Annealing temperature effects on the performance of the perovskite solar cells

A. K. Al-Mousoi, M. S. Mehde, A. M. Al-Gebori
Department of Applied Science, University of Technology, Baghdad, Iraq
*Corresponding author email: alialmousoi2006@yahoo.com

Abstract

In this work, perovskite solar cells were fabricated with one-step method by using spin coating technique. These solar cells were in the structure form of FTO/compactTiO_2/mesoporousTiO_2/CH_3NH_3PbI_3/Au. Different annealing temperatures were applied to investigate the effect of the annealing temperature on the properties of the fabricated solar cells since it lead to affect the crystallization degree of the CH_3NH_3PbI_3 layer. Three temperatures were used for annealing the perovskite layer typically: 60°C, 80°C and 100°C and the best result found at 100°C where the efficiency was 5.68%, FF = 0.55, J_sc = 12.637 mA/cm² and V_oc = 0.817 V.

Keywords: Perovskite solar cells, CH_3NH_3PbI_3, Lead Iodide perovskite.

1. Introduction

Nowadays halide organic-inorganic perovskite solar cells attract a big deal of interest of solar cells researches society since incredibly development have been done in the solar cells efficiency from 3.8% to 22.1% since 2009 [1,2]. Perovskite materials earned great attention as an alternative to silicon solar cell, which took the most predominant position in the current solar cell market, of efficiency around 26% [3]. Perovskite solar cells attract the modern attention specifically from the researchers with experiences in dye sensitized-solar cell or organic-solar cell since various materials could be employed mutually in perovskite and organic-solar cell. The configuration form of perovskite solar cell is similar to that exist in the structure of dye sensitized solar cell [1]. The band gap of perovskite materials is tunable (e.g., lead halide perovskite has a band gap from 1.5eV to 2.3eV) [4] and moderately high absorption coefficient (about 10⁴ cm⁻¹) [5,6], which is closer to other thin film solar cell materials such as CdTe [7] and copper zinc tin sulfide (CZTS) [8]. The relatively low cost and simple fabrication technique play significant role to make a competitive device that made from silicon, which requires complicated and costly high-vacuum deposition methods. The efficiency of Perovskite solar cells that fabricated with spin coating method were found highly dependent on the deposition parameters such as the annealing temperature, spinning speed, spinnning time and type of anti-solvent.

2. Experiment section

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 15min. 9- Applying UV light to the substrate for 30 min.

2.2. Materials preparation

The chemicals used to prepare TiO2 are listed in the table below

| Solvent              | Stabilizer             | Precursor                   |
|----------------------|------------------------|-----------------------------|
| Absolute Ethanol     | Hydrochloric acid (HCl)| Titanium isopropoxide (TIP) |

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 1 g 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 461mg in 0.635 ml of DMF and 0.071ml 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 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 30min 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 = 1.5406°A 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

All the characterization in this work was achieved to study the CH$_3$NH$_3$PbI$_3$ layer since it represents the important layer of the perovskite solar cells. The XRD patterns of the CH$_3$NH$_3$PbI$_3$ films formed by spin coating method on FTO glass substrates at different annealing temperatures, and make the other parameters fixed (spinning time = 60s , anti-solvent = Diethyl ether and rotation speed = 4000rpm ), are shown in Figure 1. The patterns display seven diffraction peaks at 20 values of approximately (14º.1ˊ, 20º, 24º.45ˊ, 28º.4ˊ, 40º.45ˊ and 43º.05ˊ) which correspond to the diffraction plans (110), (112), (202), (220), (400) and (411) crystalline planes of the CH$_3$NH$_3$PbI$_3$ tetragonal phase respectively. All the X-ray patterns show that the fabricated films are polycrystalline and it is clearly seen that diffraction intensities increased with annealing temperatures, which may due to the increasing of grain size and thickness.

The most preferred orientation found at 20 values of approximately 14º.1ˊ and 28º.4ˊ that corresponding to (110) and (220) diffraction planes respectively, the lattice parameters which corresponding to these values are: a=8.87 Å° and c=12.7 Å°. Some of peaks appeared in the X-ray patterns that belong to PbI$_2$ (at 20 about 12.6) and FTO, the peak of PbI$_2$ tend to be less with higher annealing temperature due to improvement in the reaction and crystallization degree. The intensities of the minor peaks are decreased with increasing of the annealing temperature as shown in Figure 1 [9]. The lattice constant (a and c) are calculated using the relation

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad \text{and} \quad d \sin \theta = n \lambda$$

where hkl are miller indices, d is the inter planar spacing, n is a positive integer (usually equal to 1), λ is the x-ray wavelength and θ is the diffraction angle.

The close calculated value to the standard lattice constant (a$_0$≈8.8Å° and c≈12.6 Å°)[10] found at annealing temperature of 100ºC.

Figure 1: X-ray patterns of the CH$_3$NH$_3$PbI$_3$ films at different annealing temperatures: 60ºC, 80ºC and 100ºC.
The surface morphology of films has been investigated using AFM images, which produces images of surfaces at very high magnification. Figure 2 shows the topography of the CH$_3$NH$_3$PbI$_3$ film deposited at different annealing temperature which be considered a significant parameter that influence the formation of the perovskite in one step method. The surface morphology has different shape for each perovskite film that prepared with a certain temperature. It is obvious that the particles, on the surface of the film, have different diameter values, however the CH$_3$NH$_3$PbI$_3$ film deposited at 60º C has average grain size of about 160nm, also the geometry of the surface has a high degree of regularity. As the annealing temperature increases the grain size will increase as obvious from images of samples prepared with annealing temperature of 80º C and 100º C which found to have average grain size of 187nm and 204nm respectively.

Figure 2: AFM images of CH$_3$NH$_3$PbI$_3$ film prepared with different annealing temperature, the letters here refer to the image scale  a) 0.5 µm , b)1µm ,c) 5 µm  and d) 10 µm

Figure 3 shows the SEM images of samples prepared with different annealing temperature to study the surface morphologies. It is clearly obvious that all samples are highly dense with full coverage. The surface of sample prepared with annealing temperature of 60 ºC is not very smooth and its surface homogeneity is not uniform, this may due to less temperature established to fully formation of the perovskite layer, however, the average particle size is about 51nm and these particles found to be in group. By increasing the annealing temperature the surface of the samples begin to have a smooth and more homogeneity and the particles becomes to assemble in bigger crystals as shown in Figure 3. The average particle size for the samples prepared with annealing temperature 80 ºC and 100 ºC are 178 nm and 208 nm respectively.
Figure 3: FE-SEM images of CH$_3$NH$_3$PbI$_3$ film prepared with different annealing temperature, the letters here refer to the image scale a) 0.2 µm , b) 0.5µm , c) 1 µm and d) 2 µm.

The transmittance spectra of the CH$_3$NH$_3$PbI$_3$ films deposited at different annealing temperatures are shown in Figure 4. We notice that the films have high transmission at long wavelengths approximately (60 – 70 %), and decreasing transmission to (20-35%) at short wave lengths (typically at about 750nm wavelength which corresponding to approximately 1.5 eV of energy gap).
**Figure 4:** Transmittance as a function of wavelength for CH₃NH₃PbI₃ thin films deposited at different annealing temperatures.

It was observed that the transmission of the film decreased with increasing in annealing temperature, this may due improvement of the crystallization and orientation degree and.

Figure 5 shows the optical energy gap estimated by using Tauc plot, As expected the increasing the annealing temperature will lead to increase the value of energy gap due to crystallization improvement, the value of $E_g$ of the sample annealed with 100° C is about 1.51 eV whereas there is a slightly difference in samples annealed with temperature of 80° C and 60° C which each has value of $E_g$ about 1.5 eV and 1.25eV respectively, this differences of $E_g$ of samples prepared with different annealing temperature may attributed to the different perovskite formation for each temperature.

**Figure 5:** Shows the estimated energy gap of CH₃NH₃PbI₃ thin films deposited at different annealing temperature.

It can be noticed from the Figure 6 that the junction exhibits rectifying behavior, this rectifying behavior is attributed to heterojunction potential barrier at the TiO₂/CH₃NH₃PbI₃ interface. The formation of the heterojunction structure is referred to the difference in energy gap between the TiO₂ and CH₃NH₃PbI₃ [11]. Some of electrical characteristics of TiO₂/CH₃NH₃PbI₃ sandwich structure can be calculated from dark I-V measurements, such as ideality factor ($n$) and saturation current density ($J_s$). 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 $I_s$. 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 $V_{oc}$ of the devices. A lower value of $n$ will lead to reduction in $V_{oc}$ value but that will help to increase the fill factors of the devices.
Figure 6: Dark I-V characteristics of FTO/c-TiO₂/mp-TiO₂/CH₃NH₃PbI₃/Au solar cell at different annealing temperature of CH₃NH₃PbI₃ film.

Table (2): describes the ideality factor and the saturation current of TiO₂/CH₃NH₃PbI₃/Au solar cells prepared at different parameters of the absorber layer (CH₃NH₃PbI₃).

| Parameters              | Values | Ideality Factor | Saturation current (µA) |
|-------------------------|--------|----------------|------------------------|
| Annealing Temperature(°C) | 60     | 3.47           | 2.71                   |
|                         | 80     | 3.05           | 2.06                   |
|                         | 100    | 2.18           | 0.731                  |

The (J–V) characteristics of the solar cells under illumination of intensity power of 100 mW/cm⁻² with FTO/c-TiO₂/mp-TiO₂/CH₃NH₃PbI₃/Au structure, at different annealing temperature of CH₃NH₃PbI₃ film, are shown in Figure (7). The effect of the annealing temperature on the solar cell parameters is very clear as Table (3) shows that, from the table one can notice that the increase in the J_sc and V_oc with increasing the annealing temperature, this may be due to improvement in the formation of the perovskite layer and this will cause high absorption of light which lead to high photocurrent generated. The efficiency of the solar cell is basically affected by series and shunt resistance which are established by the resistance of contact and leakage at the edge of device, the lower value of R_s and higher value of R_sh found to be in a solar cell prepared at annealing temperature of 100°C, the lower efficiency of the solar cell that fabricated at 60°C and 80°C may results from the incompleteness of the perovskite layer.
Figure 7: J-V characteristics of the solar cells under illumination of 100 mW/cm$^2$ with different annealing temperature.

Table 3: shows the parameters of the fabricated solar cells that prepared with different annealing temperature.

| Temperature (°C) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | $FF$ | PCE (%) | $R_s$ (Ω.cm$^2$) | $R_{sh}$ (Ω.cm$^2$) |
|-----------------|-------------|---------------------|------|---------|----------------|-----------------|
| 60              | 0.423       | 5.277               | 0.429| 0.958   | 32.98          | 189.5           |
| 80              | 0.781       | 9.647               | 0.368| 2.782   | 36.17          | 194             |
| 100             | 0.817       | 12.637              | 0.556| 5.684   | 9.6            | 315.73          |

4. Conclusions

The different annealing temperatures 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 annealing temperature of 100°C. AFM and SEM analysis showed that there is big effect on the structure and morphology of the perovskite film that prepared with different annealing temperature; it is found that the grain size becomes larger when the annealing temperature increases. From the dark I-V measurements, the ideality factor and the saturation current will decrease with increase the temperature of annealing.
Finally the efficiency of the solar cell fabricated with annealing temperature of 100°C was found to have the maximum value among the other solar cells.

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