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Semiconductor TiO2 Coating Deposited by Microwave Plasma Method

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Abstract. Transparent conducting glass is a crucial layer of Dye Synthesized Solar Cell (DSSC), due to it allows sunlight penetrating to the solar cell. DSSC has a low efficiency until semiconductor Titanium Dioxide (TiO2) was employed as the anode material. TiO2 has high photosensitivity, high structure, stability under solar irradiation and in solution, and low cost. In this study, TiO2 was deposited on the conductive glass using microwave plasma method. Plasma was generated using electromagnetic waves from microwave magnetron. TiO2 powder was dissolved using pure water and ethanol at different concentrations. The coating process was conducted on a 2.5 x 2.5 cm of conductive glass, and the effect of plasma generation time was observed at 0.5, 1, 2, 3, and 5 minutes. The thickness, roughness, and microstructure of TiO2 coating on the conductive glass were observed using a 3D measuring laser OLS4100. The result shows that the fabrication of TiO2 coatings using microwave plasma is feasible. The concentration of solution and plasma generation time plays an important role in the thickness, roughness, and microstructure of TiO2 coatings. An optimum result was obtained at a plasma generation time of 0.5 minutes with 12.49 µm and 3.398 µm of thickness and roughness respectively using 10 g TiO2 + 50 ml ethanol and 40 ml H2O.

Introduction

Dye Synthesized Solar Cell (DSSC) has been extensively considered a promising photovoltaic device recently due to the low fabrication cost, optical properties, and high efficiency of power conversion [1, 2, 3]. It consists of a conductive glass substrate, a dye-synthesized metal oxide semiconductor electrode, a catalyst counter electrode, and an electrolyte solution inserted between the two electrodes. The conductive glass substrate should possess good electrical conductivity to provide a gateway for solar radiation to absorb also as a current collector [4].

There are some prominent metal oxides with band gaps higher than 3 eV that have good photo-corrosion resistance and superior electronic properties such as TiO2, ZnO, SnO2, SrTiO3, Zn2SnO4, WO3, and Nb2O5 to name a few [5]. TiO2 is widely used as a semiconductor in DSSC due to high thermal, and chemical stability, low cost, favorable charge carrier properties, and high transparency in the solar spectrum [1]

The fabrication of TiO2 nanoparticles on conductive glass plays an important role in the solar cells' efficiency since the thickness of the TiO2 coating affects it. Various surface coating methods using TiO2 were reported such as sol-gel [6], spray deposition [7], sequential dip spin[8], and chemical vapor deposition[9]. However, those methods often require high temperatures, multiple steps, and vacuum processing to produce a film.

The plasma method has been applied widely in nanoparticle production [10, 11]. This development has heightened the research on the plasma coating process. A plasma spray copper coating has been presented using two different plasma power of 20 kW and 25 kW. The result showed that 25 kW plasma power possesses higher density and hardness, advancing contact angle, and parahydrophobic behavior that helps in better heat transfer at higher high flux [12]. The plasma electrolytic oxidation method successfully achieved high photocatalytic ability for the TiO2 coating with a pulsed power mode in a range of 200 to 400 V using NaPO3 as an alkaline electrolyte [13]. Atmospheric pressure plasma-enhanced chemical vapor deposition was applied to the TiO2 coating on transparent plastic. An amorphous structure without any crack was successfully formed without damaging the polymer structure [14].

In this study, the feasibility of the TiO2 coating using the microwave plasma method was investigated with various TiO2 solutions and plasma irradiation time.

Experimental Procedure

The coating process of TiO_2 was conducted using a 2.45 GHz microwave plasma with an input power of 160 Volt. The electromagnetic wave from microwave magnetron was used to generate plasma. A transparent conductive glass 2.5 x 2.5 cm was hung inside a stainless steel reactor. Plasma was generated at the tip of the tungsten electrode with 2.5 cm space from the transparent conductive glass as shown in Fig. 1.

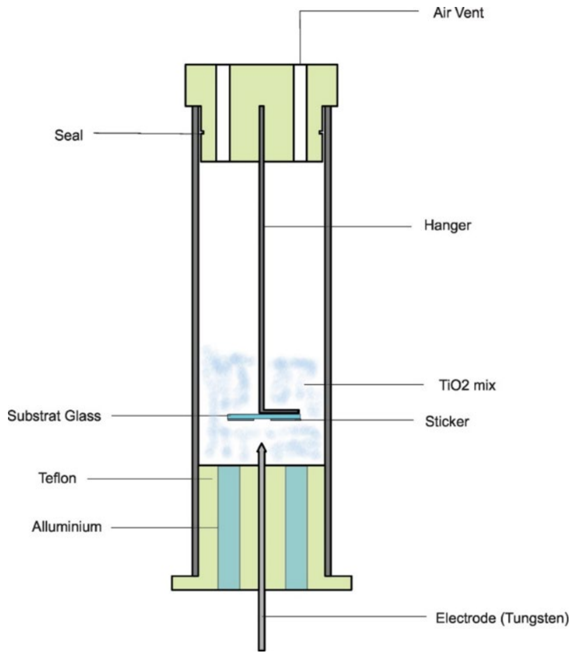

Fig. 1. Schematic illustration of TiO_2 coating by plasma

Table 1. Various concentrations of titanium dioxide solution

Solution	TiO_2 powder (g)	Ethanol (ml)	Deionized water (ml)
I	5	100	40
II	10	100	40
III	20	100	40
IV	10	50	40

The solution was prepared by making various concentrations of titanium dioxide (TiO_2) with ethanol and pure water as shown in Table 1. A commercial non-branded Titanium Dioxide powder with a nominal particle size of 15 nm was used as a feedstock. The solution was then stirred for 2 h using a magnetic stirrer and poured inside the reactor, then plasma was generated within 2 minutes of irradiation time to compare the thickness and roughness of the coating result. The solution yields an optimum coating result then used to observe the effect of plasma irradiation time of 0.5, 1, 2, 3, and 5 minutes. The thickness, roughness, and microstructure of TiO_2 coating deposited on the conductive glass were then observed using a 3D measuring laser OLS4100.

Results and Discussion

TiO_2 Coating Results in Various Concentration of a Solution. Figures 2 and 3 shows a roughness measurement record and roughness average with a variation of solution after 2 min of plasma irradiation. The average roughness (Ra) is a coating surface roughness quantity that is defined as the arithmetic mean of departures of the profile from the mean line. The average roughness was 0.74 µm, 4.11 µm, 12.3 µm, and 3.67 µm for a solution I, II, III, and IV respectively.

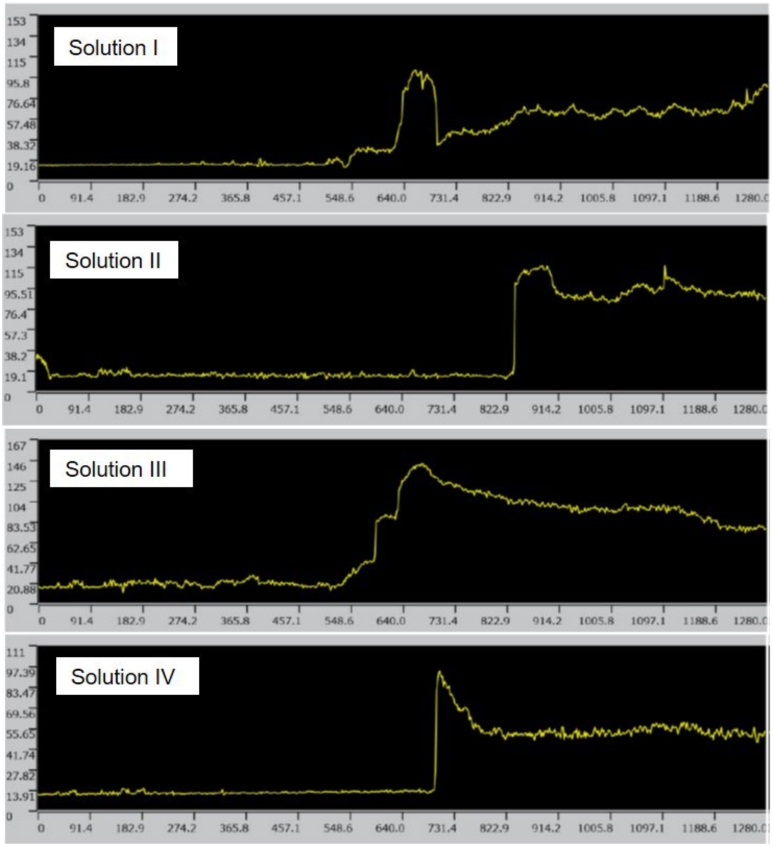

Fig. 2. Roughness measurement record of TiO_2 coating at various TiO_2 solution

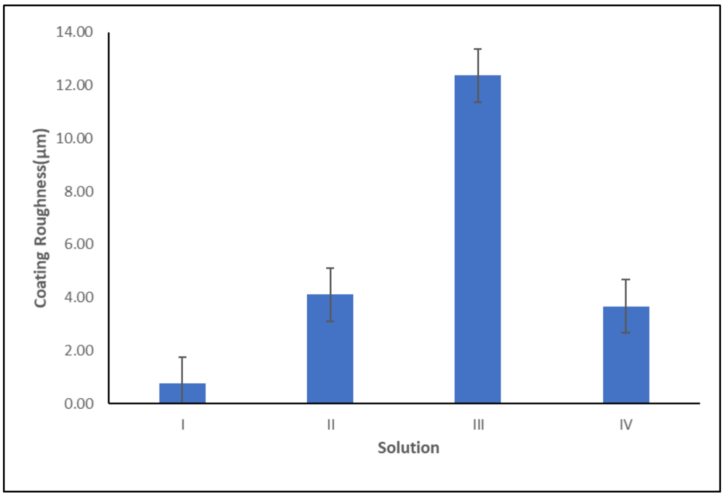

Fig. 3. Coating roughness average with a variation of TiO_2 solution

Increasing the amount of TiO_2 exhibits high roughness of the coating layer. The highest roughness was obtained when using solution III (20 g TiO_2 + 100 ml ethanol + 40 ml pure water). Following the present result, previous studies have demonstrated that the roughness of the coating surface was enhanced by increasing the particle concentration [15]. Research on micro-arc oxidation coupled with electrophoretic deposition processing of HA/ TiO_2 coating indicated that the number of HA particles integrated into the coating layer increased as the HA concentration increased [16] When plasma electrolytic oxidation was applied to ceria nanocomposite coating and ZrO_2 nanoparticle on titanium substrate, it was reported that by increasing the concentration of nanoparticle the average size of surface roughness values was increased. It is assumed that they were not deposited in the pores but a few particles attached to the surface attributed to the increase of coating surface [17], [18]. However, when the amount of ethanol in the solution was decreased in solution IV (10 g TiO_2 + 50 ml ethanol + 40 ml pure water), the coating roughness decreased to 3.672 µm. Compared to other plasma coating methods, alumina coating by the air plasma spraying process reported the coating roughness in a range of 6.84 µm to 10.23 µm [15].

Figure 4 shows a coating thickness average with a variation of solution. Coating thickness was 58.03 µm, 64.91 µm, 84,18 µm, and 15.50 µm for a solution I, II, III, and IV, respectively. The same trend with coating roughness was also observed, the coating thickness was increased as the concentration of TiO_2 in solution I to III, then decrease when the amount of ethanol was decreased in solution IV. Although some researchers stated that adding particles into the electrolyte did not affect the thickness of the coating[19, 20, 21], in several papers, the increase in the coating thickness in exchange for the addition of concentration has been mentioned. Micro arc oxidation coatings with the addition of Al2O3 particles, MgO microparticles, and CeO_2-doped TiO_2 nanostructured composite revealed that the coating thickness result was increased. The finding from these studies indicates that the perceived increment in thickness might be related to the coating band gap declining, an increase in electrolyte conductivity, and the augmenting formation voltage of coating affected by increasing concentration [22, 23, 24].

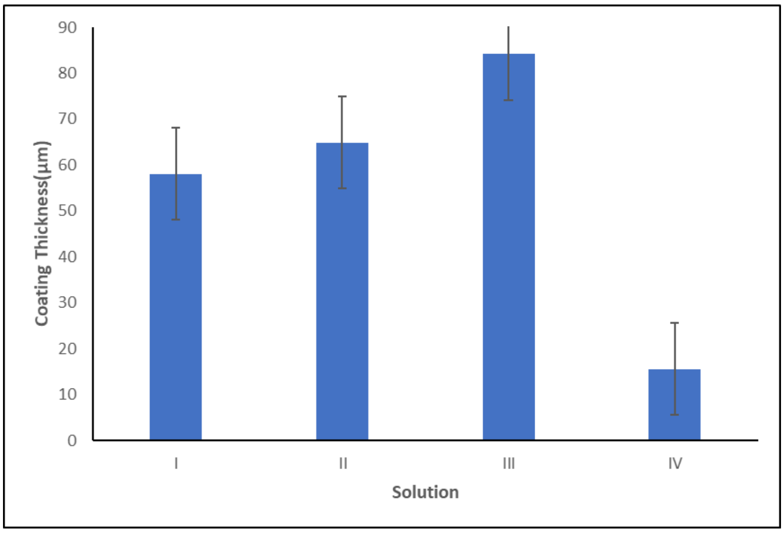

Fig. 4. Coating thickness average with a variation of TiO_2 solution

By varying the TiO_2 concentration, the optimum condition of thickness and roughness of 15.903 µm and 3.672 µm respectively was obtained using solution IV (10 g TiO_2 + 50 ml ethanol + 40 ml pure water). This solution was then used to observe the effect of plasma irradiation time.

The microstructure and 3D topography of TiO_2 coating with solution variation are shown in Figs. 5 and 6. Most coatings had the usual microstructure such as a porous surface with many micropores over the surface [15]. The formation of porous morphology was in consequence of molten materials left from the discharge channels and agglomerating around the opening due to the electric micro-discharge [25]. As can be seen in Fig. 5, increasing concentration resulting smaller pore and so does when the ethanol concentration decrease. In solution IV, pores with an average size of 7.42 µm were detected. A compact columnar structure was observed with similar morphology to other plasma coating methods [26, 14]. Coating of alumina nanoparticles on titanium substrate via plasma electrolytic oxidation also confirmed that increasing the concentration of nanoparticles promotes the peak intensity and shifts the peak position to smaller pores with pores diameter in a range of 3 to 10 μm [20].

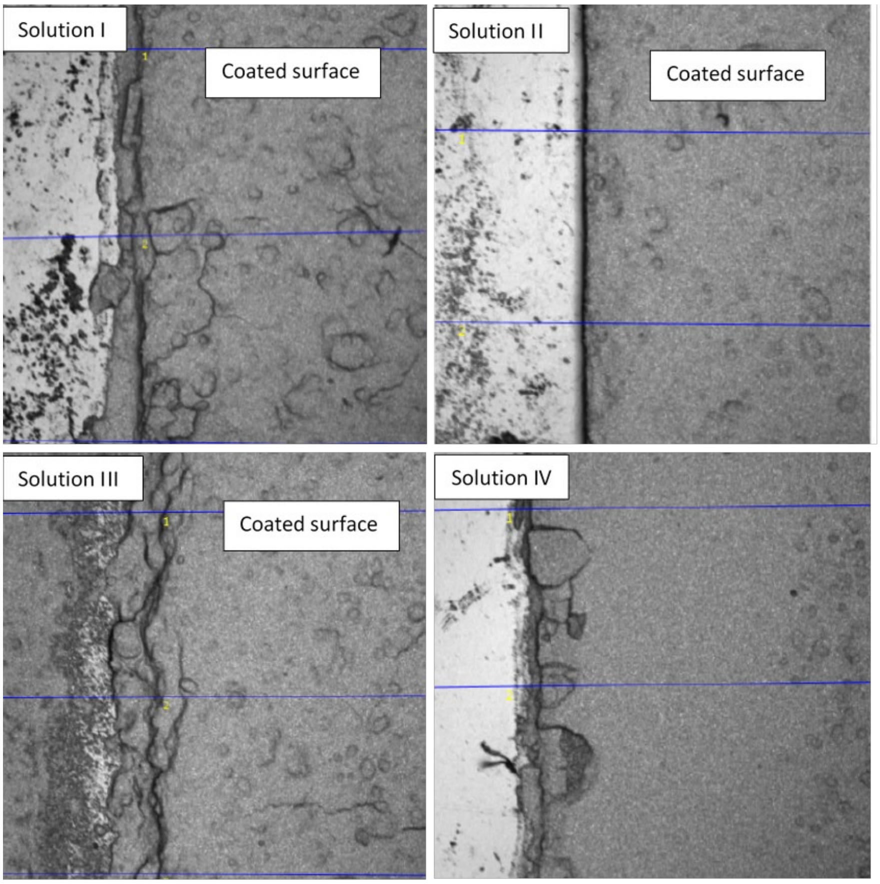

Fig. 5. Microstructure surface TiO_2 coating at various TiO_2 solution

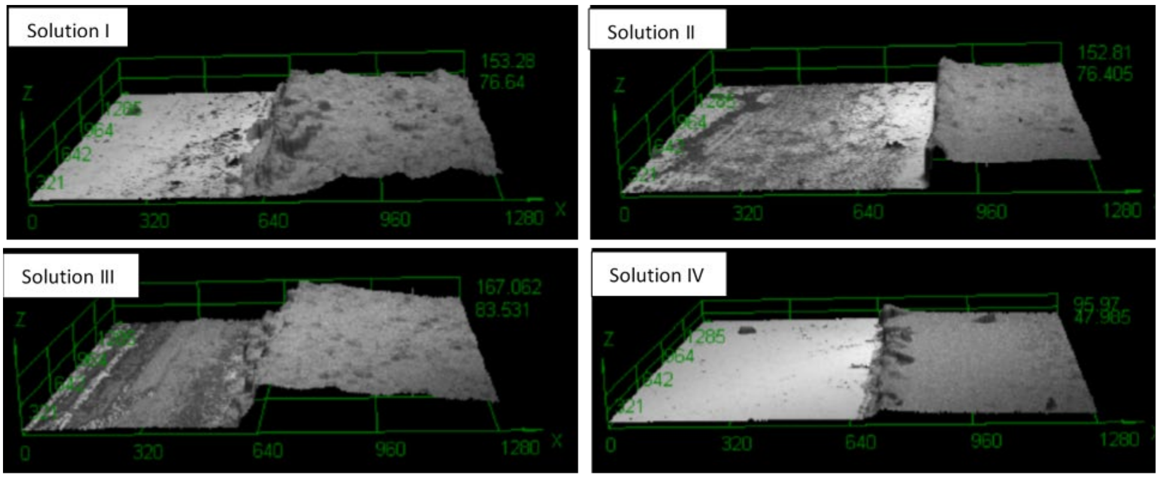

Fig. 6. 3D surface topography of TiO_2 coating at various TiO_2 solution

TiO_2 Coating Results at Various Plasma Irradiation Time. Using solution IV, the coating process was then conducted by varying plasma irradiation times of 0.5, 1, 2, 3, and 5 minutes. Roughness measurement record and roughness average are present in Figs. 7 and 8. The roughness average was increased as the plasma irradiation time. It was 3.39 μm, 4.37 μm, 4.06 μm, 5.12 μm, and 6.46 μm at plasma irradiation times of 0.5, 1, 2, 3, and 5 minutes, respectively. Figure 9 shows the thickness of the coating layer with a variation in plasma irradiation time. It was found to be 12.49 μm, 23.41 μm, 36.15 μm, 57.92 μm, and 77 55 μm at plasma irradiation times of 0.5, 1, 2, 3, and 5 minutes, respectively.

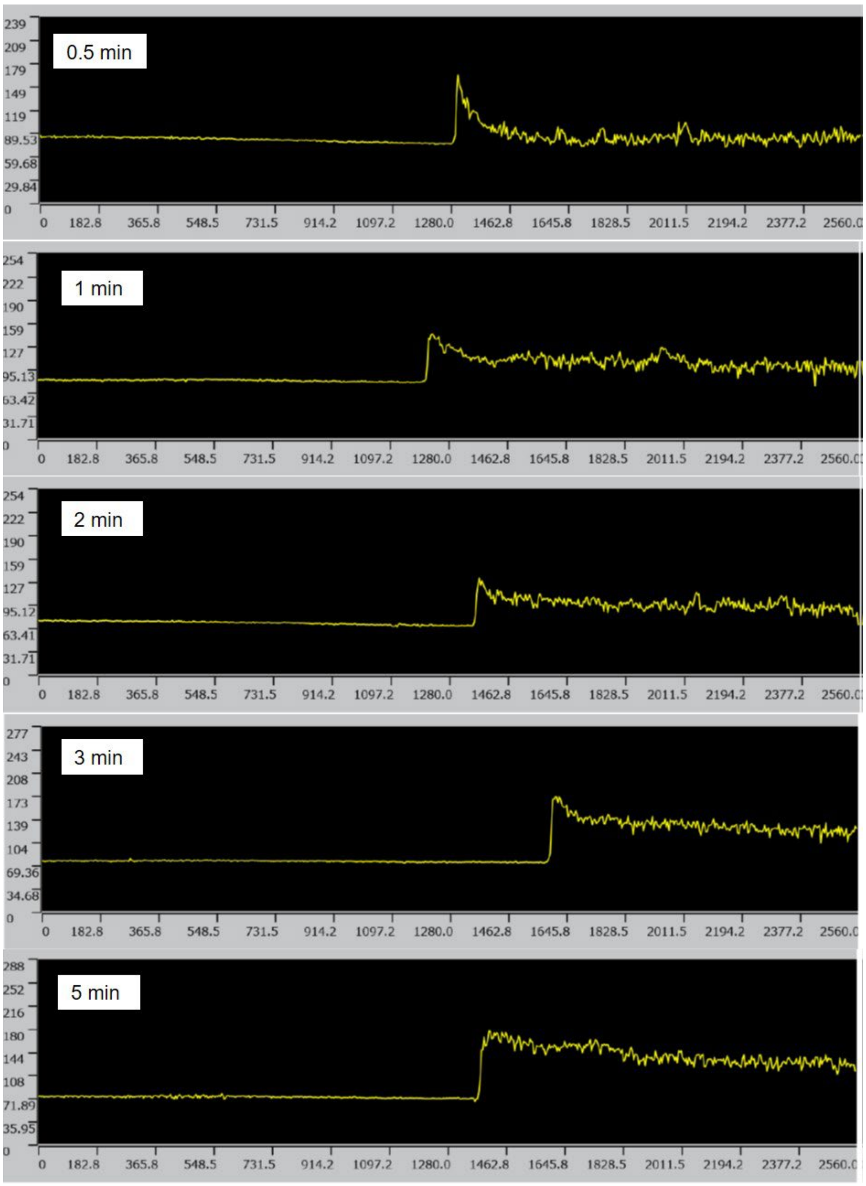

Fig. 7. Roughness measurement record of TiO_2 coating at various plasma irradiation times

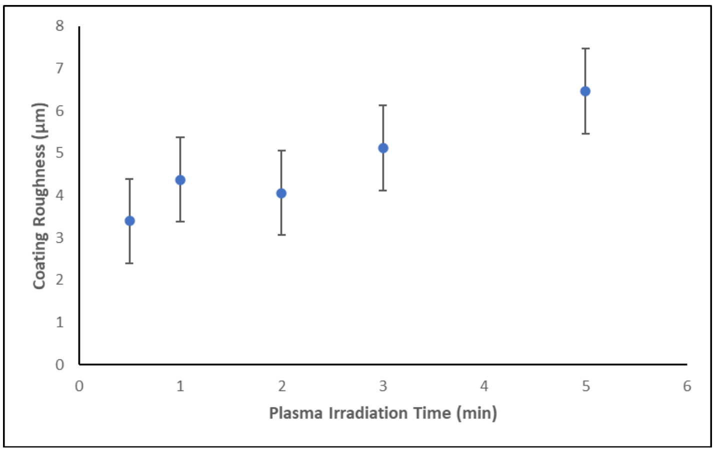

Fig. 8. Coating roughness average at various plasma irradiation time

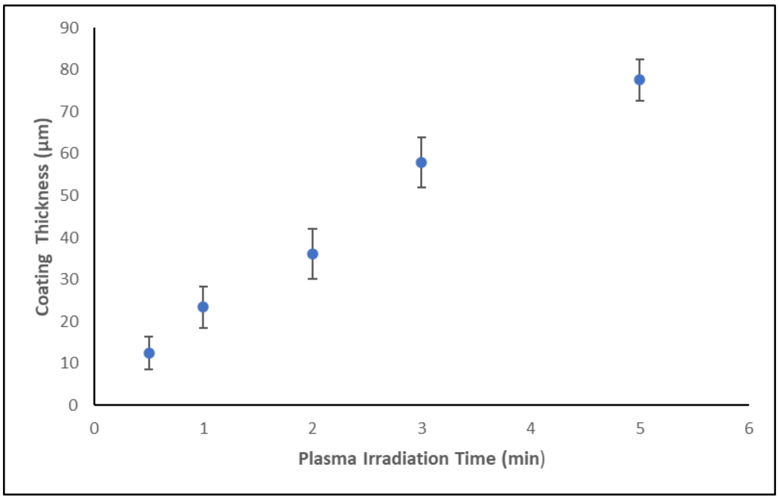

Fig. 9. Coating thickness average at various plasma irradiation time

Numerous papers deal with the influence of treatment time on roughness, thickness, and porosity. Research on the micro-arc oxidation coating method confirmed that as the oxidation time increase, the roughness and thickness constantly increase [27]. Increasing anodizing time of porous titania coating from 10 to 360 s resulting in a further increase of coating thickness, roughness, and porosity with 60 s of anodizing time is the most suitable for mechanically resistant titania coating [28].

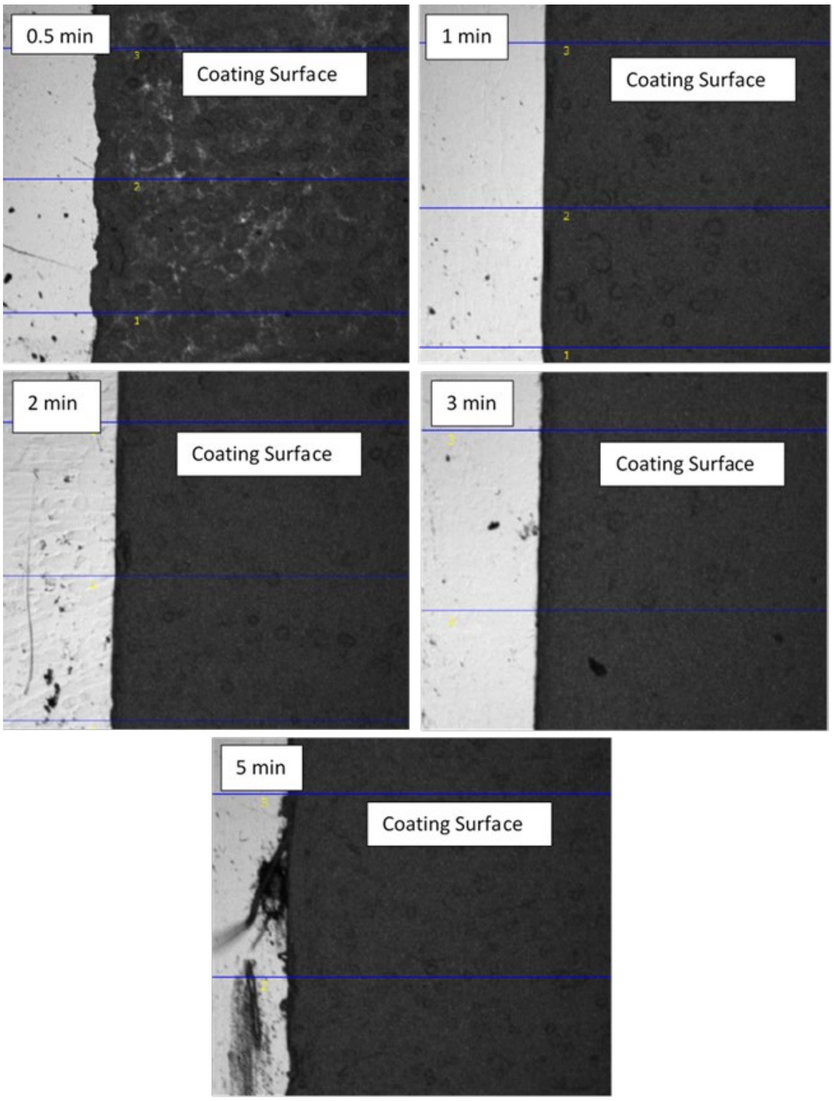

Fig. 10. Microstructure surface of TiO_2 coating at various plasma irradiation times

The thickness layer plays an important role in the efficiency of DSSC. Many studies have reported the optimum thickness for DSSC application. Research on TiO_2 deposited using the doctor blade method found that the best thickness ranged from 11 to 17 µm [29]. The single-layer TiO_2 photoanode deposited using the screen printing technique revealed that the average thickness of 12 µm can achieve the highest conversion efficiency of 5.13% [30]. Radio frequency (RF) plasma and Water Stabilized Plasma (WSP) methods reported that average coating thickness was obtained in a range of 0.47 to 3.02 µm [31]. In other work, several DSSCs were prepared with different semiconductor thicknesses to obtain the thickness-surface charge density dependence and it was found that the resistance of electrolyte solution was maximum at a thickness between 10 and 16 µm [32]. In this study, the optimum coating result was obtained when plasma was irradiated for 0.5 minutes with roughness and thickness of 3.398 µm and 12.499 µm respectively.

The morphology of the coating surface with a variety of plasma irradiation times is shown in figure 10. It was seen that the smaller pores obtained in 0.5minute plasma irradiation time with an average size of 9.92 µm. In the plasma coating process, the TiO_2 solution was heated by plasma generation. A bubble containing plasma was touched and coated onto a conductive glass surface. Chemical reactions are initiated next, and then nucleation and growth of the grains occur, resulting in the formation of dense particles. Interactions among these highly active particles lead to the formation of either 'large' particles/crystals, agglomerates, or aggregates [33]. Another study reported that the plasma mechanism for coating formation occurred as the coating was shocked by bubble explosion due to the plasma heat [18].

Conclusion

As a preliminary investigation, the feasibility of TiO_2 coating on semiconductor conductive glass using the microwave plasma method has been conducted. An optimum coating result was obtained at a plasma generation time of 0.5 minutes with 12.49 µm and 3.398 µm of thickness and roughness respectively using 10 g TiO_2 + 50 ml ethanol and 40 ml H_2O. Further, the analysis will be conducted on the TiO_2 crystalline structure and coating mechanism of the microwave plasma method.

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