EFFECTS OF SOLVENT ON TiO_2 SOL-GEL THIN FILMS

This report is submitted in accordance with requirement of the UniversitI Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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I hereby, declared this report entitled "Effect of Solvent Parameters on TiO_2 Sol-gel Thin Films" is the results of my own researches except as cited in references.

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Date	:	22th JUNE 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for the degree of Bachelor of Manufacturing Engineering (Engineering Material) (Hons.). The members of the supervisory committee are as follows:

………………………………………………..

(Supervisor)

(Associate Professor Dr. Zulkifli Bin Mohd Rosli)

ABSTRAK

Kajian ini melibatkan mengkaji kesan pelarut dan suhu penyepuhlindapan pada sifat-sifat lapisan sol-gel titanium dioksida, filem nipis TiO_2. Terdapat beberapa kajian yang dibincangkan tentang kesan pelarut dan pengaruh yang berbeza suhu rawatan haba anneal pada lapisan TiO_2. Walau bagaimanapun, tidak ada penyelidikan yang sistematik pada tajuk ini. Dalam kaedah sol-gel, titanium tetraisopropoxide (TTiP) digunakan sebagai pelopor untuk menghasilkan filem nipis TiO_2. asid hidroklorik (HCl) bertindak sebagai pemangkin berasid dan etanol perbuatan (EtOH) sebagai pelarut yang dimanipulasi untuk menyiasat pengaruh jumlah yang berbeza kepekatan pelarut kepada sifat-sifat struktur morfologi filem nipis TiO_2. TiO_2 filem nipis akan disimpan di substrat kaca dengan menyesuaikan teknik kemiringan lapisan. Kemudian, TiO_2 sampel filem nipis adalah haba yang dirawat pada suhu yang berbeza, terutamanya 500°C dan 600°C untuk menganalisis kesan suhu penyepuhlindapan morfologi dan fasa transformasi filem nipis TiO_2 melalui jumlah yang berbeza kepekatan pelarut. Di samping itu, ia juga diperhatikan bahawa pengagihan zarah TiO_2 berkelakuan berbeza apabila suhu penyepuhlindapan yang berbeza telah digunakan pada filem. Ia telah mendapati bahawa penumpuan adalah lebih tersebar pada suhu yang lebih tinggi.

ABSTRACT

This research involves studying the effect of solvent and annealing temperature on the coating properties of sol-gel titanium dioxide, TiO_2 thin films. There are several studies discussed about the effect of solvent and the influences of different anneal heat treatment temperature on the TiO_2 coating. Nevertheless, there is no systematic research on this title. In the sol-gel method, titanium tetraisopropoxide (TTiP) is used as a precursor to produce TiO_2 thin film. Hydrochloric acid (HCl) act as acidic catalyst and ethanol (EtOH) act as solvent that manipulated to investigate the influence of different amount of solvent concentration on the morphological structure properties of TiO_2 thin films. The TiO_2 thin films will then deposited on glass substrate by dip-coating technique. Then, the TiO_2 thin film samples are heat treated at different temperatures, particularly 500°C and 600°C to analyse the effect of annealing temperature on the morphology and phase transformation of TiO_2 thin films through different amount of solvent concentration. In addition, it is also worth noting that the allocation TiO2 particles behave differently when different annealing temperatures were used in the film. It has been found that the concentration is more widespread in higher temperatures.

DEDICATIONS

Dedicated to
my beloved father, Abdul Hamid bin Hj. Arshad
my appreciated mother, Noor Saliza binti Alias
my adored sister and brother, Nurul Aina, Nurul Aisyah, Nur Afifah and Ahmad Adam for giving me moral support, money, cooperation, encouragement and also understandings
Thank You So Much For All Of You

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I would like to express the deepest appreciation and thanks to my supervisor, Associate Prof. Dr. Zulkifli bin Mohd Rosli, lecturer at Faculty of Manufacturing Engineering (UTeM) who had guided me a lot, encourage me, and give full support of task during FYP1 and FYP 2. With his support, this research would not have been possible.

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Thank you.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

cm	-	Centimetre
DI	-	Deionizing Water
EtOH	-	Ethanol
HCl	-	Hydrochloric Acid
H_2O	-	Water
kV	-	Kilovolt
ml	-	Millilitre
pH	-	Potential of Hydrogen
rpm	-	Revolution per Minute
SEM	-	Scanning Electron Microscopy
TiO_2	-	Titanium Dioxide
TTIP	-	Titanium (iv) Isopropoxide
XRD	-	X-Ray Diffraction
$^{\circ}$	-	Degree

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Titanium dioxide or titania (TiO_2) was first produced commercially in 1923. It is obtained from variety of ores. The bulk material of TiO2 is widely nominated for three main phases of rutile, anatese and brookite based on Kim T.K. *et al.,* 2005. The titania films have excellent properties such as good durability, high thermal and chemical stability (B Karunagaran *et al.,* 2005, M.J. Alan *et al.,* 2001, S.S. Kale *et al.,* 2006, A.M. Sze *et al.,* 2010); therefore, they are suitable for producing antireflection and optical coatings (D.Dastan *et al.,* 2014). TiO_2 has been used instead of toxic lead oxides as pigments for white paint, printing ink, plastics, paper, food and cosmetics (S.P. Yew *et al.,* 2006). It is used as a biomaterial because it has a good compatibility with the human body (D. Carp *et al.,* 2006).

Titania is a versatile material and has been extensively studied in photocatalysis (A. Ranjitha *et al.,* 2013), photonic crystals, sensors (S.S.Kale *et al.,* 2006, D. Dastan *et al.,* 2014), light scattering (D. Dastan *et al.,* 2014) and liquid crystals displays (M.J Alan *et al.,* 2001). TiO_2 based coating have been prepared via several methods such as sol-gel technique (P. Kajitvichyanukul *et al.,* 2005, M. Hofer *et al.,* 2011, B. Yu *et al.,* 2011), spray pyrolysis (A conde-Gallardo *et al.,* 2005, i. Oja Acik *et al.,* 2009) and chemical vapour deposition (B.C Kang *et al.,* 2000, D.J. Kim *et al.,* 2010). For this project, it has been specified to use sol-gel as a method to make titania coating.

In materials science, the sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. The sol–gel method is used because easy handling, higher contact efficiency of substance to the catalyst and higher utilization efficiency of lights of the reactor (J. Ida *et al.,* 2007).

In this project, we will prepare TiO_2 coating with this parameters precursor + acid catalyst + solvent + distilled water. The perspective in TiO_2 coating will be examined to see the effect parameters and microstructure using sol-gel method and tested for effect solvent to see is there any reactions. This project will focus more on the influence of ethanol (solvent).

1.2 Problem Statement

TiO_2 demonstrates diverse qualities and properties in various stages. Anatase, brookite, and rutile are three unique stages (crystalline structures) of TiO_2. In the sol-gel route, TiO_2 is prepared from the hydrolysis of its precursor titanium (IV) isopropoxide (TTiP), with the aid of solvent and catalyst. Studies reveal that the final size and the uniformity of TiO_2 nanoparticles are greatly dependant on the speed of hydrolysis in the chemical reaction. According to Lu *et al.,* 2012 noted that pH values play an important role in controlling the hydrolysis speed. There have different thermal stability, crystal size, and responsive surface area. Surface zone and microstructure of TiO_2 effortlessly influence its photocatalysis properties study done by Hanaor Sorrell *et al.,* 2010.

Appropriate preparing strategy and parameters are critical to create TiO_2 film that suits to specific applications. Nevertheless, the decision of synthesis technique we controlled by cost control, nature of item, security issues, and so on. Current accessible creation blend, for example, physical vapour affidavit technique is expensive or including entangled process (Erol et al., 2014).

Thus, impact of solvent will be the primary subject in this review concentrating more on the basic and morphological of TiO_2 thin films created by sol-gel strategy. It is additionally pointed that by controlling the utilization of dissolvable is required. Therefore, a reasonable improvement can be accomplished. Precusor + Catalyst + Solvent + Distilled water as main part is used in making titanium dioxide (TiO_2) coatings with Titanium (IV) Isopropoxide (TTIP) process that will be in our project. Solvent that we used in this experiment was ethanol and the catalyst used was hydrochloric acid (HCl). Furthermore, we have specified to find a problem that we want to look for the solvent where we will set the solvent at (0ml, 8ml, and 16ml). For distilled water we will remain 32ml distilled water.

1.3 Objectives

During this final year project, there are objectives that occur relate to this projects and the main purpose of this research is to identify the effects of parameters TiO_2 coating film using sol-gel method. Below are the specific objectives for this research:

1) To synthesize TiO_2 solutions by varying the amount of ratio of the solvent and by using TTIP precursor via sol-gel dip method.

2) To characterize the properties of the deposited TiO_2 thin film coating in term of crystal phase, crystallite size and surface morphology of film deposited in understanding the relationship between materials properties and its synthesizing process.

1.4 Scope

This research is focus on developing an optimum TiO_2 thin film coating. In the stage 1, the interrelation of ethanol as a solvent, hydrochloric acid (HCl) as a catalyst, TTIP precursors and amount of water ratio on the hydrolysis and condensation reaction will synthesize toward phase formation during sol-gel synthesis. The sample will prepare with three different amount of ethanol: 0 ml, 8 ml, and 16 ml. The samples will be calcined at two different temperatures: 500 ˚C and 600 ◦C with soaking time reaction 1 hour. Next, the thin film will deposit in the glass substrates with 10 layers in understanding the relationship between material properties and its synthesizing process. In the stage 2, the sample will characterize based on its surface morphology using scanning electron microscopic (SEM), crystalline phase and crystallinity of thin film with XRD and Raman spectroscopy and crystal size is calculate by using Scherrer equation.

CHAPTER 2

LITERATURE REVIEW

The literature review of the titanium dioxide (TiO_2) was discussed in this chapter. The TiO_2 material and its general is discussed in the first section. Sol-gel is discussed for fabrication techniques.

2.1 Introduction

Titanium dioxide occurs in three crystalline stages, the two tetragonal structures anatase and rutile and a less regular orthorhombic frame brookite. The crystal structures of anatase, rutile and brookite are shown in figure 2.1.

2.2.2 Catalyst

(Sayilkan, F et al., 2005) has found that HCl, as a hydrolysis impetus, expect a crucial part in the advancement of the anatase crystalline kind of TiO2 at low temperatures. The most ideal assurance of union parameters and the technique for prepare materials is of pressing essentialness in fruitful sol–gel mix; in this manner high bore of coatings is principal. The pH estimation of the sol–gel response blend, which is liable to the used impetus, impacts the hydrolysis and buildup reaction, besides impacts the edge and structure of the got materials. Acids add to protonate alkoxide masses and heighten the hydrolysis reaction vitality. While different investigates, (M. Alzamani et al., 2013) inspected the effect of impetus on the properties of TiO_2 sol–gel films and they saw the impetus effect on the stage and atom measure present in tests. The results demonstrated that materials masterminded with the use of a destructive impetus showed better photocatalytic activity and contained the greatest share of the anatase structure.

Sol–gel materials are in like manner consistently adjusted in light of oxide system standoffish quality (N. Boucharat et al., 2001, P. Susmita et al., 2014). The sol–gel strategy relies on upon hydrolysis and build-up reactions (Brinker and Scherer, et al., 1990). By far most of the written work data suggests the sol–gel reactions for prepares silica. Commonly used impetus increment the rate of hydrolysis. The kind of impetus chooses the pH of sols and impacts the sort of sol–gel materials, getting the movies, powders or stone monuments. Figure 2.2 exhibits the relative build-up and vitality of hydrolysis reactions of silica sol–gel materials and their dependence on reaction condition pH, regardless of the way that figure 2.2 presents associations for silica materials; it is remarkable that the pH of condition has effect on hydrolysis and build-up vitality of all metal alkoxides, e.g. titanium and zirconium alkoxides considered along these lines

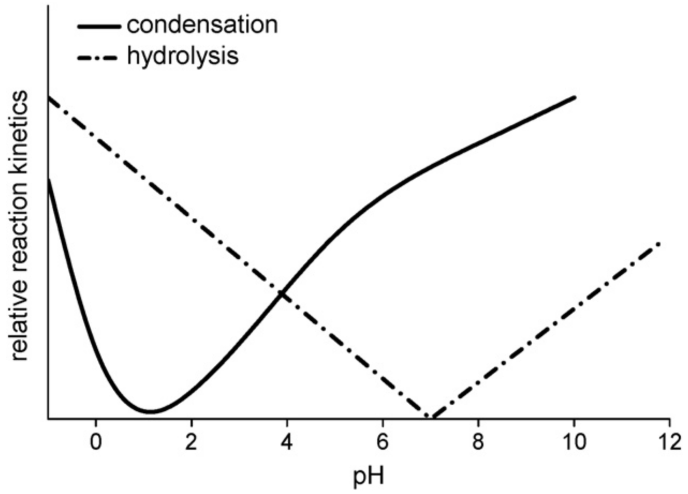

Figure 2.2: Relative hydrolysis and condensation kinetics of alkoxysilanes as a function of reaction mixture pH (B. Babiarczuk *et. al,* 2016).

2.2.3 Precusor

The span of nanoparticles was not influenced by the decision of precursor. The wide perspective of the examples arranged utilizing titanium (IV) isopropoxide indicated film-like structures. The molecule morphology and particle size distribution demonstrate consistency regardless of the precursor utilized for setting up the sample. The molecule morphology and particle size distribution have indicated consistency regardless of the precursor utilized for setting up the specimen. In any case, the wide perspective of SEM micrographs of the specimens arranged utilizing titanium isopropoxide has indicated film like structures, though the examples arranged utilizing titanium butoxide have demonstrated circular granules (Manasi Manoj Karkare *et al.,* 2014).

2.2.4 Water

TiO_2 is an extremely famous material utilized as a part of the expansive region of photo catalytic procedures, for example, water and air purification, self-cleaning surfaces and microorganisms' deactivation (A. Fujishima *et al.,* 2015, D.M.A. Alrousan *et al.,* 2009, K. Hashimoto *et al.,* 2005). There are numerous techniques for TiO_2 readiness, for example, aqueous, sol-gel, spray pyrolysis and others. However many components influence the rate of

TiO_2 hydrolysis and polycondensation procedures, for example, sort of precursor, pH of arrangement, the presence and kind of alcohol used, the environment of planning, temperature, natural added substances, blending conditions, and so forth.

Sol-gel technique gives tremendous probability of altering the properties of TiO_2 by changing the pH value of source arrangement and doping both metals and non-metals. Other than the stage creation of TiO_2, its crystallites size, surface area, morphology and particles shape, there is likewise another variable, which impacts the photocatalytic movement of TiO_2, for example, corrosive and essential character of surface destinations. The impact of the pH of titania precusors arrangement on the development of TiO_2 crystallites, phase composition and the electrokinetic capability of the particles surface was noticed (A. Molea *et al.,* 2014). It was encountered, that arrangement of TiO_2 at low pH, for example, pH = 3 brought on faster change of anatase to rutile amid heat treatment handle. Estimation of negative charge of the particles diminished with the expansion of the pH of the arrangement (A. Molea *et al.,* 2014).

2.3 Parameters

2.3.1 Sol-gel Synthesis

The most widely used method to prepare hollow nanostructured titanium dioxide particles is sol-gel synthesis. In general, the sol-gel process involves inorganic precursors (a metal salt or organometallic molecule) that undergo various reactions resulting in the formation of a three-dimensional molecular network. A common example is the hydrolysis and condensation reaction of metal alkoxides to form larger metal oxide molecules (Caruso *et al.,* 2001).

Hydrolysis:

$$M(OR)_4 + H_2O \rightarrow HO{-}M(OR)_3 + ROH \cdots\rightarrow M(OH)_4 + 4ROH$$

Condensation:

$$(OR)_3M{-}OH + HO{-}M(OR)_3 \rightarrow (RO)_3M{-}O{-}M(OR)_3 + H_2O$$

$$(OR)_3M{-}OH + RO{-}M(OR)_3 \rightarrow (OR)_3M{-}O{-}M(OR)_3 + ROH$$

Figure 2.3: Sol-gel reaction of metal alkoxides (Collins *et al.,* 2003)

Where M represents the metal and R the alkyl group. Titanium alkoxide precursors rapidly undergo hydrolysis and condensation in the presence of water. Thus, coating in nonaqueous solvents is required. Hollow submicrometer sized titania spheres have been formed by coating colloidal templates through the hydrolysis and condensation of titanium alkoxides on the particle surface to produce amorphous titania shells followed by calcination at high temperature to remove the core and to crystallize the titania. A principle disadvantage of the sol-gel method is the high reactivity of the titania precursors. This reactivity makes it difficult to control precipitation and can lead to particle aggregation and formation of separate titania particles (Imhof, 2001). Other disadvantages of the sol-gel process include the formation of irregular coatings, little control over coating thickness, and the need for precise control over reaction conditions to maximize coating uniformity (e.g. concentration of reagents, pH, temperature, mixing conditions) (Caruso *et al.,* 2001).

The sol-gel method is a cheap and easy technique for synthesizing colloidal suspension, particularly metal oxide materials. (Stöber *et al.,* 1968) was the first to synthesize silica particles with uniform sizes (100-1000 nm in diameter) using the sol gel method. From a chemical and material perspective, sol-gel derived materials have many advantages. Materials in various configurations, such as films, fibers, monoliths, and powders can be readily made. The properties of sol-gel materials, such as transparency, porosity pore size 5 distributions and surface functionality, are strongly dependent on the preparation method (Wright and Sommerdijk, 2001).

Based on studies previously researcher have done, for planning of TiO_2 coating, titanium (IV) isopropoxide (TTiP) (Sigma Aldrich Co.), ethanol, hydrochloric corrosive (HCl) and deionized water were utilized as titanium precursors, solvent, catalyst and hydrolysis medium individually. As a rule, two sorts of arrangements were set up at room temperature, predominantly Sol A and Sol B. For Sol A planning, a blend of ethanol and deionized water was mixed for 30 minutes, trailed by the expansion of 0.2, 0.5, 1.0 and 1.7 ml HCl separately. At the same time, TTiP and ethanol was blended vivaciously for 30 minutes to deliver Sol B. Both arrangements were then combined under consistent blending for 1 hour before they were kept in dull for the maturing procedure. The dip coating technique was done and the covered substrates were then permitted to dry for 24 hours took after by stove dry while the surface morphology and EDX investigation of the coatings were analysed utilizing Hitachi 1303 Convenient SEM-EDX (M.A. Musa *et al*., 2016).

2.3.2 Dip-coating

Dip-coating is a wet-chemical method that has been broadly applied in obtaining thin films. Accesscience.com, 2014 define that dip-coating is a coating which may apply to ceramic ware or metal by submersion into a tank of melted non-metallic material, such as resin or plastic, and then chilling the adhering melt. Dip-coating is a very simple process used to deposit a thin film from non-metallic material. In this process, a specified substrate is soaked in a uniform solution. One of the advantages of this method is, the substrate used can have planar, cylindrical or complex geometries (Tikkanen *et al.,* 2011). After that, it is retracted from the solution at a controlled withdrawal speed, dried, and thermal treated. Many researches repeat the coating annealing procedure for several times in order to self

2.3.3 Effect of solvent on titania coating using sol-gel technique

Based on studies conducted by previous researchers, different parameters conditions can affect the formation of metal oxides which consequently affect performances of titania in sols.

For instance, (Francesca Piccinini *et al*., 2013) in his article have reported all the mixture coatings created were flawlessly straightforward and homogeneous at the considered thickness. This is because of the great surface smoothness and by the non-appearance of clear stage partition marvels amongst natural and earthenware stages. The specimen containing the most noteworthy measure of titania (S0T63) displayed, in the thicker regions, separation and weakness.

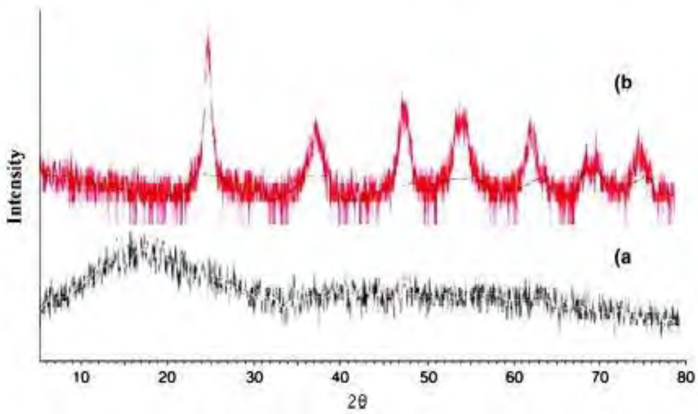

Figure 2.4: XRD analysis of coatings heat treated at (a) 300°C and (b) 500°C by (Farzad Malekmohammadi *et.al,* 2011)