# EFFECT OF CALCINATION TEMPERATURE ON BILAYER $TiO_2$/ZnO AND ZnO/$TiO_2$ THIN FILMS

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For my beloved

Mother, Ramlah binti Mehat

Father, Zulkiflee bin Md Akhir

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## ABSTRACT

Thin film is a thin material that resulting from the condensation of species through the deposition of atoms on substrate. Thin films are usually used in the production of electronic devices, optical coatings, solar cells, and for decorative items. The result of thin film from titanium dioxide ($TiO_2$) and zinc oxide (ZnO) have good photocatalytic properties, high refractive index, a high dielectric constant, and good thermal stability. In this study, bilayer $TiO_2$/ZnO and ZnO/$TiO_2$ thin films were produced using sol-gel synthesis with titanium (IV) butoxide as the precursor for $TiO_2$, while zinc acetate dehydrate as precursor material for ZnO. Thin films are produced on glass substrate via spin coating method at speed of 3000 rpm and were calcined at different calcination temperatures that are 400 $^oC$, 500 $^oC$, and 600 $^oC$. The X-ray diffraction (XRD) technique revealed that hisghest anatase crystalline phase for $TiO_2$ growth with orientation (1 0 1), while the ZnO crystal phase, zincite occurred at the highest intensity with (1 0 1) orientation. Thin film morphology analysis through field emission scanning electron microscope (FESEM) has shown that particle distribution of thin film is more uniform when the temperature increased. Based on the characterization and analysis of the atomic force microscope (AFM), the root-mean-square (RMS) value for $TiO_2$/ZnO and ZnO/$TiO_2$ decreases as the calcination temperature increase. Meanwhile, the transmittance spectra increase when the calcination temperature increases. With further increase in temperature, the band gap energy were about 3.21 eV to 3.36 eV for $TiO_2$/ZnO thin films and 3.26 eV to 3.74 eV for ZnO/$TiO_2$ thin films. The bilayer $TiO_2$/ZnO thin film had the highest reaction rate, K which is 0.0972 $h^{-1}$ for photocatalytic activity. The characteristics of bilayer $TiO_2$/ZnO and ZnO/$TiO_2$ thin-film is strongly influenced by the calcination temperature and the presence and combination between the two types of materials.

## ABSTRAK

Filem nipis adalah suatu bahan nipis yang terhasil daripada proses pemeluwapan spesies melalui pemendapan atom-atom pada substrat. Filem nipis digunakan dalam menghasilkan alat-alat elektronik, lapisan optik, sel solar, dan barangan hiasan. Filem nipis yang terhasil daripada titanium dioksida ($TiO_2$) dan zink oksida (ZnO) mempunyai sifat fotokatalitik yang baik, indeks biasan yang tinggi, pemalar dieletrik yang tinggi, dan kestabilan terma yang baik. Filem nipis dwilapis $TiO_2$/ZnO dan ZnO/$TiO_2$ dihasilkan menggunakan kaedah sintesis sol-gel dengan bahan mula titanium (IV) butoksida untuk $TiO_2$, manakala zink asetat dehidrat digunakan sebagai bahan mula untuk ZnO. Filem nipis ini dihasilkan pada substrat kaca melalui kaedah penyalutan putar dengan kelajuan 3000 rpm dan kemudian dikalsinkan pada suhu pengkalsinan 400 ºC, 500 ºC, dan 600 ºC. Melalui XRD, struktur fasa hablur anatas bagi $TiO_2$ muncul pada semua jenis filem nipis dengan orientasi tertinggi (1 0 1), manakala ZnO dengan fasa hablur zinkit pada keamatan paling tinggi pada orientasi (1 0 1). Analisis morfologi filem nipis melalui FESEM menunjukkan taburan partikel filem nipis semakin seragam apabila suhu meningkat. Berdasarkan pemerhatian dan analisis daripada AFM, nilai *root-mean-square* (RMS) filem nipis dwilapis $TiO_2$/ZnO dan ZnO/$TiO_2$ berkurang apabila suhu pengkalsinan meningkat. Ketelusan cahaya oleh filem nipis meningkat apabila suhu pengkalsinan meningkat. Dengan peningkatan suhu pengkalsinan, jurang jalur adalah dari 3.21 eV hingga 3.36 eV oleh filem nipis $TiO_2$/ZnO, dan 3.26 eV hingga 3.74 eV oleh filem nipis ZnO/$TiO_2$. Filem nipis $TiO_2$/ZnO mempunyai kadar tindak balas tertinggi, K, iaitu 0.0972 $h^{-1}$ untuk aktiviti fotokatalitik. Kesimpulannya, filem nipis dwilapis $TiO_2$/ZnO dan ZnO/$TiO_2$ sangat dipengaruhi oleh suhu pengkalsinan dan dengan adanya penggabungan antara dua jenis bahan.

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## LIST OF SYMBOLS AND ABBREVIATIONS

| | | |
|---|---|---|
| $TiO_2$ | - | Titanium dioxide |
| ZnO | - | Zinc Oxide |
| nm | - | nanometre |
| µm | - | micrometre |
| mm | - | millimetre |
| Å | - | Angstrom |
| θ | - | Theta (angle) |
| % | - | Percent |
| RMS | - | root-mean-square |
| XRD | - | X-ray diffraction |
| AFM | - | Atomic force microscope |
| UV-vis | - | Ultraviolet visible |
| MB | - | Methylene blue |
| K | - | Reaction rate |
| °C | - | degree Celsius |
| eV | - | Electronvolt |
| ppm | - | Parts per million |
| ml | - | Millilitre |
| FESEM | - | Field emission scanning electron microscope |
| FWHM | - | Full width at half maximum |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

Thin film is defined as a thin material resulting from an atom or molecule, ion or cluster via the condensation of species [1, 2]. Thin film is produced by deposition of atoms on various substrates such as microscope glass [3], silicon wafer [4], and quartz glass [5]. Thin film is used in the production of electronic devices, optical coating, cutting tool enhancement, solar cells, large-scale architectural automotive, and biomedical application using thin film in the production [6, 7].

The development of thin film grew rapidly in 1930s. The growth in thin film researches is due to their extensive applications in electronics [6], optics [8], space science , and other industries [2, 9]. The earliest evolution of optical modern thin film was developed by Robert Boyle and Robert Hooke on colours [10]. The colours were exhibited from the materials in thin film form. Thin film properties are sensitive not only to their structures, but also to other properties such as electronic [6], dielectric, and optical properties [9]. Optical coating has been interpreted to produce items such as antireflection and high reflectance properties [8].

Thin film can be prepared from various type of materials such as metals [11], semiconductors [12], and insulators [9] or dielectrics [13]. Most of thin film applications require the properties to be associated with inorganic and nonmetallic material such as ceramic materials. Due to the existing of the wide range of ceramic compounds and the ability to initiate additives into their structure, their electric and optical properties can be modified to make them semiconductors and electro-optic materials as wave guides, modulators and detectors. Most of ceramics have high bonding strength between atoms that result in high degree of hardness, stiffness and strength. Furthermore, most ceramics have good resistance to corrosion and oxidation at high temperatures [14].

The growth of new materials has affected ceramic film and coating technology. Performance of thin film especially in optical properties is enhanced when the coating consists of bilayer or multiple layers having varying refractive indices. These bilayer or multilayer ceramic materials, consisting layers of $TiO_2$ and ZnO thin film have been widely developed for optical [15-20] and solar cell application [21]. Bilayer coatings can have extraordinary mechanical properties and good thin films to make devices such as laser devices [15], ultraviolet (UV) light-emitting devices [16] and optoelectronic devices [18].

The ceramic materials identified are titanium dioxide ($TiO_2$) and zinc oxide (ZnO). $TiO_2$ is one of the semiconductor material that had been used by many researchers as an alternative for producing nanoporous thin film. $TiO_2$ is known as a photocatalytic material and is used for degradation of environmental pollution. $TiO_2$ properties have high photocatalytic activities, without the presence of toxicity, and excellent chemical stability in various conditions [22, 23]. $TiO_2$ is formed in three different type of crystallographic structures, namely anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [24].

On the other hand, ZnO also act as a photocatalytic material for degradations of various environmental pollutants. The properties of ZnO has been proven similar with the $TiO_2$ and is extensively used in the production of electronic devices [22]. ZnO is a semiconductor material with a large band gap 3.37 eV that can crystallizes in a hexagonal wurtzite structure with oxygen atoms in the hexagonal and zinc atoms in the tetrahedral sites [25]. Consequently, the bilayer or multilayer of $TiO_2$ and ZnO would potentially provide enhancement of properties such as band edge emission and crystalline quality.

Optical systems are becoming more complex and require more attention in antireflection coatings. Both of telescope and binocular are the example of applications improved by antireflection coatings [8]. Thin films can been produced by different deposition techniques. These deposition techniques can be divided into two categories; physical vapor deposition and non-vacuum deposition or chemical deposition [26].

Based on previous studies, $TiO_2$/ZnO and ZnO/$TiO_2$ thin films were prepared in various methods such as chemical vapor deposition [27], spray pyrolysis [28], magnetron sputtering [29], atomic layer deposition [3], and sol-gel method [22].

## 1.2 Problem statement

Bilayer thin films are becoming increasingly important in the rapid development of smaller and more efficient electronic and optoelectronic devices. One of the intention in applying bilayer structures of thin film is to modify the optical properties of materials. Hence, bilayer of $TiO_2$ and ZnO have been studied in order to improve the crystallinity and optical properties of both materials, which include crystalline quality and enhancement of band edge emission of bilayer thin films.

$TiO_2$ has two major flaws in the quality of photocatalytic activity due to band edge emission: (i) the low use of solar spectrum and (ii) the rate of recombination between the electron columns is relatively high. One of the solution to overcome this problem is to combine $TiO_2$ with other materials [23]. The $TiO_2$ thin films calcined at relatively low temperature as 300°C shows the existence of very poor crystallinity of $TiO_2$ phase [5].

The challenge in ZnO thin film applications used in ultraviolet light emitting devices is to improve photodegradation of ZnO thin films and to control the composition of the ZnO thin films which are difficult to manage [30, 31]. Low used of calcination temperature on ZnO thin film will cause defect due to insufficient grain size of ZnO thin film, which cause voids on the structure and the dislocation density defect will be increased [32].

Therefore, to improve the photodegradation of ZnO thin films, $TiO_2$ is introduced in order to optimize the parameters and to improve the crystal quality of the thin film. The result of $TiO_2$ with ZnO layer on a substrate can increase the level of ultraviolet light beam [30, 31]. The performance of thin film properties will be enhanced when the thin film coating consists of bilayer of different materials is coated on substrate having varying thicknesses and refractive indices. Hence, as the temperature increase, the intensities also increase, implying an improvement of the crystalline structure and the increase in the crystallite size.

## 1.3 Objectives

The main objectives of this research are as follows:

i. To growth bilayer nanostructured $TiO_2$/ZnO and ZnO/$TiO_2$ thin films.

ii. To optimize the calcination temperatures for deposition of $TiO_2$/ZnO and ZnO/$TiO_2$ thin films, and

iii. To characterize the structural, physical, optical properties, and photocatalytic activities behavior of bilayer $TiO_2$/ZnO and ZnO/$TiO_2$ thin films.

## 1.4 Scope of study

The scope of this study includes the following:

i. Growth of two types of bilayer thin film: $TiO_2$/ZnO thin film and ZnO/$TiO_2$ thin film.

ii. Growth of bilayer thin films using spin coating deposition technique on glass substrate.

iii. $TiO_2$ sol-gel form by using titanium (IV) butoxide and butanol as the precursor with concentration of 0.2 mol/L, while ZnO sol-gel form by using zinc acetate dehydrate as the precursor with concentration is 0.06 mol/L.

iv. The spinning speed used is 3000 rpm in 30 sec.

v. Each layer of thin films dried at 100 °C.

vi. The different calcination temperature for bilayer thin films are used; pre-calcined at 400 °C, 500 °C, and 600 °C; post-calcined at 500 °C and 600 °C.

vii. The thin films were characterized using X-Ray Diffractometer (XRD), Atomic Force Microscope (AFM), Field Emission Scanning Electron Microscope (FESEM), and Ultraviolet Visible Spectroscopy (UV-Vis).

viii. Photocatalytic activities was using methylene blue (MB) with 10 ppm concentration and carried out under 20 W ultraviolet light.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction to thin film

The term of thin film is widely used in scientific studies, which states that thin film is not only available in the form of solid layer but also found in form of liquid or gas phase [9]. Thin film is typically found in the form of solid layer having thickness varying from a few nanometers to several micrometers in thickness [1, 2].

According to Freud and Suresh [33], when the film thickness is very thin compared to the substrate thickness (typically by factor of 50 or more), the thin film is known as mechanical thin film. When a small dimensional structure of the material is comparable to the scale of the microstructure size, the thin film is described as microstructure thin film. Most of the thin films used in microelectronic devices and magnetic storage media is an example of the microstructure thin films. Microstructure thin film has thickness significantly larger than the dimensions of the atom or molecule. Meanwhile, atomic thin film is the thin film with thickness of one layer or a few atomic layers. A monolayer of atoms adsorbed gas on the surface is a sample of atomic thin film [33].

Rapid increase in the study of thin films is mainly contributed by the widespread application in various fields such as electronics [6], optics [8], space sciences [9], aircraft and other industries [2]. Thin films have been used in various engineering systems and have been adapted to meet variety of functions and applications [34]. The main applications benefiting from thin film construction is the electronic semiconductor devices [13] and the optical coatings [35]. In addition, thin film is also used as wear resistance [36], corrosion resistance [37], and chemical resistance [38]. Thin film materials can minimize the use of toxic substances because the quantity of thin film materials usage are limited to the surface only. Energy consumption in the production of thin film also can be saved [6].

Since the late of 1930s, thin films have been widely studied because of high demand in the production of electronic goods. In the early 1960s, thin film transistors (TFTs) which is a device of thin film have been proposed to substitute by using cadmium sulfide (CdS) semiconductor as the material. In the 1970s, a number of devices from thin films have been developed such as acoustic wave devices (SAW) and bulk acoustic integrated wave devices (BAW) [6]. Since then, variety of thin film devices have been developed by using various type of materials such as $TiO_2$ and ZnO.

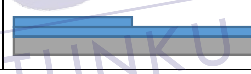
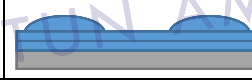
## 2.2 Nucleation and growth of thin film



Thin film growth through deposition of material on substrate works for various purposes including physical protection, decoration, insulation, and corrosion resistance [39]. The production of thin film typically involves nucleation and growth stages. The nucleation and growth stages includes the process of adsorption, surface diffusion, chemical bonding, and other atomic processes on surface [40]. Nucleation is the process where nuclei or seeds act as template for crystal growth. The nucleation and the growth of thin film generally occur when individual atoms strike on the substrate surface. The homogenous nucleation and growth during monolayer stage plays an important role in determining the morphology and properties of the thin film [41]. Thin film growth occurs if pressure is administrated to the molecule momentum, which results in the generation of kinetic energy. In addition, the impact on molecule energy causes the thin layer formation on the substrate [39]. The growth of thin film determines the crystal phase and the crystal orientation of thin film.

According to Moshfegh [41], there are three major growth mechanisms that occur in the early stages of film formation such as two dimensional layer-by-layer, island growth mechanism, and mixed layer island. The two dimensional layer-by-layer or known as Frank-Van der Marwe mode has greater bonding strength between atoms and is used to grow metal or semiconductor structure. While island growth mechanism (Volmer-Weber) involve the smallest stable clusters nucleate on substrate to form island in three dimensions. In the island growth mechanism, the atoms of thin film are strongly bound to each other than the substrate atom. While the mixed layer-island (Stranski-Krastanov) mode is the intermediate mixture of layer-by-layer and island growth [41]. Table 2.1 shows the schematic view of three type of film growth mechanism.

Table 2.1: Thin film growth mechanism schematic view [41]

| **COVERAGE** | **$\theta < 1$ ML** | **$1 < \theta < 2$** | **$\theta > 2$ ML** |
|---|---|---|---|
| 2-D Layer-by-Layer Mechanism |  |  |  |
| 3-D Island Growth Mechanism |  |  |  |
| Mixed Layer-Island |  |  |  |

$\theta$ = Substrate surface coverage

ML = Monolayer

## 2.3 Deposition growth parameter

Thin film structure is dependent on the parameter used for thin film growth. Thin film deposition allows the formation of structural properties and chemical properties of the material through the control of the parameter [42]. Among the thin film growth parameters that need to be considered are the crystal structure deposition rate, the calcination temperature, and the type of the substrate used [2, 6, 9].

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