UNIVERSITI TEKNIKAL MALAYSIA MELAKA

FABRICATION OF TITANIUM DIOXIDE (TiO_2) BY HIGH TEMPERATURE OXIDATION OF PHYSICAL VAPOUR DEPOSITION (PVD) TITANIUM FILM

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

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The members of the supervisory committee are as follow:

………………………………
(Prof. Dr. Mohd Razali bin Mohamad)

………………………………
(Dr. Lau Kok Tee)

ABSTRAK

Tujuan laporan ini adalah untuk mencadangkan satu kaedah baru untuk menghasilkan lapisan titanium dioksida (TiO_2) nipis pada substrat kaca untuk aplikasi cermin yang membersihkan secara sendiri. Terdapat beberapa kaedah yang digunakan untuk menghasilkan lapisan TiO_2 nipis dan yang selalu menjadi pilihan adalah melalui kaedah pemendapan wap fizikal (*PVD*) melalui pengeluaran atom reaktif. Oleh kerana terdapat beberapa kelemahan dalam kemasukan gas oxygen dengan menggunakan kaedah pengeluaran atom raeaktif *PVD* , kajian ini bertujuan untuk menyelidik teknik sintesis alternatif pembuatan lapisan nipis TiO_2 melalui dua proses iaitu; (i) pendepositan lapisan nipis titanium (Ti) melalui pengeluaran atom arus terus (ii) pengoksidaan lapisan Ti nipis didalam relau tiub (*ex-situ*) dengan 100 peratus oksigen pada persekitaran. Suhu pengoksidaan telah ditetapkan kepada 200 ºC, 300 °C dan 400 °C. Teknik ujian dan pencirian yang digunakan dalam kajian ini adalah mikroskop optik untuk pemerhatian mikrostruktur, Mikroskop Electron Kedua (*SEM*) untuk pembentukan permukaan dan ketebalan lapisan, kaedah pembelauan X-Ray (*XRD*) untuk stoichiometri lapisan tersebut, dan *UV-VIS* untuk jurang jalur. Pemerhatian yang utama kajian ini ialah pembentukan sifat yang dimiliki oleh lapisan nipis yang disintesis didominasi semasa proses pendepositan lapisan nipis Ti daripada sewaktu proses pengoksidaan. Terdapat kecacatan nodular dalam bentuk sfera dan serpihan pada sampel sebelum pengoksidaan dan menigkat pada jumlah kecilselepas pengoksidaan. Kecacatan ini mempengaruhi intergriti lapisan nipis Ti yang dideposit kerana hasil ujian *XRD* menunjukkan Ti bukan kandungan utama. Selain itu, ujian UV-VIS menunjukkan sampel tidak mempunyai jurang jalur sterusnya mengesahkan laisan nipis oksida tersebut bukan separa konduktor.

ABSTRACT

The purpose of this research is to develop a new synthesis method of titanium dioxide (TiO_2) thin film coating on glass substrates for self-cleaning glasses application. There are several method use to fabricate the TiO_2 thin film but the most favorable is via Physical Vapour Deposition (PVD) reactive sputtering. Due to the disadvantages in controlling the oxygen incorporation using PVD, the current work explores an alternative synthesis technique of TiO_2 thin film which consisted of two steps, which are: (i) deposition of titanium (Ti) thin film via DC magnetron sputtering, and then (ii) oxidation of the Ti thin film in tube furnace (ex-situ) with 100 percent oxygen enviroment. The temperature of the oxidation were set to 200 ºC, 300 ºC and 400 ºC. Oxidized Ti coated glass samples were characterized using optical microscope for microstructural observation, Secondary Electron Microscope (SEM) for surface morphology and thickness, X-Ray Diffraction (XRD) method for the stoichiometry of film, and UV-VIS spectrometry for band gap. The main observation of this study was properties of the synthesised film predominantly depended on the deposition process rather than the oxidation process. Nodular defect in form of spheres and flakes can be seen on the samples before oxidation and increasing significantly after the oxidation process. These defect also affected the intergrity of the deposited Ti film onto the glass where titanium were not shown as the main constituent based on the XRD results. Besides that, UV-VIS test shows that the samples does not have bandgap, thus indicated the oxidized film on the glass was not a semiconductor.

DEDICATION

for the one and only...for all the smile from thee...

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Bismillahirrahmanirrahim,

I would like to convey my gratitude to Allah S.W.T for giving me strength and willingness to be able to completed this final year project. I am indebted to many people during this research. I would like to express my special gratitude, appreciation and thanks to Dr Lau Kok Tee as my co-supervisor in this project where he teach a lot of knowledge that is new for me, helping me upon the completion of this research and assist me all the time. Not forgetting my principal supervisor Prof, Dr Razali bin Mohamad, technicians, Mr Sarman, Mr Azhar, Mr Hairulhisyam, Mr Bahatiar and all the technicians and friends that involved upon completing this project.

Last but not least, I would like to say thousand thanks to my parent, Mr Mohamad Noor binOthman, and Pn Fauziah bte Mustapha where without them, I won’t be here. Their love and care are always in my heart.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

AC	-	Alternate Current
Ar	-	Argon
C	-	Carbon
c	-	Speed of light
cm	-	centimeter
CVD	-	Chemical Vapour Deposition
DC	-	Direct Current
E	-	Energy
g	-	gram
H	-	Hydrogen
h	-	Planck's constant
IBAD	-	Ion Beam Assisted Deposition
K	-	Kelvin
min	-	minutes
mbar	-	milibar
mPa	-	milipascal
N	-	Nitrogen
Nm	-	nanometer
O	-	oxygen
PVD	-	Physical Vapour Deposition
Sccm	-	standard cubic centimeter
SEM	-	Scanning Electron Microscope
SiO_2	-	Silicon Dioxide
SSIM	-	Static Secondary Ion Mass
Ti	-	Titanium
TiN	-	Titanium carbide
TiO_2	-	Titanium Dioxide

UHV	-	Ultra High Vacuum
UV	-	Ultra Violet
v	-	velocity
W	-	Watt
XRD	-	X-Ray Diffraction
HCP	-	Hexagonal Closed Packed
Â	-	Angstrom
λ	-	Wavelength

CHAPTER 1

INTRODUCTION

This chapter will introduce the background of the study as well as problem statement, objectives and scopes. The content of this chapter explained about why this research was carried out.

1.1 Background of Study

Nowadays the self-cleaning glasses are the common engineering materials used as for building, tower, car windshield *etc*. It is due to the ability to self-clean without the use of any human labour. The self-cleaning occurs naturally with the help of sun and rain. Imagine the labours that are hired to clean the windows of Kuala Lumpur Twin Tower (KLCC). These people need to be paid in huge amount of salary due to the dangerousness of their work. By using the self-cleaning glass, the danger and cost can be reduce to zero.

The magic behind the self-cleaning glasses is the titanium dioxide (TiO_2) thin film coating applied on the surface of the glass where TiO_2 is a special compound material that has photocatalyctic properties that can decompose any air borne toxic organic matter. The further discussion of this topic will be discussed in this report.

Aside from that, this report will also discuss the fabrication of the tin film coating of TiO_2 that later will be used in this research. Physical vapour deposition (PVD) is one of the favourable method to fabricate the TiO_2 thin film coating but due to some of its disadvantages, the fabrication method need to be altered. This report will propose and experiment on the TiO_2 thin film coating fabrication method.

1.2 Problem Statement

Titanium Dioxide (TiO_2) thin film coating can be fabricated by various methods and techniques. The method are Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), sol-gel dip coating, spin coating, and spray pyrolysis. Among all these method, PVD and CVD are the common method to fabricate thin film coating. Whilst between these two common method, PVD is most favourable due to its advantages on operating on low temperature, finer coating grain size, smooth surface, low crack initiation and propagation on the coating (Campbell, 2008). Despite all the advantages, PVD has its own on disadvantages in controlling the oxidation rate for efficient oxidation coating (Heinrichs *et al*. 2008). In order to obtain stoichiometry of TiO_2, several parameter need to be pre-determined before the deposition. One of the parameter is the oxygen flux must be control efficiently. If the amount of oxygen is high, the growth rate of the thin film is slower and if the amount of oxygen is low, it will result in an incomplete oxidation. The nucleation growth of oxide layer causes agglomeration and amorphous TiO_2. During deposition, the sputtered atoms from the target tend to lost during transfer from target to substrates due to argon-oxygen mixtures that result in loss of TiO_2 stoichiometry of the deposited film materials (Donald, 1998). It is expected that by two steps method will create a decent stoichiometry of the TiO_2 thin film layer. The two step method use in this report is defined by thin film deposition and oxidation process are done separately where the titanium thin film is deposit using PVD machine and the oxidation process of the thin film takes place in the tube furnace (*ex-situ*). The term *ex-situ* in this report is defined by oxidation process of titanium thin film takes place outside the PVD chamber in order to eliminate the effect of argon-oxygen mixture.

1.3 Objective

The purpose of this research is to synthesize TiO_2 thin film on glass substrates using two steps method which is; (i) Deposition of titanium (Ti) film on glass substrate by DC magnetron sputtering, and (ii) High temperature oxidization of the TiO_2 film in tube furnace (*ex situ*). Below are the specific objectives for this research;

i. To synthesize the titanium dioxide (TiO_2) thin film using *ex-situ* oxidation of DC magnetron sputtered titanium film.
ii. To study the microstructure, surface morphology and phase composition of the TiO_2 film at different temperature.
iii. To determine the band gap of the fabricated TiO_2 thin film.

1.3 Scope and limitation

The deposition of the Ti thin film were done using DC magnetron sputtering in a vacuum chamber with pressure of $5x10^{-3}$ mbar, chamber temperature setting, 300 °C, sputtering power, 3000 W and deposition time, 30 minutes. For the oxidation process, it will be conducted in controlled oxygen flow environment (oxygen partial pressure = 100%) the oxygen flow were set to 15 psi. The oxidation temperatures were made as the manipulated variable which is 200 °C, 300 °C and 400 °C. The temperature ramp rate were made constant at 1 °C/min as well as the cooling rate at -1 °C/min. Characterization of the TiO_2 thin film were done by the optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-VIS spectrometry.

CHAPTER 2

LITERATURE REVIEW

This chapter will discuss further on the literature review that is related to the general info of titanium dioxide (TiO_2). The later section will focus on the Tio_2 material and its general physical properties and crystallography. Next is the photocatalyst properties that are the main reason why TiO_2 is being used as the thin film coating on glass. The fabrication used in this research is physical vapour deposition (PVD). There are many types of PVD method. In this research, the PVD method use is DC magnetron sputtering.

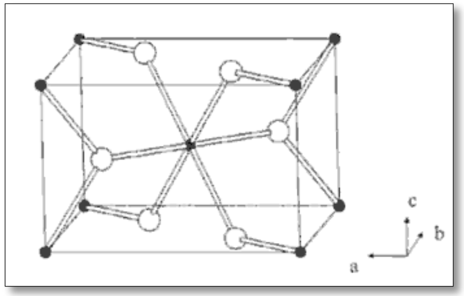
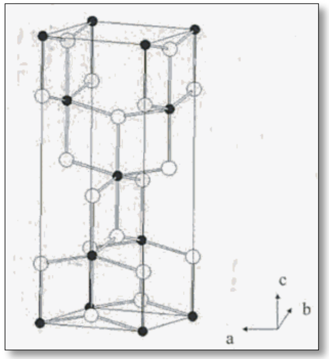
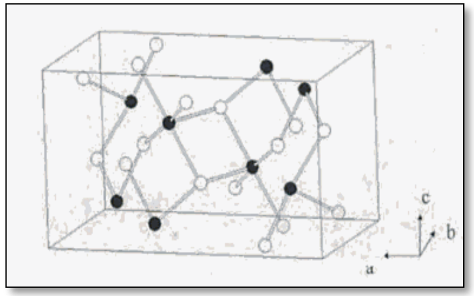
2.1 Titanium Dioxide (TiO_2)

Titanium dioxide (TiO_2) has been commercialized since the early 20^{th} century and it is widely used as pigment, sunscreen, paint, ointment and *etc* (Xiabo, 2007). In 1972, Fujishima and Honda discovered the photocatalyst phenomenon where water is splitting on the TiO_2 electrode under the ultraviolet light (UV). Since this discovery, a lot of research has been done that led to new technology such as photovoltaic, photocatalysis, photochemical and sensors. All the discovery mention has fulfil the needs in energy and environment area. The TiO_2 is very versatile material and it depends not only on the properties itself but also on the modification of TiO_2 host. TiO_2 exists in three phase that has different crystal structures and physical properties. There are rutile, anatase, and brookite.

2.1.1 Basic Properties of Titanium Dioxide (TiO_2)

Titanium Dioxide occurs naturally in three modification form which is rutile, anatase and brookite. Between these three, rutile, and anatase are the most common form. The crystallographic arrangements of this modification are titanium atom surrounded octahedrally by oxygen atom. Rutile has the hexagonal close packing of the oxygen atoms, in which half of the octahedral space filled with titanium. It has the highest refractive index and highest density compare with other TiO_2 form. Anatase is a cubic close packing of the oxygen atoms, in which half of the tetrahedral space filled with titanium. Anatase has the lowest refractive index and density. Among all the three form of TiO_2, there is not much different in term of refractive index and density. Lastly, Brookite has the orthorhombic crystal structure where the titanium atom at the centre surrounded by six oxygen atoms. Anatase and Brookite will transform into rutile at the temperature above 973°K where it is thermodynamically stable. Table 2.1 show the summarization of basic physical properties of the TiO_2 of three different forms.

Table 2.1: Basic properties of TiO_2 (Nakaruk, 2010)

Properties	Rutile	Anatase	Brookite
Crystallographic Titanium : black sphere Oxygen : white sphere			
Crystal Structure	Tetragonal	Tetragonal	Orthorhombic
Lattice constant (Ǎ) a b c	 4.59 - 2.96	 5.36 - 9.53	 9.15 5.44 5.14
Space Group	$P4_4/mmm$	$14_1/amd$	Pbca
Symmetry	D_{2h}	D_{2d}	C1
TiO bond length	1.95, 1.98	1.94, 19.97	1.87, 1.92, 1.94, 1.99, 2.00, 2.04
Density (g/cm^3)	4.13	3.79	3.99
Refractive index	2.61	2.56	2.58
Hardness (Mohs)	7-7.25	5.5-6.0	5.5-6.0

2.2 Photocatalysis of Titanium Dioxide (TiO_2)

Photocatalysis is an action when a source of light that acts as the catalyst to activate a substance *i.e* TiO_2 and create electron-hole pair result in formation of free radical anion. The act radical anion, O^{2-} and OH when activated by UV light and with help of water (H_2O) allows the substrates to self-clean. The substrates of TiO_2 is use to eliminate harmful substances attached on the substrates such as organic compounds or nearby bacteria when it is exposed to the sun or fluorescent lamp. A figure 2.1 describes the general concept of photocatalytic action of TiO_2.

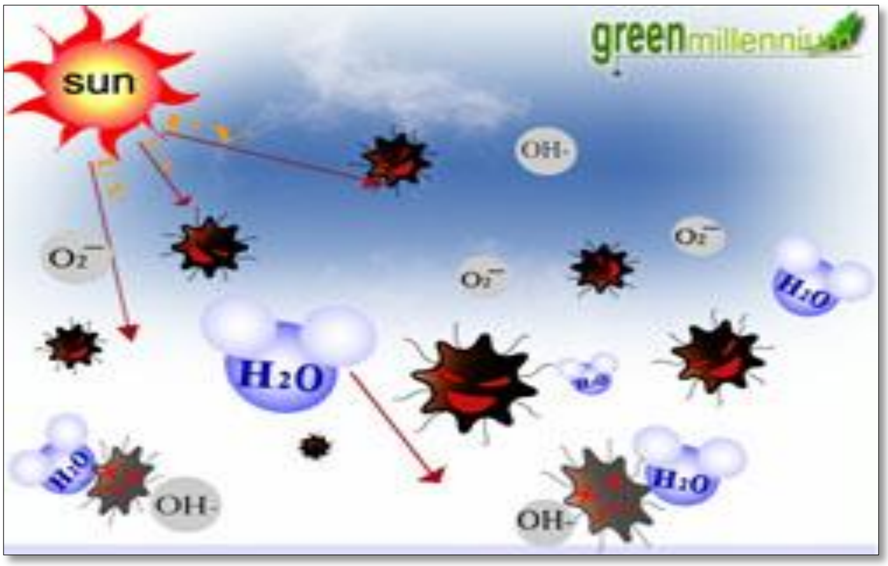


Figure 2.1: Photocatalyctic action of TiO_2 (Green Millenium, 2013)

Photocatalysts of TiO_2 were found out to be effective as purifying agent. For examples, if catalytically active TiO_2 powder put in a contaminated pool and allowed it to be illuminated with sunlight, the water will gradually become purified (Fujishima *et al.* 2000). In details, their function of the can be divided into five major categories as follows; i) Purifying water, ii) Preventing contamination, iii) Anti bacteria, iv) Deodorizing, and v)Purifying air.

The mechanism of the TiO_2 thin film photocatalyst is when the adsorbed light is below the wavelength ≈388nm; it will promote the electron in the valence band to jump into the conduction band due to TiO_2 semiconducting properties. This will leave hole in the valence band and create vacancy. Nakaruk (2010) stated that based on the occurrence, these photon-generated electron-hole pair can either recombine or take part in redox (reduction of oxygen). The majority of the electron will recombine with dissipation of heat while some of them migrate to the surface and will react with adsorbed electron donor. Shown below is the calculation of light wavelength:

$$E = hv$$

E = Energy of TiO_2 (3.3 eV = 5.12 x 10^{-19} J)

h = Planck's constant (6.63 x 10^{-34} J)

v = c/λ

c = light speed (3.0x10^8 m/s)

λ = wavelength

Thus,

λ = c/ (E/h)

= 3.0x10^8 / (5.12 x 10^{-19}/6.63 x 10^{-34})

= 388 nm #

*Therefore, the light wavelength that need to activate TiO_2 photocatalyst is 388 nm.

When TiO_2 thin film exposed to the light source that has a UV light, it will generate electron hole pair where electron are excited and released from the surface and bind with the oxygen in ambient air to produce super oxide radical anion (O^{2-}). At the same time, the TiO_2 surface becomes positively charge and combined with the electron from moisture in the air. The moisture that lost an electron caused it to become super hydroxyl radical (OH). The existence of two super radical reactions (O^{2-} and OH) will decompose organic substance on the surface such as oil, dirt, unwanted bacteria, most and *etc*. Figure 2.2 describe the mechanism of photocatalysis.

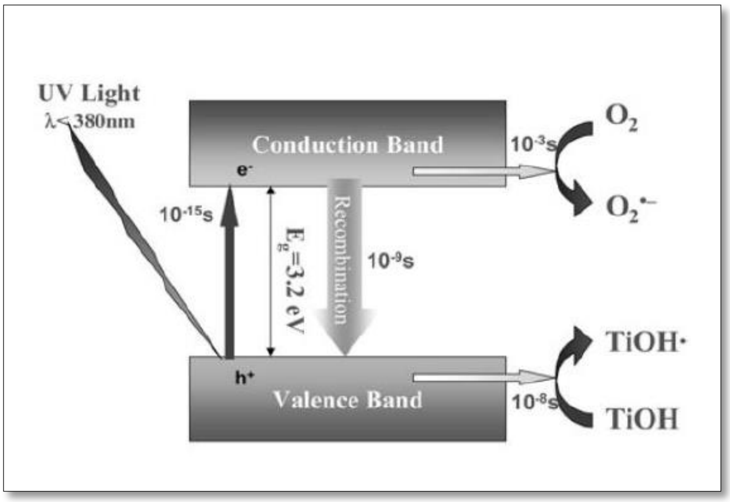


Figure 2.2: Band theory of mechanism of Photocatalysis (Nakaruk, 2010)

2.3 Physical Vapour Deposition (PVD)

PVD is a process where coating material in form of solid or liquid in are vaporized and transferred in vacuum chamber or low pressure gaseous environment it onto the desired substrate (deposition). PVD is one of the methods of surface coating technique used to change the surface or near surface to desired criteria. Generally this process also called surface coating. PVD coating thickness is in range of few nanometres to a thousand of nanometres (thin film). Besides that, it is also used to synthesize multilayer coatings, graded composition deposits, very thick deposits and freestanding structures. PVD can coat a substrate in many sizes from large to small and various shapes from flat to complex geometry. Typical PVD deposition rates are 10–100Å (1–10 nanometres) per second (Donald, 1998)

The vaporized materials that were transferred to the substrate are in an atomic level. It works in 4 basic principal steps which are;