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Sol-gel Synthesis of TiO_2 Thin Films from In-house Nano-TiO_2 Powder

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Abstract**—** This paper presents the optimization process in sol-gel technique to synthesize Titanium dioxide (TiO_2) thin films using in-house Nano-TiO_2 powder. Nano-TiO_2 powder was previously synthesized in our lab from ilmenite which is a tin mining byproduct using a modified hydrothermal method. By varying the mass of Nano-TiO_2 powder and acetic acid (catalyst) concentration in the sol-gel process, highly transparent TiO_2 thin films were obtained. The thin films were characterized by field effect scanning electron microscope (FESEM), atomic force microscopy (AFM), thickness profiler, ultra-violet-visible spectrometer (UV-Vis) and current-voltage (*I-V*) measurement system. This paper also demonstrates the TiO_2 thin films are sensitive towards isopropanol (IPA) solution where the *I-V* response of the thin films changed sharply as IPA was dropped onto the thin film's surface. The electrical property shows the thin film has potential applications for chemical sensors and solar cells.

Keywords**-** Titanium dioxide; Ilmenite; Sol-gel; Tin mining;

1. Introduction

Tianium dioxide (TiO_2) or known as titania has been reported widely for its numerous applications from optoelectronics to cosmetics [1-3]. TiO_2 has excellent photocatalytic oxidative properties that depend on the crystallinity and crystal form [4]. Due to the photocatalytic activity, TiO_2 has been used in water and air pollution treatments [5]. It also exhibits unique electrical and chemical properties that can be utilized in various technological and engineering applications such as humidity sensor, gas sensor and membrane [6-7]. In addition, TiO_2 is also proposed for solar cells and laser diodes for its high refractive index and stability [8]. Although the starting material of TiO_2 powder can be obtained easily in the market, the price is quite expensive especially for research purposes in Malaysia. Therefore, an alternative way of using in-house nano-TiO_2 powder (anatase) synthesized from Ilmenite powder (from Malaysian Tin mining waste), is proposed. Using this in-house nano-TiO_2 powder, the cost of the starting material can be reduced up to 80%.

The problem of using nano-TiO_2 powder is the low solubility in organic solvent such as ethanol and isopropanol. Therefore, optimization on the mass of the starting material and catalyst is required. Sol-gel process is proposed since it is a convenient and versatile method for preparing transparent thin film at low temperature [9]. The sol-gel process involved many complex processes for both chemical and structural nature. Before gel formation (polymerization), two stages are indentified: (i) hydrolysis of the organometallic group precursor, and (ii) polycondensation. The physical, chemical and mechanical properties are much dependant on the properties of the precursor solution [10]. Therefore, optimizing the precursor solution may produce great results of TiO_2 thin film. Sol-gel process is very convenient to deposit transparent materials in combination with spin coating technique. The resulting coatings are of high purity and structural homogeneity depending on the parameters optimization.

2. Experimental

Indium Tin Oxide (ITO) was used as the substrate which has dimension of 1.5 cm x 1.5 cm. The substrate was cleaned using acetone in ultrasonic bath for 5 minutes at 50ºC. Then, it was blown dry with nitrogen gas.

Different TiO_2 solution was prepared using different mass of nano-TiO_2 powder which is 1g, 0.4 g, 0.1 g and 0.05 g. Each powder will be stirred in 30 ml of ethanol mixed with 6 ml of acetic acid. After underwent ageing process for 20 hours, the solution was spin coated onto the ITO substrate for 10 layers. The deposition was using 2-steps spin coating (1000 r.p.m. for 30 s and 3000 r.p.m. for 60 s). Every layer was preheated at 100ºC for 3 minutes. The thin films were annealed at 500ºC for 1 hour to improve the structural property. Again, after underwent slow cooling at room temperature, the thin films were characterized to find the optimum Nano-TiO_2 mass.

The acetic acid concentration was optimized using different acetic acid volumes which are 0 ml, 6 ml, 10 ml and 30 ml. It was mixed with nano-TiO_2 powder using the optimum mass in the previous experiment. It was stirred in 30 ml of ethanol for 20 hours. Using the same spin coater step, the TiO_2 thin films were deposited onto the ITO substrates. After annealing at 500ºC for 1 hour, the thin films were undergoing slow cooling at room temperature.

The thickness of each sample was characterized using KL Tenko surface profiler. The surface topology and roughness were characterized by an XE-100 Park system atomic force microscope (AFM). The optical property was characterized with a Lambda-750 Perkin Elmer ultra violet-visible spectrometer (UV-Vis). The structural property was characterized by an Advance Bruker X-ray diffractometer (XRD) and the electrical property of the sample was measured by a 2400 Keithley current-voltage (*I-V*) measurement system.

3. Results and Discussion

A. Nano-TiO_2 Mass Optimization

Figure 1 shows the AFM topography of the sample deposited using different mass of nano-TiO_2 powder. Generally, the film's roughness changes as the mass of the nano-TiO_2 powder changed. All films exhibit particles-packed morphology rather than sheet-packed. Lowering the mass of nano-TiO_2 powder contribute to the reduction of the surface roughness of the films. The surface roughness for film deposited using 1g, 0.4g, 0.1g and 0.05g of nano-TiO_2 powder is 55.6, 18.6, 23.8 and 26.6, respectively. It is found that the optimum mass of nano-TiO_2 powder for optimum roughness is 0.4g. The thicknesses of the sample deposited using 1g, 0.4g, 0.1g and 0.05g of nano-TiO_2 powder is 230, 140, 110 and 98 nm, respectively.

Figure 2 shows the transmittance of the TiO_2 thin films using different mass of nano-TiO_2 powder. As shown in the figure, it is clearly observed that the transmittance increases as the mass of the nano-TiO_2 powder decreases. This may due to the reduction of the thin film's thickness as the mass of nano-TiO_2 powder reduced. The TiO_2 thin film absorbed light which has energy greater than 3.4 eV (~365 nm). However for 0.4g sample, it absorbed photon energy greater than 3.83 eV (~324 nm) or in other word, extends the transparency in which applicable for photovoltaic application. Figure 3 shows the XRD spectra of the TiO_2 thin films. It is proven that all TiO_2 films exhibit anatase form. The intensity of the XRD spectra differs due to the mass difference of nano-TiO_2 powder.

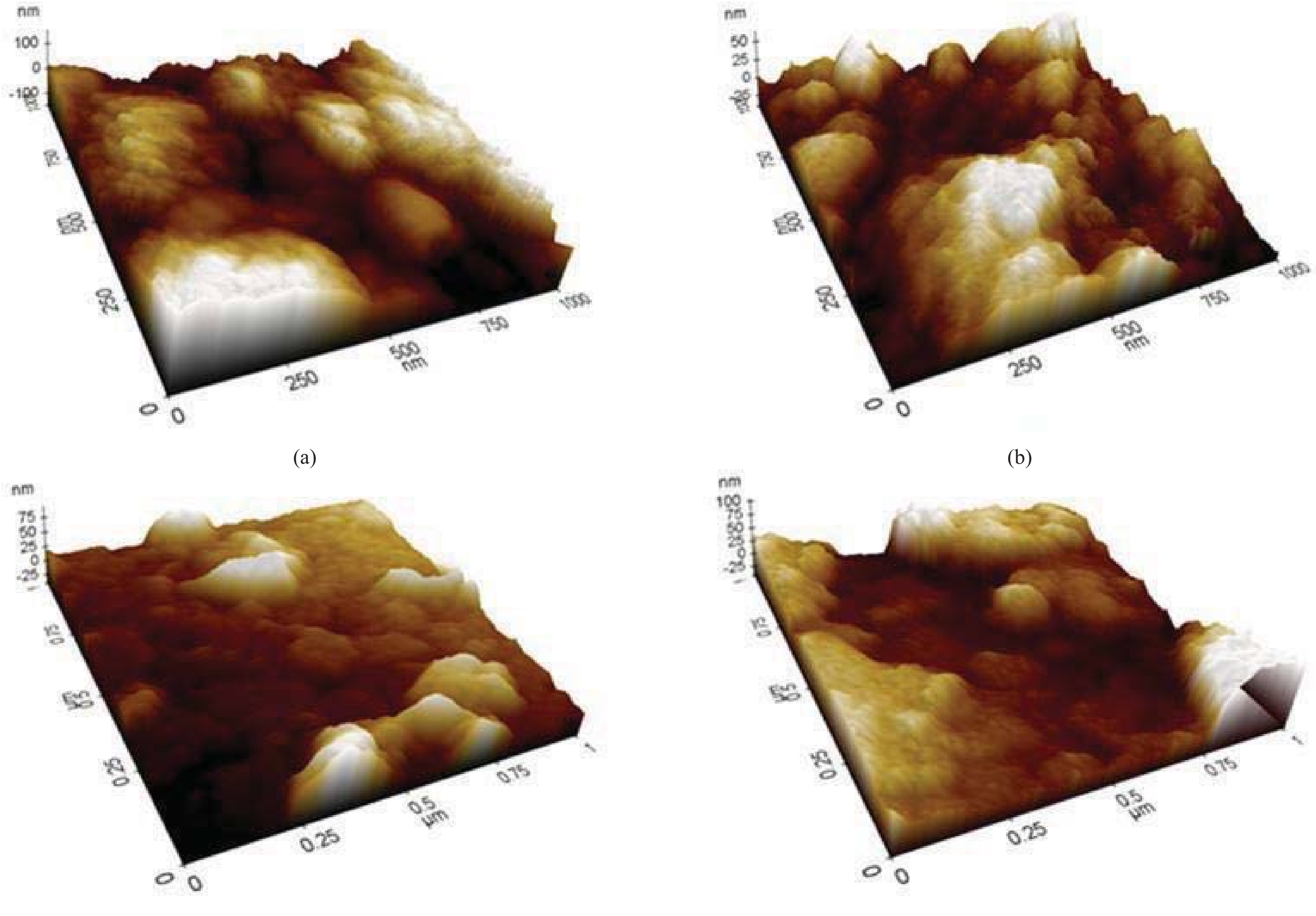

Figure 1. The AFM topography of TiO_2 thin films using different mass of nano-TiO_2 powder; (a) 1g; (b) 0.4g; (c) 0.1g; (d) 0.05g.

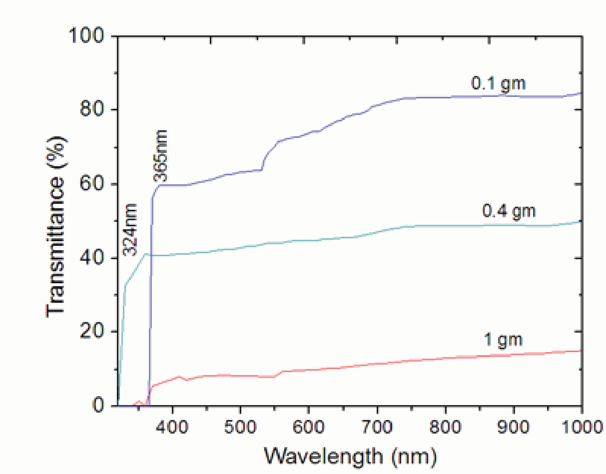

Figure 2. The UV-Vis spectra of TiO_2 thin films deposited using different mass of nano-TiO_2 powder

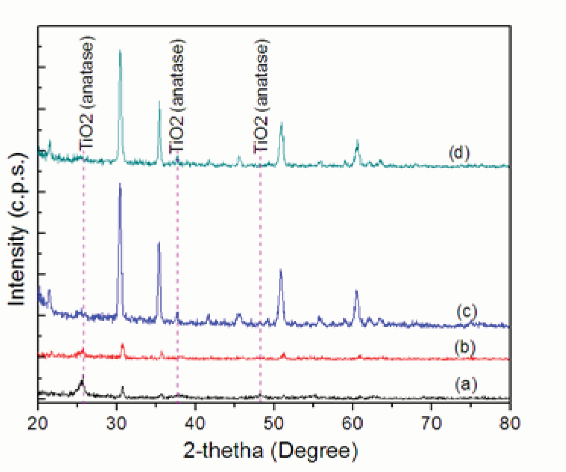

Figure 3. The XRD spectra of TiO_2 thin films using different mass of nano-TiO_2 powder; (a) 1g; (b) 0.4g; (c) 0.1g; (d) 0.05g.

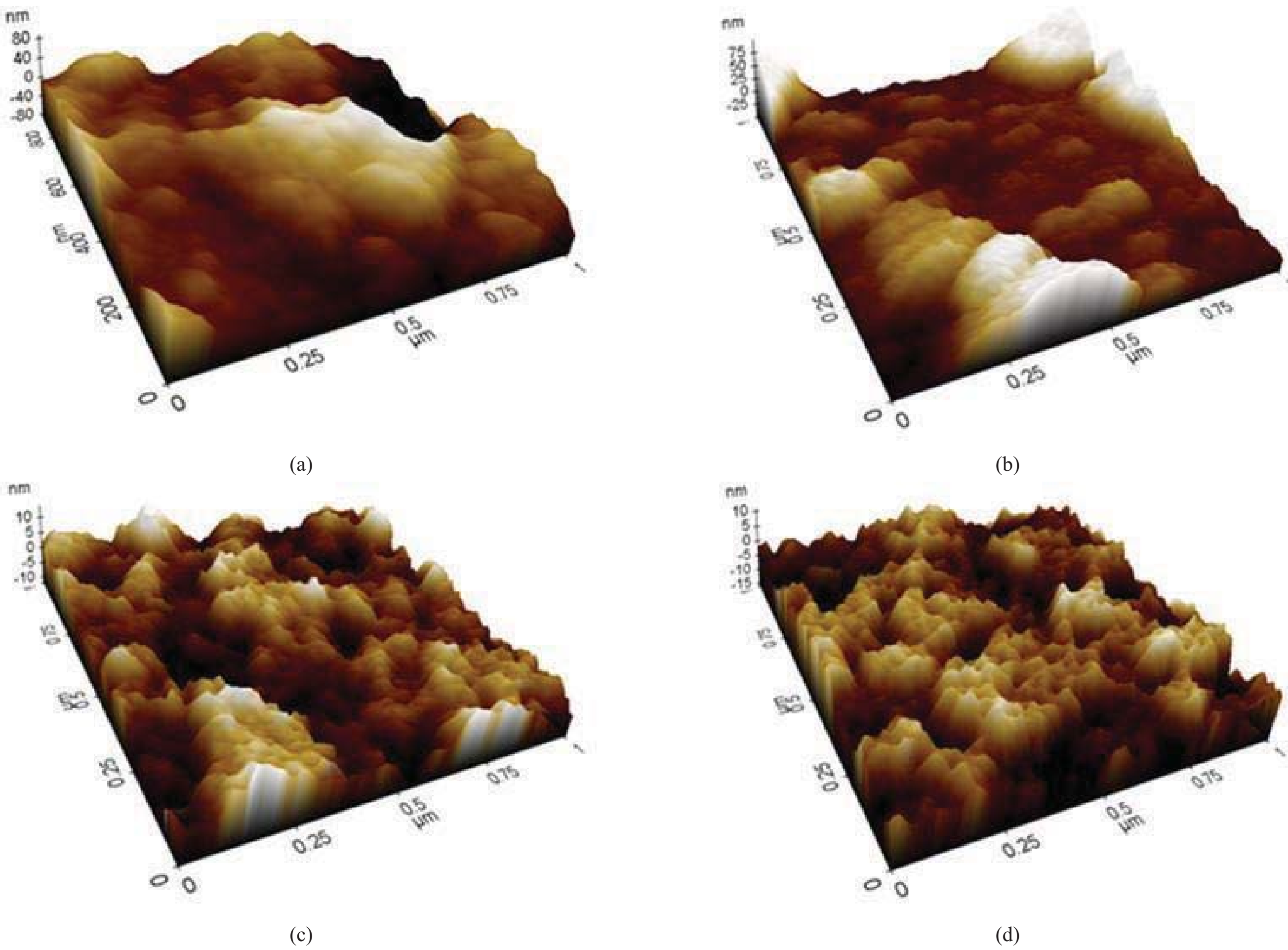

Figure 4. The AFM topography of TiO_2 thin films using different acetic acid concentration; (a) 0 ml; (b) 3 ml; (c) 10 ml; (d) 30 ml.

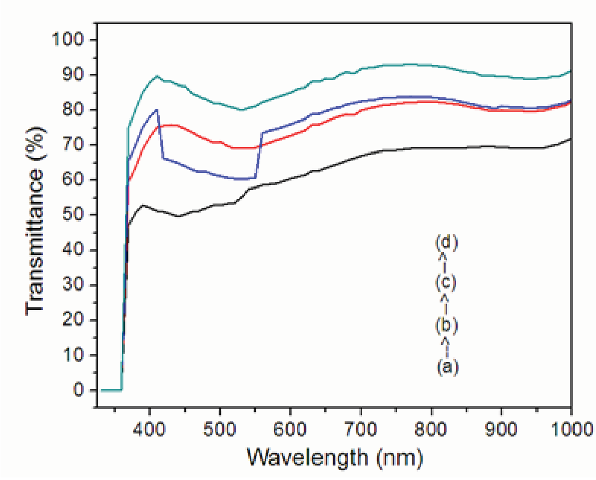

Figure 5. The transmittance spectra of TiO_2 thin films using different acetic acid concentration; (a) 0 ml; (b) 3 ml; (c) 10 ml; (d) 30 ml.

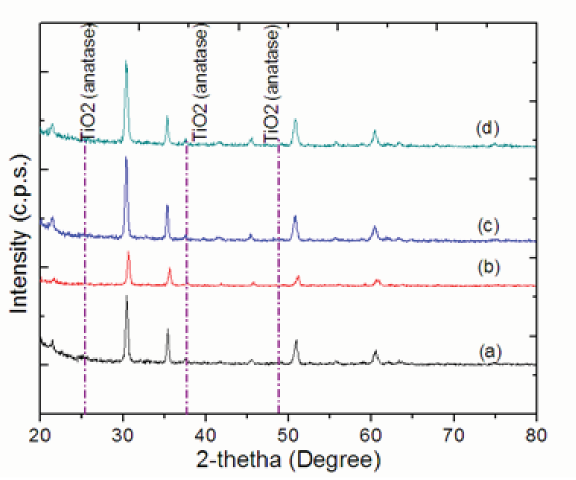

Figure 6. The XRD spectra of TiO_2 thin films using different acetic acid concentration; (a) 0 ml; (b) 3 ml; (c) 10 ml; (d) 30 ml.

B. Acetic Acid Concentration Optimization

Figure 4(a) shows the AFM topography of the sample deposited using 0.4g of nano-TiO_2 powder without the presence of acetic acid catalyst. The surface roughness obtained from AFM is 32. Figure 4(b) shows the topography of TiO_2 thin film when 3 ml of acetic acid was added in the solution. The surface roughness is reduced to 25.9. However, figure 4(c) show different morphology of TiO_2 thin film when 10 ml of acetic acid was used. The particle morphology is obviously seen and the surface roughness is reduced to 3.8 when the acetic acid volume was increased to 10 ml. On the other hand, figure 4(d) shows almost similar morphology with that of figure 4(c). The surface roughness increased slightly to 4.9 when the acetic acid volume was 30 ml. It is found that the optimum acetic acid volume is 10 ml which results a uniform TiO_2 thin films as shown in figure 4(c). All samples exhibit almost similar thickness which is approximately 130 nm.

Figure 5 shows the transmittance spectra of the sample deposited using different acetic acid concentration. Generally, as the acetic acid volume increases, the transmittance of the TiO_2 thin film also increased. However for 10 ml sample, the transmittance for wavelength from 419 to 547 nm decreased below the transmittance of 3 ml sample. The effect of adding acetic acid on the band gap is evaluated using Tauc's plot from the equations;

$$\alpha = (1/t) \times \ln[1/T] \quad (1)$$

and

$$E_g = hc/\lambda \quad (2)$$

Where α, t and T are the absorption coefficient, film's thickness and transmittance, respectively. While E_g, h, c and λ are the energy gap, plank constant (4.136×10^{-15} eV), speed of light (3×10^8 m·s^{-1}) and wavelength, respectively. It has been found that the band gap of the TiO_2 thin films for 0, 3 and 30 ml samples is around 3.2 eV. However, the 10 ml sample has different band gap value which is around 2.2 eV. Figure 6 shows the XRD spectra of the samples which indicates all TiO_2 thin films are still in anatase form although the intensity is low. This low intensity of the film is due to the low thickness of TiO_2 thin film.

C. Sensing Properties of TiO_2 Thin Film

In order to test current-voltage (*I-V*) characteristic of the sample, Platinum (Pt) electrodes were deposited on the TiO_2 thin film using a d.c. sputter coater. With Pt thickness around 15 nm, *I-V* probes were contacted and supplied with voltages from -2 V to +7 V using Keithley 2400 source meter. Figure 7 shows the *I-V* characteristic of the optimized TiO_2 films (nano-TiO_2 powder: 0.4g, acetic acid: 10 ml) when dropped with IPA. As shown in the figure, the TiO_2 thin film exhibits Schottky response with Pt due to large difference of work function. The threshold voltage is around 6.7V. The threshold voltage increased to 2.4V as IPA was dropped on the thin film. The current value was gradually decreased by time and obviously seen after 30 second. The *I-V* response returned back to origin after 5 minutes. This phenomena is due to the chemical reaction between TiO_2 particles and the IPA. The sensitivity of

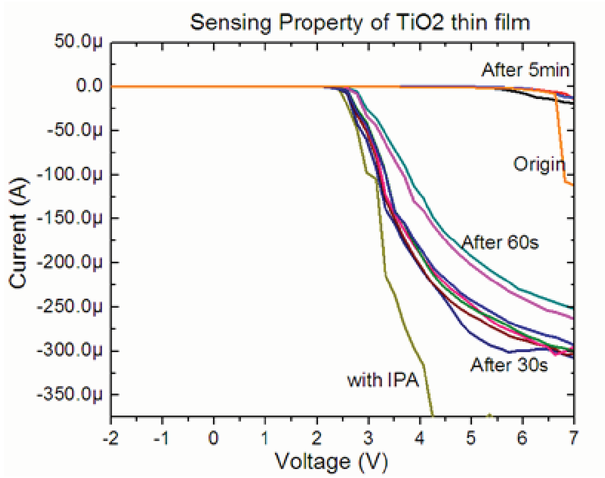

Figure 7. The sensing property of TiO_2 thin film toward IPA solvent.

structural stability, porousity and surface-to-volume ratio. TiO_2 thin films prepared by sol-gel process provide a backbone that can be use as a microporous support in which analyte-sensitive species are trapped and into which analyte molecules may effectively diffuse and interact [11].

4. Conclusion

This paper presents the results of the optimization process to produce uniform and transparent TiO_2 thin films using sol-gel technique. Two types of optimizations were performed. First was the mass of nano-TiO_2 powder and second was the acetic acid concentration.

The results from the AFM analysis confirmed that 0.4 g sample has the least TiO_2 thin film roughness. Then by adding 10 ml of acetic acid has resulted optimum uniformity and roughness of the TiO_2 thin film. The transmittance for the optimum film is around 80% which is sufficient for optoelectronic application especially for solar cell. The XRD result indicates that all films are in anatase form. Finally, it has been demonstrated in this paper that the prepared TiO_2 thin film is sensitive towards organic solvent which could increase the current value. Therefore, it is applicable for chemical sensing application.

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