Optical, Electrical and Structural Investigation on Different Molarities of Titanium Dioxide (TiO_2) via Sol-Gel Method

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***Abstract*—Titanium dioxide (TiO_2) solution having different molarities were synthesized and deposited on glass substrates by using sol-gel spin-coating method. The variation in thickness, optical, electrical and structural properties of TiO_2 thin films were investigated by surface profiler (SP), UV-Vis spectroscopy, two-point probes and atomic force microscopy (AFM), respectively. The result show that the thickness of TiO_2 thin film increases as the molarities increases. The optical band gap energy decreases from 3.78 eV to 3.07 eV as the TiO_2 molarities increases from 0.01M to 0.20M. The maximum value of the absorption coefficient was 16.27 x 10^4 cm^{-1} at 0.20M with surface roughness of 21.45 nm. Thin films deposited with 0.01M show lower absorption coefficient (3.87 x 10^4 cm^{-1}) within visible region with surface roughness of 5.21 nm. The improvement in optical and structural properties of TiO_2 thin films affects the electrical properties as the highest conductivity 9.62 x 10^2 S/m is obtained by 0.20M.**

***Index Terms*—Sol-Gel; TiO_2; Thin Film; Properties.**

I. INTRODUCTION

Titanium dioxide (TiO_2) is an insulator metal oxide of material that used in many areas including solar energy [1]. It also known as titania which exists in amorphous and phases of crystalline structures (anatase, rutile and brookite) which exhibit different photocatalytic characteristics [2]. The anatase crystal phase (E_g = 3.32 eV) is usually used for production of photocatalyts [3,4]. Under illumination, it can help break down hazardous gases and organic pollutants via photo-catalysis [5]. In nano titanium dioxide, high purity can be obtained and enhance UV absorption due to the average particle size of less than 100nm [6]. Absorption coefficient in thin film is momentous in photocatalytic application as it indicated how much photons or UV light can be absorbed in average distance travelled by a photon before it gets absorbed by the thin film [7]. The magnitude of absorption coefficient in TiO_2 is influenced by many factors such as; changes in phase-transformation, grain sizes, thickness of thin film and others [8-10].

Sol-gel process is a liquid-phase method of synthesizing inorganic, organic-inorganic network such as powders, ceramics, glasses, films at ambient temperature. The sol-gel process is unique due to the ability to produce TiO_2 at low-processing temperature compared to plasma synthesis and flame pyrolysis [10,11]. Sol-gel involved the process of solid nanoparticles dispersed in a liquid and agglomerate together to form a continuous three-dimensional network and extending throughout the liquid. The main advantage of this process is the desired properties are easily obtained by modifying the microstructure through the process of sol-gel. Sol-gel process involved the hydrolysis of titanium (IV) isopropoxide precursor through condensation, forming the titanium dioxide nanoparticles [12]. There are many factors that influence the changes in microstructure of TiO_2 nanoparticles synthesize by sol-gel such as the nature of precursor and solvent, hydrolysis ratios, pH and synthesizing temperature [13-16]. Owing to the fact that TiO_2 is a wide-band gap semiconductor, it contributes to low absorbance of light and has limited to UV range of the electromagnectic spectrum [17-18]. In this work, molarity of TiO_2 solution is being controlled to improve the microstructure to enhance the absorbance of light. The effect of different TiO_2 molarities by sol-gel process was presented and their influences on the performance of thin films were discussed.

TiO_2 nanoparticles is further growing and form a soul that can be deposited on the substrates to form a film by using spin-coating, dip-coating, doctor-blading and spray-pyrolysis [19-22]. By using spin-coating to deposit thin film, it has ability to produce uniform films and control thickness from a nanometers to a microns. It is used for coating substrates for transparent conductive oxide (TCO), insulators, photoresists, nano-materials, organic semiconductors and metal oxides precursors [23].

II. EXPERIMENTAL PROCEDURE

A. Glass Substrates Preparation

Glass substrates were cut in dimension of 2.5cm x 2.5cm. Then, the glass substrates were ultrasonically cleaned in methanol, acetone and distilled water in 10 minutes each. The substrates were dried using nitrogen gas (N_2) blower.

B. Synthesis of TiO_2 by Sol-Gel Method

Synthesizing of TiO_2 nanoparticles were done by sol-gel that used titanium isopropoxide ($C_{12}H_{28}O_4Ti$) as main

precursor and others organic chemicals such as absolute ethanol (C_2H_6O) and glacial acetic acid ($C_2H_4O_2$). The chemical steps involved in sol-gel are hydrolysis and condensation result in formation of a network Ti-O-Ti. Hydrolysis occurs when titanium (IV) isopropoxide and deionized water are mixed in ethanol (Equation (1)). In this phase, molarities of titanium (IV) isopropoxide were varied from 0.01M, 0.05M, 0.10M, 0.15M and 0.20M. Poly-condensation of titanium (IV) isopropoxide (Equation (2) and (3)) were took place to produce TiO_2 [23].

$$Ti\text{-}OR + H_2O \rightarrow Ti\text{-}OH + ROH \quad (1)$$

$$Ti\text{-}OH + OR\text{-}Ti \rightarrow Ti\text{-}O\text{-}Ti + ROH \quad (2)$$

$$Ti\text{-}OH + HO\text{-}Ti \rightarrow Ti\text{-}O\text{-}Ti + H_2O \quad (3)$$

where, R = $C_{12}H_{28}O_3$.

One-drop of non-ionic surfactant triton X-100 was added at the end of sol-gel process. The solution was stirred at 60℃ with 600rpm for one hour using stirrer to get clear and transparent sol. Finally the solution was continuously stirred at room temperature for one day.

C. Deposition of TiO_2 thin film by Spin-Coating Technique

For deposition process, spin-coater was set to 6000 rpm for 30 seconds and carried out at room temperature. The glass was placed and aligned on the vacuum chuck. A plastic dropper was used to dispense the aged-TiO_2 solution of ten drops. After one cycle of spin-coat, the substrate was kept in oven at 150°C for 10 minutes to evaporate the solvent in the TiO_2 thin films. The process of spin-coat-dry was repeated for five times. The samples were annealed at 450°C for one hour. The overall process of sol-gel spin-coating is as shown in Figure 1.

D. Deposition of TiO_2 thin film by Spin-Coating Technique

The thickness of films were measured with surface profiler (SP) Veeco Deetak 150. The optical properties of the deposited TiO_2 thin films were studied using UV-Vis spectroscopy. Atomic Force Microscopy (AFM) was used to investigate the roughness and surface topology of TiO_2 thin films. Electrical properties of TiO_2 thin films were measured using KEITHLEY 2420 sourcemeter.

III. Results and Discussion

A. Optical Properties

The optical properties of the deposited TiO_2 thin films were measured using UV-Vis spectroscopy in the wavelength range of 300nm - 800nm as shown in Figure 2. From the transmittance data, optical absorption coefficient, α, of TiO_2 thin films were calculated using the Lambert law relation in Equation (4) [7].

$$\alpha = \frac{1}{t}\ln(\frac{1}{T}) \quad (4)$$

where: α = Absorption coefficient
t = Thickness of TiO_2 thin film
T = Transmittance of TiO_2 thin fim

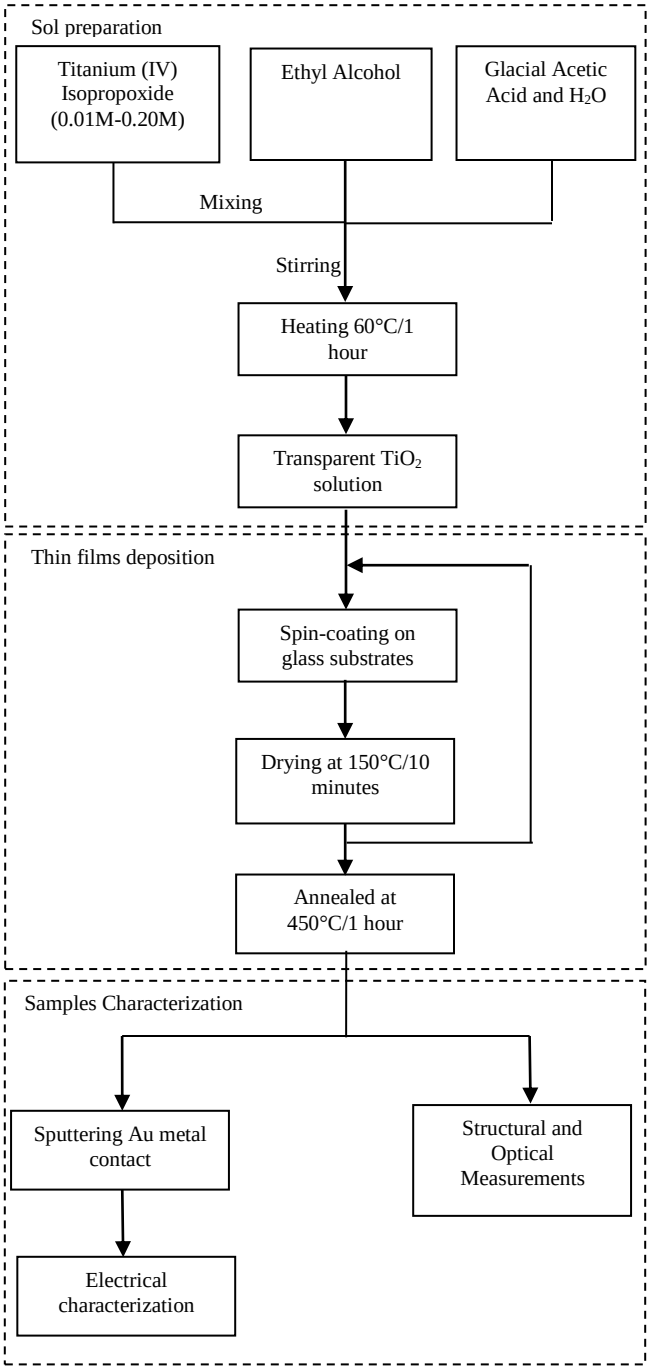


Figure 1: Flow Chart of Overall Process

The relationship between absorption coefficient and incident photon energy is written as Eq. 5 [7]. The optical band gap of TiO_2 thin films were determined by extrapolating the linear portion of the curve as shown in Figure 3.

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (5)$$

where: h = Planck constant (6.626 x 10^{-34} J.s)
v = Speed of light (c = 3 x 10^8 ms^{-1})
A = Constant for indirect transition
E_g= Energy band gap

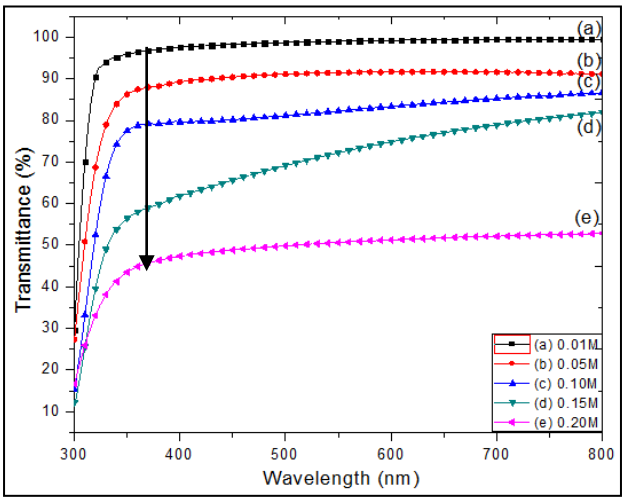


Figure 2: Optical transmittance spectra of TiO_2 thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

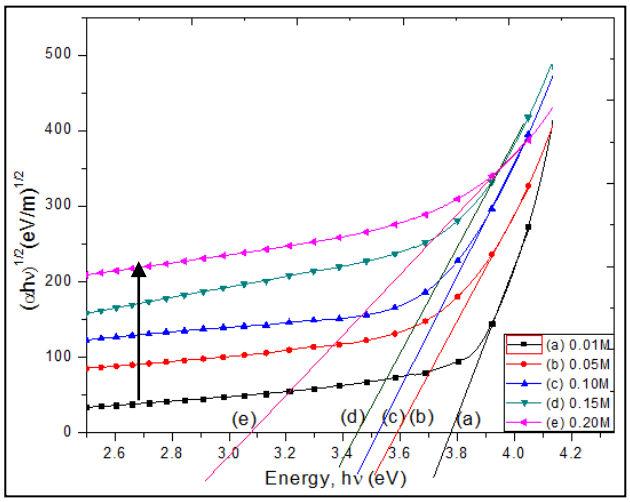


Figure 3: Optical band gap of TiO_2 thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

The variation of transmittance and absorption coefficient of TiO_2 thin films are strongly influence by the thickness of thin films and surface films. As can be seen in Figure 2, it was observed that 0.01M of TiO_2 thin film exhibits high transparency in visible region, average up to 90%. The average transmittance gradually decreased to 45% as the molarity of TiO_2 increases to 0.20M. In contrast, thin films having the lowest TiO_2 molarity (0.01M) exhibits the lowest absorption coefficient (3.87×10^4 cm^{-1}) compared to the highest TiO_2 molarity (0.20M) which give the highest absorption coefficient (16.27×10^4 cm^{-1}) of thin film. Increasing the molarity of TiO_2 during the solution preparation cause the films thickness (Table 1) increases due to the viscosity of solution increases [24]. This might be due to the bonding experienced by the hydrolyzed titanium isopropoxide (Ti-OH) network become stronger and high flexibility for the TiO_2 to undergo densification during the anneal treatment [25]. 0.01M has the lowest of absorption coefficient that may be due to the films has a large band gap. However, the values of optical band gap energy gradually decreases from 3.78eV to 3.07eV as TiO_2 molarity increases. The decreases of optical band gap with respect to TiO_2 molarity can be attributed to the improvement in surface roughness and increases in grain boundaries as reported by L. Patil *et al*. [26].

B. Electrical Properties

The samples were tested under illumination and the results were taken in the range between -10V to 10V. The resistivity, ρ and photoconductivity, σ of TiO_2 thin films under illumination were calculated using Equation (6) and (7), respectively [16].

$$\sigma = \frac{V}{I}\left(\frac{Wt}{l}\right) \quad (6)$$

$$\rho = \frac{1}{\sigma} \quad (7)$$

where: w = Width of the metal contact
ℓ = Length between two metal contacts.
t = Thickness of thin film

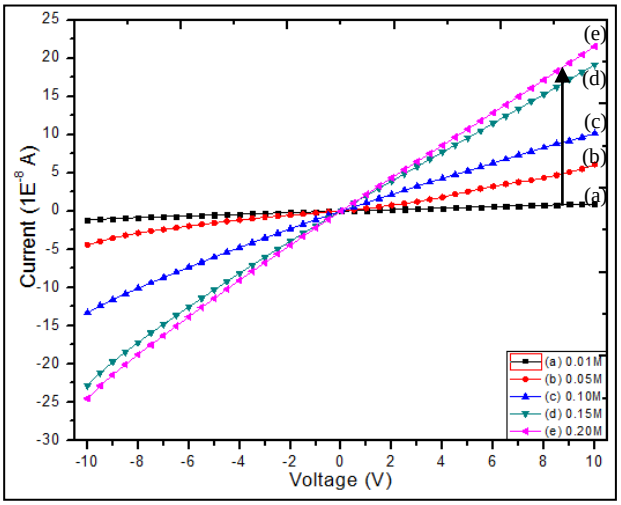


Figure 4: I-V characteristics of TiO_2 thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

The I-V characteristics shows increasing trends with TiO_2 molarity which the current obtained for 0.01M, 0.05M, 0.10M, 0.15M and 0.20M at 10V are 9.47×10^{-9} A, 6.08×10^{-8} A, 1.02×10^{-7} A, 1.95×10^{-7} A and 2.16×10^{-7} A, respectively. From the data collected in Table 1, the conductivity of TiO_2 thin film shows improvement from 2.05×10^{-3} S/m (0.01M) to 9.62×10^{-3} S/m (0.20M).

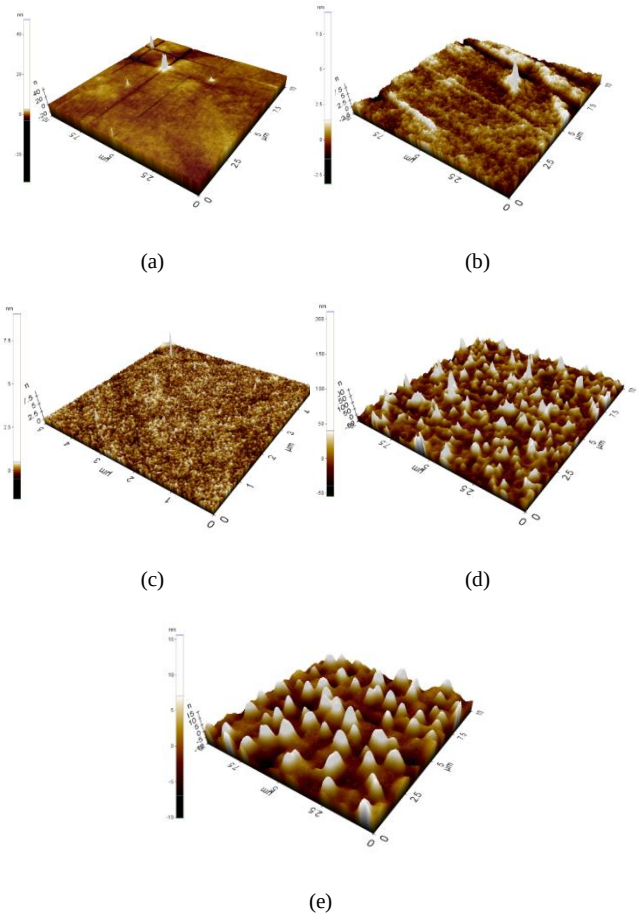
On the other hand, the resistivity of thin films improved as the molarity increased. TiO_2 thin film having the lowest molarity (0.01M) has the highest resistivity (4.89×10^2 Ω.m) and get improved as the molarity of TiO_2 increased to 0.20M (1.04×10^2 Ω.m). This improvement of conductivity and resistivity in respect of increasing molarities were due to increases the formation of grains sizes and improved the migration of electrons within TiO_2 thin films [27,28].

Table 1
Effect of TiO_2 molarity on properties of TiO_2 thin film

Entry	TiO_2 Molarity, M	Film thickness, t (nm)	Absorption coefficient, α (10^4 cm^{-1})	Optical Band Gap, E_g (eV)	Resistivity, ρ (10^2 Ω.m)	Conductivity, σ (10^3 S/m)	Surface Roughness, R_a (nm)
(a)	0.01	10.22	3.87	3.78	4.89	2.05	5.21
(b)	0.05	24.48	8.97	3.59	1.79	5.59	7.64
(c)	0.10	32.11	9.80	3.53	1.43	6.99	9.88
(d)	0.15	48.13	13.99	3.45	1.11	9.01	18.34
(e)	0.20	50.75	16.27	3.07	1.04	9.62	21.45

C. Structural Properties

Figure 5 shows the AFM surface topography of 3-dimensional (3D) images of TiO_2 thin films taken at the scan rate of 10μms^{-1}. The surface roughness, R_a of TiO_2 thin films having different molarities are shown in table 1. An increment of molarities of titanium (IV) isopropoxide causes surface roughness to increase with the maximum value of 21.45 nm obtained by 0.20M.



(a) (b) (c) (d) (e)

Figure 5: AFM topology 3-dimensional images of TiO_2 thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

The lowest three molarities (0.01M, 0.05M and 0.10M) showed the surface roughness below ~10nm. The lowest surface roughness 5.21nm was obtained by 0.01M TiO_2. AFM images in Figure 5 (a) shows less film formation when 0.01M TiO_2 was used. When TiO_2 molarities increased to 0.05M and 0.10M, the AFM images show smooth films of columnar grains. The results shows that by less addition of TTIP during the sol-gel process causes less weak interconnected porous matrix and porosity and get shrinks as the solution undergo anneal treatment [28,29].

IV. CONCLUSION

TiO_2 thin films having different molarities were deposited on glass substrates by sol-gel spin-coating technique. It was notified that the increasing in the TiO_2 molarity affects the thickness of thin films. The highest absorption efficient is obtained by 0.20M with band gap energy, E_g = 3.07eV which is lower than the TiO_2 anatase reported (E_g = 3.32eV). In addition, the highest conductivity of 0.20M TiO_2 thin films show the improvement in migration of electrons within the thin films. This is due to the high surface film roughness and uniformity growth of TiO_2 nanoparticles on the substrates.

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