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INFLUENCES OF DEPOSITION LAYER ON THE PROPERTIES OF TITANIUM DIOXIDE THIN FILMS FABRICATED BY DIP COATING TECHNIQUE

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ABSTRACT

Titanium dioxide (TiO_2) thin films were deposited on silicon substrates by using a sol-gel dip coating technique. In order to study the influences of the deposition layer on the properties of TiO_2 films, the number of layer was varied. Then, the TiO_2 films were analyzed by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and four- point probe. Generally, all films are uniform without the presence of any grain or grain boundary. The TiO_2 films were confirmed by energy-dispersive X-ray spectroscopy (EDS) which indicates the presence of titanium (Ti) and Oxygen (O). It was found that, the thickness and crystallite size of the films increases as the deposition layers increased. On the contrary, the resistivity of the TiO_2 films decreases in the range of 5.80×10^2 Ω.cm and 1.45×10^2 Ω.cm as the deposition layer increased. Therefore, it has been determined that the properties of TiO_2 films were strongly correlated with the thickness of the films.

Keywords: TiO_2 film, sol-gel dip coating, crystal structure.

INTRODUCTION

Titanium also known as titania has a wide band gap energy and is a non-toxic material. The band gap energy is different according to their crystallographic polymorphs of the titanium dioxide (TiO_2). TiO_2 are extensively studied because of their interesting properties such as high photocatalytic activity, high refractive index, and good physical and chemical stability (Ahn, Kim, Kim, & Hahn, 2003). The unique properties of the TiO_2 make this metal oxides material suitable for many applications, particularly as dye-sensitized solar cells (Moon, Sung, and Han, 2013), gas sensor (Castañeda, López-Suárez, and Tiburcio-Silver, 2010), white pigment for paints (Valencia *et al.*, 2010) and photocatalyst (Hanaor and Sorrell, 2011). TiO_2 has three different crystallographic polymorphs which is rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) (Diebold, 2003; Fröschl *et al.*, 2012; Luís, Neves, Mendonça, and Monteiro, 2011). Rutile have been reported as the stable phase while anatase and brookite are metastable phase (Di Paola, Bellardita, and Palmisano, 2013). In high temperature (~1300 °C and above) (Hanaor and Sorrell, 2011), the anatase and brookite which is metastable form are readily transformed to rutile. The band gap energy of rutile is 3.02 eV, anatase is 3.23 eV and brookite is 3.14 eV (Di Paola *et al.*, 2013).

TiO_2 thin films have been fabricated on several kind of substrates such as Indium Tin Oxide (ITO), glass (Paez and Matoušek, 2004), alumina, silicon and even on substrate with low thermal resistance like plastics and textiles (Sisti *et al.*, 2012). In this work, silicon have been used due to its special features such as available in large diameter and have good electrical and thermal properties (Pal and Jacob, 2004).

Different techniques have been used for the fabrication of TiO_2 such as reactive magnetron sputtering (Piwo, Kisielewska, Szczukocki, Krawczyk, and Sielski, 2014), chemical vapor deposition (Zheng, Gu, Sun, Mo, and Chen, 2010), spray pyrolysis (Castañeda *et al.*, 2010), hydrothermal (Wang, Li, Zhi, Manivannan, and Wu, 2008) and sol-gel method. Among of these technique, the sol-gel method has some advantages such as reproducibility (Mechiakh, Sedrine, Chtourou, and Bensaha, 2010), can deposited large area of substrate, can control film thickness and easy control of chemical composition of thin film layers (Sonawane, Kale, and Dongare, 2004). Sol-gel coating method has been classified as two different methods such as spin coating and dip coating. The dip coating have been widely used for fabricated TiO_2 nanostructured thin films (Barati, Sani, Ghasemi, Sadeghian, and Mirhoseini, 2009; K, Ramli, Amri, and Maarof, 2012; Mechiakh *et al.*, 2010).

In this paper, we report the influence of deposition layers of TiO_2 films on the surface morphology, structural and electrical properties.

EXPERIMENTAL PROCEDURE

Preparation of the coating solution

Flow chart of the experiment is shown in Figure-1. A starting solution for the dip coating process was prepared from titanium (IV) butoxide Ti-$(OC_4H_9)_4$ (97%, Sigma Aldrich) as a precursor and ethanol as a solvent. Precursor solutions for TiO_2 films were prepared by the following method: at room temperature titanium (IV) butoxide and glacial acetic acid were dissolved in ethanol. Deionized water was added to the solution under continuous stirring. The mixture was stirred and heated to 40 °C for about 10 minutes. The reaction process between the materials in the solution were increased during the heating process. Then the solution was continuously

stirred at a constant speed for 3 hours to complete the reaction.

Deposition of thin films

For the deposition of the film, a single sided polished n-type silicon wafer (500 µm thick, (100) orientation, obtained from semiconductor wafer, inc.) were used as a substrate. The substrate were cut in to (20 mm X 30 mm). Silicon substrates were cleaned with diluted hydrofluoric acid (HF) (HF-water) with molar ratio of 1:10 before depositing the films to remove native oxide from the substrates. The substrates were then washed with deionized water and dried with nitrogen (N_2) gas. Afterwards, the substrates were dipped and withdrawn from the precursor solution at a withdrawal speed of 180 mm/min by using a dip coater machine (PTL-MM01 Desktop Dip Coater). Immediately after dipping process, the sample was pre-heated at 100 °C for 5 minutes in hot plate. The process was repeated for several times to obtain a desired coating. Finally, the sample was annealed at 500 °C for 1 hour in furnace to improve the structural property.

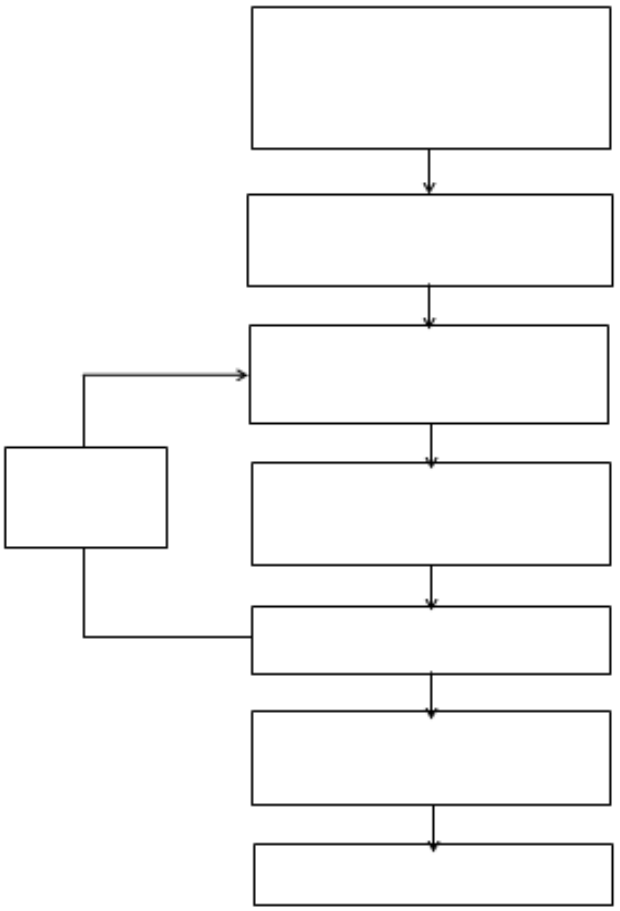


Figure-1. The flowchart of the experiment methodology.

Surface characterization

The TiO_2 films on silicon substrates were characterized for crystalline properties using X-ray diffractometer (XRD, model; PANalytical X-Pert Powder) with a Cu- Kα radiation source at a setting of 40mA and 40 kV. The diffraction patterns were collected in the range 2θ = 20°-70° with a 0.01° step size. The surface morphology of the coating layer was characterized using Field Emission Scanning Electron Microscope (FESEM, model; JSM-7600F) with an accelerating voltage of 15kV. Approximate film thickness was measured by using Alpha-Step IQ Surface Profiler (KLA Tenkor) with scan length 4000 µm and scan speed 50µm/s while the resistivity of the thin films were measured by using four point probe.

RESULTS AND DISCUSSIONS

Structural properties

To compare the effect of different deposition layer on structural properties of TiO_2 films, the films were fabricated on the silicon substrates by the dip-coating method. Figure-2 shows the XRD pattern in the range of 2θ = 20°-70° of the samples with 5, 7, 9 and 11 layers. Measurements with XRD confirmed that anatase with tetragonal lattice structure is the only crystalline phase present for each layer. All peaks match well with Bragg reflections of the standard anatase nanocrystalline structure (ICSD file no. 98-015-4604). A weak silicon peak was also observed in all samples at position 2θ = 52.4° (ICSD file no. 98-004-1991).

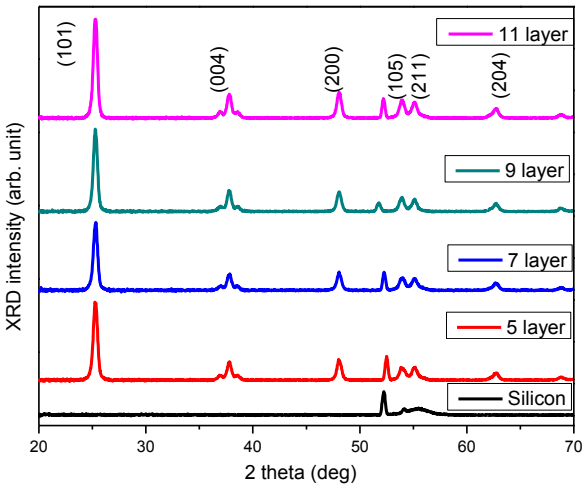


Figure-2. XRD pattern of TiO_2 films with different deposition layer.

Strong XRD peaks corresponding to TiO_2 anatase (101) were clearly observed at 2θ= 25.2°, along with generally low intensities of 2θ values at about 37.6° (004), 48.0° (200), 53.9° (105), 55.2° (211), and 62.7° (204) diffraction peaks. The increase in the intensity of these peaks indicates an improvement of the crystalline structure, by a rearrangement phenomenon and the increase in TiO_2 particle size (Luís *et al*., 2011). From the results, it can be seen that the intensities of the anatase TiO_2 (101) peak were increased as the 9 deposition layers of the film is increased to 11 deposition layers. This can be

explained by the improvement of the crystal quality. In fact, the improvement of the crystal quality may be due to the increase of the film thickness.

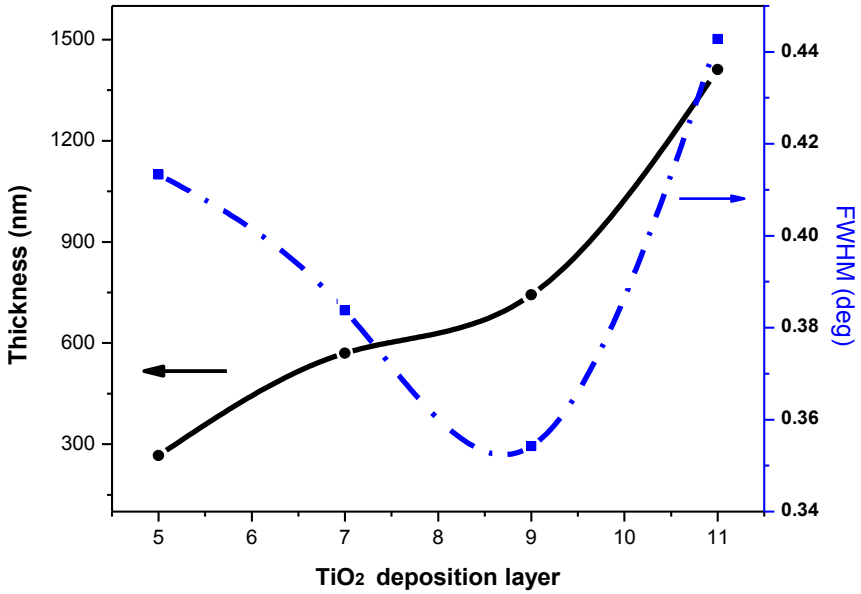


Figure-3. Variation of thickness and FWHM at various TiO_2 films.

Table-1. Evaluated structural parameters of TiO_2 films.

TiO_2 layer	**Position** (2 θ°)	**FWHM, deg**	**Crystallite size,d** (nm)	**Thickness** (nm)
5	25.2	0.4133	22.47	265.86
7	25.3	0.3838	24.25	569.93
9	25.2	0.3542	26.33	743.39
11	25.3	0.4428	20.94	1411.29

The thickness of each sample was characterized using surface profiler. It can be seen that the average thickness of the thin film were changed from 265.86 nm to 569.93 nm, 743.39 nm, and 1411.29 nm for 5, 7, 9 and 11 deposition layers, respectively. These results agree well with those of the increasing peak intensity as a function of deposition layer at the XRD measurements.

Figure-3 shows the thickness and full width at half maximum (FWHM) values of the anatase TiO_2 (101) peak as a function of TiO_2 deposition layers. From the figure, it can be seen that when the deposition layer is increased the thickness also increases while from the XRD

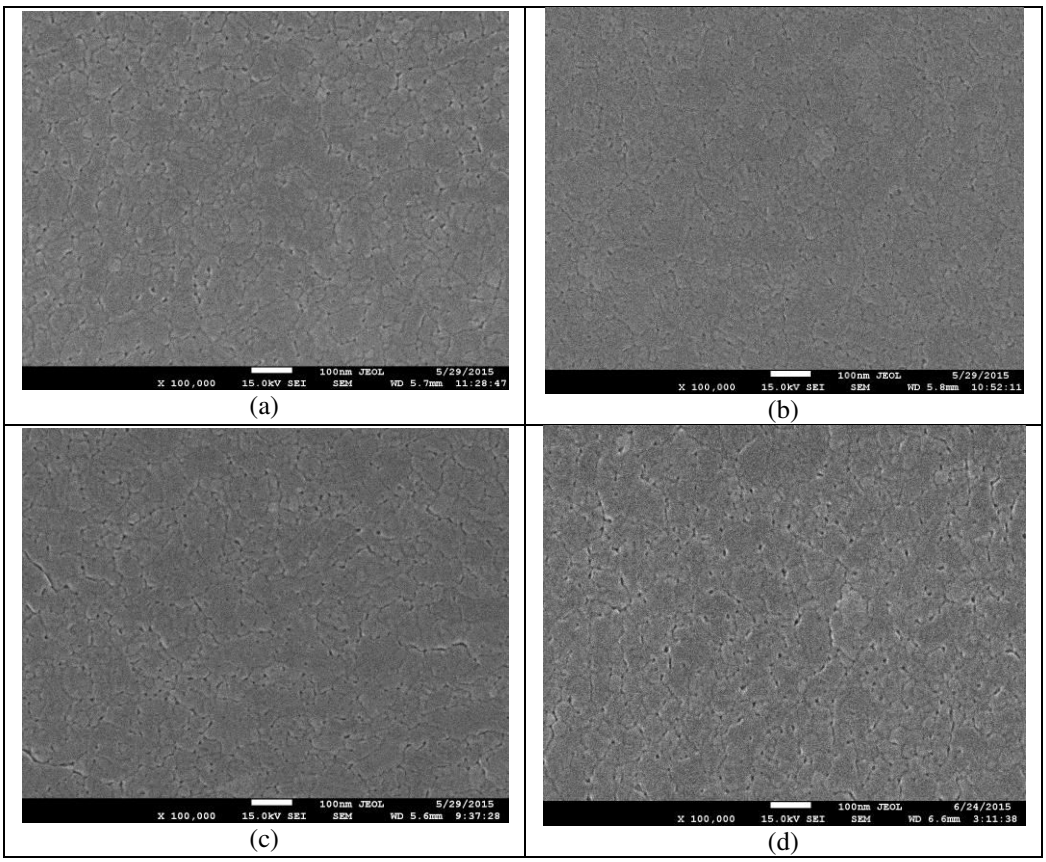
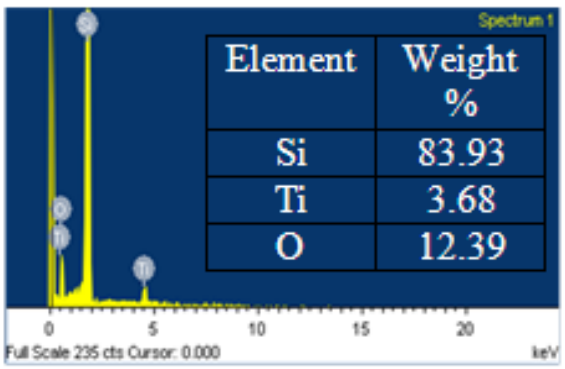
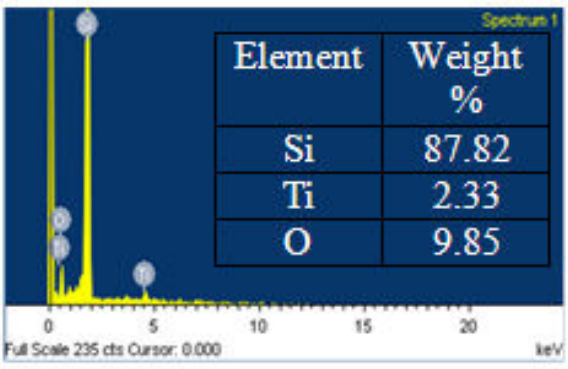


Figure-4. FESEM images for different layer dip coating (a) 5 layer (b) 7 layer (c) 9 layer (d) 11 layer.



(a)



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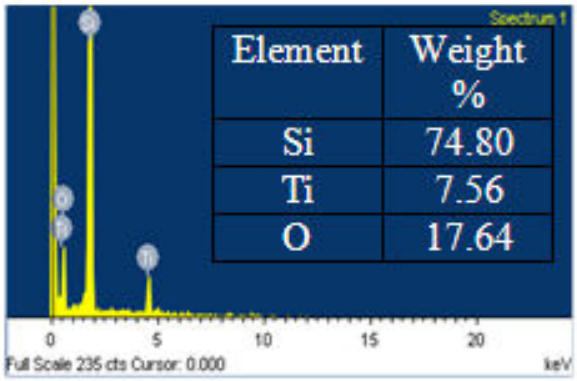
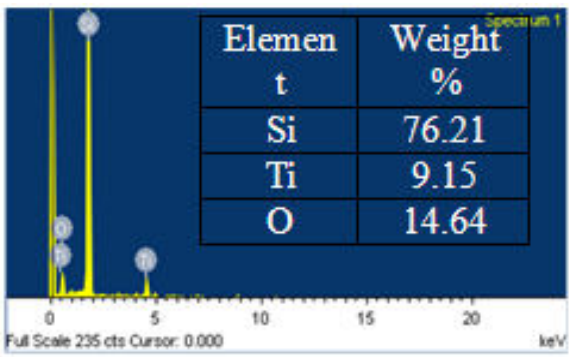


(b)



(d)

Figure-5. EDS images for different layer dip coating (a) 5 layer (b) 7 layer (c) 9 layer (d) 11 layer.

data, it is also observed that the FWHM decreases with an increase in deposition layers and approaches a minimum value at 9 layers deposition (film thickness at - 743 nm). As the film thickness increase further, the width of the peaks increase. This information indicates an increase in the crystallite size of the TiO_2 thin films was produced at higher deposition layer.

The crystal quality was improved by increasing the deposition layers. The average crystallite size of anatase TiO_2 (101) at 2θ =25.2° was estimated from the FWHM of the XRD peak using Scherrer's formula (Malek *et al*., 2013).

$$d = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

Where d is the crystallite diameter of TiO_2 thin film, k is the shape constant (0.94), λ is the wavelength of X-Ray (CuKα = 1.5406 Å), θ is the Bragg angle and β is the observed peak width at half-maximum peak height. The TiO_2 crystallite size values estimated during this work are presented in Table-1. The calculated values of the crystallite sizes changed from 22.47 nm to 26.33 nm. It is observed that the crystallite size increases with an increase in the deposition layer. However, for 11 layer of TiO_2 films, the crystallite size decreased.

Morphological properties

Figure-4 shows the FESEM images at 100 k magnification with 15 kV applied voltage of the TiO_2 films prepared on silicon substrates, corresponding to the deposited layer of 5, 7, 9 and 11 layers. It can be seen that TiO_2 films with different deposition layer (Figure-4 (a-d)) show almost similar morphology. There is no obvious grain or grain boundary on the sample. (Figure-5 (a-d)) show the energy-dispersive X-ray spectroscopy (EDS) spectrum indicating the presence of Titanium (Ti), Oxygen (O) and Silicon (Si) element. A high peaks of Si in all samples resulting from the silicon substrate. Thus, prove that TiO_2 has been formed as being supported by XRD data in Figure-2.

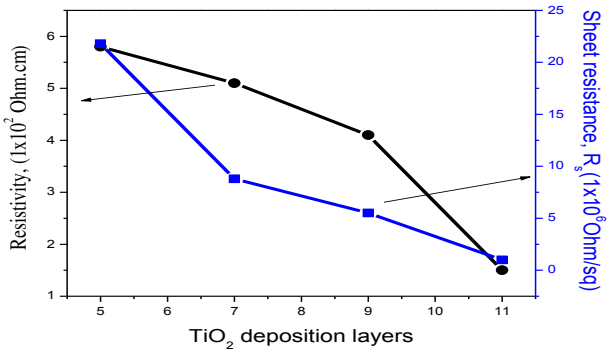


Figure-6. Variation of resistivity and sheet resistance at various TiO_2 thin films.

Figure-6 shows the resistivity and sheet resistance of TiO_2 thin film as a function of TiO_2 deposition layers. The resistivity and the sheet resistance of the TiO_2 films appear to be decreasing with the increment of the deposited layer of the TiO_2 films. The 11 layers deposition which is the highest deposition layers shows the lowest resistivity (1.45 x 10^2 Ω.cm) and sheet resistance (2.6 x 10^6 Ω/sq) compared to others. The resistivity is calculated using the formula below:

$$\rho = 2\pi s \frac{V}{I} \quad (2)$$

Where ρ is the resistivity, s is the spacing between the probe, V is the voltage and I is the current. The sheet resistance is measured by four-point probe. The sheet resistance can be determined based on the resistivity and thickness of the films according to the equation:

$$R_{s=\frac{\rho}{t}} \quad (3)$$

Where ρ is the resistivity and t is the thickness. The conductivity of the TiO_2 thin film is the reciprocal of the resistivity as shown by the following equation:

$$\sigma = \frac{1}{\rho} \quad (4)$$

Where σ is the conductivity and ρ is the resistivity. The samples were deposited from 5 until 11 layers indicate improvements of the conductivity according to the deposition layer applied. The highest conductivity can be found at thin film with 11 deposition layers. This is may be due to the improvement of the anatase TiO_2 crystal quality. When the crystal quality is improve, the electron movement from one particles to another improve.

The growth rate of the TiO_2 films deposited with 5 layers deposition is small compared to the growth rate deposited with 11 layers deposition. When this phenomenon occurs which is at 11 layers deposition, the empty space around the particles is reduced, causing a more physical contact within the film that resulted in decrease the resistivity of the films, as has been shown previously.

CONCLUSIONS

TiO_2 thin films have been successfully prepared by sol-gel dip coating method and the effect of deposition layer on their structural and electrical properties were examined. It was found that the TiO_2 films were primarily composed of anatase-phase TiO_2. The crystalline quality of the films improves at 11 layer deposition. Based on Scherrer's formula calculations, the crystallite size of the anatase phase increased from 22.47 nm to 26.33 nm with increasing deposition layer from 5 to 9 layers. With increasing the deposition layer from 5 to 11 layers, the resistivity of TiO_2 films decreased from 5. 80 x 10^2 Ω .cm to 1.45 x 10^2 Ω. cm due to the improvement in the crystallinity. The results show that the deposition layer

clearly affects the structural and electrical properties of TiO_2 films.

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