EFFECT OF CATALYST AND HEAT TREATMENT TEMPERATURE ON THE COATING PROPERTIES OF SOL-GEL TiO_2 THIN FILMS

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

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DECLARATION

I hereby, declared this report Entitled "Effect of Catalyst and Heat Treatment Temperature on the Coating Properties of Sol-Gel TiO_2 Thin Films" is the results of my own research except as cited in references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfilment of the requirements for the Degree of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory committee is as follow:

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(Supervisor)

(Associate Professor Dr. Zulkifli Bin Mohd Rosli)

ABSTRAK

Kajian ini membincangkan kesan penggunaan pemangkin dan suhu pengolahan haba atas sifat-sifat lapisan sol – gel filem nipis titanium dioksida TiO_2. Terdapat beberapa kajian yang telah membincangkan mengenai kesan pemangkin dan pengaruh suhu pengolahan haba pada ciri salutan TiO_2. Walau bagaimanapun, tiada kajian sistematik pada tajuk ini. Dalam proses pengeluaran sol - gel , titanium tetraisopropoxide (TTIP) digunakan sebagai pelopor untuk menghasilkan filem nipis TiO_2. Asid hidroklorik (HCl) bertindak sebagai pemangkin berasid dan ammonium hidroksida (NH_4OH) bertindak sebagai pemangkin alkali akan dimanipulasi untuk mengaji pengaruh pelbagai pemangkin - jenis pada mikrostruktur dan sifat morfologi filem nipis TiO_2. Filem nipis TiO_2 akan didepositkan pada substrat kaca dengan mengaplikasikan teknik dip-coating . Kemudian, sampel filem nipis TiO_2 akan haba dirawat pada suhu yang berbeza, terutamanya 500℃ dan 700℃ untuk menganalisis kesan suhu penyepuhlindapan pada morfologi dan transformasi fasa filem nipis TiO_2 dengan aplikasi pemangkin berbeza. Dalam kajian ini, ia telah mendapati bahawa filem nipis TiO_2 menunjukkan morfologi permukaan yang berbeza apabila pemangkin yang berbeza telah digunakan (pH berbeza). Apabila terdapat penggunaan pemangkin alkali, filem ini mempamerkan bentuk zarah daripada bentuk helaian. Di samping itu, ia juga diperhatikan bahawa pengagihan partikel TiO_2 berkelakuan berbeza apabila suhu penyepuhlindapan yang berbeza telah digunakan ke atas filem. Didapati bahawa pengumpulan adalah lebih tersebar pada suhu yang lebih tinggi.

ABSTARCT

This research involves studying the effect of catalyst and heat treatment temperature on the coating properties of sol-gel titanium dioxide TiO_2 thin films. There are several studies discussed about the effect of catalyst and the influence of heat treatment temperature on the TiO_2 coating properties. Nonetheless, there is no systematic research on this title. In the sol-gel production route, titanium tetraisopropoxide (TTIP) is used as a precursor to produce TiO_2 thin film. Hydrochloric acid (HCl) act as acidic catalyst and ammonium hydroxide (NH_4OH) act as alkaline catalyst are manipulated to investigate the influence of various catalyst-type on the microstructure and morphological properties of TiO_2 thin films. The TiO_2 thin films will then deposit on glass substrate by adapting dip-coating technique. Then, the TiO_2 thin film samples are heat treated at different temperatures, particularly 500℃ and 700℃ to analyze the effect of annealing temperature on the morphology and phase transformation of TiO_2 thin films through different catalyst. It was found that TiO_2 thin film exhibits different surface morphology when different catalysts were used (distinct pH). When there is use of alkaline catalyst, the film exhibits particle shape instead of sheet-form. In addition, it was also observed that the distribution of TiO_2 particles behaved differently when different annealing temperatures were applied on the films. It was found that the agglomeration is more dispersed at higher temperature.

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DEDICATION

Dedicated to
my beloved father, Christopher Wong
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for giving me moral support, cooperation, encouragement and also understandings.

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LIST OF ABBREVIATIONS

CVD	-	Chemical Vapour Deposition
DEA	-	Diethanolamine
HCl	-	Hydrochloric Acid
HNO_3	-	Nitric Acid
H_2SO_4	-	Sulphuric Acid
NaOH	-	Sodium Hydroxide
NH_4OH	-	Ammonium Hydroxide
OR	-	Alkoxy group
PVD	-	Physical Vapour Deposition
R	-	Alkyl
ROH	-	Alcohol
SEM	-	Scanning Electron Microscopy
$Ti(OR)_4$	-	Titanium alkoxides
TiO_2	-	Titanium Dioxide
TTIP	-	Titanium Tetraisopropoxide
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

ρ	-	density
℃	-	degree Celsius
℃/min	-	degree Celsius per minute
%	-	percent
h(m)	-	film thickness
ml	-	millilitre
mm	-	millimetre
min	-	minute
mm/s	-	millimetre per second
mm/min	-	millimetre per minute
Pa· s	-	viscosity
t(s)	-	spinning time
wt. %	-	weight percent

CHAPTER 1

INTRODUCTION

This chapter describes the background of the research, the problem statement and the objectives of the research. Furthermore, it also states the scope covered by student in this research.

1.1 Background of Study

In recent decade, titanium dioxide, TiO_2 thin film has been intensively studied because of its various potential applications including optoelectronic applications, solar cells, gas sensors, and photocatalytic activities (for example self-cleaning glass). TiO_2 has been focus of extensive studies in view of environment, medical, electrical and biological application and it is normally existed in the form of anatase, rutile and brookite.

In comparison with TiO_2 powder, TiO_2 film does not create conglomeration and has higher surface activity, allowing the material use in wide industrial application such as self-cleaning and antibacterial (Chen *et al.*, 2009). Thus, this study will focus on investigating the coating properties of TiO_2 thin films.

TiO_2 thin films can be prepared by numerous techniques such as chemical vapor deposition, hydrolysis deposition, electrodeposition, chemical spray pyrolysis and sol-gel method. However, sol-gel method is usually preferable because of its ability to shows excellent homogeneity, has advantage on controlling the particle size and morphology, easy to control film thickness, has advantage of purity and relatively cheaper. Therefore, in order to deposit the TiO_2 thin film on a substrate, a dip-coating method is going to apply in this study. Dip-coating method is widely adopted and suitable for TiO_2 thin films because it is time- saving and involve low cost.

The performance of titania thin films rely not only on the preparation technique (details of synthesis parameters), but also on the coating conditions. In the sol gel production route, optimization of synthesis parameters such as sol reactivity, viscosity, pH, metal precursor concentration, types of solvent and heat treatment temperature is essential as they determine nucleation and the growth of crystal phase of TiO_2 which directly affect the properties of TiO_2 thin films. Thus, the influence of the catalyst and heat treatment temperature on the microstructure, reaction morphology and phase transition of TiO_2 thin film is of great interest and will be investigated in this study.

The pH control act as a catalyst in sol-gel preparation as it plays effective parts in manipulating hydrolysis and condensation reactions. A study done by Alzamani *et al.* (2013) shows that thin films prepared from sols using acidic catalysts mainly consists of anatase at 500°C. As the heat treatment temperature rises to 700°C, the anatase phase shortly transforms into rutile phase. In other words, the catalyst used in the sol synthesis reaction significantly activates phase transformation of amorphous to anatase TiO_2, and anatase to rutile phase.

Meanwhile, the heat treatment temperature plays vital role in determining the phase exists in TiO_2 thin film. Previous results reveal that the particle size of TiO_2 increases with an increase temperature in the heat treatment as crystallization takes place (Arıer and Tepehan, 2011). The increased particle size promotes phase transformation from amorphous to anatase phase and to rutile phase.

The crystal phase influences TiO_2 thin film properties for their widespread range of application. For an instance, at low heat treatment temperature, there is an increase of photocatalytic activity. This is due to particles have smaller diameter at lower calcinations temperature, results in quantum side effect. Indirectly, the quantum side influence results in widening the band gap of semiconductor; hence photocatalytic activity increases (Behnajady, Eskandarloo, Modirshahla and Shokri, 2011).

Thus, it is crucial to study the effect of catalysts and calcinations temperature apply in the synthesis of TiO_2 thin film as they are interrelated and play decisive role in determine the crystal growth.

1.2 Problem Statement

The microstructure and properties of TiO_2 thin films depend upon particulars of deposition parameters such as the pH controlled in the sol-gel process, heat treatment temperature, solvent, precursor and additive selected for the process. The deposition parameters are decisive in determining nucleation and growth of the crystal phase in which influence its properties for their wide potential applications. In general, titanium oxide (TiO_2) has three (3) crystalline forms which are anatase, rutile and brookite. The crystalline structure of these TiO_2 thin films is believed strongly depends upon catalyst-type and annealing temperature.

According to Callister and Rethwisch (2011), a catalyst is a substance that accelerates the chemical reaction rate without participating in the reaction itself. In the sol-gel route, TiO_2 is prepared from the hydrolysis of its precursor titanium (IV) isopropoxide (TTIP), with the aid of catalyst. Studies reveal that the final size and the uniformity of TiO_2 nanoparticles are greatly dependent on the speed of hydrolysis in the chemical reaction. In addition, Lu *et al.* (2012) noted that pH value plays an important role in controlling the hydrolysis speed. At this point, numerous acids or alkalis were used to adjust the pH value during the sol preparation. However, there is no systematic study is done on the influence of acid and alkali catalyst on the quality and the morphologies of TiO_2 thin film.

Heat treatment temperature, on the other hand, has an explicit effect on the ultimate properties of TiO_2 thin film. For example, study done by Pomoni *et al.*

(2011) observed that the TiO_2 sample annealed at 400°C shows an amorphous phase, whereas annealing at 500°C and 600°C results in the formation of anatase phase. With further increase of the thermal treatment temperature to 800 °C, rutile phase is developed, with anatase remaining the dominant phase. High temperature is required in order to achieve desired phase. Moreover, there is limited study was done on the effect of heat treatment temperature on the morphology of TiO_2 thin film.

Hence, the simultaneous influence of catalyst and heat treatment temperature will be the main subject in this study focusing more on the structural and morphological of TiO_2 thin films produced by sol-gel method. It is also aimed that by controlling the use of catalyst, lower heat treatment temperature is needed. Indirectly, a sustainable development can be achieved.

1.3 Objectives

The objectives of this study are:-

1. To deposit TiO_2 thin films via sol-gel method.
2. To investigate the influence of hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) as catalyst on the microstructure and morphological properties of TiO_2 thin films.
3. To analyze the effect of annealing temperature on the morphology and phase transformation of TiO_2 thin films through different catalyst.

1.4 Scope

The scope of this research will be focused on the coating properties of TiO_2 thin films under the influence of catalyst and heat treatment temperature of sol-gel. Analysis of coating properties of thin films which derived from three different solutions with different pH (by controlling the use of catalyst) will be carried mainly on the morphological properties of TiO_2 thin films.

In addition, this research will only discuss on the sol-gel method used to synthesis TiO_2 thin film. The TiO_2 thin film is going to be deposited on a surface of glass substrate by using dip-coating technique. The samples will then be heat treated at two different temperatures: 500℃ and 700℃ to determine the influence of heat treatment temperature on the surface morphology of TiO_2 thin film.

CHAPTER 2

LITERATURE REVIEW

This chapter will mainly discuss the broad view of titanium dioxide, thin film preparation techniques and the important parameters in sol-gel process. In this chapter, there will be summative and formative evaluation on previous thin film synthesis methods and the sol-gel derived deposition techniques. Strengths of each method will be indicated and appraised in this section. Furthermore, this chapter is aimed to have a clear and cohesive structure on each of the stages in sol-gel process in order to assist student in deciding the parameters to be used in the research later. Most importantly, two of the variables that will be employed in the path of producing titania (TiO_2) thin films – types of catalyst and heat treatment temperature will be covered and critically studied in this chapter.

2.1 Titanium Dioxide

Among the ceramic coatings, titanium dioxide (TiO_2) has been studied extensively in recent years due to the fact that TiO_2 is a multifunctional material having diverse potential application. Interestingly, there is a study indicating that more than 70 articles were published on the TiO_2 surface solely in year 2000. TiO_2 has been reviewed extensively and is preferable in pursuing research because it has high versatility for various experimental techniques.

Generally speaking, TiO_2 has three (3) crystalline forms: anatase, brookite and rutile. According to Ahn (2003), phase transformation in titanium dioxide has been greatly investigated due to the fact that the phase exists in TiO_2 plays a decisive role in defining the properties of TiO_2, indirectly deciding its applications. Based on a research done by Diebold (2003), author suggested that the most stable rutile phase of TiO_2 falls certainly into the 'self-promising' effect category because it can be reduced easily, which brings the benefit of preventing charging of its wide band gap semiconductor.

Likewise, titanium dioxide which has high refractive index, good physical and chemical stability and high photocatalytic activity also the reasons why it is discussed widely particularly in electronic and optical field (Ahn, 2003). Other than that, TiO_2 has many potential applications for example - used as photocatalyst, used in solar cells, as gas sensor, as white pigment, as a corrosion-protective coating, as an optical coating, as well as self-cleaning coatings on windows.

By far, the most active study is done on the use of titania for photo-assisted degradation of organic molecules. TiO_2 as an n-type semiconductor has attracted growing interests when a new corrosion protection mechanism was reported since the early 90s.

In short, titania thin films are of interest as it contributes various potential applications in different field.

2.2 Thin Film Synthesis Techniques

There are variety methods in thin film preparation such as chemical vapor deposition, chemical spray pyrolysis, pulsed laser deposition, sol-gel method, plasma electrolytic deposition, electrochemical deposition, microwave activated chemical bath deposition and many more.

Basically, the deposition of thin film to a substrate surface is divided into two groups: chemical deposition and physical deposition. Specifically, chemical vapor deposition (CVD) which derived from chemical deposition; physical vapor deposition (PVD) and sol-gel will be discussed in this section.

In comparison with other methods, sol-gel process has been frequently adopted to prepare TiO_2 due to its notable advantages such as low temperature synthesis, easily controlled reaction condition and able to synthesis homogeneous film in a cheaper manner.

Table 2.1: Comparison of Thin Film Synthesis Techniques

	Chemical Vapor Deposition (CVD)	Physical Vapor Deposition (PVD) (DU and Choy , 2004)	Sol-gel
Basic principle	• This method includes a setup of transmitting mixture of one or more precursors particularly in gas phase (normally hydrogen or nitrogen) together with alkoxides, deposited over the substrate. • The film deposition normally employed at desired temperature. • Can be achieved by thermal decomposition, oxidation and hydrolysis (Khatib and Oyama, 2013)	• Coating involves spraying atomized precursor droplets across an electric field. • During the spraying process, droplets decomposes and chemical reaction takes place in the vapor phase near the vicinity if the heated substrate.	• Generally involves the preparation of sol, gelation of the sol, and removal of the solvent. • Involves the conversion of monomers into a colloidal solution which also call as sol • Undergoes chemical reactions such as hydrolysis and condensation to obtain the sol, which then acts as precursor for gel formation, an integrated network.