

**OPTICAL AND SENSING PROPERTIES OF SPUTTERED INDIUM TIN
OXIDE (ITO) THIN FILMS**

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OPTICAL AND SENSING PROPERTIES OF SPUTTERED INDIUM TIN OXIDE
(ITO) THIN FILMS

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*Dedicated to my beloved parents,
Abd Mubin Bin Othman and Kalsom Begum Binti Fazal Ahmad,
to my siblings and family,
to my fiance, Nur Fatin Binti Sulaiman,
to my friends,
thank you so much,
for their patience, support, love and encouragement.*

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In the name of Allah s.w.t, the most gracious and the most merciful

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ABSTRACT

Two sets of indium tin oxide thin film were prepared at different thicknesses onto the corning glass substrates using radio frequency magnetron sputtering method. Set one is for single configuration sample and set two is for sensor array sample. All samples were annealed at temperature of 600°C for 4 hours inside a furnace. A surface profiler was used to measure the thickness of the samples while a UV-VIS spectrophotometer was used to measure their optical properties. The gas sensing characterization system was used to determine the gas sensing properties in 200 ppm of nitrogen dioxide, NO₂. The thickness of the sample was found to be in the range of 132 nm to 424 nm. The transmittance and the optical band gap decrease as thickness increases. The resistance decreased to several kilo ohms when the operating temperature increased for all samples. The highest sensitivity for single configuration was found in sample C with thickness 227 nm (45 minutes deposition time). Sample H has the highest sensitivity (combination of 15 minutes + 90 minutes deposition times) for array configuration. Thus, the response time and the corresponding recovery time for sample C were 66.6 seconds and 133.2 seconds respectively; while for sample H, the response time was 60 seconds and recovery time was 333.6 seconds.

ABSTRAK

Dua set saput tipis indium timah oksida telah berjaya dihasilkan di atas kaca korning dengan menggunakan kaedah percikan magnetron frekuensi radio. Set pertama untuk sampel konfigurasi tunggal dan set kedua untuk konfigurasi pelbagai. Kesemua sampel tersebut disepuh lindap pada suhu 600°C selama 4 jam di dalam relau. Alat profil permukaan telah digunakan untuk mengukur ketebalan sampel manakala spektrofotometer UV-VIS digunakan untuk mengukur sifat optik. Sistem penderia gas telah digunakan untuk menentukan sifat penderia gas pada 200 ppm nitrogen dioksida, NO₂. Ketebalan sampel adalah dalam julat 132 nm ke 424 nm. Kehantaran dan jurang tenaga optik berkurang dengan pertambahan ketebalan. Rintangan berkurang kepada beberapa kilo ohms apabila suhu operasi untuk kesemua sampel bertambah. Sensitiviti tertinggi untuk konfigurasi tunggal didapati pada sampel C dengan ketebalan 227 nm (45 minit masa pemendapan). Sampel H mempunyai sensitiviti tertinggi (gabungan antara 15 minit + 90 minit masa pemendapan) untuk konfigurasi pelbagai. Oleh itu, masa gerak balas dan masa pemulihan untuk sampel C masing-masing adalah 66.6 saat dan 133.2 saat; manakala untuk sampel H, masa gerak balas adalah 60 saat dan masa pemulihan adalah 333.6 saat.

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LIST OF SYMBOLS

E_c	-	Covalent band edge
E_D	-	Position of the donor level
E_F	-	Fermi level position
E_g	-	Energy band gap
E_v	-	Valence band edge
R	-	Resistance
R_L	-	Load resistance
R_{sa}	-	Resistance of sample in synthetic air
R_{sg}	-	Resistance of sample in test gas
R_s	-	Resistance of the sample
S	-	Sensitivity
T	-	Temperature
t	-	Thin film thickness
V	-	Voltage
V_C	-	Supply Voltage
V_L	-	Load Voltage
P	-	Charge density
Φ	-	Work function
$\varphi(x)$	-	Electrostatic potential
χ	-	Electron affinity
λ	-	Wavelength
ΔR	-	Resistance different
h	-	Planck's Constant
ν	-	Frequency
α	-	Adsorption coefficient
	-	

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Indium tin oxide, ITO or the other synonym tin-doped indium oxide is a mixture of 90% indium oxide, In_2O_3 and 10% tin dioxide, SnO_2 by weight percentage. It has slightly yellow to grey colour in powder form and almost colourless when already being deposited onto the substrate as a thin film. Nowadays, many companies and industries used indium tin oxide in the form of thin film as a gas sensing monitoring system in order to maintain the exposure of the toxic gasses in the surrounding environment. Indium tin oxide has already being adapted in almost many industries in the world because it is cost effective. Furthermore, indium tin oxide is a very stable element and has good stability after long term usage. It also has fast response time and very sensitive towards toxic gasses.

Indium tin oxide thin film has high optical transmittance in the visible region that gives high conductivity. Because of the almost transparent properties of indium tin oxide, it yield low resistivity and give good conductivity due to its addition and increment of carrier concentration. Tin-doped indium oxide has many other applications in industry for examples, liquid crystal display (Pankove *et al.*, 1980), development in television and computer screen. Besides, it also has been used in anti-static coating, solar cell, heat mirror (Chopra *et al.*, 1983; Hamburg *et al.*, 1986), light emitting diode (Kim *et al.*, 1998), flat panel display (Lee *et al.*, 1977) and electroluminescent devices (Meng *et al.*, 1987).

Nowadays, many techniques and methods have been used to deposit metal oxide thin film onto the substrate such as thermal heat evaporation, pulse laser beam exposure, chemical vapor deposition, electron beam thermal evaporation, spray pyrolysis and radio frequency magnetron sputtering. This research work has focused on the uses of radio frequency magnetron sputtering method to deposit indium thin oxide, ITO thin film.

To improve the electrical properties of indium tin oxide thin film to be functional, interdigitated aluminum electrode was deposited onto the sensing layer by using electron beam evaporation machine. Interdigitated electrode was used in order to enhance the sensitivity of the electrical properties and it will amplified the signal because of the small separation between the comb-like design of a few micrometer and less.

1.2 Statement of Problem

In the 21st century, many industries have developed rapidly, especially that result in poor ventilation in humans such as factories that produced electronic devices, medical devices and also universities that runned the experiments using hazardous gases. It is very important to detect those hazardous gases precisely and rapidly. By alerting and monitoring the presence toxic gases, it can prevent or minimize accidents to almost 90% involving poisoning or explosions. Toxic gases, including carbon monoxide, hydrogen sulfide, chlorine, bromine, hydrogen chloride, hydrogen fluoride, nitric oxide, nitrogen dioxide, sulfur dioxide, ammonia, hydrogen cyanide, phosgene, benzene, formaldehyde and methyl bromide are found in a wide range of industries including chemical, petroleum, electronic and also coal, gas, mines, vehicles, sewerage, waste disposal, atmosphere, houses and even battle fields. In the past, certain color changing reagents were adopted to detect these gases by tedious and time-consuming colorimetric or more complicated chromatographic methods. However, in the last ten to twenty years, many techniques have progressed

rapidly and more sensors have been developed for the fast precise detection of various toxic gases.

In this research, nitrogen dioxide, NO₂ gas was chosen because it is one of the most dangerous gases. Thus, to overcome this problem, indium tin oxide, ITO thin film was fabricated to study the sensitivity of the film towards nitrogen dioxide gas at different operating temperature in the laboratory. However, some of the studies have high operating temperature for undoped material and also high response times. (Steffes *et al.*, 2000; Jaswinder Kaur *et al.*, 2007; and Forleo *et al.*, 2005).

1.3 Objectives of the Study

The main objective of this research is to detect the nitrogen dioxide, NO₂ gas by using indium tin oxide, ITO thin film that carried out by radio frequency magnetron sputtering method. Therefore, the research objectives are to:

- a) To deposit the indium tin oxide, ITO onto the corning glass substrate to form thin film layer.
- b) To characterize the optical properties indium tin oxide, ITO thin film.
- c) To detect nitrogen dioxide, NO₂ gas by using Gas Sensor Characterization System (GSCS) for single and sensor array sample.

1.4 Significant of Research

Research towards thin film as a gas sensor will give a lot of benefits to all the heavy industry in Malaysia especially the one that handle or contribute to producing hazardous gasses such as nitrogen oxide, NO, carbon monoxide, CO, nitrogen dioxide, NO₂ and methane. This hazardous gas is very harmful and fatal to human being and will caused chronic diseases such as asthma, brain cancer, chemical

poisoning and genetic damage. Thus, this research is to prevent these accidents from occurring.

1.5 Scope of the Study

The scope of this research can be divided into five major aspects. The first aspect was to prepare the indium tin oxide thin film by using radio frequency magnetron sputtering at different thickness that was varied by the deposition times which were 15, 30, 45, 60, 75 and 90 minutes.

The second aspect was to apply the heat treatment to indium tin oxide thin film by setting the temperature to 600°C for 4 hours. The purpose of the heat treatment was to produce the fine thin film structure to enhance the electrical properties due to its decrements in resistivity and increase the conductivity by increasing of carrier concentration. This is because the thin film structure already transform from amorphous to crystal (Bhatti *et.al.*, 2002).

The third aspect was to deposit the pair of aluminium interdigitated comb-like electrodes onto the thin film in order to amplify the electrical signal to be detected. The fourth aspect was to characterize the prepared thin film by using UV-Vis spectroscopy and surface profiler to determine the exact thickness. The last aspect was to detect nitrogen dioxide, NO₂ gas by using indium thin oxide, ITO thin film using the Gas Sensor Characterization System (GSCS). The samples were divided into two categories, single configuration samples and sensor array combination.

REFERENCES

- Balasubramaniam, N. and Subramanyam, A. (1988). Effect of Substrate Temperature on the Electrical and Optical Properties of Reactively Evaporated Indium Tin Oxide Films. *Material Science and Engineering*. B1., pp. 279-281
- Bube and Richard, H., (1992). *Electrons in Solids: An Introduction Survey*. 3rd Edition, California: Academic Press Inc.
- Chopra, K.L., Major, S. and Panday, D.K. (1983). *Thin Solid Films*. 102.
- Chopra, K.L., Major, S. and Pandya, D.K. (1983). Transparent Conductor - A status Review. *Thin Solid Films*. 102., pp. 1-46
- Demarne, V. and Sanjines, R. (1992). Thin Film Semiconducting Metal Oxide Gas Sensor. *Gas Sensor-Principles, Operation And Developments*, London: Kluwer Academic. pp. 89-116
- Dunlap, W.C. (1957). *An Introduction to Semiconductor*. Wiley, New York. pp 96
- Fan, J.C.C. and Goodenough. (1977). X-Ray Photoemission Spectroscopy Studies of Sndoped Indium Oxide Films. *Journal of Applied Physics*. pp. 3524-3531
- Forleo. A, Francioso. L, Epifani. M, Copone. S, Taurino. A. M, and Siciliano. P. (2005). NO₂-gas sensing properties of mixed In₂O₃-SnO₂ thin films. *Thin Solid Films*.
- Gospel, W. and Scierbaum, K.D. (1995). SnO₂ sensors: current status and future prospects. *sensors and actuators*. B 26-27., pp. 1-12

- Gupta, L., Mansingh, A. and Srivastava, P.K. (1989). Narrowing and the Band Structure of Tin Doped Indium Oxide Films. *Thin Solid Films*. 176., pp. 33-44
- Hamburg, C.G. and Granquist. (1986). *J. Applied Physics*. R123.60
- Henish, H.K. (1957). Rectifying Semiconductor Contacts. *Oxford Univ. Press London and New York*. pp 251
- Jaswinder Kaur, Somnath Roy. C, and Bhatnagar. M. C. (2007). Highly sensitive SnO₂ thin film NO₂ gas sensor operating at low temperature. *Sensors and Actuators B*.
- Kim, J.S., Granstorm, M., Friend, R.H., Johansson, N., Salaneck, W.R., Daik, R., Feast, W.J. and Cacialli, F. (1998). *J. Applied Physics*. 84.6859
- Lee, B.H., Kim, I.G., Cho, S.W. and Lee, S.H. (1977). *Thin Solid Films*. 25.302
- Meng, L.J., Li, C.H., Zhong, G.Z. and Lumin. J. (1987). 11
- Muhammad Yahaya. (1997). Teknologi Filem Nipis. *Cetakan Pertama, Selangor:Universiti Kebangsaan Malaysia*.pp 30
- Norton, D. (2004). *Mater. Sci. Eng*. R 43-139
- Pankove, J.I., (1980). *Topic in Applied Physics*, Springer, Berlin. vol. 40
- Patel, N.G., Panchal, C.J., and Makhija, K.K. (1994). Use of Cadmium Selenide Thin Film as a Carbon Dioxide Gas Sensor. *Cryst. Res. Technol*. 29., pp. 1013-1020
- Rao, C.N.R., Raveau, B. (1998). Transition Metal Oxide, 2nd edn. *Wiley-VCH, New York*. pp220

Ruddlesden, S.N. and Popper, P. (1958). Acta. Crystallogr. 11-54

Shamsuri, W.N.W. (2006). Development of Carbon Monoxide Gas Sensing System Using Tin Oxide Thin Films As a sensor. *Universiti Teknologi Malaysia, Skudai, PhD Thesis.*

Steffes. H, Imawan. C, Solzbacher. F and Obermeier. E. (2000). Fabrication parameters and NO₂ sensitivity of reactively RF-sputtered In₂O₃ thin films. *Sensors and Actuators B.*

Szczyrbowski, J., Dietrich, A. and Hoffman, H. (1983). Optical and Electrical Properties of R.F. Sputtered Indium-Tin Oxide Films. *Phys Stat Sol (a)*. 78., pp. 243-252

Tariq Bhatti, M., Anwar Manzoor Rana., Abdul Faheem Khan and Iqbal Ansari, M., (2002). Effect of Annealing on Electrical Properties of Indium Tin Oxide (ITO) Thin Film. *Pakistan Journal of Applied Sciences*. 2(5):570-573.

Theodor, D. (2003). Semiconducting Oxides as Gas Sensitive Resistors. *sensor and actuator*. B 57., pp. 1-16

Turnbull, W.R. (1968). Semiconducting Thin Films. *an annotated bibliography, NOLC Rept.* 712-745

Yacobi, B.G. (2003). An Introduction to Basic Principles. *Semiconductor Materials*. ISBN 0306473615., pp. 1-3

Yamazoe, N. and Shimano, K. (2007). Overview of gas sensor technology. *Science and Technology of Chemiresistor Gas Sensor, Nova Publisher Inc.*

Zhang Xin, Song Xia Hui, Zhang Dian-Lin. (2010). Thickness Dependence of Grain size and Surface Roughness for dc magnetron sputtered Au films. *Chin. Phys. B.*