A Study Of Tio_2 Thin Film Using Sol-Gel Method

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Abstract

This paper reports on a study of titanium dioxide (TiO_2) thin films. TiO_2 thin films were prepared by sol-gel method using nano- TiO_2 powder dissolved in Isopropanol solution. The nano- TiO_2 powder was previously extracted from local mineral waste which is known as ilmenite. Using the aqueous solution containing 0.1g of nano-TiO_2 powder, several acids which are acetic, hydrochloric (HCI) and nitric were used to study its effects. Each sample was mixed with Triton X-100. Using spin-coating technique the thin films were deposited with 1000 r.p.m for 30s and 3000 r.p.m for 60s. The thickness of each sample was characterized using KL surface profile. The surface topologies 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). It was found that by using nitric acid more uniform and transparent TiO_2 thin film has been produced.

Keywords: Titanium dioxide, Nitric acid, Sol-gel method

1. Introduction

One of nanomaterial type is titanium dioxide (TiO_2), features a strong adsorption of TiO_2 due to the high chemical motion of the surface. Titanium dioxide (TiO_2) is also known as titania and among its properties are chemically stable, nontoxic and low cost material. Pure TiO_2 does not arise in natural world but is obtained from ilmenite or leuxocene ore. Nowadays, many researchers have been explored TiO_2 in various fields due to its many applications such as photocatalyst (Keshma, 2004), solar cell (Colgan, 2004) and gas sensor (Skubal et al., 2004). It is a wide band gap semiconductor material (Eg~3.2eV), and depending on their chemical composition, it shows a great variety of electrical conductivity (Kwon et al., 2004).

Sol–gel methods have been extensively used for preparation of TiO_2 particle powder and thin films. This study based on TiO_2 thin film using sol-gel method. TiO_2 thin-film solar cells are essentially thin layers of semiconductor materials useful for backing material. Thin films greatly reduce the amount of semiconductor material required for each cell when compared to silicon wafers and hence lowers the cost of production of solar cells.

In this research, nano- TiO_2 powder obtained from tin mining waste (Illmenite) is used. This will reduce the cost of nano- TiO_2 to 99% compared to the market price of nano- TiO_2 powder. Sol-gel spin-coating is used to produce aqueous solution and then to deposit thin film. However, nano- TiO_2 powder has low solubility. It does not fully dissolve in a solvent. This can be a problem for producing a highly transparent thin film that is the most effective for absorbing light. Thus, the nano- TiO_2 powder needs to be soluble in an aqueous solution. Therefore, acids as catalyst in solution were used by many researchers.

The aim of this research is to optimize TiO_2 composition and phase in TiO_2 thin films. This research comprises of several objectives;

a) To find the process recipe of substances that can dissolve TiO_2 in IPA.
b) To optimum the physical and optical properties of TiO_2 thin film.

2. Literature Review

Sugimoto et al. (1987) stated the method of using sol-gel TiO_2 nanoparticles in the formation of various sizes and shapes by tuning parameters of the reaction. Epperson et al.(1988*)* prepared TiO_2 nanoparticle using condensation technique of Ti vapors into clusters with

Hellium pressure and after that exposed to dioxygen atmosphere. Bücher et al. (1989) found TiO_2 pigments were obtained by adding older sulfate and newer chloride processes. Two economic processes were highly dependent on the raw materials available. Ilmenite and titaniferous slag were used in sulfate processes whereas leucoxene, rutile, synthetic rutile and probably anatase in chloride processes.

Legrand-Buscema et al. (2002) investigated TiO_2 thin film obtained via sol-gel dip coating method on a silicon substrate. The stable solution were synthesized using titanium alkoxide in acetic acid and using acetylacetone asa chelating agent. The rutile phase appeared at 700°C in the xerogel whereas the anatase phase up to 800°C. However, the particle size increases around 40nm at 800°C.

Su et al. (2005) prepared nanosized TiO_2 by a sol-hydrothermal process using titanium (IV) n-butoxide in isopropyl alcohol was used as precursor of TiO_2 . Acetylacetone (acac) was added to control the reaction kinetics. After that, the solution was added with HNO3 dropwise and finally a clear solution was obtained. The sol mixture was inserted into a Teflon-lined autoclave, 45% filled and heated at 150°C or 200°C. After all, the products were obtained by filtration and dried at 150°C for 5 hours. Nevertheless, the fraction of rutile phase increases with increasing hydrothermal temperature and time.

Mohammadi et al. (2008) investigated sol-gel route nanostructured TiO_2. The solution contains titanium tetraisopropoxide, hydrochloric acid, and deionised water. Two major parameters were peptisation and drying temperature identified that accountable for delaying the anatase to rutile phase transformation. The prepared solution had a narrow particle size distribution in the range 20-33 nm and the synthesized powder had crystallite size before annealing in the range 2.2-3.2 nm and after annealing, 3.5-4nm. Nevertheless, drying temperature effect on anatase to rutile phase transformation was larger than peptisation temperature.

Suzana et al. (2011) studied synthesis, characterization and photocatalytic properties of sol-gel TiO_2 films. Two solutions were prepared in which the first solution was without polyethylene glycol (PEG) and other one was prepared by adding of PEG. As the result, the solution with the addition of PEG has a higher ratio of the anatase/rutile crystal phases than the second solution without the addiition of PEG. Nevertheless, the weight loss of the sample large than without PEG due to exothermic process. The exothermic process due to combustion of PEG.

Wetchakun et al. (2012) prepared TiO_2 nanoparticles modified by sol-gel method. The solution consist of titanium tetraisopropoxide and nitric acid. The mixture solution was loaded into a cellophane membrane and suspended for 1 hour in transparent solution contains ethylenediaminetetraacetic (EDTA) and ammonia solution. TiO_2 nanoparticles calcined at 400°C for 3 hours using cellophane membrane at the highest specific area 97 m^2g^{-1} with the smallest particle size of 10nm-20nm. However, the surface area extremely decreased at the high calcination temperature from 97m^2 g^{-1} at 400°C to 97m^2 g^{-1} at 700°C.

Golobosstanfard et al. (2013) prepared TiO_2 thin film on glass substarates from alkoxide solution by sol-gel spin coating technique. The solution contains with titanium isopropoxide, deionized water, different acids and different solvents. However, the use of acids causes the refractive index and porosity of the films were intensely affected by the acid type in a way that hydrochloric acid always leads to higher refractive index and lower porosity.

3. Methodology

3.1 Materials

The study of TiO_2 thin film using sol-gel method started with materials as the follows: Nano- TiO_2 powder as precursor; Isopropanol as solvent; Acid and triton X-100 as catalyst to increase conductivity of thin film. The types of acid were acetic acid (AC), nitric acid (NA) and hydrochloric acid (HCL).

3.2 Substrate

The glass substrates were cleaned with acetone in an ultrasonic bath for 5 minutes at 50°C and dried with nitrogen gas.

3.3 Preparation of TiO_2 Solution

The TiO_2 solution was prepared using sol-gel method. The materials were mixed in a beaker with their specific order. Nano- TiO_2 powder was mixed in Isopropanol and each acid catalyst and triton X -100 and the solutions was stirred for 20 hours ageing process at room temperature. Table 1 shows the molar ratio of acid solutions. This solutions were heterogeneous mixing. Then, the solutions were filtered.

Table 1. Molar ratio of acid solution

Sample	Molar ratio
HCL	2.44
NA	0.32

AC	0.349

3.4 Thin Film Deposition Method
TiO_2 thin films were deposited by 2-steps spin coating method (1000 r.p.m for 30s and 3000 r.p.m for 60s) for 10 layers. TiO_2 solution was dropped 10 times onto the substrates. Each layer was preheated at 250°C for 5 minutes.

3.5 Annealing Process
The thin films were annealed at 500°C for 1 hour. Annealing also produces better physical attachment which improves the electronic contact between all the particles of the thin films. After annealing at 500°C for 1 hour, the thin films were undergoing slow cooling at room temperature.

3.6 Gold Electrode Coating Process
Then thin films were coated with electrode by using sputter coater. The sputter coater was set to of 40mA and 20 seconds. Then, TiO_2 thin films were characterized

3.7 Characterization Method
The thickness of each sample was characterized using KL surface profile. The surface topologies 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).

4. Result And Discussion
Figure 1 shows the thickness of the three samples using 0.1g nano- TiO_2 powder indicates HCI (33 nm), nitric (21nm) and acetic (115 nm). Nitric acid has the smallest thickness compared with others. However, low intensity of the film is due to the low thickness of TiO_2 thin films.

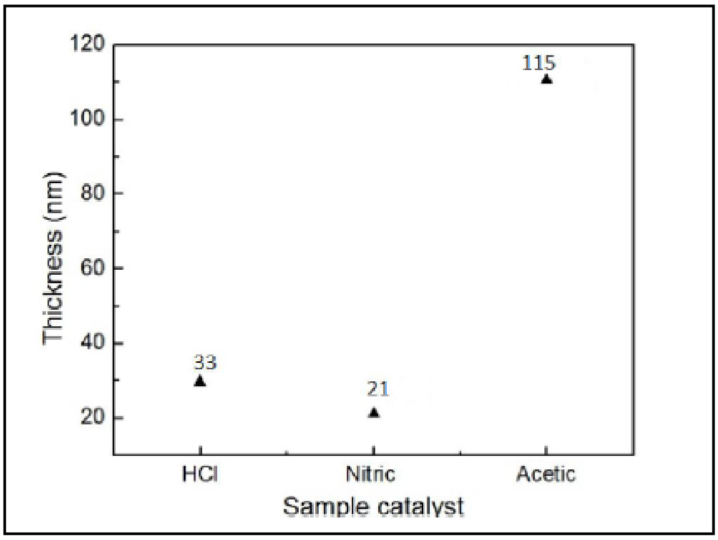

Figure 1. The tickness of three samples

Figure 2 shows the surface topography of TiO_2 thin film for different acids. The roughness of TiO_2 thin film increased with the thickness of TiO_2 thin film

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also increased. The roughness of sample acetic, HCI and nitric acid were 56.942 nm, 16.353 nm and 9 nm respectively. It was observed that sample nitric acid had optimum uniformity due to the roughness that the smallest grain size than others. The surface roughness of topography obtained from AFM analysis. The lower roughness value represents good homogeneity of the TiO_2 particles on the surface.

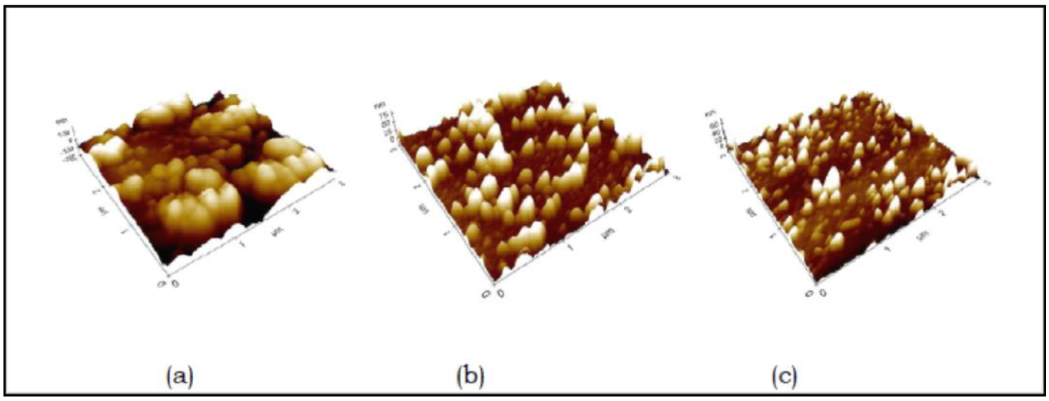

Figure 2. AFM topography (a) Acetic (b) HCI (c) Nitric

Figure 3 shows the transmittance spectra of TiO_2 thin film deposited using different acids. Transmittance spectra were measured in the wavelength range of 300-1000 nm. The optimum TiO_2 thin films spectra exhibit high visible transmittance, up to 95 %, for nitric acid when the energy band gap 3.44 eV. TiO_2 has high absorption at the wavelength of 360 nm because of optical band gap. The TiO_2 thin film absorbed light which has energy greater than 3.42 eV at 364 nm for HCI sample. However, it absorbed photon energy greater than 3.26 eV at 380 nm for acetic acid. However, the transmittance for wavelength from 310 to 320 nm decreased below the transmittance of sample. The energy band gap equation as the following:

$$Eg = \frac{hc}{\lambda} \quad (1)$$

While h, c and are plank constant (4.136×10^{-15} eV), speed of light (3×10^{8} ms^{-1}) and wavelength, respectively. Energy band gap (*Eg*) normally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in semiconductors. From the measured transmittance T given, assuming the absorption coefficient α using the following relation:

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (2)$$

Where d is the thickness of the film and T is its transmittance. The absorption coefficient defines how far into a material of a certain wavelength of light can penetrate before it was absorbed. The absorption coefficient for nitric acid, HCI and acetic were $2.4\text{x}10^{4}$ cm^{-1}, $5.6\text{x}10^{4}$ cm^{-1} and $3.1\text{x}10^{4}$ cm^{-1}.

In a material with a low absorption coefficient, only light was poorly absorbed, and if the material is very thin, would appear transparent for that wavelength. The absorption coefficient based on the material and wavelength of the light that was absorbed.

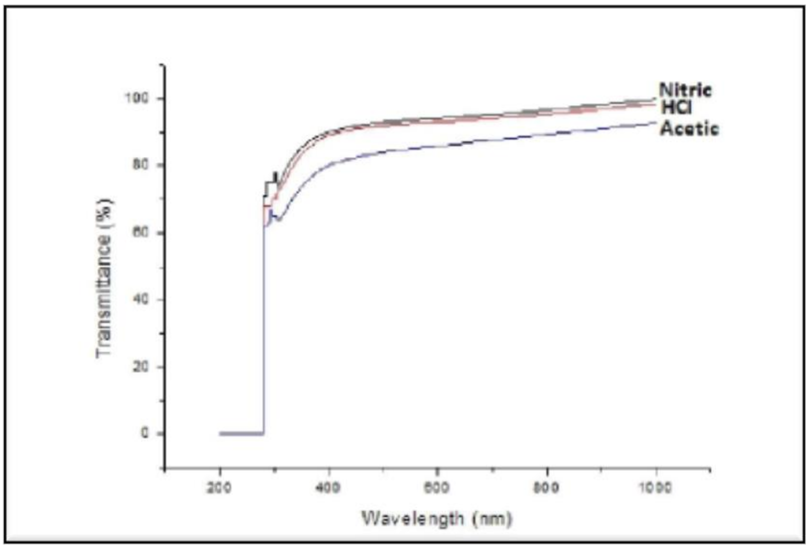

Figure 3. The transmittance spectra of TiO_2 thin film with different acids

5. Conclusions

Transparent TiO_2 thin films have been prepared using sol gel method on glass substrates from solution with different acids catalyst. However, the porosity of the films were strongly affected by the acid type in a way that nitric acis always leads lower porosity than HCI and acetic acid. The use of triton-X 100 was also better the characteristic aspect. When the thickness of the thin film was reduced, the transmittance was increased and the particles size become smaller. The transmittance for the optimum of TiO_2 thin film contains nitric acid is about 95% which was acceptable for solar cell application.

References

Bucher K. & Fricke *J. Phys. in unserer* Zeit (1990), 21. Jahrg., Nr.6.

Legrand-Buscema C., Malibert C.& Bach B. (2002). Elaboration and characterization of thin films of TiO_2 prepared by sol–gel process, *Thin Solid Films* 418: 79–4.

Chul Han Kwon, Je Hun Kim, In Sun Jung, Hyunmin Shin, & Ki Hyun Yoon. (2003). Preparation and characterization of TiO_2 –SiO_2 nano-composite thin films. *Ceramics International*, Volume 29, Issue 8: 851-856.

Colgan M.J. and Jbrett M. (2005). Sol. Energy Master, Sol.Cell 85: 321-331

Epperson J.E., Siegel R.W. & White J.W. (1988). Sintering of nanophase TiO_2 at 550°C. *Mater Res Soc Symp Proc.*132: 3–7.

Golobostanfard M.R. & Abdizadeh H. (2013). Effects of acid catalyst type on structural, morphological, and optoelectrical properties of spin-coated TiO_2 thin film. *Journal of Physica B* 413: 40–46.

Keshma M., Mmohseni, Trocrynski T., *Appl.Catal.*, B53. (2004). 209-219.

Mohammadi M.R., Fray D.J., & Mohammadi A. (2008). Sol-gel nanostructured titanium dioxide: Controlling the crystal structure, crystallite size, phase transformation, packing and ordering, *Micporous materials* 112: 392-402.

Natda Wetchakun, Burapat Incessungvorn, Khatcharin Wetcakun, & Sukon Phanichphant. (2012). Influence of calcination temperature on anatase to rutile phase transformation in TiO_2 nanoparticles synthesized by the modified sol-gel method. *Materials Letters*: 195-198.

Sahdan, Mohd Zainizan & Nayan, Nafarizal and Dahlan, Samsul Haimi and Mahmou, Mahdi Ezwan and Hashim, *Uda Sol-gel synthesis of TiO_2 thin films from in-house Nano- TiO_2 powder.* In: World Congress on Engineering and Technology 2012 (CET 2012), 26-29 Oktober 2012, Beijing, China.

Skubal, L.R.N.K. Meshkov & M.C. Yogt. (2002). Detection and identification of gaseous organics using a TiO_2 sensor. *J. Photochem.* Photobiol, A(148):103-108.

Su C., Tseng C.M., Chen L.F., You B.H., Hsu B.C., & Chen S.S. (2006). Sol–hydrothermal preparation and photocatalysis of titanium dioxide, *Thin Solid Films* 498: 259 – 265.

Sugimoto, T. AdV. *Colloid Interface Sci.* (1987) 28, 65.

Suzana Segota, Lidja Curkovic, Davor Ljubas, Vesna Svetlicic, Ivona Fiamengo Houra, & Nenad Tomasic (2011). Synthesis, characteristic and photocatalytic properties of sol-gel TiO_2 films, *Ceramic International* 37: 1153-1160.