000,4000), the letters here refer to the image scale A:0.2 µm, B:0.5µm, C:1 µm and D:2 µm
3.3 Optical Measurements

To evaluate the optical properties of the perovskite films prepared by spin coating method at different conditions, we measured the UV-visible to calculate the transmittance, absorption coefficient and the energy gap. The speed of rotation in the spin coating process has influence in the resultant film morphology, this is due to the effect of diffusion of solution through the substrate that vary depending on the rotation speed, which would change the centrifugal force that responsible on the spread of solution. It can be clearly observed from Fig. 5 that transmittance is higher in speed rotation of 4000 rpm, and has maximum transmittance (about 65%) at long wavelength and then the transmittance begin to decrease at about 750nm wavelength to 35% then remain constant in short wavelengths. This result of lower transmittance at high rotational speed (4000 rpm) explains that the thickness and the morphology of thin films prepared by spin coating method are changed significantly due to small solution amount remained during the process.

The absorption coefficient versus wavelength, of samples fabricated at different rotational speed, is shown in Fig. 6. At the short range wavelength the absorption coefficient, for sample prepared at 4000 rpm spinning, appears to have lower value compared to the other samples, in the other hand, as the wavelength increased, the 4000 rpm sample has higher absorption coefficient (in the range between 600 nm and 1100 nm) relative to samples prepared with lower speed. The energy gap of CH$_3$NH$_3$PbI$_3$ thin films deposited at different spinning speed are almost equal value of about 1.53 eV, this result may be explained as the spinning speed has no big influence on the optical energy gap of the fabricated samples as shown in Fig. 7.

![Figure 5. Transmittance as a function of wavelength for CH$_3$NH$_3$PbI$_3$ thin films deposited at different rotational speed.](image)
3.4 Electrical Measurements

3.4.1 Capacitance–Voltage (C-V) Measurement

In order to obtain efficient energy conversion in solar cells with low mobility LHM, a high build in potential ($V_{bi}$) is necessary to prevent significant losses due to carrier recombination processes competing with charge extraction processes [1]. The capacitance equation is given by

$$\frac{1}{C^2} = \frac{2}{qA^2\varepsilon_0} \left( \frac{1}{N\varepsilon_r} \right) \left( V_{bi} - V_{bias} + \frac{k_BT}{q} \right)$$  \hspace{1cm} (1)

Where $C$ is the junction capacitance, $A$ is the junction area, $\varepsilon$ is the vacuum permittivity, and $N$ is the activated dopant density in semiconductor and $\varepsilon_r$ is the relative permittivity. Fig. 8 shows the change in junction capacitance with applied voltage for FTO/compactTiO$_2$/mpTiO$_2$/CH$_3$NH$_3$PbI$_3$/Au solar cells prepared at different parameters of the absorber layer (CH$_3$NH$_3$PbI$_3$). It’s clear from this figure that there is an increase in capacitance with
increasing voltage bias and this variation of capacitance, as the bias change, is caused by changes of the width of the depletion region. As the bias reversely increases, the extension of the depletion region starts at the CH$_3$NH$_3$PbI$_3$/Au interface, then goes through the CH$_3$NH$_3$PbI$_3$ and finally into the TiO$_2$ because of the different N and $\varepsilon_r$ values in both CH$_3$NH$_3$PbI$_3$ and TiO$_2$. C-V curves under reverse bias are bent into two stages. Similar phenomena were observed for III-V semiconductors [11]. The roughly constant capacitance at stage II is due to the heavy doping level in TiO$_2$, in comparison with the smaller slope related to the small doping level in CH$_3$NH$_3$PbI$_3$. The sharp edge of the curves in Fig. 9 corresponds to the transition point of the depletion region from stage I to stage II. According to equation (1), the V$_{bi}$ of a finite CH$_3$NH$_3$PbI$_3$ layer is extracted from the intersection. The fluctuations in some curves found in Fig. 9 of stage II can be explained by non-uniform doping in the TiO$_2$ layer. Because of the huge effective surface area of nano-porous TiO$_2$ and the rough surface of CH$_3$NH$_3$PbI$_3$ layer. The diffusion potential or built in potential (V$_{bi}$) can be estimated by plotting between V and $1/C^2$ (Mott-Shottky plot) and intercept the linear portion of the line with x-axis. Table 2 shows the summary results obtained from C-V measurements basically included the built in potential values.

![Figure 8](image_url)

**Figure 8.** Capacitance as a function of applied voltage for FTO/c TiO$_2$/mp TiO$_2$/CH$_3$NH$_3$PbI$_3$/Au solar cell at different synthesis Speed of spinning.
Figure 9. Estimation of built in potential from the relationship of voltage and $1/C^2$ for FTO/c TiO$_2$/mp TiO$_2$/CH$_3$NH$_3$PbI$_3$/Au solar cell at different Speed of spinning of CH$_3$NH$_3$PbI$_3$ film.

Table 2. Values of built in potential of FTO/c TiO$_2$/mp TiO$_2$/CH$_3$NH$_3$PbI$_3$/Au solar cells prepared at spinning speed of the absorber layer (CH$_3$NH$_3$PbI$_3$).

| Parameters                  | Values | Built—in voltage (diffusion potential) $(V)$ |
|-----------------------------|--------|--------------------------------------------|
| Spinning Speed(rpm)         |        |                                            |
| 2000                        |        | 0.85                                       |
| 3000                        |        | 0.9                                        |
| 4000                        |        | 0.91                                       |

3.4.2 Dark Current-Voltage Measurements (I-V)

It can be noticed from the Fig. 10 that the junction exhibits rectifying behavior, this rectifying behavior is attributed to heterojunction potential barrier at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface. The formation of the heterojunction structure is referred to the difference in energy gap between the TiO$_2$ and CH$_3$NH$_3$PbI$_3$. Some of electrical characteristics of TiO$_2$/CH$_3$NH$_3$PbI$_3$ sandwich structure can be calculated from dark I-V measurements, such as ideality factor and saturation current that were calculated according to the equations in previous work [10]. Both $I_s$ and $n$ provide important information on the predominant current transport mechanism in a device. There are a number of ways to obtaining these parameters, although the most consistent method involves their determination using the dark J-V curves. The slope of the J-V curve gives the $n$, whereas the y-intercept gives the $J_s$. They are usually considered together as there is great deal of correlation between these two parameters. It is desirable that $J_s$ be as low as possible, so that higher voltages are required for the dark current to equal the light generated current. This increases the Voc of the devices. A lower value of $n$
will lead to reduction in Voc value but that will help to increase the fill factors of devices. Table 3 describes the ideality factor and the saturation current of TiO₂/CH₃NH₃PbI₃/Au solar cells prepared at different rotation speed of the absorber layer (CH₃NH₃PbI₃).

![Figure 10. Dark I-V characteristics of FTO/c TiO₂/mp TiO₂/CH₃NH₃PbI₃/Au solar cell at different Speed of spinning of CH₃NH₃PbI₃ film.](image)

Table 3. shows the values of parameters of the solar cell extracted from the dark (J-V).

| Parameters          | Values | Ideality Factor | Saturation current (µA) |
|---------------------|--------|----------------|------------------------|
| Spinning Speed(rpm) |        |                |                        |
| 2000                |        | 2.86           | 1.7                    |
| 3000                |        | 2.58           | 1.26                   |
| 4000                |        | 2.153          | 0.69                   |

4. Solar Cell Measurements

Fig. 11 presents the (J-V) characteristics of FTO/c TiO₂/mp TiO₂/CH₃NH₃PbI₃/Au structure solar cells with different spinning speed of the prepared CH₃NH₃PbI₃ film. The detailed photovoltaic parameters such as open-circuit voltage (Voc), FF, short-circuit current density (Jsc), PCE, Rs and Rsh are given in Table 4. It is obvious from the table that the solar cell, which prepared with spinning speed of 2000 rpm, had higher Rs and lower Rsh, this result will lead to lower the photocurrent which lowers the efficiency of the solar cell. By increasing the spinning speed to 3000 rpm and 4000 rpm the value of Jsc is drastically increasing to higher values as well as the other parameters will improve, this may be due to the good interaction between the spinning speed and the anti-solvent diffusion process that occurs during the formation of the perovskite layer. On the other hand, the FF of the device prepared at 4000 rpm has the higher value, this may be attributed to good quality formation of perovskite at this spinning speed as presented in Table 4.
Figure 11. J-V characteristics of the solar cells under illumination of 100 mW/cm² with different spinning speed.

Table 4. Illustrates Parameters of the fabricated solar cells that prepared with different spinning speed.

| Spinning Speed (rpm) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | FF | PCE (%) | $R_s$ (Ω.cm²) | $R_{sh}$ (Ω.cm²) |
|----------------------|--------------|-------------------|----|---------|---------------|------------------|
| 2000                 | 0.551        | 7.612             | 0.514 | 2.156 | 18.53         | 233              |
| 3000                 | 0.834        | 11.708            | 0.508 | 4.96   | 12.2          | 347              |
| 4000                 | 0.859        | 12.188            | 0.577 | 5.857  | 10.04         | 380.17           |

5. Conclusions

The different rotation speeds play an important role on the quality of the perovskite films and lead to different influence of the fabricated solar cells. The best efficiency of the solar cells found at speed of 4000 rpm. AFM and SEM analysis showed that there is big effect on the structure and morphology of the perovskite film that prepared with different speeds, it is found that the grain size becomes smaller when the rotation speed increases. From the dark I-V measurements, the ideality factor and the saturation current will decrease with increase the rotation speed.

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