

SUBSTRATES EFFECT ON STRUCTURAL AND
OPTICAL PROPERTIES OF INDIUM TIN OXIDE
(ITO) THIN FILMS BY SOL GEL METHOD

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
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SUPERVISORS' DECLARATION

I hereby declare that I have checked the thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Honor)Material Technology.

Signature

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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DEDICATION

This thesis is dedicated to my beloved family, supervisor and friends for their unconditional love, endless support, encouragement and enthusiasm since the beginning of my studies and throughout my project until finishing this thesis.

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LIST OF SYMBOLS

%	-	percent
λ	-	wavelength
2θ	-	Bragg's angle
$^{\circ}\text{C}$	-	degree celcius
\AA	-	angstrom (10^{-10})
t	-	substrates' thickness
α	-	absorption coefficient
β	-	FHWM
h	-	Planck's constant
ν	-	frequency

LIST OF ABBREVIATIONS

ITO	-	indium tin oxide
CBD	-	chemical bath decomposition
CVD	-	chemical vapor deposition
FESEM	-	field emission electron scanning microscopy
PL	-	photoluminescence
XRD	-	X-ray diffraction
UV-Vis	-	ultraviolet-visible
FHWM	-	full half width maximum
SnO	-	tin oxide
SnO ₂	-	tin dioxide
Sn	-	tin
InCl ₃	-	indium chloride
Cu-K α	-	copper K-alpha
rpm	-	rotation per minute
E _g	-	band gap energy
g	-	grams
h	-	hour
cm	-	centimeter (10 ⁻²)
eV	-	electron volt
kV	-	kilovolt
mA	-	milliampere
nm	-	nanometer (10 ⁻⁹)
μ L	-	micro liter

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ABSTRACT

Metallic oxides are one of the transparent semiconductors that having abundant application in industry. Indium tin oxide (ITO) is an example of metallic oxide which commonly referred to ITO thin films. ITO thin films were prepared by sol-gel method and then annealed in the temperature of 500 °C in order to improve their structural and optical properties. In this study, ITO thin films were deposited on different substrates which are quartz and glass. Characterization techniques of X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV-visible, and photoluminescence (PL) spectra measurements were performed to investigate the effects of substrate on the structural and optical properties of ITO thin films. The XRD results indicated that the highest intensity peak for ITO thin film on glass substrate is (222) while ITO thin film on quartz substrate is (211). FESEM characterization showed the grain size for ITO thin film on glass substrate is smaller than grain size of ITO thin film on quartz substrate. Transparency of the films, over the visible light region showed that ITO thin film on quartz substrate has better transparency compared to ITO films on glass substrate as the absorption edge of ITO thin films on quartz substrate shifted towards more longer wavelength compared to absorption edge of ITO thin film on glass substrate. The transmittance spectra showed that the thin film for ITO thin films on glass substrate has highest transmittance than quartz substrate. The optical band gap for ITO thin films on glass substrate and ITO thin films on quartz substrate are 4.30 eV and 4.10 eV respectively. Photoluminescence (PL) spectra of ITO film deposited on glass and quartz substrate observed strong ultraviolet emission at same value which is only at 580 nm indicating the emission of yellow light.

ABSTRAK

Logam oksida ialah salah satu semikonduktor lutsinar yang digunakan secara meluas dalam industri. Indium timah oksida (ITO) ialah satu contoh logam oksida yang biasanya dirujuk kepada filem nipis ITO. Filem nipis ITO disediakan melalui kaedah sol-gel dan dibakar pada suhu 500 °C untuk mengkaji struktur dan ciri-ciri optic mereka. Dalam kajian ini, filem nipis ITO dilapiskan ke atas dua substrat yang berbeza iaitu kaca dan kuarza. Teknik-teknik pencirian seperti sinaran x-ray (XRD), imbasan mikroskop elektron (FESEM), spektroskopi ultraviolet dan spektrum fotoluminasi (PL) telah digunakan untuk mengkaji bagaimana penggunaan substrat yang berbeza memberi kesan kepada struktur dan ciri-ciri optic filem nipis ITO. Hasil sinaran x-ray menunjukkan keamatan tertinggi bagi filem nipis ITO pada substrat kaca ialah (222) manakala bagi filem nipis ITO pada substrat kuarza ialah (211). Imbasan mikroskopelektron menunjukkan saiz zarah filem nipis ITO pada substrat kaca lebih kecil berbanding saiz zarah filem nipis ITO pada substrat kuarza. Sifat lutsinar filem, merentasi cahaya yang dapat dilihat, menunjukkan filem nipis ITO pada substrat kuarza mempunyai sifat lutsinar yang baik berbanding filem nipis ITO pada substrat kaca. Hal ini kerana filem nipis ITO pada substrat kuarza menyerap cahaya pada gelombang yang tinggi berbanding penyerapan cahaya oleh filem nipis ITO pada substrat kaca. Spektrum tansmisi menunjukkan filem nipis ITO pada substrat kaca mempunyai transmisi yang tinggi berbanding filem nipis ITO pada substrat kuarza. Jurang tenaga optik filem nipis ITO pada substrat kuarza ialah 4.30 eV dan jurang tenaga filem nipis ITO pada substrat kaca ialah 4.10 eV. Spektrum fotoluminasi filem nipis ITO yang dilapiskan pada substrat kaca dan kuarza memperlihatkan kewujudan pancaran ultraungu yang kuat pada nilai panjang gelombang yang sama iaitu 580 nm. Panjang gelombang itu merupakan penyerapan cahaya berwarna kuning.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF PROBLEM

Metallic oxides are one of the transparent semiconductors that having abundant application in industry. Indium tin oxide (ITO) is an example of metallic oxide which commonly referred to ITO thin films. Some of us did not aware of extraordinary chemical and physical properties which are characterize in ITO' particles. The spectral transmittance and simulation software can be used to determine the real significant of ITO in terms of its presence as n-type conductivity and a wide bandgap.

As already mentioned above, ITO has a wide bandgap which is about >3.5 eV. It is n-type semiconductor with excellent substrate adherence and great electrical conductivity (Ojo Adurodija, 2002). That is why coating electrodes for optoelectronics especially films in solar cells used ITO as its primary source (Harith Ibrahim et al., 2013). Here tin acts as a cationic dopant and a substitute on the indium sites to bind with the interstitial oxygen.

Indium Tin Oxide is known as beneficial semiconductor which contributes more in industry when it is synthesized as a thin film. Thin film is known as a very thin layer of material coating. Thin film deposition is one of the procedures used to apply a very thin film of material onto a substrates' surface. This process is mainly used in optical devices and semiconductor industries. Thin film deposition commonly divided into two groups which are physical and chemical decomposition. Zhou et al., 2007 has reported that vacuum-based deposition method is costly and require complicated equipment. Chemical vapor deposition (CVD), laser ablation, spray pyrolysis and

sputtering are some examples of vacuum-based deposition. In addition, physical deposition or also known as solution-based deposition methods used thermodynamic, electrochemical and mechanical procedure where the releasing material from a source is deposited on a substrate. Chemical bath decomposition (CBD), electrodeposition, hydrothermal and sol gel process are the examples of solution-based deposition method (BIAN et al., 2008). Among these solution-based deposition, sol-gel method becomes the greatest choice in industry due to its ability in obtaining high purity materials using simple equipment with reasonable price (Harith Ibrahim, 2013).

To the best of my knowledge, the study of ITO synthesized by sol gel method on quartz substrate have rarely reported. Thus, in this contribution, we study the properties of ITO deposited on two different substrates which are glass and quartz. In particular, we have focused on morphologies and optical properties of ITO thin films.

1.2 STATEMENT OF PROBLEM

Historically, ITO films are used widely and becomes priority in semiconductor industry. As concrete integrated apparatus used ITO as its main source, fine patterning is required in order to gain quantified fine patterns. These patterns are quite hard to quantify via wet and dry etching which both are the example of chemical etching methods (Park et al., 2005). The study before reported that various procedures like spray pyrolysis and thermal hydrolysis are used to obtain ITO nanoparticles. However, these methods were unsuccessful because the oxide produce high degree of agglomeration. Among these techniques, the sol-gel method has its own benefits which are the possibility of obtaining high purity materials using modest equipment and the ability to synthesis ITO in the form of thin films (Silva et al., 2012).

In this work, sol gel method is used to fabricate ITO films on two different substrates and hence the structural and optical properties will investigated.

1.3 OBJECTIVES OF STUDY

The objectives of this study are:

1. To synthesis ITO thin film deposited on two different substrates.
2. To study the structural characteristics of ITO thin films deposited on two different substrates using XRD and FESEM.
3. To determine the band gap of ITO thin films and study their optical effect on two different substrates using UV-Vis spectrometry and PL spectroscopy.

1.4 SCOPE OF THE STUDY

This study is mainly focus on characterizing the structural and optical properties of sol gel Indium Tin Oxide (ITO) thin films using different substrates. The substrates are concentrated on glass and quartz only.

For structural studies, the structural characteristics of ITO are investigated using non- destructive method such as FESEM and XRD. Apart from that, for optical studies, the optical effect of ITO are investigated using UV-vis spectrometry and PL spectroscopy.

The attention of this study is to focus on substrate effects on structural and optical properties of Indium Tin Oxide thin films by sol-gel method.

REFERENCE

- A Singh, A. K. (2009). Structural and Optical Characterization of ZnO Thin Films Deposited by Sol-gel Method. *Journal of Optoelectronics and Advanced Materials*, 790-793.
- C. Su*, T.-K. S.-T.-A.-C.-C. (2005). Preparation of ITO Thin Film by Sol-gel Process and Their Characterization. *Synthetic Materials* .
- H.Y. Valencia, L. M. (2014). Structural, electrical and optical analysis of ITO thin films prepared by sol-gel. *Journal of Microelectronics*, 1356-1357.
- Han, S.-J. H.-I. (2004). Fabrication of Indium Tin Oxide (ITO) Thin Film with Pre Treated Sol Coating. *Journal of the Korean Physical Society*, 634-637.
- Harith Ibrahim1, M. M. (2013). Preparation of ITO thin film by Sol-Gel method.
- K. Daoudi, B. C. (2002). Tin-doped Indium Oxide Thin Films Deposited by Sol-Gel Dip-Coating Technique. *Elsevier Material Science & Engineering*, 313-317.
- Liliana Rodriguez Paez, J. M. (2004). Properties Of Sol-Gel TiO₂ Layers On Glass Substrate. *Original Journal*, 1-6.
- P.Sujatha Devi, M. C. (2002). Indium Tin Oxide Nanoparticles through an emulsion technique. 205-210.
- Sung-Jei Hong, J.-I. H. (2004). Fabrication Of ITO Thin Film with Pre Treated Sol Coating. 634-637.
- Timoumi, A. (2013). Properties and Electrical Study of In₂S₃/SnO₂/Glass Substrates. *International Journal of Advanced Researched in Electrical, Electronics and Instrumentation Engineering*, 2278-8875.
- Ting-Ting Liu, G.-J. S.-T. (2013). Research Progress in Nanostructured MnO₂ as Electrode Materials for Supercapacitors. *Asian Journal of Chemistry*, 7065-7070.
- Yasmeen Z. Dawood*, M. H. (2014). Effect Of Solution Concentration On Some Optical Properties Of Indium Oxide Doped with SnO₂ Thin Films Prepared by Chemical Spray Pyrolysis Technique. *International Journal of Pure and Applied Physics*, 1-7.
- Al-Dahoudi, N., Aegerter, M.A., 2006. Comparative study of transparent conductive In₂O₃:Sn (ITO) coatings made using a sol and a nanoparticle suspension. *Thin Solid Films*, Selected Papers from the 5th International Conference on Coatings on Glass (ICCG5)-Advanced Coatings on Glass and Plastics for Large-Area or High-Volume Products ICCG5-Selected Papers from the 5th International Conference on Coatings on Glass (ICCG5)- Advanced Coatings on Glass and Plastics for Large-Area or High-Volume Products 502, 193–197.
- Bian, Z.Q., XU, X.B., Chu, J.B., Sun, Z., Chen, Y.W., Huang, S.M., 2008. Study Of Chemical Bath Deposition Of ZnS Thin Films With Substrate Vibration. *Surf. Rev. Lett.* 15, 821–827.

- Cho, H., Yun, Y.-H., 2011. Characterization of indium tin oxide (ITO) thin films prepared by a sol-gel spin coating process. *Ceramics International* 37, 615–619.
- Faraj, M.G., Ibrahim, K., Eisa, M.H., Ali, M.K.M., Azhari, F., 2010. Investigation on Molybdenum Thin Films Deposited by DC-Sputtering on Polyethylene Terephthalate Substrate. *International Journal of Polymeric Materials and Polymeric Biomaterials* 59, 622–627.
- Frank, G., Köstlin, H., 1982. Electrical properties and defect model of tin-doped indium oxide layers. *Appl. Phys. A* 27, 197–206.
- Hong, S.-J., Kim, J.-W., Lim, J.-W., Choi, G.-S., Isshiki, M., 2010. Characteristics of Printed Thin Films Using Indium Tin Oxide (ITO) Ink. *Materials Transactions* 51, 1905–1908.
- Kwon, C.H., Kim, J.H., Jung, I.S., Shin, H., Yoon, K.H., 2003. Preparation and characterization of TiO₂-SiO₂ nano-composite thin films. *Ceramics International* 29, 851–856.
- LI, Z., KE, Y., REN, D., 2008. Effects of heat treatment on morphological, optical and electrical properties of ITO films by sol-gel technique. *Transactions of Nonferrous Metals Society of China* 18, 366–371.
- LI, Z., REN, D., 2006. Preparation of ITO transparent conductive film by sol-gel method. *Transactions of Nonferrous Metals Society of China* 16, 1358–1361.
- N. M. Khusayfan, M.M.E.-N., 2013. Study of Structure and Electro-Optical Characteristics of Indium Tin Oxide Thin Films. Hindawi Publishing Corporation 2013, 8.
- Ojo Adurodija, F., 2002. Chapter 3 - Laser applications in transparent conducting oxide thin films processing A2 - Nalwa, Hari Singh, in: *Handbook of Thin Films*. Academic Press, Burlington, pp. 161–217.
- Park, J.-O., Lee, J.-H., Kim, J.-J., Cho, S.-H., Cho, Y.K., 2005. Crystallization of indium tin oxide thin films prepared by RF-magnetron sputtering without external heating. *Thin Solid Films* 474, 127–132.
- Seki, S., Ogawa, M., Sawada, Y., 2001. Indium-Tin-Oxide Thin Films Prepared by Dip Coating; Dependence of Resistivity on Film Thickness and Annealing Atmosphere. *Japanese Journal of Applied Physics* 40.
- Silva, G.M., Faria, E.H. de, Nassar, E.J., Ciuffi, K.J., Calefi, P.S., 2012. Synthesis of indium tin oxide nanoparticles by a nonhydrolytic sol-gel method. *Química Nova* 35, 473–476.
- Tak, Y.-H., Kim, K.-B., Park, H.-G., Lee, K.-H., Lee, J.-R., 2002. Criteria for ITO (indium-tin-oxide) thin film as the bottom electrode of an organic light emitting diode. *Thin Solid Films, Proceedings of the 2nd International Symposium on Transparent Oxide Thin Films for Electronics and Optics* 411, 12–16.
- Zhou, H., Yi, D., Yu, Z., Xiao, L., Li, J., 2007. Preparation of aluminum doped zinc oxide films and the study of their microstructure, electrical and optical properties. *Thin Solid Films* 515, 6909–6914.