

Optical, Electrical and Structural Investigation on Different Molarities of Titanium Dioxide (TiO₂) via Sol-Gel Method

Angelina Harry¹, Marini Sawawi¹, Muhammad Kashif¹, Siti Kudnie Sahari¹ and Mohammad Rusop²

¹Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS), 94300 Kota Samarahan, Sarawak, Malaysia.

²NANO-Scitech Centre (NST), Institute of Science, Universiti Teknologi Mara (UiTM), 40450 Shah Alam, Selangor, Malaysia.
angelinavivianaharry@gmail.com

Abstract—Titanium dioxide (TiO₂) 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 TiO₂ 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 TiO₂ thin film increases as the molarities increases. The optical band gap energy decreases from 3.78 eV to 3.07 eV as the TiO₂ molarities increases from 0.01M to 0.20M. The maximum value of the absorption coefficient was $16.27 \times 10^4 \text{ cm}^{-1}$ at 0.20M with surface roughness of 21.45 nm. Thin films deposited with 0.01M show lower absorption coefficient ($3.87 \times 10^4 \text{ cm}^{-1}$) within visible region with surface roughness of 5.21 nm. The improvement in optical and structural properties of TiO₂ thin films affects the electrical properties as the highest conductivity $9.62 \times 10^2 \text{ S/m}$ is obtained by 0.20M.

Index Terms—Sol-Gel; TiO₂; Thin Film; Properties.

I. INTRODUCTION

Titanium dioxide (TiO₂) 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 ($E_g = 3.32 \text{ eV}$) is usually used for production of photocatalysts [3,4]. Under illumination, it can help break down hazardous gases and organic pollutants via photocatalysis [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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ is a wide-band gap semiconductor, it contributes to low absorbance of light and has limited to UV range of the electromagnetic spectrum [17-18]. In this work, molarity of TiO₂ solution is being controlled to improve the microstructure to enhance the absorbance of light. The effect of different TiO₂ molarities by sol-gel process was presented and their influences on the performance of thin films were discussed.

TiO₂ 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

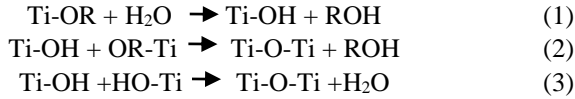
A. Glass Substrates Preparation

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 (N₂) blower.

B. Synthesis of TiO₂ by Sol-Gel Method

Synthesizing of TiO₂ nanoparticles were done by sol-gel that used titanium isopropoxide (C₁₂H₂₈O₄Ti) as main

precursor and others organic chemicals such as absolute ethanol (C₂H₆O) and glacial acetic acid (C₂H₄O₂). 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. Polycondensation of titanium (IV) isopropoxide (Equation (2) and (3)) were took place to produce TiO₂ [23].



where, R = C₁₂H₂₈O₃.

One-drop of non-ionic surfactant triton X-100 was added at the end of sol-gel process. The solution was stirred at 60°C 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 TiO₂ 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-TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ thin films were studied using UV-Vis spectroscopy. Atomic Force Microscopy (AFM) was used to investigate the roughness and surface topology of TiO₂ thin films. Electrical properties of TiO₂ thin films were measured using KEITHLEY 2420 sourcemeter.

III. RESULTS AND DISCUSSION

A. Optical Properties

The optical properties of the deposited TiO₂ 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 TiO₂ thin films were calculated using the Lambert law relation in Equation (4) [7].

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

where: α = Absorption coefficient
 t = Thickness of TiO₂ thin film
 T = Transmittance of TiO₂ thin film

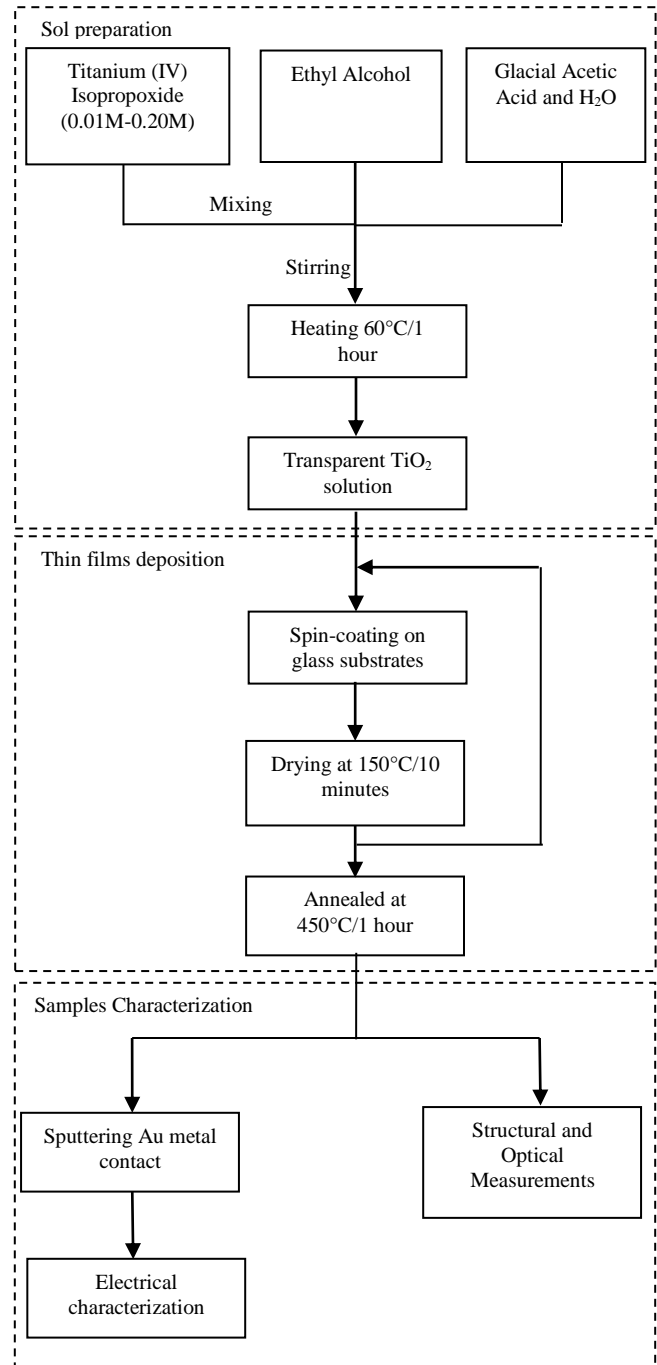


Figure 1: Flow Chart of Overall Process

The relationship between absorption coefficient and incident photon energy is written as Eq. 5 [7]. The optical band gap of TiO₂ 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)
 ν = Speed of light (c = 3 x 10⁸ ms⁻¹)
 A = Constant for indirect transition
 E_g = Energy band gap

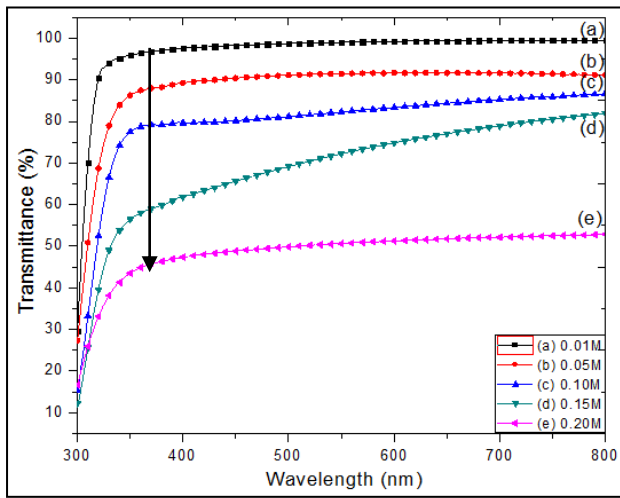


Figure 2: Optical transmittance spectra of TiO₂ thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

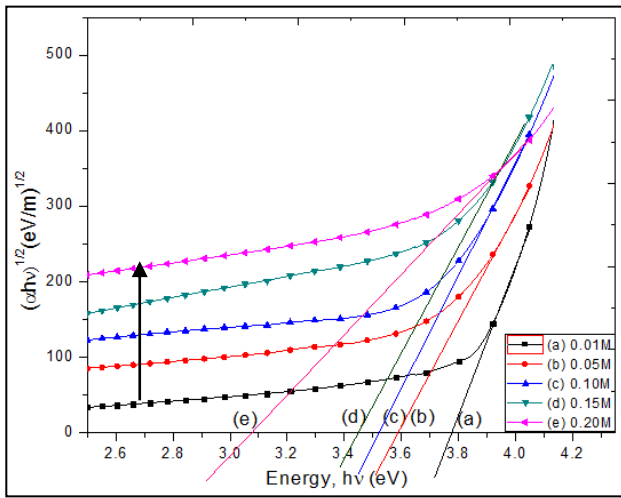


Figure 3: Optical band gap of TiO₂ thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

The variation of transmittance and absorption coefficient of TiO₂ 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 TiO₂ thin film exhibits high transparency in visible region, average up to 90%. The average transmittance gradually decreased to 45% as the molarity of TiO₂ increases to 0.20M. In contrast, thin films having the lowest TiO₂ molarity (0.01M) exhibits the lowest absorption coefficient ($3.87 \times 10^4 \text{ cm}^{-1}$) compared to the highest TiO₂ molarity (0.20M) which give the highest absorption coefficient ($16.27 \times 10^4 \text{ cm}^{-1}$) of thin film. Increasing the molarity of TiO₂ 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 TiO₂ 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 TiO₂ molarity increases. The decreases of optical band gap with respect to TiO₂ 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 TiO₂ 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

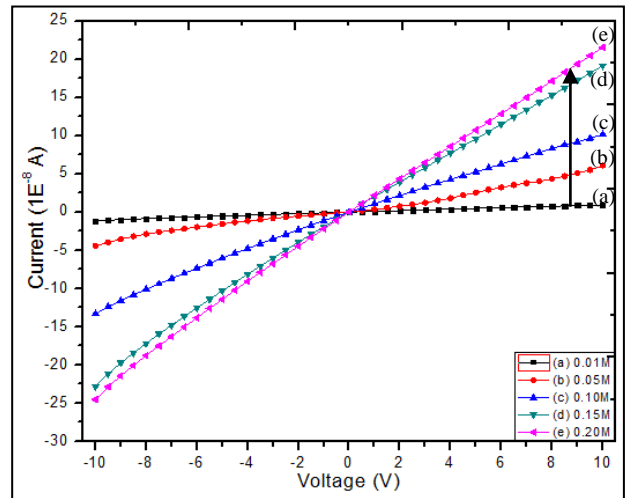


Figure 4: I-V characteristics of TiO₂ thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

The I-V characteristics shows increasing trends with TiO₂ molarity which the current obtained for 0.01M, 0.05M, 0.10M, 0.15M and 0.20M at 10V are $9.47 \times 10^{-9} \text{ A}$, $6.08 \times 10^{-8} \text{ A}$, $1.02 \times 10^{-7} \text{ A}$, $1.95 \times 10^{-7} \text{ A}$ and $2.16 \times 10^{-7} \text{ A}$, respectively. From the data collected in Table 1, the conductivity of TiO₂ thin film shows improvement from $2.05 \times 10^{-3} \text{ S/m}$ (0.01M) to $9.62 \times 10^{-3} \text{ S/m}$ (0.20M).

On the other hand, the resistivity of thin films improved as the molarity increased. TiO₂ thin film having the lowest molarity (0.01M) has the highest resistivity ($4.89 \times 10^2 \text{ } \Omega \cdot \text{m}$) and get improved as the molarity of TiO₂ increased to 0.20M ($1.04 \times 10^2 \text{ } \Omega \cdot \text{m}$). 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 TiO₂ thin films [27,28].

Table 1
Effect of TiO₂ molarity on properties of TiO₂ 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 TiO₂ thin films taken at the scan rate of $10\mu\text{ms}^{-1}$. The surface roughness, R_a of TiO₂ 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.

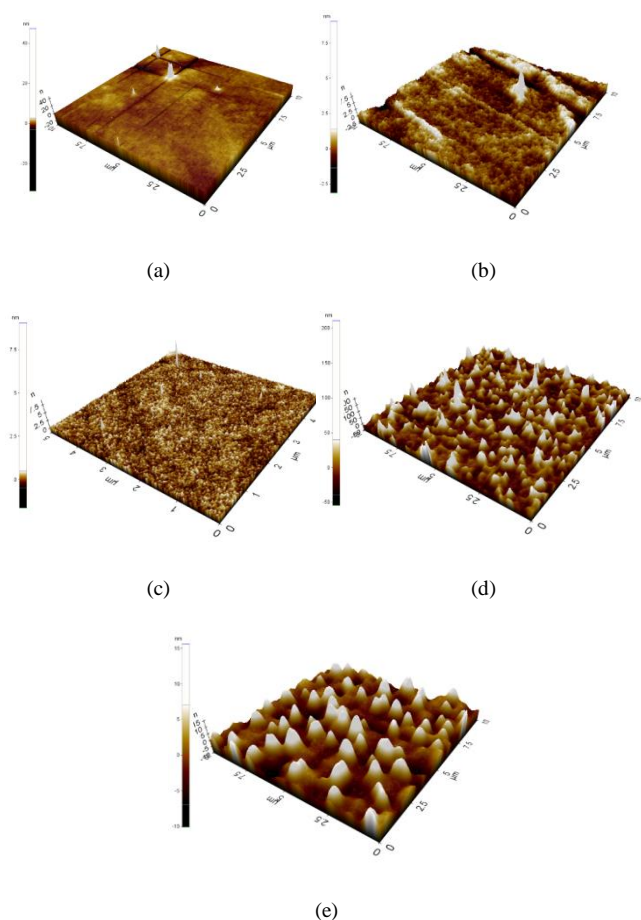


Figure 5: AFM topology 3-dimensional images of TiO₂ thin films for (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M and (e) 0.20M

The lowest three molarities (0.01M, 0.05M and 0.10M) showed the surface roughness below ~ 10 nm. The lowest surface roughness 5.21nm was obtained by 0.01M TiO₂. AFM images in Figure 5 (a) shows less film formation when 0.01M TiO₂ was used. When TiO₂ 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

TiO₂ thin films having different molarities were deposited on glass substrates by sol-gel spin-coating technique. It was notified that the increasing in the TiO₂ molarity affects the thickness of thin films. The highest absorption efficient is obtained by 0.20M with band gap energy, $E_g = 3.07\text{eV}$ which is lower than the TiO₂ anatase reported ($E_g = 3.32\text{eV}$). In addition, the highest conductivity of 0.20M TiO₂ 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 TiO₂ nanoparticles on the substrates.

ACKNOWLEDGMENT

The author would like to thank supervisors for the support, encouragement and guidance given throughout this study. The author would also like to thank to the members of Nano-SciTech Laboratory (NST) and Nano-ElecTronic Centre (NET) for the assistance and technical support in this research. The research was also supported by Universiti Malaysia Sarawak (UNIMAS) via Special Short Term Grant F02/SpSTG/1376/16/18.

REFERENCES

- [1] Sasani, M., and Bahramian, A. 2008. High Transparent Sol-Gel derived Nanostructured TiO₂ Thin Film. *Materials Letters*. 62(3): 361-364.
- [2] Trong, N., and Ngoc, D. 2015. Preparation of TiO₂ Nanocrystals in Anatase and Rutile Phase. *Journal of Science, Natural Science*. 60(4): 14-20.
- [3] Welte, A., Waldauf, C., Brabec, C., and Wellmann, P. 2008. Application of Optical for the Investigation of Electronic and Structural Properties of Sol-Gel Processed TiO₂ Films. *Thin Solid Films*. 516(20): 7256-7259.
- [4] Monllor-Satoca, D., Gómez, R., González-Hidalgo, M., and Salvador, P. 2007. The "Direct-Indirect" model: An Alternative Kinetic Approach in Heterogeneous Photocatalysis based on the Degree of Interaction of Dissolved Pollutant Species with the Semiconductor Surface. *Catalysis Today*. 129(1-2): 247-255.
- [5] Porkodi, K., and Arokiamary, S. 2007. Synthesis and Spectroscopic Characterization of Nanostructured Anatase Titania: A photocatalyst. *Materials Characterization*. 58(6): 495-503.
- [6] Bellucci, A. 2004. Overview of the TiC/TiO₂ (Rutile) Interface. *Solid State Ionics*. 172(1-4): 369-375.
- [7] Li, G., Yang, L., Jin, Y., and Zhang, L. 2000. Structural and Optical Properties of TiO₂ Thin Film and TiO₂+2 wt.% ZnFe₂O₄ Composite Film prepared by R.F. Sputtering. *Thin Solid Films*. 368(1): 164-167.
- [8] Zhao, W., Bala, H., Chen, J., Zhao, Y., Sun, G., Cao, J., and Zhang, Z. 2013. Thickness-Dependent Electron Transport Performance of

- Mesoporous TiO₂ Thin Film for Dye-Sensitized Solar Cells. *Electrochimica Acta*. 114: 318-324.
- [9] Xu, W., Zhu, S., Fu, X., and Chen, Q. 1999. The Structure of TiO_x Thin Film Studied by Raman Spectroscopy and XRD. *Applied Surface Science*. 148(3-4): 253-262.
- [10] Acayanka, E., Tiya Djowe, A., Laminsi, S., Tchoumkwé, C., Nzali, S., and Poupi Mbouopda, A. 2013. Plasma-Assisted Synthesis of TiO₂ Nanorods by Gliding Arc Discharge Processing at Atmospheric Pressure for Photocatalytic Applications. *Plasma Chemistry and Plasma Processing*. 33(4): 725-735.
- [11] Chiarello, G., Selli, E., and Forni, L. 2008. Photocatalytic Hydrogen Production over Flame Spray Pyrolysis-Synthesized TiO₂ and Au/TiO₂. *Applied Catalysis B: Environmental*. 84(1-2): 332-339.
- [12] Zhang, X., Li, X., Wu, J., Yang, R., Tian, L., and Zhang, Z. 2009. Simple Sol-Gel Route to Synthesis of Mesoporous TiO₂. *Journal of Sol-Gel Science Technology*. 51(1): 1-3.
- [13] Hong, Y., Cheng, K., Weng, W., Song, C., Du, P., Shen, G., and Han, G. 2011. Low Temperature Preparation of TiO₂ Nanodot Film on Substrates. *Thin Solid Films*. 519(15): 4641-4646.
- [14] Zhang, Q., Gao, L., and Guo, J. 2000. Effect of Hydrolysis Conditions on Morphology and Crystallization of Nanosized TiO₂ Powder. *Journal of European Ceramic Society*. 20(12): 2153-2158.
- [15] Lim C. S. 2014. Effect of pH on the Microstructural Morphology and Phase Transformation of TiO₂ Nanopowders Prepared by Sol-Gel Method. *Asian Journal of Chemistry*. 26(6): 1843-1847.
- [16] Halim Affendi, I., Ahmed Azhar, N., Mohamad Saad, P., Alrokayan, S., Khan, H., and Rusop, M. 2015. Electrical and Physical Property of TiO₂ Films Prepared at Different Deposition Time. *Advanced Materials Research*. 1109:524-528.
- [17] Ong, W. and Ho, G. 2016. Enhanced Photocatalytic Performance of TiO₂ Hierarchical Spheres Decorated with Ag₂S Nanoparticles. *Procedia Engineering*. 141:7-14.
- [18] Ansari, S. and Cho, M. 2016. Highly Visible Light Responsive, Narrow Band gap TiO₂ Nanoparticles Modified by Elemental Red Phosphorus for Photocatalysis and Photoelectrochemical Applications. *Scientific Reports*. 6:25405.
- [19] Lewkowicz, A., Synak, A., Grobelna, B., Bojarski, P., Bogdanowicz, R., and Karczewski, J. 2014. Thickness and Structure Change of Titanium (IV) Oxide Thin Films Synthesized by the Sol-Gel Spin Coating Method. *Optical Materials*. 36(10): 1739-1744.
- [20] Mechiakh, R., Sedrine, N., Naceur, J., and Chtourou, R. 2011. Elaboration and Characterization of Nanocrystalline TiO₂ Thin Films Prepared by Sol-Gel Dip-Coating. *Surface and Coatings Technology*. 206(2-3): 243-249.
- [21] Lee, W., Lee, D., Song, J., and Min, B. 2005. Effect of Process Parameters on the Efficiency of Dye Sensitized Solar Cells. *Metals and Materials International*. 11(6): 465-471.
- [22] Dhanapandian, S., Arunachalam, A., and Manoharan, C. 2015. Effect of Deposition Parameters on the Properties of TiO₂ Thin Films Prepared by Spray Pyrolysis. *Journal of Sol-Gel Science Technology*. 77(1): 119-135.
- [23] Superkar A.K. 2013. Optical, Structural and Morphological Study of TiO₂ Thin film using Sol-gel Spin Coating Techniques. *IOSR Journal of Engineering*. 3(01): 38-41.
- [24] Wong, A., Daoud, W., Liang, H., & Szeto, Y. 2014. The Effect of Aging and Precursor Concentration on Room-Temperature Synthesis of Nanocrystalline Anatase TiO₂. *Materials Letters*. 117: 82-85.
- [25] Lau, L., Ibrahim, N., and Baqiah, H. 2015. Influence of Precursor Concentration on the Structural, Optical And Electrical Properties of Indium Oxide Thin Film Prepared by a Sol-Gel Method. *Applied Surface Science*. 345: 355-359.
- [26] Patil, L., Suryawanshi, D., Pathan, I., and Patil, D. 2013. Effect of Variation of precursor concentration on Structural, Microstructural, Optical and Gas Sensing Properties of Nanocrystalline TiO₂ Thin Films Prepared by Spray Pyrolysis Techniques. *Bulletin of Materials Science*. 36(7): 1153-1160.
- [27] Ge, L., Li, R., He, S., Chen, H., and Guo, L. 2012. Effect of Titania Concentration on the Grain Boundary Conductivity of Ce_{0.8}Gd_{0.2}O_{1.9} Electrolyte. *International Journal of Hydrogen Energy*. 37(21): 16123-16129.
- [28] Mohamad Saad, P., Sutan, H., Shariffudin, S., Hashim, H., and Mohd Noor, U. 2015. TiO₂ Thin Film via Sol-Gel Method: Investigation on Molarity Effect. *IOP Conference Series: Material of Science and Engineering*. 99: 012006.
- [29] Affenfi, I., Mohammad Saad, P., Salman, A. H., Haseeb A. K., and Mohammad, R. 2015. The Effect of Different Molarity on TiO₂ solution Prepared by Sol-Gel Method. *Proceedings of Malaysian International Tribology Conference 2015*, 308-309.