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Influence of Different Solvents on the Formation of Uniform Titanium Dioxide (TiO_2) Thin Film by Sol-gel

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Abstract. Uniform Titanium dioxide (TiO_2) thin film is essential for application in high performance solar cells. A low cost approach using TiO_2 nanopowder extracted from tin mining waste to deposit TiO_2 thin films is demonstrated in this paper. Furthermore, the influence of different solvents (ethanol, acetone, isopropanol and ethylene glycol) on the formation of uniform TiO_2 thin films in sol-gel technique is studied. The films were characterized by an atomic force microscope (AFM), ultra violet – visible spectrometer (UV-Vis) and a current-voltage (*I-V*) measurement system. The correlations of the structural, optical and electrical behavior to the type of solvent used were discussed in details.

Introduction

Titanium dioxide (TiO_2) or known as titania is a unique IV-VI semiconductor where it has three different polymorps. The naturally occurring polymorph is brookite and extremely difficult to synthesize. While the most commonly researched polymorphs are anatase and rutile. When the sintering temperature is over 500°C, brookite will transform to anatase form [1]. The anatase will transform to rutile when the temperature is over 600°C [2]. Anatase is proven recently as the most photocatalytically active and more ionic of the three polymorphs. In addition, the conduction band is better around 0.3 eV more positive than rutile phase [3].

In practical technological applications, anatase TiO_2 is widely used for light emitting diodes, laser diodes and solar cells [4]. It shows magnificent performance when combined with organic dye in dye-sensitized solar cells (DSCs) which demonstrated by Gratzel [5-6]. On the other hand, the emerging of organic solar cells also requires TiO_2 nanolayer to improve the solar cell performance [7]. TiO_2 films also reported to have possibility to reduce air pollution when it absorbed carbon monoxide (CO) when coat on buildings [8]. There are several more reports have been found on the relevance of TiO_2 for the application of high technological devices. Therefore, it is essential to study the process of synthesizing TiO_2 thin films to improve the performance and to reduce the processing cost for manufacturing.

There are several methods to synthesize TiO_2 thin films such as r.f. sputtering [9], laser ablation [10] and chemical vapor deposition (CVD) [11]. However, these methods require expensive and sophisticated equipments where not only the return of investment (ROI) is longer, the mass production also will be an issue. Sol-gel spin coating is a cost effective method and capable for mass production [12]. In this paper, nano-TiO_2 powder which was synthesized from local tin mining waste has been used as the starting material. Our initial works has been reported by M.Z. Sahdan *et al.* [13] demonstrating the effects of mass concentration and catalyst volume on the uniformity and performance of the TiO_2 thin films. In this study, different solvents have been used to synthesize more uniform TiO_2 films with better physical and optical performances. The films were characterized by an atomic force microscopy (AFM), an x-ray diffraction (XRD), an ultraviolet-visible spectroscopy, and a current-voltage testing (*I-V*) measurement system.

Experimental Setup

An aqueous solution commencing 0.1g of nano-TiO_2 powder was mixed with 10 ml of acetic acid (CH_3COOH) in 30 ml of four different solvents which are ethylene glycol, acetone, ethanol and isopropanol. Then, all solutions were undergoing ageing process for 20 hours at room temperature. After that, the solution were spin coated on Indium tin oxide (ITO) coated glass substrate using 2-step coating which is 1000 r.p.m. for 30 seconds and 3000 r.p.m. for 60 seconds. Each layer consists of 10 drops of the solution and each sample was coated with 10 layer coating. Between every layer, the sample was preheated at 150°C for 3 minutes. Finally, the sample was annealed at 500°C for 1 hour to remain its anatase phase. All samples were characterized by an atomic force microscope Park System XE-100 (AFM), an x-ray diffraction Bruker Advance (XRD), an ultra violet-visible Perkin Elmer Lambda 750 (UV-Vis) and a current-voltage Keithley 2400 (*I-V*) measurement system.

Results and Discussion

Fig. 1 shows the AFM images indicating the influence of different solvents on the surface topology of the films. Referring to Fig. 1(a-d), it is obviously seen that TiO_2 film deposited using IPA has the most uniformity and least roughness compared to the other solvents. By using AFM, the roughness and grain size of the sample can be determined. The roughness for sample from solvent ethylene glycol, acetone, ethanol and IPA are 277 nm, 84 nm, 135 nm and 140 nm respectively while the grain size observe for each sample are 734 nm, 691 nm, 683 nm and 336 nm respectively. It was found that using IPA, the grain size and roughness are the smallest.

The transmittance property of the TiO_2 films is depicted in Fig. 2 below. Since their thicknesses may vary, the effects of using different solvents cannot be compared. Therefore, the absorption coefficient versus energy is plotted to analyze their optical properties. The absorption coefficient, α is due to the inter band transition near band gap and can be calculated from transmittance using equation,

$$\alpha = (1/t) \text{ x } \ln[1/T] \qquad (1)$$

where t is the thin film thickness and T is the transmittance value. The photon energy, (E) is calculated using formula,

$$E = hc/\lambda = h\upsilon \qquad (2)$$

Fig. 3 shows the Tauc's plot of the TiO_2 films deposited using different solvents. From the Tauc's plot, the optical band gap of each film can be estimated. As indicated in the figure, the band gap of TiO_2 film deposited using IPA has nearly the same value as its bulk around 3.2 eV. The band gap increases to a value of 3.22 eV using ethanol and further increases to 3.28 eV when ethylene glycol was used. However, the TiO_2 band gap decreases to a value of 3.0 eV when acetone was used.

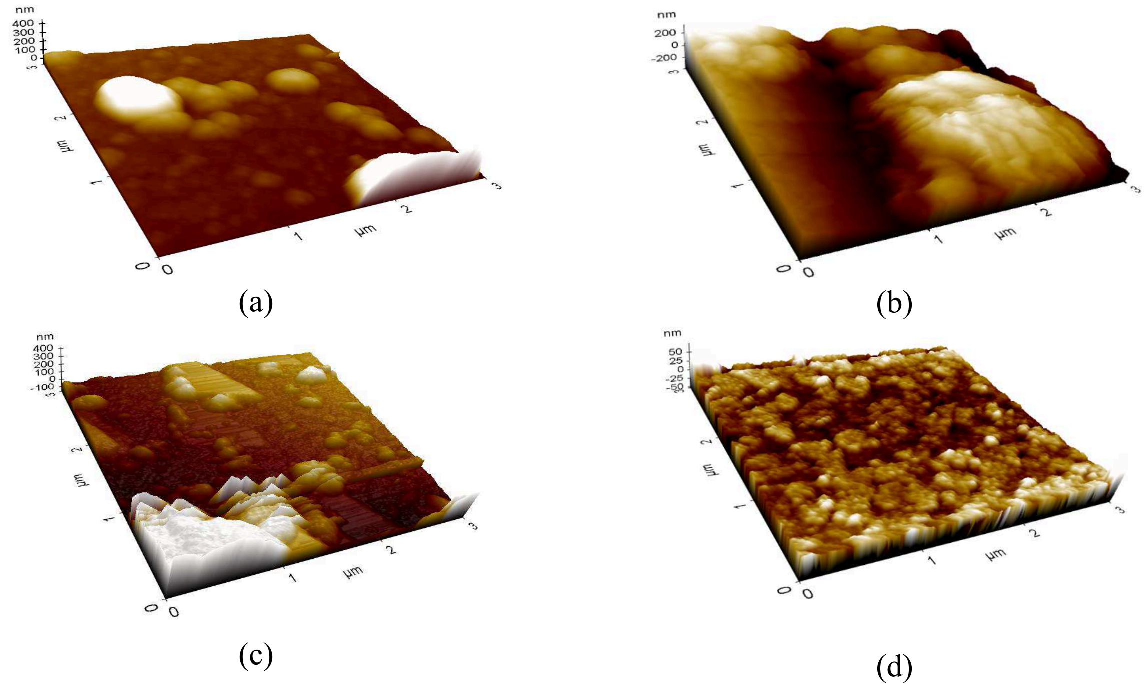

Fig. 1 The AFM images of TiO_2 films with 3 um scan area; (a) Ethylene Glycol; (b) Acetone; (c) Ethanol and (d) Isopropanol

From our observations, we proposed that the increasing of the optical band gap is due to the oxygen interstitial where for ethylene glycol there are two oxygen ions which results in obvious changes. On the other hand, the decreasing of band gap is due to the carbon ions in acetone where it might substitute the Ti and reduced its band gap.

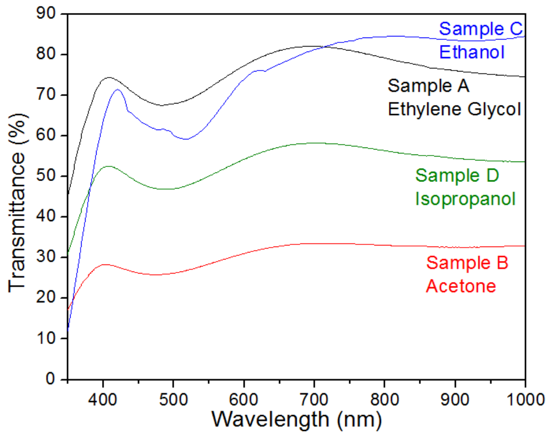

Fig. 2 The transmittance spectra of TiO_2 films deposited using different solvents

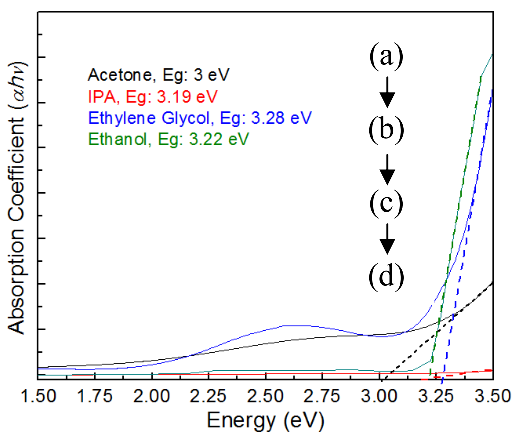

Fig. 3 The band gap approximation using Tauc's plot; (a) ethanol; (b) ethylene glycol; (c) acetone and (d) IPA

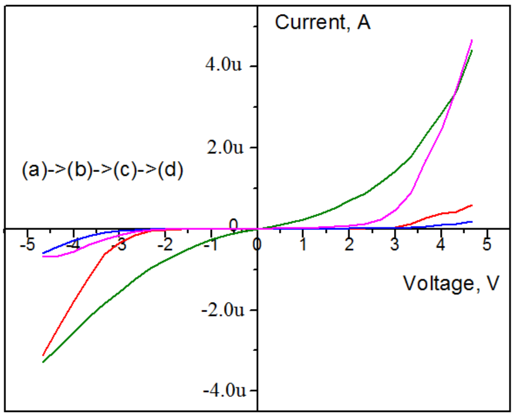

Fig. 4 The *I-V* characteristics of TiO_2 films using different solvents; (a) ethanol; (b) acetone; (c) IPA, and (d) ethylene glycol

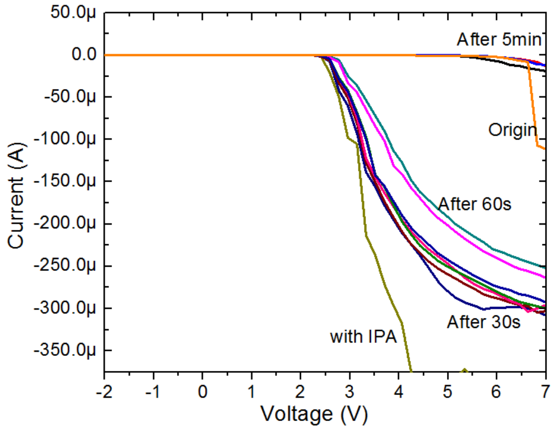

Fig. 5 The sensing property of TiO_2 film towards IPA

Fig. 4 shows the *I-V* characteristics of TiO_2 films deposited using different solvents. Using silver (Ag) as the electrode, the thin film was bias with voltage from -2.0 to 2.0 V to the ITO electrode. The current obtained is in the range of micro-ampere. It is found that except for film deposited using ethylene glycol, all films shows diode characteristics with different threshold voltage. TiO_2 film deposited using ethanol has threshold voltage of 2.87 V and followed by film deposited using IPA with threshold voltage of 2.67 V. The fastest response is shown by TiO_2 deposited using acetone with threshold voltage of 0.9 V. Even though acetone shows good positive current rectification, however IPA shows very good negative breakdown voltage with -2.28 V. Therefore, TiO_2 film deposited using IPA has been selected as for the next experimentation to study the sensing property towards organic solvent which is also IPA. Generally, the films topology and the band gap energy influenced the electrical property of TiO_2 films. Higher surface roughness of the film contributes to uneven attachment between the Ag electrode and the film. Referring to the AFM topology and surface roughness, IPA is the optimum and acetone is the second. However, referring to the band gap of the films, acetone has the lowest band gap followed by IPA. Therefore, these maybe the reasons why IPA shows good electrical response at negative voltage while acetone at positive voltage.

Fig. 5 shows the sensing property of TiO_2 films deposited using IPA towards IPA solution. Originally, the current response of the film is indicated by orange color. When, IPA was dropped onto the film, the current rectification increases sharply. As the IPA vaporized, it is clearly seen that the current rectification slowly drops and back to original state.

Conclusion

A new precursor of producing TiO_2 thin films using Ilmenite from local tin mining waste is introduced in this study. In order to tailor its property for electronic and optoelectronic applications, several works have been commenced. In this paper, the influences of using different solvents to cast the TiO_2 thin films on the surface topology, optical and electrical properties were explored and discussed. From the XRD and AFM results, the optimum structural, surface uniformity and roughness has been depicted by TiO_2 film deposited using IPA solvent. This film also exhibits sensing property towards IPA solution in which has potential application in gas sensor or odour detector.

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