Effect of Band Gap on TiO$_2$ Thin Film with Different Layer using Dip Coating Technique

S.F.A Samat, M.S.P Sarah and M.F.M Idros

Abstract— Titania or titanium dioxide (TiO$_2$) thin films were prepared using a simple sol-gel dip-coating method on a glass substrate. Titanium (IV) tetraisopropoxide, (TTIP) was used as a titania precursor. The purpose of this work is to study the behavior of optical band gap with the different number of layer and the phase present of each sample. From the result, all samples are amorphous phase have their value of optical band gap in the range of 3.21 eV until 3.80 eV depends on transition. The number of layers increased caused the surface morphology of TiO$_2$ to agglomerate and the roughness of the samples increased. The single layer sample shows higher transmittance value than multiple layer samples which is the best for optical sensor application.

Keywords—Dip Coating; Sol-gel; TiO$_2$; Optical Sensor

I. INTRODUCTION

TITANIUM DIOXIDE, TiO$_2$ is an important $n$-type semiconducting material that has interesting properties. It had been used in a large variety of applications which are solar cells [1], photocatalyst [2], electro chromic devices [3], chemical sensors [4] and electronic applications. It also has good chemical stability, optical, physical properties, and high refractive index [5]. It can be found in nature and non-toxic metal oxide [6]. There are several deposition techniques that can be used to fabricate TiO$_2$ such as chemical vapour deposition (CVD) [7], hydrothermal [3], sol-gel [8][9], and physical vapour deposition (PVD) [10]. Sol-gel is a technique that is easy to handle, low cost and simple experimental setup. In sol-gel process, hydrolysis and condensation reaction would lead to the formation of TiO$_2$ network in the solution. These reactions can be represented as follows:

$$\text{Ti(OR)}_x + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_x + 4\text{ROH} \quad \text{(hydrolysis)} \quad (1)$$

$$\text{Ti(OH)}_x \rightarrow \text{TiO}_x\text{H}_2\text{O} + (2-x)\text{H}_2\text{O} \quad \text{(condensation)} \quad (2)$$

Where $R$ is ethyl alcohol, $i$-propyl, $n$-butyl, etc [11]. In general, the conditions for preparing TiO$_2$ thin films using sol–gel process can strongly affect the physical and optical properties of the film [1]. In this work, the sample prepared by sol-gel dip coating technique. Sol-gel dip coating technique is an oldest commercially applied in thin film and has some advantages such as good uniformity, coated in large substrates, excellent thickness and good adhesion on substrate [9]. Dip coating has three important stages; which are immersion, deposition and evaporation. The substrates were immersed into the solution reservoir at a constant withdrawal speed and dipping cycle [8]. Performance of TiO$_2$ depends on deposition method applied, film thickness, band gap, crystallite size and morphology [12][13]. The band gap is calculated from absorbance coefficient ($\alpha$) for direct and indirect transition [14]. Then the deposited TiO$_2$ thin film are characterized by optical detector using Surface Profiler (SP) for measure the thickness, Atomic Force Microscopy (AFM) to determine the surface roughness, Field Emission Scanning Electron Microscopy (FESEM) for analyzing the morphology surface and transmittance by using UV-Vis Spectrometer.
II. EXPERIMENTAL PROCEDURE

A. The sol-gel technique
The glass substrate preparation started with cleaning 2cm x 2cm dimension immersed in a beaker with the chemical solution. There are acetone, methanol and deionizer water (DI) sonication with ultrasonic cleaner consecutively. It took 10 minutes for each step. Then, they were blown with nitrogen gas for drying purpose to ensure the substrates are free from other particles. The preparation of 0.01M TiO$_2$ solution involved ethyl alcohol as a solvent and titanium (IV) tetraisopropoxide (TTIP) which acts as precursor for synthesizing crystalline TiO$_2$ particles. Glacial acetic acid (GAA) and distilled water (DI) for TTIP hydrolysis meanwhile Triton X-100 as a surfactant. The solution was stirred and heated at 60ºC with 600rpm for one hour using a hot plate stirrer.

B. Sample Deposition
The thin films prepared by dip coating technique with regulation speed of 0.6cm$^{-1}$. After deposited each layer, the substrates undergo drying process at 100ºC for 15 minutes. The thin film was dip with 20 dipping cycles. Then, they were annealed at 450ºC for one hour to restructure the grain size.

C. Sample Characterization
An Ultraviolet-Visible (UV-VIS Spectrophotometer), (JASCO, FLH-740) is used to record the transmittance between wavelengths of 300nm and 800nm. The thickness of the thin film was measured using Surface Profiler, SP (Dektak-150). The surface topology was examined by field-emission scanning electron microscope, FESEM by JEOL (JSM-J600F) meanwhile the surface morphologies and surface roughness of the thin film was investigated using Atomic Force Microscopy, AFM.

III. RESULT AND DISCUSSION

A. Phase Crystallinity of TiO$_2$ thin film
Figure 1 shows the XRD pattern of TiO$_2$ thin films when annealed at 450ºC. The result is amorphous phase for all samples at characterized at angle of 2 theta (θ). As claimed by Savas Sonmezoglu et al said that the amorphous is formed when n-TiO$_2$ thin films annealed from 200ºC to 600ºC [18]. The amorphous is start to agglomerate and form a particle at 3$^{th}$ layer. This is due to small particle and low thickness. This is proven by R. Mechiakh et al said that the absence peaks of diffraction due to the low of thickness and high in speed withdrawal [19]. Even the samples are amorphous, the peak of XRD pattern are tends to form crystalline size at angle 25º.

B. Thickness of different layer TiO$_2$ thin film
Figure 2 depicts the thickness of each sample. The reading of the samples (a), (b), (c), (d) and (e) are 164.91nm, 152.98nm, 142.42nm, 136.44nm and 96.94nm respectively. The thickness is increasing with increasing the number of layer. Each layer of the film is deposited with 15 dipping cycles, dried and annealed. The process of the cycle dipping, coating, and drying are repeated as necessary to reach the number of desired thickness. The TiO$_2$ thin film is exhibited good adhesion to the glass substrate [18].
When in this transition, the electron momentum is conserved, the transition is direct, but if the momentum does not conserve this transition must be attended by a photon, this is an indirect transition \[20\]. Figure 3(a) and 3(b) are energy band gap, $\Delta E_g$ for direct and indirect transition by plotting the optical absorption ($\alpha h\nu$) and ($\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$), unit eV and extrapolating the linear portion of the TiO$_2$ transmittance curves in the UV region to 0 respectively \[20\]. The data for both direct and indirect band gap are increasing with increasing of layer but different value of each sample tabulated in Table 1. The energy band gap for indirect transition from 3.21 eV to 3.41 eV meanwhile the direct transition are 3.66 eV until 3.80 eV. The value band gap of indirect transition is much smaller than direct transition. As claimed from Sergio Valencia et al, the amorphous band gap is higher than crystalline band gap however, this study showed that the amorphous state is still in the range of TiO$_2$ band gap as reported in many research \[20\]. In some cases, the optical band gap cannot be calculated for amorphous. However in this case of amorphous has been to consider band edges which have localized states near valence band and conduction band energies or appropriate term is mobility gap. This is because the structure sharp band edges are not present due to the absence of long range. For amorphous materials the values of the band gap are above 3.4eV independent of the transition type, which is in agreement with the XRD. Dip coating method can clearly showed the good morphology and topology surfaces and even the peak of crystallinity however the annealing temperature and the molarity of solution are not in the desired scaled.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap, E (eV)</th>
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<tbody>
<tr>
<td></td>
<td>Direct</td>
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<tr>
<td>(a)</td>
<td>3.66</td>
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<tr>
<td>(b)</td>
<td>3.71</td>
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<td>(c)</td>
<td>3.76</td>
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<td>(d)</td>
<td>3.78</td>
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<td>(e)</td>
<td>3.80</td>
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C. The Optical Band gap of TiO$_2$ thin film

When a semiconductor absorbs photons of energy larger than the gap of the semiconductor, an electron is transferred from the valence band to the conduction band where there occurs an abrupt increase in absorbency of the material to the wavelength corresponding to the band gap energy. For optical properties of the synthesized TiO$_2$ nanoparticles, the energy band gap, $\Delta E_g$ of a semiconductor with large band gap can be determined from its absorption coefficient ($\alpha$) \[17\]. The absorption coefficient ($\alpha$) are calculated using Eq. (1)

$$\alpha = \frac{\ln(T)}{d}, \text{eV m}^{-1}$$  \hspace{1cm} (1)

Where T is the transmittance, d is the film thickness. The relation of absorption coefficient ($\alpha$) to the incidental photon energy depends on the type of electronic transition.
Figure 4: The surface is very clearly shown the particle size increases by increasing layer in (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers and (e) 5 layers.
D. Optical Transmittance of TiO₂ Thin Films

The sample (a) is transmitted at 79.51%, meanwhile (b) 51.66%, (c) 48.42%, (d) 63.30%, and (e) 64.54%. The optical transmittance of one layer is the highest due to low the thickness of film. This is due to the different in scattering efficiency depending on light-scattering particle sizes and semitransparent layer film thickness might be related to the wavelength of the transmitted light. As reported by M.F. Malik et al, the variations in film thickness improved the transmittance percentage [21]. This might be due to the grain boundaries of TiO₂ thin film deposited with different layer deposition. The grain boundaries decrease with the low number of thickness, thus improved the light absorption in that region [13]. The optical detector need high transmittance, however the structure is low in crystalline.

E. Surface Morphologies

The microstructures surface of TiO₂ thin film shown in Figure 4. The surface structure effect the crystal layers grow in the sample with their sizes [22]. The overall structures are quite dense and the coating is crack-free due to well-distribution of particles to form a crystalline phases. The layers of particles are agglomerate and uniform. It is a corresponding between thickness and annealing temperature. The annealing time is one hour for each sample. The purpose of annealing temperature is to restructure the surface of the films. However, in other research, when the temperature is hike the film is cracking due to the expansion of TiO₂ nanostructure [23].

F. Surface Topology

Figure 5 shows representative AFM images of the surfaces of 5 sample TiO₂ films with different layers. The sample in Figure 4 (a), (b), (c), (d) and (e) are 1 layer, 2 layers, 3 layers, 4 layers and 5 layers. The surface plots (three-dimensional representations) 3D, revealed that the surface morphologies. The distinctive bright spots are determined of the highest height from the scan area. All TiO₂ thin films exhibit a smooth surfaces and uniform grain size. As the layers are increasing in number, the surface roughness are increased due to the bigger clusters formed by the coalescence of two or more grains. The surface roughness are plotted in Figure 7 and is evaluated by the Root Mean Square (RMS). The Rq readings starting from the 1st layer until 5 layers are 2.911nm, 7.303nm, 12.368nm, 17.592nm and 23.00nm respectively. The result from AFM is in accordance with the results from FESEM and thickness, as discussed previously. The amorphous of TiO₂ thin film can be seen in Figure 1 that characterized by XRD analysis.

IV. CONCLUSION

The sol-gel dip coating method of TiO₂ thin films with different number of layers with annealing process at 450°C and molarity solution 0.01M had been studied. The results obtained showed that all fabricated samples have amorphous-crystalline phase. Moreover, the thickness and surface roughness are increased as the number of layer increased. The increasing layer have low of percentage transmittance. The optical band gap for TiO₂ thin film are different for each layers starting from 3.21 eV until 3.80 eV. For an amorphous material the band gap is independent transition types. All the synthesized materials depended on molarity solution and annealing temperature.