

OPTICAL PROPERTIES OF DYE SENSITIZED ZINC OXIDE THIN FILM  
DEPOSITED BY SOL-GEL METHOD

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**UNIVERSITI TEKNOLOGI MALAYSIA**

With lots of love and gratitude, I dedicate this to my beloved parent and siblings and  
my closest friend.

Each and every one of you always makes me feel special and thank you for  
believing me.

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## ABSTRACT

Metal oxide semiconductor has been widely studied due to its varied properties and application. Among metal oxides, ZnO semiconductor is of great interest due to its wide band gap (3.2-3.4 eV) with hexagonal wurtzite structure. This study involves the comparison of optical properties of ZnO thin films when doped with erbium and terbium. The optical properties were studied using Photoluminescence and Direct Reflectance Ultraviolet (DR-UV). FESEM image shows that the irregular shape and there is variation in the surface morphology of undoped and doped ZnO thin film. The grain size increased with addition of erbium and terbium. The transmission spectra for all samples show high transmission with more than 90%. However, the band gap increases for doped ZnO thin film sensitized with eosin B. The band gap value also decreases with the addition of erbium and terbium for sensitized eosin Y. The XRD patterns of these samples are in close agreement with the JCPDS standard (No. 36-1451). It was observed that all deposited films were polycrystalline with hexagonal wurtzite structure with diffraction peaks oriented along the (100), (002), (101), (102), (110) and (103) planes. The preferred orientation for ZnO thin film sensitized with eosin Y and B is (101) plane. The discrepancy may be caused by different preparation conditions. The PL emission in the UV bands was observed, peaking at the range of 365-387 nm, centered at 380 nm at near band edge emission, due to  $\text{Er}^{3+}$  transition from  ${}^4\text{F}_{7/2} \rightarrow {}^4\text{I}_{15/2}$  and  $\text{Tb}^{3+}$  transition from  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_1$ .

## ABSTRAK

Semikonduktor logam oksida telah dipelajari dengan meluas kerana kepelbagaian sifat dan aplikasinya. Antara logam oksida, semikonduktor zink oksida dipelajari kerana ruang jalur yang luas (3.2-3.4eV) dengan struktur heksagonal wurtzite. Kajian ini melibatkan perbandingan sifat optikal zink oksida saput tipis apabila didop dengan erbium dan terbium. Sifat optikal ini dikaji menggunakan Photoluminescence dan Direct Reflector ultraviolet (DR-UV). Imej FESEM menunjukkan bentuk tak tersusun dan terdapat variasi pada sifat permukaan zink oksida dan dop-zink oksida saput tipis. Saiz partikel meningkat dengan pertambahan erbium dan terbium. Transmisi spektra bagi semua sample menunjukkan transmisi tinggi lebih 90%. Walaubagaimanapun, ruang jalur meningkat untuk dop zink oksida saput tipis yang dipekakan dengan eosin B. Namun begitu ruang jalur zink oksida berkurang dengan pertambahan erbium dan terbium yang dipekakan dengan eosin Y. Bentuk XRD untuk semua sampel ini mengikuti taraf JCPDS 36-1451. Ia menunjukkan semua saput tipis adalah polikristal dengan struktur heksagonal wurtzite dengan puncak tersusun mengikut tapak (100), (002), (101), (102), (110), dan (103). Orientasi terpilih untuk zink oksida saput tipis yang dipekakan dengan eosin Y dan B adalah tapak (101). Perbezaan orientasi terpilih mungkin disebabkan perbezaan penyediaan bahan. Pancaran PL pada jalur UV diperhatikan dan puncaknya wujud dalam lingkungan 365-387nm, berpusat pada 380nm dekat dengan pancaran jalur disebabkan transisi  $\text{Er}^{3+}$  dari  ${}^4\text{F}_{7/2} \rightarrow {}^4\text{I}_{15/2}$  dan transisi  $\text{Tb}^{3+}$  dari  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_1$ .

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**LIST OF SYMBOLS**

DRUV	-	Direct reflector-ultraviolet
Er	-	Erbium
FESEM	-	Field emission scanning electron microscope
Nm	-	Nanometer
Tb	-	Terbium
XRD	-	X-ray diffraction

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# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Zinc comes from d-block element from periodic table. Within this group, in each case the d orbital are filled. Group IIB elements decrease in electropositive tendencies with increasing atomic number, although the change is not marked between zinc and cadmium. These two metals oxidize only superficially in air at room temperature, and are used as plating metals. They will however, oxidize readily in dilute temperatures. Zinc normally dissolves readily in dilute acids but pure samples are much more resistant to attack than commercial metal. Zinc and cadmium form many compounds involving direct links to carbon, as well as nitrogen, sulphur, etc., but zinc appears to form more stable links with oxygen than cadmium (Cooper, 1968). ZnO belongs to a group of hexagonal wurtzite, 6 -mm symmetry, wide band gap ( $E_g = 3.35$  eV, 300K). ZnO has been used in a wide range of device applications due to its semiconducting electrical, optical and piezoelectric properties (Wen and Jing, (2007).

Metal Oxide semiconductor films have been widely studied and have received considerable attention in recent years due to their optical and electrical properties. Some of them are good candidates for transparent conductive oxide films. Among them ZnO is one of the metal oxide semiconductors suitable for use in optoelectric devices. It is an alternative material to tin oxide and indium tin oxide, which have been most used to date (Jin Hong and Byong Ok, (2003). Zinc oxide is an important oxide semiconductor for toxic and combustible gas sensing

applications. ZnO gas sensor elements have been fabricated in various forms, such as, single crystals, sintered pellets, thick films, thin films and heterojunctions (Mitra *et al.*, 1998). Among the metal oxides, SnO<sub>2</sub> semiconductor gas sensor is of great interest from a scientific and technological point of view. In fact, commercially available gas sensors are mainly based on SnO<sub>2</sub> in the form of thick films, pellets or thin films (Rella *et al.*, 1997).

The development of solid-state chemical sensors, and more specifically gas sensors, is currently being carried out intensively since environmental pollution and security in the work and domestic ambient atmospheres represent acute problems with a high social impact (Rella *et al.*, 1997). Materials that change their properties depending on the ambient gas can be utilized as gas sensing materials. Usually changes in electrical conductance in response to environmental gases are monitored. Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases. However, the most commonly used gas sensing materials are ZnO and SnO<sub>2</sub> (Matthias and Ulrike, 2005).

Undoped and doped zinc oxide thin films have a wide range of applications as an important semiconductor material such as solar cells, electrical, piezoelectric or luminescent devices and also as gas sensors and chemical sensors (Musat *et al.*, 2008). It is well known that chemical doping greatly influences the electronic and optical properties of ZnO. Al, In and Ga-doped ZnO thin films are one of the promising transparent conductive oxides for advanced applications such as displays and electrochromic devices (Ka Eun *et al.*, 2009).

Terbium was discovered by C.G. Mosander in 1843 in Stockholm, Sweden. Terbium with the symbol Tb and atomic number 65 is a silver-grey metal, malleable, ductile, and soft enough to be cut with a knife. Terbium can be recovered from the mineral monazite by ion exchange and solvent extraction, and from euxenite, a complex oxide containing 1% or more of terbium. It is usually produced commercially by reducing the anhydrous fluoride or chloride with calcium metal. Terbium is used to dope calcium fluoride, calcium tungstate and strontium

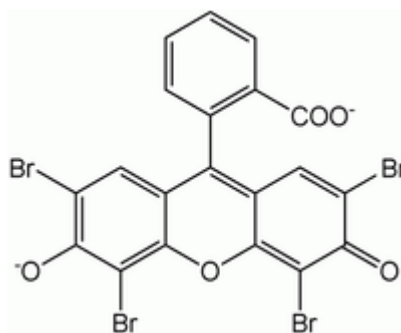
molybdate, all used in solid-state devices. Terbium salts are used in laser devices, but otherwise this element is not widely used.

Erbium is a chemical element in the lanthanide series with the symbol Er and atomic number 68. Natural erbium is always found in chemical combination with other elements on earth. Erbium's principle uses involves its pink-colored ions, which have optical fluorescent properties particularly useful in certain laser application. Erbium is a trivalent element, pure erbium metal is malleable (easily shaped), soft yet stable in air and does not oxidize quickly as some other rare-earth metals. The principle commercial sources of erbium are from the minerals xenotime and euxenite same as other lanthanides. Erbium compounds are of low to moderate toxicity. Erbium-doped optical silica glass fibers are the active element in erbium-doped fiber amplifiers (EDFAs), which are widely used in optimal communication.

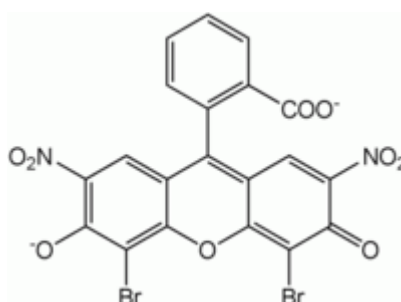
Dye-sensitized solar cell (DSSC) is a relatively new class of low-cost solar cell, which belongs to the group of thin film solar cells. It's based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a photoelectrochemical system. A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require mordant to improve the fastness of the dye on the fiber.

Eosin is a fluorescent red dye resulting from the action of bromine on fluorescein. There are actually two much related compounds commonly referred to as eosin. Most often used is eosin Y. It has a very slightly yellowish cast. The other eosin compound is eosin B; it has a very faint bluish cast. The two dyes are interchangeable where Eosin Y is a tetrabromo derivate of fluorescein and eosin B is a dibromo dinitro derivate of fluorescein.





**Figure 1.1:** Eosin Y



**Figure 1.2:** Eosin B

The properties of films are strongly dependent upon the method of preparation. As a result, a wide range of different deposition techniques have been investigated. These include chemical vapor deposition, spray pyrolysis, electron beam evaporation, and sputtering. The sol gel technique offers many advantages over other method, such as low temperature processing, precise control of the doping level, and simplicity not requiring expensive deposition facilities. The sol-gel method is a “wet chemistry” approach to make thin films. A sol is a colloidal mixture of solid particles dissolved in a solvent. After a stable sol is prepared with the desired composition, this precursor solution can be easily deposited onto surface and spin-coated to make a thin film. The film is then heated to drive the formation of a gel. Subsequent high temperature annealing removes organic residues and makes solid thin film denser (Ken, 2004). The films obtained by the sol gel technique have a porous structure consisting of ultra-fine particles, thereby offering a large specific surface area. Such a structure is desirable for gas sensor application (Racheva and Critchlow, 1997).

## 1.2 Background of Problem

Metal Oxide Semiconductor have been widely studied the properties and application. Zinc oxide thin film is extensively studied because of its potential application in various fields such as gas sensor, solar cells, photo-detector, light emitting diodes and laser system. Due to its non-toxicity, abundance and chemical stability even under a reducing environment, zinc oxide thin film could surpass the performance of indium oxide and tin oxide in some applications. Zinc oxide thin film with band gap value of 3.42eV at 300K, and as result of oxygen efficiency and/or zinc interstitials shows intrinsic n-type conductivity.

Magnetron sputtering is generally accepted as an optimum method for preparing zinc oxide based film. However, sputtering requires a complex and expensive vacuum technique and has its distinct challenges when it comes to large area coating and film deposition on substrates featuring a complex geometry. An alternative deposition technique that can easily overcome these issues is sol-gel method. The sol-gel method has distinct potential advantages over other technique due to its lower crystallization temperature, ability to tune microstructure via sol-gel chemistry, conformal deposition ability, compositional control and large surface area coating capability (Shane et al., 2007).

The numerous factors that affect the properties of sol gel based ZnO films fall into three main categories. They are: (1) the chemistry of the sol gel method, (2) the interaction between the film and the substrate during the coating process, and (3) post heat treatment. All these factors have a distinct effect on the films microstructure. This especially holds true in the case of sol-gel based multi-layer coatings which are utilized to overcome cracking issues in thick layers. The main parameters of interest have been heating temperature and heating time.

The used of anhydrous zinc acetate, which avoids the introduction of large amounts of water to the sol-gel, enabling control over reactions taking place within the sol-gel method (Shane *et al.*, 2007). One of the most promising materials for room temperature ferromagnetism is transition metal-doped zinc oxide.

Ferromagnetism operates via mechanism by which itinerant carriers are spin polarized and mediate ferromagnetic ordering between the widely spaced dopant ions. Nowadays, Mn-doped ZnO has been extensively studied for its expected ferromagnetism and magneto-optical application at room temperature. But Mn doping severely suppresses the luminescence of  $Zn_{1-x}Mn_xO$  even at a very low doping level (Srinivasan and Kumar, 2008).

Photoactive materials in dye-sensitized solar cells are typically prepared by stepwise processing starting with the formation of porous films of inorganic semiconductors by colloid coating and heat treatment (around 450°C) followed by dye adsorption by dipping the film in the dye solution.

### 1.3 Statement of Problem

The use of anhydrous zinc acetate, which avoids the introduction of large amounts of water to the sol-gel, enabling control over reactions taking place within the sol-gel method. Magnetron sputtering is generally accepted as an optimum method for preparing ZnO based film. Sputtering requires a complex and expensive vacuum technique and has its distinct challenges when it comes to large area coating and film deposition on substrates featuring a complex geometry. The sol-gel method is preferred due to its lower crystallization temperature, ability to tune microstructure via sol-gel chemistry, conformal deposition ability, compositional control and large surface area coating capability. Even though Mn-doped has been extensively studied before it severely suppresses the luminescence of  $Zn_{1-x}Mn_xO$  at very low doping. The quick decrement of isolated  $Mn^{2+}$  with increasing  $x$  is considered to be responsible for the severe suppression of the blue and ultraviolet luminescence. The green emission is also quenched, which is generally attributed to the passivating action of Mn on surface defects (Srinivasan and Kumar, 2008).

The two main drawbacks of the colloidal process is an active control of the crystallographic structure and pore sizes of the inorganic phase is difficult which

resulting in electron traps and resistance to the electron percolation. Besides that heat treatment limit the substrate choice to heat-resistant materials, thus excluding temperature-sensitive materials such as polymers. Sol gel technique has its own problem concerning annealing temperature because too high temperature may lead to overgrown dopant precipitates, while annealing at too low temperature would lead to insufficient pyrolysis, crystallization thus poor film properties. The problem is rather serious for TiO<sub>2</sub> composite films because a relatively high temperature is required to remove the organic byproduct and to crystallize the oxide. In this experiment this problem is not serious since the main solvent is volatile and ZnO can easily crystallize out at relatively low temperature (Xiang Hua *et al.*, 2003).

#### **1.4 Research Objectives**

Based on the research background and problem statement mentioned above, the objective of this study is to investigate the influence of addition of dopants in zinc oxide thin films as well as their optical properties when sensitized with Eosin Y and Eosin B.

#### **1.5 Scope of Study**

In order to achieve the above objective, this study starts with the preparation of zinc sol precursor. Zinc sol precursor was prepared by sol gel method. Zinc sol was prepared by using zinc acetate dehydrate as starting material and dissolved in absolute ethanol and diethanolamine (DEA) at room temperature. The solution was stirred vigorously and yields a clear and homogenous solution. The solution was prepared in three conditions as undoped zinc oxide thin films, erbium doped zinc oxide thin films and terbium doped zinc oxide thin films. Each solution was prepared in two samples as each sensitized with eosin Y and eosin B respectively. Characterization of structure, morphology and optical properties was

measured by X-Ray diffraction (XRD), field-emission scanning electron microscope (FESEM), photoluminescence (PL), and direct reflector ultraviolet (DRUV). Comparison of characterization will be made between zinc oxide thin films, erbium doped zinc oxide thin film and terbium doped zinc oxide thin films with different dye.