Investigation on Morphology and Optical Properties of TiO_2 Blocking Layer Deposited in Ambient Air for Perovskite Solar Cell Application

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Abstract*— Titanium dioxide (TiO_2) is a synonym material that acted as electron transport medium in Perovskite Solar Cell (PSC). The electron transport layer (ETL) was deposited using simple, time-saving spin coating technique. The two factors that have been focused in this paper are different concentrations of TiO_2 blocking layer (BL) and different number of coating layers. Different TiO_2 BL precursor solution concentrations were prepared by mixing TiO_2 BL precursor with ethanol at ratio of 1:1 and 1:9. Then, different coating numbers were deposited on FTO glass substrate for one until four layers. The first layer was constant at 3000 rpm for all samples and the other layers were set at 4000 rpm. The morphology of obtained films was studied through Atomic Force Microscopy (AFM), scanning electron microscopy (SEM) and profilometer. Optical absorption for TiO_2 is investigated by UV-visible (UV-vis) spectroscopy within absorption range of 300-1100 nm. Effect of TiO_2 BL concentrations and number of coatings on the surface morphology and optical properties of these films have been studied in this paper. The results obtained proved that both the surface morphology and optical properties are closely related to the concentrations and numbers of TiO_2 BL deposited layers.

Keywords—TiO_2 blocking layer; spin coating; ambient air; morphological properties; optical properties; Perovskite Solar Cell application

I. INTRODUCTION

Few years back, the urge of researches towards Perovskite solar cells (PSC) has gained great concern in the solar cell research field. This statement was supported by the latest efficiency performance that managed to achieve up to 22.1 % most recently [1] and PSC also offers low economic impact on production cost [2], [3] as the production involves low temperature processes. Electron transport layer (ETL), absorber layer, hole transport layer (HTL) and contacts are the essential components to complete the conventional Perovskite Solar Cell (PSC) structure. The structure of PSC is illustrated in Figure 1.

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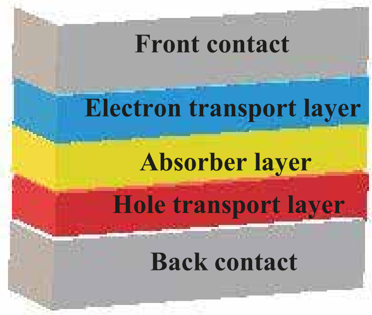


Fig. 1. The basic structure of conventional Perovskite Solar Cell (PSC).

There are two types of PSC that are n-i-p and p-i-n which p-i-n is normally named as inverted PSC. The inverted PSC (p-i-n) arrangement is always starts from front contact, p type layer, absorber layer, n type layer and back contact. The conventional PSC usually in n-i-p form (either planar or mesoporous) which the light travels into FTO glass and pass through different layers until the last silver, Ag contact as shown in Figure 2.

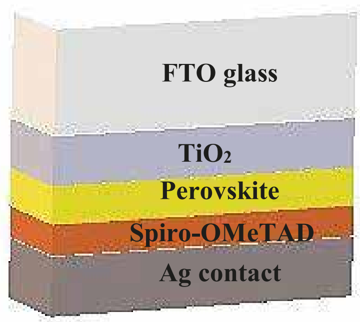


Fig. 2. The common structure of planar n-i-p type Perovskite Solar Cell (PSC).

From previous research, titanium dioxide (TiO_2) is one of the most regularly used electron transport material (ETM) among SiO_2, SnO_2, ZrO_2 and ZnO [4] as TiO_2 is a reliable and cost effective material. There are useful applications of TiO_2 within ultra violet (UV) region as TiO_2 has wide bandgap of 3.2 eV [5].

There are wide varieties of ETL depositing techniques that include chemical vapour deposition, spin coating, sputtering and spray pyrolysis [6]. Spin coating technique is chosen due to simple and able to reduce time constraint. This spin coating technique is mainly involves rotation speed adjustment in order to get optimum thickness of desired ETL. Besides that, the rotation time also important to make sure enough time for the layer to spread well on top of the substrate. A homogenous layer of ETL can helps in enhancing the power conversion efficiency (PCE) of PSC.

Generally, ETL is one of the most important layers in PSC. ETL is functioned as the layer to transport the electrons absorbed by absorber layer [4] and make sure the electrons flow smoothly in order to produce high efficiency solar cell. This paper has highlighted the importance of morphology and optical factors in ETL that are the essential baseline to achieve good PSC performance. The morphology and optical properties of TiO_2 BL are analysed using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), profilometer and UV-visible (UV-vis) spectroscopy.

II. EXPERIMENTAL SECTION

A. FTO Glass Cleaning

FTO glass was cleaned using three types of glass cleaning agents that were ethanol, acetone and propanol. The substrate was ultrasonic bathed for 15 minutes at room temperature within each type of cleaning agent. Then, the substrate was dried using nitrogen, N_2 purge.

B. TiO_2 Blocking Layer Solution Preparation

TiO_2 blocking solution was prepared by mixing TiO_2 blocking layer precursor with ethanol. There were two types of TiO_2 BL layer concentrations that were prepared for ETL deposition process. The first type of concentration was the concentrated version with ratio of 1:1 of TiO_2 precursor to ethanol. Meanwhile, the ratio of 1:9 of TiO_2 precursor to ethanol was for diluted version.

C. TiO_2 Blocking Layer Deposition

ETL was deposited on FTO glass substrate using spin coating technique that is the rotation speed was set at 3000 rpm for 35 seconds for all first layers and followed by 4000 rpm at 35 seconds for the other consecutive layers. The simplified sample deposition steps were listed in Table 1 and Table 2. One layer deposited was heated at 150°C for 15 minutes before the next layer was deposited. When depositions of all layers were finished, all the samples were annealed gradually to the temperature of 500°C for 60 minutes. The TiO_2 ETL was formed on the glass substrate as the ethanol content in TiO_2-ethanol mixture solution was evaporated during the high heat applied. Then, the samples were cool down gradually until achieved the room temperature. All the processes were taken place in ambient air.

TABLE I. SAMPLE PREPARATION FOR BOTH CONCENTRATED (1:1) AND DILUTED (1:9) TIO_2 BL LAYER.

Number of Layers	Sample 1	Sample 2	Sample 3	Sample 4
	Rotation speed (rpm)[a]			
First layer	3000	3000	3000	3000
Second layer	-	4000	4000	4000
Third layer	-	-	4000	4000
Fourth layer	-	-	-	4000

a. Different rotation speed at fixed rotation time (35 seconds).

III. RESULTS AND DISCUSSION

A. Profilometer

From the data analyze by profilometer, the average thickness of TiO_2 BL layer increased with the addition of each layer for both ratio of 1:1 and 1:9. There were slightly changes in thickness value when each layer was added for diluted TiO_2 ratio (1:9). Conversely, there were noticeable changes in thickness when more layers were deposited for ratio of 1:1. This was because higher concentration precursor solution had high viscocity compared to the diluted ratio and thus formed thicker layer of TiO_2 BL when spin coated.

TABLE II. SIMPLIFIED DATA ON AVERAGE THICKNESS OF TIO_2 BL LAYER.

Ratio (TiO_2:CH_3NH_2OH)	1 Layer	2 Layers	3 Layers	4 Layers
	Average thickness(nm)			
1:1	28.50	59.43	77.60	102.05
1:9	16.33	21.47	26.13	32.53

B. Atomic Force Microscopy (AFM)

Figure 3, 4, 5 and 6 had showed the results of surface roughness for 1, 2, 3 and 4 layers of TiO_2 BL deposited on FTO glass respectively. All the left (a) parts were the images for concentrated (1:1) ratio precursor solution and all the right (b) parts were the images for the diluted (1:9) ratio precursor solution. The simplified data obtained were recorded in Table III. The general trends for different number of layers had indicated that the surface roughness decreased as the number of deposited layers increased. Besides, the concentration of TiO_2 BL precursor solution also can affect the surface roughness values. From the acquired data, the surface for FTO glass that deposited with higher concentration (1:1) precursor solution was smoother rather than the lower concentration (1:9) TiO_2 solution. Generally, the thickness of the TiO_2 ETL depends on the number of spin coated layers and TiO_2 BL concentrations.

3(a) (b)

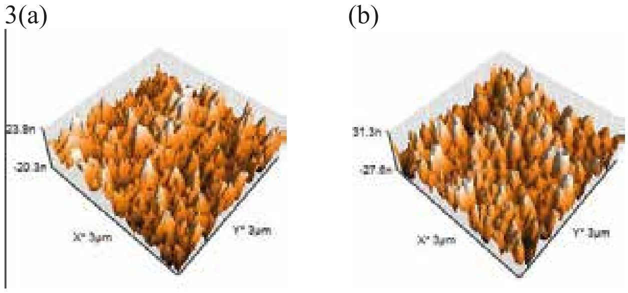


Fig. 3. The topography of 1 layer of TiO_2 with ratio of (a)1:1 and (b)1:9 deposited on FTO glass.

4(a) (b)

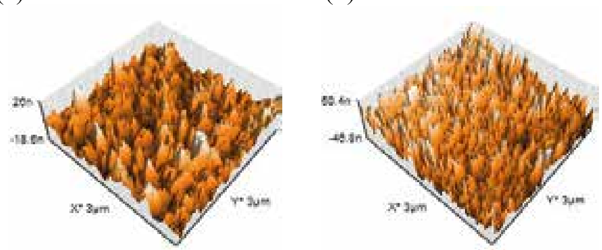


Fig. 4. The topography of 2 layers of TiO_2 with ratio of (a)1:1 and (b)1:9 deposited on FTO glass.

5(a) (b)

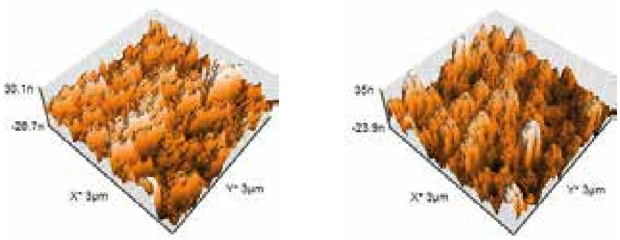


Fig. 5. The topography of 3 layers of TiO_2 with ratio of (a)1:1 and (b)1:9 deposited on FTO glass.

6(a) (b)

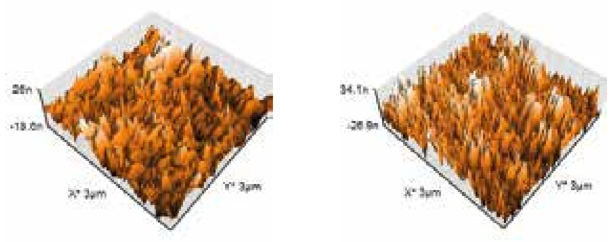


Fig. 6. The topography of 4 layers of TiO_2 with ratio of (a)1:1 and (b)1:9 deposited on FTO glass.

TABLE III. SIMPLIFIED DATA ON SURFACE ROUGHNESS OF TIO_2 BL LAYER.

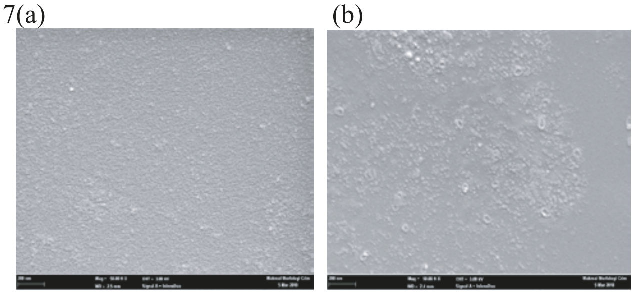
Ratio (TiO_2:CH_3NH_2OH)	**1 Layer**	**2 Layers**	**3 Layers**	**4 Layers**
	Surface Roughness (nm)			
1:1	5.2663	4.7929	4.1700	3.5168
1:9	11.0830	10.3330	9.0333	8.5935

C. Scanning Electron Microscopy (SEM)

Figure 7 and 8 had showed the SEM image of FTO coated TiO_2 BL layer. For 1 layer of 1:1 ratio, the grain size was within the range of approximately 38.16-47.11nm and as for 1:9, the grain size range was in the range of about 22.33-45.16nm. For 4 layers of 1:1 ratio, the grain size was within the range of approximately 67.91-110.20nm and as for 1:9, the grain size range was in the range of about 27.98-70.08nm. The particle size of higher concentration TiO_2 displayed larger grain size than the lower ratio. The same situation was applied to the increase number of deposited layers which formed larger grains.

According to the SEM result observation, the concentrated films were spread well and thus the films had formed more uniform layer than the diluted ratio precursor solution. As for cross section images obtained, the TiO_2 ETL become more adhesive after the films were exposed to high temperature during annealing process.

7(a) (b)



(c) (d)

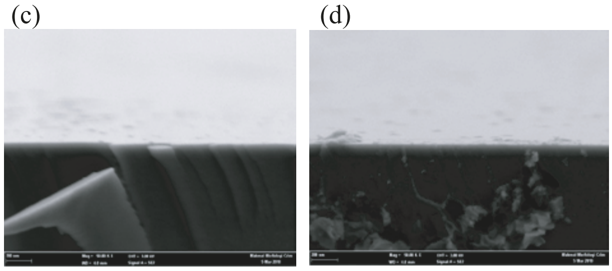


Fig. 7. The SEM surface images of 1 layer (a) concentrated (1:1) and (b) diluted (1:9) of TiO_2 BL film. The SEM cross section images of 1 layer (c) concentrated (1:1) and (d) diluted (1:9) of TiO_2 BL film.

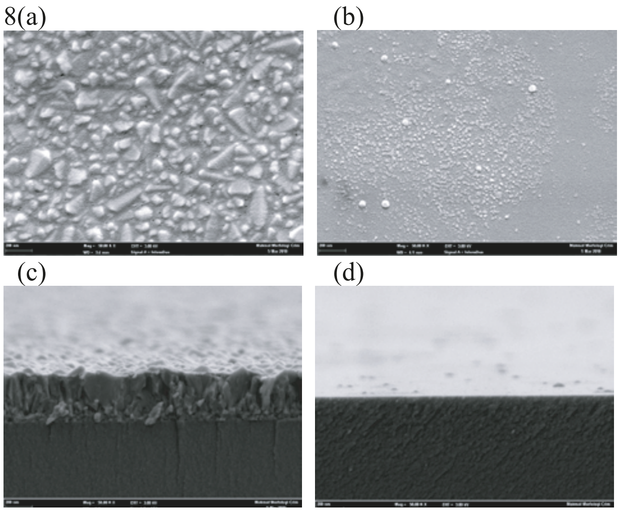


Fig. 8. The SEM surface images of 4 layers (a) concentrated (1:1) and (b) diluted (1:9) of TiO_2 BL film. The SEM cross section images of 4 layers (c) concentrated (1:1) and (d) diluted (1:9) of TiO_2 BL film.

D. *UV-visible (UV-vis) Spectroscopy*

The two UV-Vis absorbance spectra were plotted based on different TiO_2 concentrations and varied number of deposited layers to study the relationship between them.

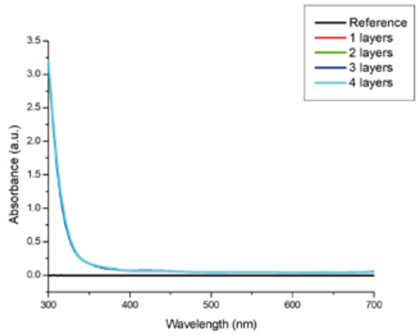


Fig. 9. The UV-Vis absorbance spectra of different numbers of TiO_2 layers for concentrated (1:1) BL precursor solution.

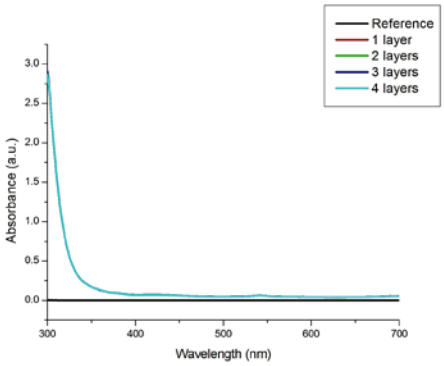


Fig. 10. The UV-Vis absorbance spectra of different numbers of TiO_2 layers for diluted (1:9) BL precursor solution.

From the plotted graph, there were no visible changes in the absorbance value for 1:1 and 1:9 when increased in the deposited layers. However, there were observable changes in absorbance value when the concentration of TiO_2 increased the prepared precursor solution from ratio of 1:9 to 1:1. There was slight increase in thickness value for 1:9 even when more layers were added and thus, no obvious absorbance changes. In contrast, there was observable difference in ETL thickness between 1:1 and 1:9, more light was absorbed during illumination and so the absorbance plotted was higher for concentrated 1:1. Therefore, this had obeyed the Beer-Lambert's Law which stated that the absorbance had linear proportional relationship with the concentration of absorbing material when exposed to the light.

IV. CONCLUSION

In conclusion, this paper had studied the effect of concentration and number of deposited layers on morphology and optical properties of TiO_2 ETL. From the characterization results, the AFM analysis found that the higher concentration (1:1) precursor solution managed to obtain more uniform and smooth films. This had indirectly translated into UV-Vis data which less light was scattered during illumination process for 1:1 rather than 1:9. Thus, the 1:1 precursor deposited film had recorded higher absorbance value than the diluted (1:9) version. However, there was no noticeable change in absorbance value when more TiO_2 layers were deposited for each concentration. This was because there was not much change in layer thickness even more layers were added.

As for SEM result, larger grain size can be produced with the use of higher concentration precursor solution and also by the addition of TiO_2 BL layers. TiO_2 was a stable and robust material that the precursor solution was prepared and then each layer was spin coated onto FTO glass substrate within the ambient air environment. A stable, uniform, large grain size with higher absorbance value material were the required characteristics that an ETL needed in order to produce a good quality solar cell especially in term of cell performance.

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