Effect of Concentration of Precursor Solution on Surface Morphology and Optical Properties of Titania Thin Film

N. Barua, J.F. Moushumi, A.K.M.B. Rashid

Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

Abstract. Titania thin film has become a great interest for the researchers due to its amazing photocatalytic activities and anti-bacterial effect. In present paper, films were deposited on normal silica glass substrate by dynamic spin coating using stable titania precursor solutions of different concentrations. Stable titania solution were synthesized by aqueous sol-gel route using titanium tetra isopropoxide. The films were calcined at 500°C were characterized with thermo gravimetry and differential scanning calorimetry to determine phase transition point. X-ray diffraction for phase analysis, UV-Visible spectrometry for optical properties analysis, surface profilometer for thickness measurement, Optical Microscope and Scanning Electron Microscopy (SEM) to determine surface morphology. The objective was to analyze the effect of concentration of titania precursor solution on the surface morphology and optical properties of titania thin films. Solution of comparatively lower concentration produced uniform and stable titania film with better optical properties. With increasing concentration, the adhesion of the film degraded along with its surface morphology and optical properties.

Introduction

Interest in titania thin film has grown rapidly in recent years due to its photocatalytic activity, availability as well as chemical inertness which has led to a global spark of interest into several applications such as water and air purification by photo catalysis, self-cleaning or anti-fogging materials (due to its superhydrophyllicity) and solar energy conversion. Many investigations have focused on its production and applications in solar energy conversion and environmental purification since Fujishima and Honda discovered the photocatalytic splitting of water on the TiO$_2$ electrodes in 1972[1]. TiO$_2$ is transparent in the visible range and has a wide optical band gap [2]. This, together with its chemical and thermal stability, makes TiO$_2$ an excellent candidate for optical coatings. Many researchers have been developing various ways to apply TiO$_2$ coatings on various substrates to avoid the use of powder, which must be separated from the water in a slurry system after photocatalytic reaction.

There are several methods for the fabrication of titania thin films including hydrothermal methods, electronbeam evaporation, DC and RF magnetron sputtering, solvo-thermal synthesis and sol–gel methods [3-7]. However, some of these methods have some disadvantages for industry applications [8] like vacuum evaporation, sputtering, and chemical vapor deposition methods require special apparatuses for deposition of films. The sol–gel process provides new approaches and a better control in the preparation of materials compared with the other methods[9]. It offers several advantages: fine powders and films with high homogeneity can be prepared using simple equipment, the thickness and
the porosity of the films can easily be controlled by changing the concentration of the sol and large surface areas can be coated by spin or dip coating. Spin coating is a simple process for rapidly depositing thin coatings onto relatively flat substrates. This technique offers many advantages over other deposition techniques due to the use of very simple large area thickness uniformity, good reproducibility, controlled growth and low temperature deposition[10].

The photocatalytic activity of TiO\textsubscript{2} thin films strongly depends on the preparing methods and process parameters like solution concentrations, calcination temperature as they have decisive influence on chemical and physical properties of titania thin films[11]. It was our interest to analyze the effect of solution concentration on the overall quality of titania thin film as not many works have been done on this. In this work both the aqueous and non-aqueous sol-gel routes for facile preparation of titania thin film were explored to find an inexpensive production route of uniform and transparent TiO\textsubscript{2} thin film via spin coating method. With this, the effect of concentration of the precursor solution on the surface morphology, quality and optical properties of titania thin film was analyzed which was our major concern.

2. Experimental

2.1 Materials
Titanium(IV) isopropoxide (TTIP) (Ti\{OCH(CH\textsubscript{3})\textsubscript{2}\}\textsubscript{4} (98.0%) were purchased from Acros Organics and acetylacetone (C\textsubscript{5}H\textsubscript{8}O\textsubscript{2} ) (99.0%), acetic acid(CH\textsubscript{3}COOH) (98.5%) were purchased from Merck Chemical Industries, Ltd. All reagents were used as received, and all the experiments were carried out under ambient conditions without eliminating the water from the atmosphere.

2.2 Preparation of Aqueous Titania Sol
Titanium (IV) isopropoxide was added to acetylacetone (\texteta_{acac}\eta_{TTIP}=1) slowly under continuous stirring at room temperature. The mixture was stirred for 10 minutes. The resulting yellow solution of TTIP/ Acac (acetylene acetone) precursor was added dropwise to an aqueous solution of AcOH under continuous stirring for 1 hour at room temperature, yielding yellow transparent solutions (20ml). The water and AcOH ratio were determined via trial and error to obtain the desired pH. 5 batches of solutions of different concentrations (0.3M, 0.5M, 1M, 1.25M, 1.5M) with pH ranging from (3.5-3.6) were produced to study the effect of concentration on the stability, uniformity, and properties of the films.

2.3 Preparation of Titania Film
Thin films of TiO\textsubscript{2} were prepared by dynamic spin-coating method. The substrate used for coating was a silica glass substrate with 25*25*1.15mm dimension. The substrates were cleaned with soft bristled brush to avoid scratches; detergent was used to get rid of oily or greasy substances. The cleaning is followed by ultrasonic bath in ethanol, acetone and water respectively, each for 10 minutes. The clean and dry substrates were then dropped with precursor solution while the substrate was rotating at 2500 rpm for 20 seconds in the spin coater (MIDAS, Model 1200T). The coated film was dried at room temperature for 10 min and then at 60°C for 10 minutes. The set of spin coating and drying was further repeated twice. The as-prepared film was then heated at 500 °C for 2 hours to yield stable and Transparent TiO\textsubscript{2} thin films.

2.4 Characterization of Titania Film
The surface morphology of the TiO\textsubscript{2} films were observed using an optical microscope, field emission scanning electron microscope (FeSEM, JEOL-7600F). Surface roughness and thickness were determined using surface profilometer (BRUKER, Model :DektakXT). Changes in the crystal phase and crystallite size were monitored using X-ray diffraction (Model EMMA) rotating anode diffractometer (45 kV, 40 mA) with CuK\textalpha radiation (1K\alpha ¼ 1.5406 Å). UV–Vis Spectrometer (Cary Win UV 50, Australia) and (Cintral 2020, GBC corporation, Australia) were used to measure absorbance of the thin film over an extended spectral range.
3. Result and discussion

3.1 Characterizations of TiO₂ films prepared by spin-coating

Preparation of titania film was attempted by both static and dynamic spin coating at different spinning speed, spinning time and different concentration. It was observed that dynamic spin coating at 2500 rpm produces more uniform film than static spinning. It was also observed that film produced from solution with lower concentration produced more stable, uniform and transparent film than the film produced from higher concentration precursor solution. A visual difference between the films made from different concentration precursor solution can be seen from Fig. 1.

![Figure 1: Effect of concentration on the uniformity and transparency of the films](image)

The thermo-gravimetry and differential thermal analysis was conducted to determine the calcination temperature. Because it was difficult to analyze precisely the changes accompanied by the crystallization and/or phase transition owing to the quite small amount of TiO₂ loaded on the glass substrate, the TG-DTA analysis was conducted on the powder samples that were obtained by the simple dryness of the precursor sol solutions. No clear peaks were observed for titania powder from 500 to 900 °C, whereas exothermic peaks corresponding to phase transition from anatase to rutile are generally observed at around 800 °C for titania powder obtained from other precursor solutions[12]. The TG-DTA result indicates the interesting nature for acac/AcOH for preventing the phase transition of anatase to rutile at high temperatures. It has been reported that the addition of acac and/or AcOH into the organic solvents containing the titania precursor effectively suppress the phase transition[12] and crystal growth[13]. However, it has also been found that the crystal growth increases with increasing calcination temperature [2] so 500°C calcinations temperature were selected for this experiment.

Figure 2 shows the thickness of TiO₂ thin film with different concentration from 0.3, 0.5M, 1M, 1.25M and 1.5M. The thickness are increasing gradually. It is found that as the thickness increase it will affect the electrostatic contact between solute particles [14]. The particles become larger and resulted in increasing the probability of more solute particles to be grouped creating agglomerate particles. This result was supported by structural analysis.

![Figure 2: Effect of concentration on film thickness](image)
Figure 3: XRD spectra of Titania thin film (C=0.3M)

The X-ray diffraction pattern of the synthesized titania film is shown in Figure 3. The absence of spurious diffractions indicates the crystallographic purity [7]. The experimental XRD pattern agrees with the JCPDS card no. 21-1272 (anatase TiO$_2$) and the XRD pattern of TiO$_2$ nanoparticles other literature [8]. Strong diffraction peaks at 25° and 48° indicating TiO$_2$ in the anatase phase [10]. The 2θ peaks at 25.27° and 48.01° confirm its anatase structure. The X-ray diffraction peaks of the powders show a significant broadening due to the small size of crystallites. The average crystallite sizes (D) were calculated from the most intense diffraction peak (101) using the Scherrer formula. It was observed that crystallite size increases with increasing concentration.

Table 1: Different Crystallite size with varying Concentration.

| Sample No | Concentration | wavelength, λ | FWHM, 2θ | Diffraction angle at 101 peak 2θ | Crystallite Size |
|-----------|---------------|---------------|-----------|---------------------------------|-----------------|
| 1         | 0.3M          | 0.154 nm      | 1.47      | 25.12                           | 486nm           |
| 2         | 0.5M          | 0.154 nm      | 1.42      | 25.2                            | 502nm           |
| 3         | 1.0M          | 0.154 nm      | 1.2       | 25.32                           | 595nm           |
| 4         | 1.25M         | 0.154 nm      | 0.95      | 25.18                           | 751nm           |
| 5         | 1.5M          | 0.154 nm      | 0.87      | 25.3                            | 820nm           |

3.2 Surface morphology of the Titania films

In Fig. 4(a) the substrate shows smooth continuous coating with few inclusion type matter that has a broken glass type morphology. It is assumed that inclusion particles during drying or heating breaks the continuity of the coating. Figure 4(b) shows absolute broken glass morphology. When observed closely a smooth and continuous layer beneath the broken glass like layer can be seen which posits a very important conclusion that with increasing concentration the continuity/uniformity of the coating decreases. This may occur due to grain coarsening or particle-agglomeration resulting in degradation of other properties too.
Figure 4: Optical micrographs showing surface morphology of titania thin film.
(a) C= 0.3M, (b) C= 1.5M.

Figure 5 shows SEM images of TiO$_2$ films at low and high concentration of the precursor solution. As described earlier, all the films were confirmed to have anatase phase after calcination (Figure 3 for the XRD patterns). The SEM image demonstrates that grain sizes of TiO$_2$ particles gradually increased with increasing concentration. The difference in crystal growth was also confirmed in the average sizes of TiO$_2$ particle calculated from the full width of half maximum intensity of the (101) diffraction peaks by the Scherrer formula (Table 1).

Figure 5: SEM micrograph of titania thin film surface. (a) 0.3M, (b) 1.25 M (at X=100k).

It is found that scarcity of sufficient amount of acid and water larger titania nano particles forms in precursor solution from alkoxide [14]. This degrades the surface property like smoothness, adhesion with substrate and causes cracking on the surface. Sufficient amount of acetic acid hinders crystal growth and phase transformation from anatase to rutile during calcinations [4]. Lower volume of acid in causes crystal growth during calcinations and degrades surface morphology.
3.3 Optical properties of Titania films

Figure 6 shows the absorbance spectra of TiO₂. The thin films from all the solutions show absorbance in UV range and it is from 290 nm to 350 nm. But they show different peak value for absorbance at different wavelength. With increasing concentration, the wavelength for the highest peak value shifts towards left side of the wavelength. That means with increasing concentration the wavelength for the highest absorbance decreases.

![Absorbance spectra of titania thin film produced from different concentration precursor solution.](image)

Figure 6: Absorbance spectra of titania thin film produced from different concentration precursor solution. (Wavelength range: from 310nm to 400nm)

It is evident from this research that precursor’s concentration affects the optical properties of the thin film to a great extent. It is because it also affects the crystallization behavior, the size, stability, and morphology of the produced sol from titanium alkoxides [3]. These are also strongly affected by the water titanium molar ratio (r=[H₂O]/[Ti]) [10]. The formation of colloidal TiO₂ at high r ratio is of great interest, because the small size of particles of titania is formed under this condition. The smaller the nanoparticles of titania the more stable the precursor’s colloidal solution of titania [7]. And this type of solution produce film of smooth, transparent surface with higher surface area due to very small titania particle size. Film with higher surface area absorbs higher amount of energy.

With increasing concentration amount of water reduces that reduces the value of r. This enlarges the particle size of titania that causes film of lower quality. So that the value of peak absorbance reduces with increasing concentration. On the other hand, with increasing concentration, TITP to acetic acid ratio decreases, Table 2.

Now, Although the TITP molecules had undergone hydrolysis and condensed in the initial period into amorphous titania nano colloids with Ti–O–Ti networks, the surface Ti species were effectively protected from further hydrolysis and condensation via the chelation of acac molecules to Ti cations [16]. This stabilization mechanism in the aqueous system seems reasonable because it is known that the chelated acac molecules can effectively suppress the hydrolysis and further condensation of various alkoxides, such as TITP, in organic solvents [21]. As for the roles of AcOH, it is probably that AcOH molecules also inhibit the condensation of tita nic colloids by affecting the surface Ti cations and/or hydroxyl groups [18–21]. In addition, it has been reported that the added AcOH molecules can
work as peptizer of TiO$_2$-sols in organic solvents[11]. Although the sole addition of acac or AcOH is effective to suppress the hydrolysis and condensation of TIPT in organic media, neither can suppress the rapid hydrolysis of TIPT in aqueous media. The co-existence of acac and AcOH in an appropriate amount specially can stabilize the amorphous titania colloid even in aqueous media through a type of concerted mechanism. Decreasing the amount of acid with increasing concentrations couldn’t supply the sufficient amount of acid for the peptizing and chelate action. That causes larger titania particle and this degrades the film quality. It has been reported that the addition of acac and/or AcOH into the organic solvents containing the titania precursor effectively suppressed the phase transition and crystal growth during the calcinations which causes higher surface area and higher absorbance[13].

| Concentration of solution | TTIP to acetic acid volume ratio |
|---------------------------|---------------------------------|
| 0.3 M                     | 1:0.4                           |
| 0.5 M                     | 1:0.37                          |
| 1 M                       | 1:0.27                          |
| 1.25 M                    | 1:0.21                          |
| 1.5 M                     | 1:0.33                          |

4. Conclusion
We developed a very simple method for preparing stable titania solution by aqueous route employing three common and cheap chemicals, TIPT, acac and AcOH, as raw materials and by mixing them with appropriate ratio and sequence to prepare solutions with different concentration. The present titania sols possess desirable properties as a precursor for fabricating TiO$_2$ thin films, such as quite high stability (for more than one year), no use of organic solvents, mild acidity (pH 4), and can indeed be easily transformed into homogeneous and transparent TiO$_2$ thin films on various substrates post calcination. Surface quality and adhesion degraded with increasing concentration of precursor solution. The value of absorbance peak reduced and shifted towards lower wavelength (UV portion) with increasing concentration. Solution with 0.3 M (pH 3.2) yielded the most stable solution and the best thin film. Effect of pH of solution on the film quality was also studied. With increasing the pH of solution surface quality and adhesion of the films degraded but the effect wasn’t as noticeable as the effect of concentration. Thin film produced from lowest pH (3.2) yielded least bandgap width. The TiO$_2$ thin films prepared from the lower concentration titania sols showed considerably higher photocatalytic activity under UV light irradiation, certainly due to the considerably smaller size of TiO$_2$ particle and the higher content of highly active anatase phase. These superior features of the newly developed aqueous titania sols will widen the application of TiO$_2$ thin films in the practical use on large scales.

Acknowledgements
The authors would like to express their deepest appreciation to all the staffs of Materials and Metallurgical department and Glass and Ceramic Engineering departments for their assistance in completing this work. Special gratitude for Dr. Muhammad Shariar Bashar, Senior Scientific Officer, BCSIR for his guidance, co-operation and giving us permission to use the lab facilities for characterization.

References
[1] Anpo, L., Yamashita, H., et al., 1995. Photocatalytic Reduction of CO$_2$ with H$_2$O on Various Titanium Oxide. Electroanalyt. Chem. 396, 21-26.
[2] Asahi, R., Morikava, T., Ohwaki, T. et al., 2001. Visible-Light Photocatalysis in Nitrogen-Doped Dioxide. Science. 293, 269-271.
[3] Bu, S.J., Jin, Z.G., Liu, X.X. et al., 2005. Synthesis of TiO$_2$ Porous Thin Films by PolyethyleneGlycol Templating and Chemistry of the Process. J. Eur. Ceramic Soc. 25, 673-679.

[4] KaploviČová, M., Bellie, P., KaploviČ, L. et al., 2012. On the True Morphology of High Photocative Anatase TiO$_2$ Nanocrystals. Appl. Cat. B.117-118, 224-235.

[5] Valencia, J.M. Martin, G. Restepo, Study of the bandgap of synthesized Titanium Dioxidanoparticles using the sol-gel method and a hydrothermal treatment. The Open Mater. Sci.Journ., 4, 2010, 9-14.

[6] M.B. Casu, W. Braun, K.R. Bauchspieb, S. Kera, B. Megner, C. Heske, R. Thull, E. Umbach, A multitechnique investigation of TiO$_2$ films prepared by magnetron sputtering. Surface Sci., 602, 2008,1599-1606.

[7] M. Sreemany, A. Bose, S. Sen, A study on structural, optical, electrical and microstructural properties of thin TiO$_x$ films upon thermal oxidation: Effect of substrate temperature and oxidation temperature. Physica B, 405, 2010,85-93.

[8] N.M.Thuy, L.T.H.Hai, T.M.Duc and N.T.H.Thanh, “A visible light activity of TiO$_2$ basedphotocatalysts”, The 5th International Workshop on Advanced Materials Science and Nanotechnology (IWAMSN2010) - Hanoi, Vietnam – Nov. 09-12, 2010.

[9] Chekhlova, T.K., Jivtsov, S.V., Grabowski, E.I., 2006. Temperature Dependence of the Sol-Gel Waveguides. J. of Com. Tech. and El. 51, 834-843.

[10] Fujishima, K. Hashimoto, T. WATANABE, TiO$_2$ Photocatalysis, Fundamentals and Applications, BKC, Tokyo 1999.

[11] Miao, L., Tanemura, S., et al., 2004. Microstructure and Bacterecidal Ability of Photocatalytic TiO$_2$ Thin Films. Appl.Surf. Sci. 238, 125-131.

[12] Mor, G.K., Carvalho, M.A., Varghese, O.K. et al., 2004. A Room-Temperature TiO$_2$ –Nanotube Hydrogen Sensor Able to Self-Clean Photoactively from Environmental Contamination. J. Mater. Res. 19, 628-634.

[13] Myata, H., Fukushima, Y., Okamoto, K. et al., 2011. Remarkable Birefringence in a TiO$_2$–Composite Film with an Aligned Mesoporous Structure. J. Am. Chem. Soc. 133,13539-13544.

[14] Negishi, N., Takeuchi, K., 2005. Preparation of Photocatalytic TiO$_2$ Transparent Thin Filmby Thermal Decomposition of Ti-Alkoxide with I- Terpinol as a Solvent. Thin Solid Films 479, 249-253.

[15] Guo, B., Liu, Zh., Hong, L. et al., 2005. Sol Gel Derived Photocatalytic Porous TiO$_2$ Thin Films. Surf. Coat. Techn. 198, 24-29.

[16] A. Kleimana, A. Marquez, M.L. Veraa, J.M. Meichtrya, M.I. Littera, Photocatalytic activity of TiO$_2$films deposited by cathodic arc, Appl. Catalysis B: Environm., 101, 2011, 676-681.

[17] W.Choi, A.Termin and M.R. Hoffmann, “The Role of Metal Ion Dopants in Quantum-SizedTiO$_2$: Correlation between Photoreactivity and Charge Carrier Recombination Dynamics”, J.Phys. Chem. 98 (1994)13669

[18] Sanni Ma,JianqiangMeng, JinghuaLi,YufengZhang,LeiNi, Synthesis of catalytic membranes enabling visible-light-driven photocatalytic degradation of dyes in water, Journal ofMembraneScience453(2014)221–229.

[19] Chen, X., Mao, S.S., 2007. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. Chem Rev. 107, 2891-2959.

[20] I. H. Andersen, K. P. Almtoft, L. P. Nielsen, M. B. Sorensen, S. Johannsen, J. Bottiger, „Photocatalytic active and antibacterial TiO2 coatings deposited by industrial scale magnetron sputtering”, paper C2, Photocatalytic and Superhydrophilic Surfaces Workshop, Manchester Metropolitan University.

[21] Van Popta, A.S., Cheng, J., Sit, J.C. et al., 2007. Thermal Annealing of Birefringent TiO2 Thin Films Formed by Oblique-Angle Deposition. Proc.SPIE 6647, Nanocoatings, 66470C.