Effect of Deposition Time on the Properties of $ZnSnO_3$ Thin Film for Humidity Sensor Application

NOOR KHADIJAH MD SHAH

Faculty of Electrical EngineeringUniversiti Teknologi MARA

40450 Shah Alam, Selangor, Malaysia

gejah_eja@yahoo.com

Abstract **- This paper presents the research on the effect of deposition time on the properties of $ZnSnO_3$ thin films for humidity sensor applications. This research involves four processes which are preparation of nanostructured ZnO thin films by using RF magnetron sputtering, preparation of $ZnSnO_3$ sol-gel solution, metal contact deposition and characterization of humidity sensor. The electrical and structural properties of $ZnSnO_3$ thin films deposited at different deposition time using Sol-gel immersion-method have been studied. The thin films were characterized using current-voltage (I-V) measurement (Keithley 2400) for electrical and field emission scanning electron microscopy (FESEM) (JEOL JSM 6701F) for structural properties respectively. The humidity measurement was conducted on Au metal contact deposited on $ZnSnO_3$ thin films connected to a circuit using copper wire. The sensor was characterized using I-V measurement (keithley 2400) in a humidity chamber (ESPEC SH-261) and the chamber had been set at room temperature of 25°C. Relative humidity (RH %) is varied in the range of 40 to 90 RH%. The sample with deposition time 2 hour shows good sensitivity material as humidity sensor. The FESEM investigation shows that cubic structure of the thin films' size increase as the deposition time increases.**

Keywords **- Zinc Oxide (ZnO); Tin Oxide (SnO_2); Sol-Gel Immersion Method; Cubic Structure;Sensitivity Humidity Sensor.**

I. INTRODUCTION

The development of nanotechnology provides excellent sensitive material for sensor [1]. Nanotechnology is a new category of technology that involved the precise manipulation of material at the molecular level or a scale of 1 to 100 nanometers, with a nanometer equalling of one-billionth of a meter [2].

In recent years, humidity sensor is becoming an important device for semiconductor manufacturing human comfort [3]. Humidity sensor based on semiconducting oxides has certain advantages when compared to other types of humidity sensor such as low cost, simple construction, small size and ease of placing the sensor in the operating environment [4].An excellent humidity sensor should have high response value, quick response and fast recovery, good reproducibility, broad range of operating and low cost [5].

Tin dioxides SnO_2, an important n-type semiconductor with a wide band gap (Eg= 3.6eV) at 300K, exhibits excellent optical, electrical, chemical properties and high thermal stability [6].Many researches have shown that the semiconductor SnO_2 material is of potential applicability in gas sensor, glass electrodes, secondary lithium batteries, solar cell, transistor and catalyst [6]. Zinc oxide is a semiconductor with a binding energy of 50 meV and band gap around 3.3 eV at room temperature and free exciton energy [7]. ZnO was chosen for this research because of its simplicity, excellent compositional control, lower crystallization temperature and large area coating at low cost [8].

ZnO/SnO_2 can be coupled to form different oxide semiconductors, ZnO and SnO_2 belong to wide direct band gap semiconductor [9]. Difference in their band gap width is also found to be very effective way to slow the recombination of electron-hole pair [9]. The mixture of ZnO and SnO_2 shows high sensitivity due to heterogeneous inter-face between them, the sensitivity, selectivity, response time will be improve for humidity sensing [12].

In recent years doped SnO_2 and SnO_2 based material such as sb doped SnO_2, Zn_2SnO_4 have been studied for special optical and electrical properties [6]. The chemical and physical properties of this material also depend on the size and shapes of particles [6]. Zirong et al reported that during the past few years, many efforts have been done to control the size and shape through lots of strategies, such as oxidation, sol-gel, hydrothermal and other method to fabricate low-dimensional nanocrystals, including nanoparticles, nanorods, nanobelts and nanowires [6]. Among all techniques, sol-gel has been used extensively, being less expensive, simple in operation and easy in control [10]. Sol-gel method includes the process of solution preparation immerse gel reaction and annealing [10]. Tien et al prepared growth of ZnO/SnO_2 nanocomposite by nucleating the nanoroads on the substrate coated with Au islands by MBE technique [11]. Rama et al prepared zinc stannate ($ZnSnO_3$) nanoparticles by a chemical precipitation method for synthesis shown that nanostructured $ZnSnO_3$ most sensitive of humidity in comparison to pure SnO_2 [12]. In this paper, $ZnSnO_3$ was prepared by using sol-gel immersion-method.

$ZnSnO_3$ have been synthesized cubic nanocrystal via a solution at low temperature shown that cubic crystal exhibited high sensitivity and fast response [5]. Coupled oxide semiconductor possess characteristic of both the component oxides and allow the possibility of tuning their material properties as per the requirement for novel applications [9].

If single component oxide is used problem may arise due to their similar sensitivity to different gases [9]. These sensors have poor long-term stability and need high operating temperature. To overcome this problem, one approach is to synthesize this sensor by coupling different oxide semiconductor [9].

In this study the effect of nanostructure $ZnSnO_3$ thin film deposition time (0.5h, 2h, 4h and 6h) on the electrical and structural properties of humidity sensor application were particularly studied. The nanostuctured ZnO thin film as seeded catalyst were prepared by rf magnetron sputtering and cubic stuctured $ZnSnO_3$ based thin film using sol-gel immersion method was investigated also studied.

II. METHODOLOGY

The device configuration in this work is as shown in Figure 1. The implementation of this project was summarized in the flow chart (Figure 2).

A Glass Substrate Preparation and Cleaning Process

The glass is cut into 2.5cm X 2.5cm and cleaned by standard cleaning method. The glass substrates were cleaned using acetone and methanol for 10 minutes in ultrasonic bath. Then DI water was used to rinse the substrates and nitrogen gas is used to dry them.

B Process 1: Preparation of Nanostructured Zno Thin Films

Preparation of ZnO thin films as layer 1 was done using R.F magnetron sputtering method. The zinc oxide thin films were deposited on glass substrate by R.F magnetron sputtering using ZnO target with high purity (99.999%). The sputter was pumped at $5x10^{-4}$ pa using a molecular pump and pure Ar gas (99.99%) at 45sccm mixed with O2 gas at 5sccm flow inside the chamber. The pressure of the system was maintained at 7mTorr. After that the ZnO thin film was annealed at 500°C. The characterization of ZnO was carried out for electrical and structural properties by using current-voltage (I-V) measurement (Keithley 2400) and field emission scanning electron microscopy (FESEM) (JEOL JSM 6701F) respectively.

C Process 2: Preparation of $ZnSnO_3$ Sol-Gel Solution.

$SnCl_4$ $5H_2O$ (60 mmol) and NaOH (400 mmol) were separated dissolved in 200 mL of distilled water. $SnCl_4$ solution was then slowly dropped into NaOH while stirring at 2rpm for 10 minute at 50°C until a transparent solution was formed. Then, the solution containing 6mmol $ZnCl_2$ dissolved in 200ml DI water was introduced to the transparent solution drop by drop under stirring. Next, the solution was sonicated by ultrasonic for 10 minute at 50°C and white slurry was obtained. The white slurry was divided into four, and transferred into a container that contained the template (ZnO thin film). Then, the container was immersed inside a water bath of DI water at 95°C under different time (0.5h, 2h, 4h and 6h). After deposition process the thin films were washed in distilled water and dried for 10 minute at 100°C. Finally, the sample was annealed for 1 hour at 500°C.

D Process 3: Metal Contact Deposition.

In this experiment, the metal contact was deposited on the thin film for I-V measurement by using thermal evaporation. Argon gas bled into a vacuum chamber was ionized in the high vacuum and accelerated towards a gold target. The collision was caused by the sputtering of the gold which was then deposited on the sample placed directly below the target.

E Process 4: Characterization of Humidity Sensor

The characterizations of humidity sensor were carried out to electrical properties, and surface morphology. Electrical characterization was done using 2 probe I-V measurements (Keithley 2400). It was used to study the sensitivity, responsisitivity and stability of the sample inside a humidity chamber (ESPEC SH -261). The temperature was set at 25°C with relative humidity (RH %) varied in the range of 40 to 90 RH%. Surface morphology was characterized using FESEM (JEOL JSM 6701F).

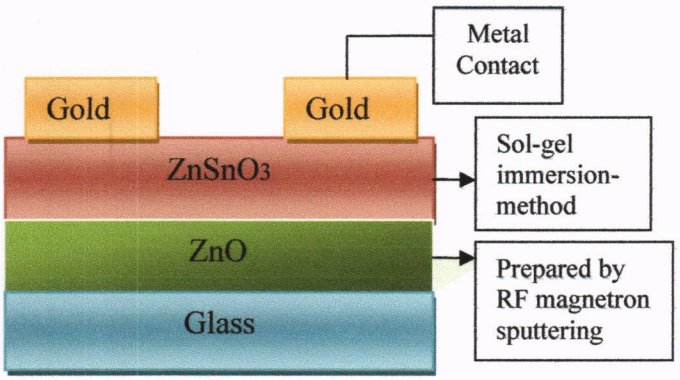

Figure 1: Figure show the device configuration in this work

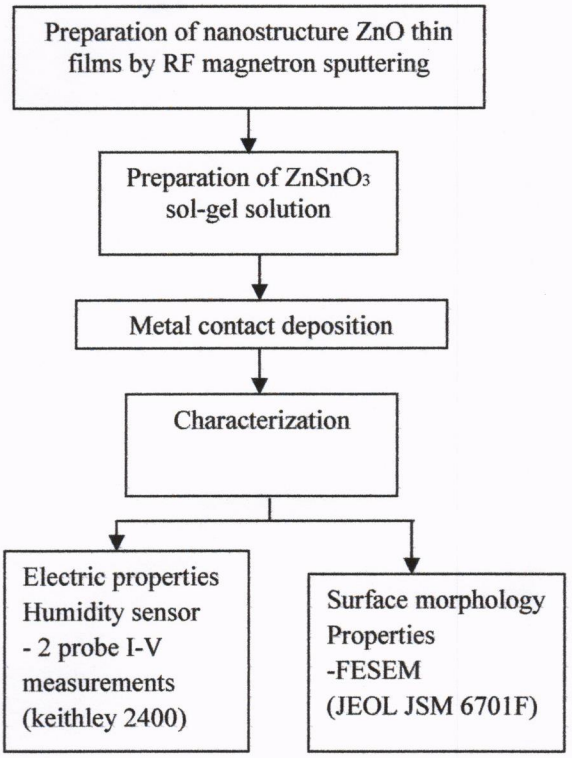

Figure 2: Flow chart of the project development

III. RESULT AND DISCUSSION

A Electrical Properties

Figure 3 shows I-V plot for ZnO prepared by RF magnetron sputtering. Figure 4, 5, 6 and 7 show I-V plots for $ZnSnO_3$ thin films deposited for 0.5 h, 2 h, 4 h and 6 h respectively at different RH% (40 to 90 RH%). 40 RH% indicate dry air 50 to 70 RH% indicate compatible air while 80 to 90 RH% indicate wet condition or moist air. Figure 3 shows ohmic behaviour and Figure 4, 5 and 6 show rectifiers characteristic. When current density increases, the percent humidity of ZnO and $ZnSnO_3$ thin film also increase. This change is due to the water absorption by the nanostructured thin film. The water vapor helps more current flow through the sample with less resistance [3]. Obviously, water vapor in air has strong influence on the conductivity of $ZnSnO_3$ thin films.

At low humidity, only a few water molecules are adsorbed by chemisorption mechanism according to Kulwicki et al. Reported reduction in impedance is due to proton hopping between hydroxyl ions on this layer [13]. But, due to absorption of a few water molecules, this layer is not continuous [13]. So, thin film exhibit higher resistance and lower current at low relative humidity. At high humidity, serial water layer are formed on the surface of the sensing film by physisorption mechanism according to Casalbore- Miceli et al. then reported proton hopping between physisorbed molecules in continuous water layer [13]. So, thin films exhibits lower impedance and higher current at high relative humidity.

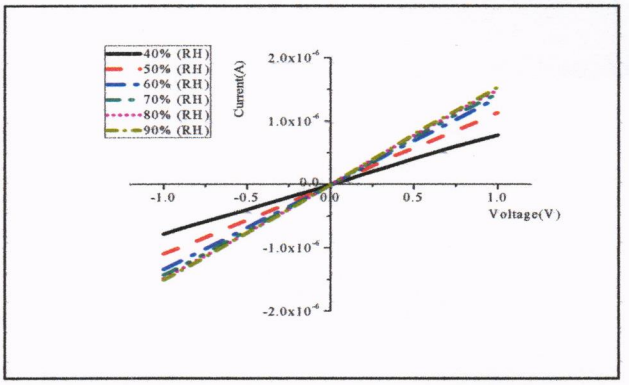

Figure 3: The I-V plot of ZnO by RF magnetron sputtering

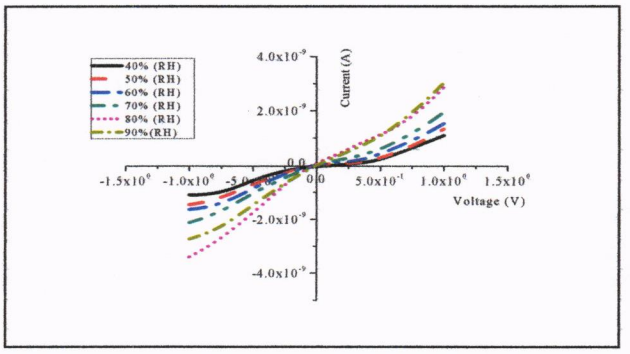

Figure 4: The I-V plot of $ZnSnO_3$ thin films with deposition time of 0.5 hour.

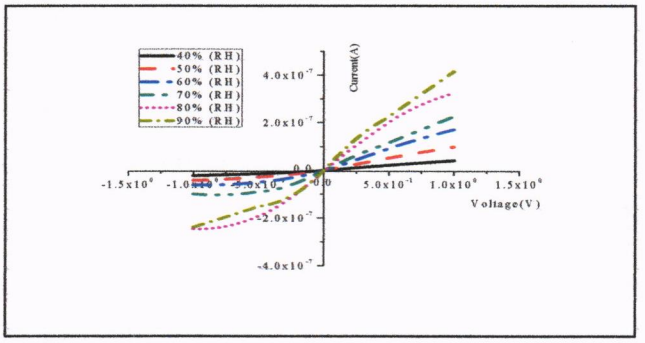

Figure 5: The I-V plot of $ZnSnO_3$ thin films with deposition time of 2 hour

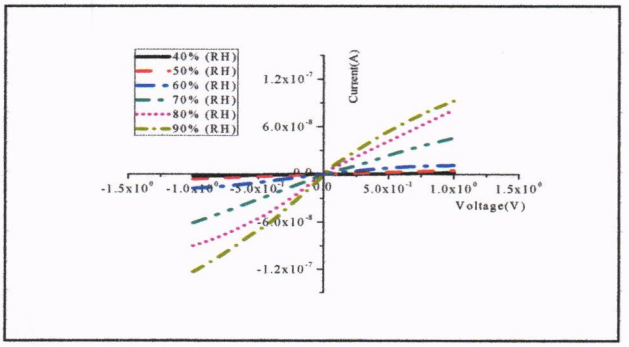

Figure 6: The I-V plot of $ZnSnO_3$ thin films with deposition time of 4 hours

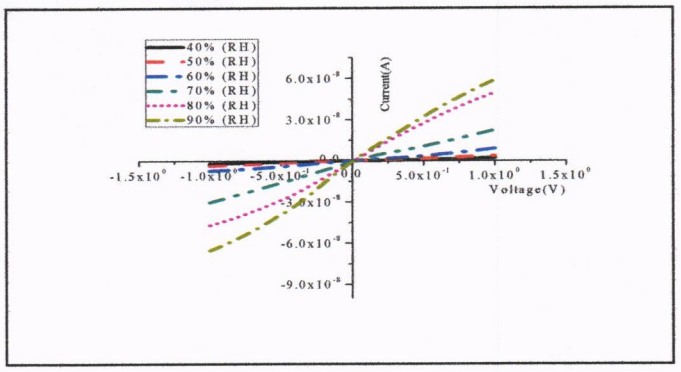

Figure 7: The I-V plot of $ZnSnO_3$ thin films with deposition time of 6 hours

The sensitivity, response, recovery, and reproducibility are important characteristics for evaluating the humidity sensor [4]. Figure 8 shows the current versus relative humidity for ZnO by RF magnetron sputtering, $ZnSnO_3$ thin films deposited for 0.5h, 2 h, 4h and 6h deposition time. The figure also shows variation of current with changes in relative humidity for 40 to 90 RH%. The current increases with increasing the relative humidity. This result shows sample with deposition time 2 hours have better sensing properties and exhibit good linearity with RH compare to other thin films. It occurs due to more water vapor that can be absorbed by the $ZnSnO_3$ sample. M.Parthibavarman et al reported that in general water molecules can be absorbed by physisorption or hydrogen bonding [4]. N.D et al reported that the sensing mechanism is based on the absorption and desorption process between the surface structure and humidity [3]. In this process, more of the surface areas of the sensing element are exposing leading to more adsorption of water molecule [14]. This process causes the sensitivity to increase.

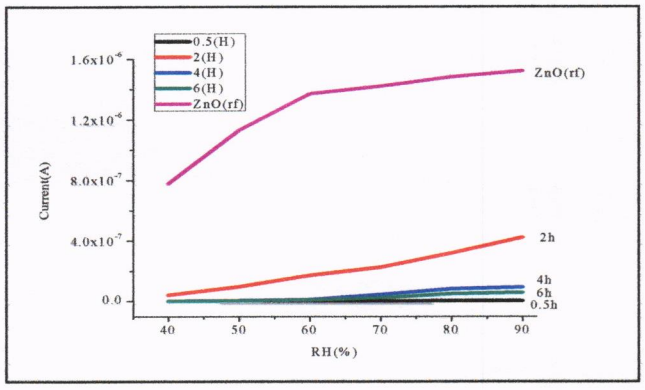

Figure 8: The current versus Relative humidity for ZnO by RF magnetron sputtering, $ZnSnO_3$ thin film with deposition time of 0.5h, 2h, 4h and 6h

In order to examine the repeatability of the sensor, the current in $ZnSnO_3$ thin films was measured for four cycles exposing it from the zero humidity to 90 RH% at 25°C inside humidity chamber and the corresponding current-time are shown in Figure 9. When the sensor was exposed to the moist air of 90 RH%, the current through the $ZnSnO_3$ thin films promptly increase and then gradually reached a relatively stable value. When the sensor was switched to zero humidity the current abruptly decreased and rapidly reached a relatively stable value.

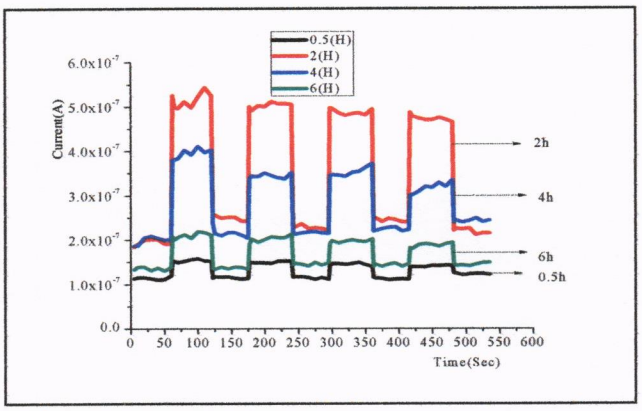

Figure 9: The current versus time $ZnSnO_3$ thin films with deposition time for 0.5h, 2h, 4h and 6h

Figure 10, 11, 12, and 13 show the response and the recovery time for sample fabrication with deposition time of 0.5h, 2h, 4h and 6h respectively. To estimate the response and the recovery time, the $ZnSnO_3$ thin films for 1 cycle with RH changing was exposed repeatedly to zero humidity and then to 90 RH% inside humidity chamber. The response time is defined as the time it takes for the current to increase to maximum value when 90 RH% is created inside the chamber. The recovery time is the time it takes for the current to decrease to minimum value when relative humidity is turned off.

All samples show response and recovery characteristic. The response and recovery time curve of $ZnSnO_3$ films were listed at table 1.

TABLE 1: THE RESPONSE AND RECOVERY TIME OF THE $ZnSnO_3$ THIN FILMS.

Deposition Time (Hour)	Response Time (Second)	Recovery Time (Second)
0.5	19.16	43.44
2	9.58	42.86
4	14.12	51.90
6	14.66	53.28

The recovery time is always greater than the response time. Compare to the other thin films, 2 hour deposition time

better sensitivity, rapid response and fast recovery time and has relatively good repeatability.

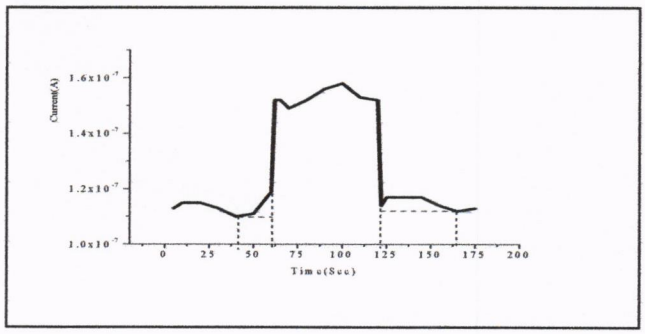

Figure 10: The respond and recovery time for 0.5 h

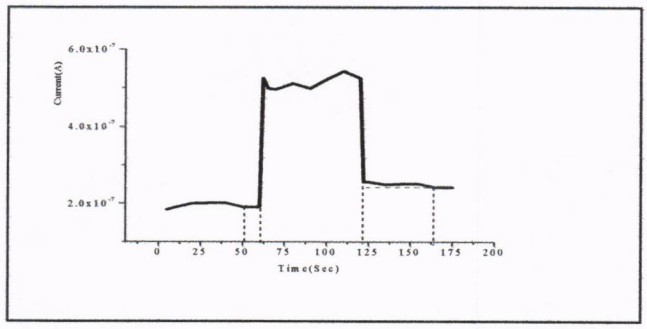

Figure 11: The respond and recovery time for 2h

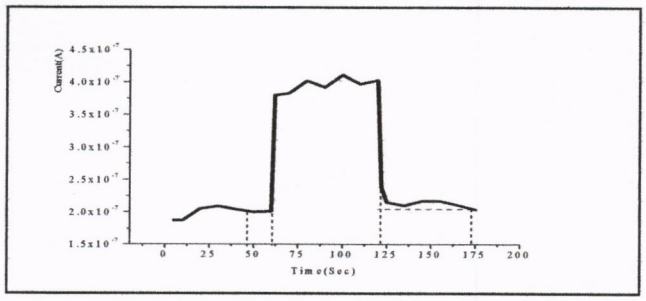

Figure 12: The respond and recovery time for 4h

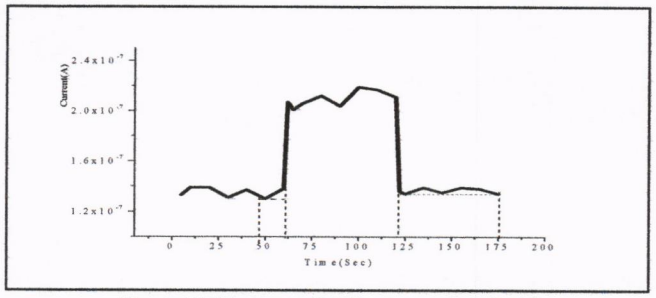

Figure 13: The respond and recovery time for 6 h

To investigate the stability, the $ZnSnO_3$ thin films based humidity sensor was exposed in air for 35 minute and measurement of the impedance once in every 5 minute was performed 90 RH% at 25°C. As shown in Figure 14. Deposition times of 2 hour sample shows more stability then other thin films. There are almost no changes in the resistance, which directly confirm the good stability of the sensor. Furthermore, the 2h sample shows minor changes in resistance, confirming the good stability of this sensor.

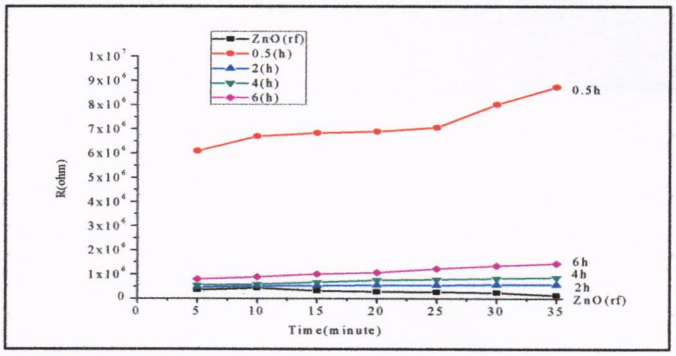

Figure 14: The resistance versus time for ZnO by RF magnetron sputtering, $ZnSnO_3$ thin films with deposition time for 0.5 h, 2h, 4h and 6h

B Structural Properties

The structural properties of the $ZnSnO_3$ were investigated by FESEM and the image 30K magnification in Figure 15 shows ZnO by RF magnetron sputtering and Figure 16, 17, 18 and 19 shows the deposition time for 0.5h, 2h, 4h and 6h. The concentration of NaOH is a very important factor during the reaction. When high concentration of NaOH was added Zn^{2+} will react with OH^- and produced $Zn(OH)_4^{2-}$ phase, which can restrain the formation of $Zn[Sn(OH)_6]$ [6]. The effect of concentration of Zn^{2+} and OH^- on the precipitation phase the action restrain of zinc impurities as generator of the shape controlled structure [6].

The cubic structure size of the $ZnSnO_3$ was evaluated at Table 2.

TABLE 2: THE CUBIC STRUCTURE SIZE OF $ZnSnO_3$ THIN FILMS

Deposition Time (Hour)	Cubic Structure Size (nm)
0.5	99.2 to 139
2	114 to 162
4	147 to 166
6	151 to 168

Because of the non-uniformity of the crystallites, concentration of solutes (or growth nutrients) across the bulk solution varies [15]. Furthermore, for water soluble nanoparticles with solvent that has slow evaporation rate, large scale area assembly with ordered features is typically hard to obtain [16]. In this study, when the deposition time increase the cubic structure size increase.

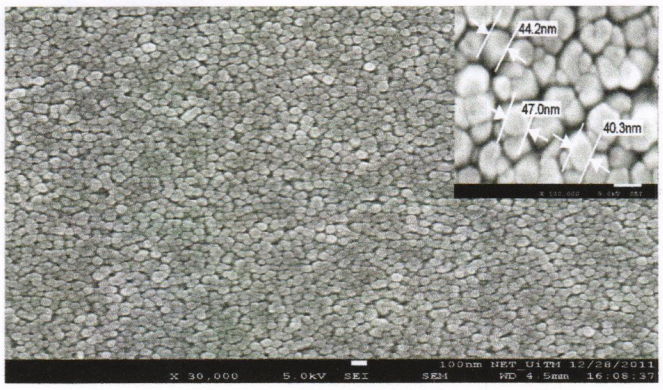

Figure 15: FESEM image of ZnO by RF magnetron sputtering

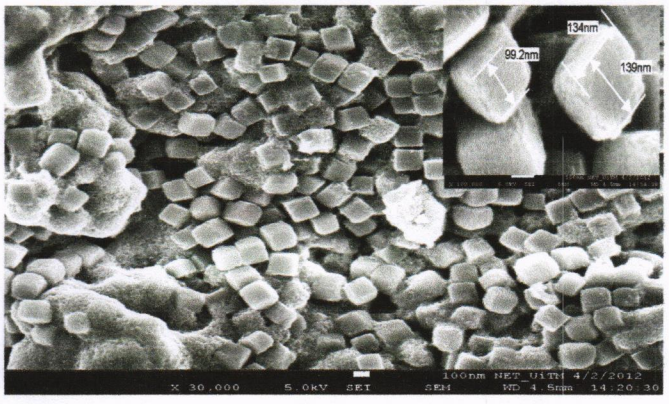

Figure 16: FESEM image of $ZnSnO_3$ thin films deposit for 0.5 hour

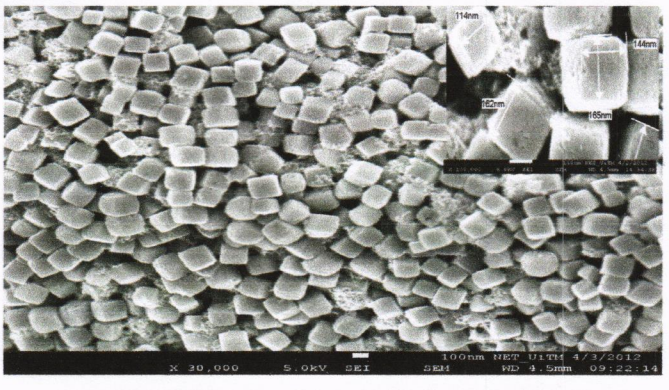

Figure 17: FESEM image of $ZnSnO_3$ thin films deposit for 2 hour

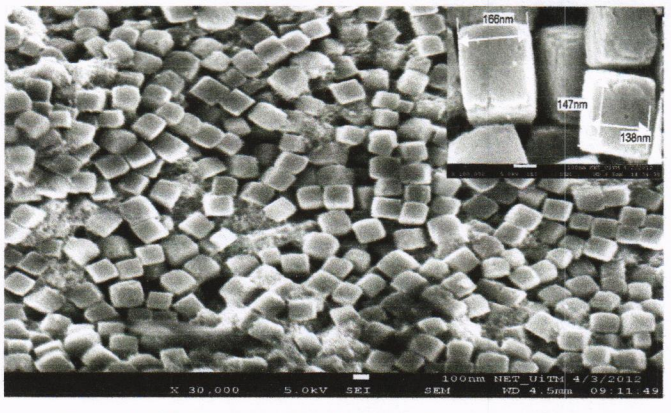

Figure 18: FESEM image of $ZnSnO_3$ thin films deposit for 4 hour

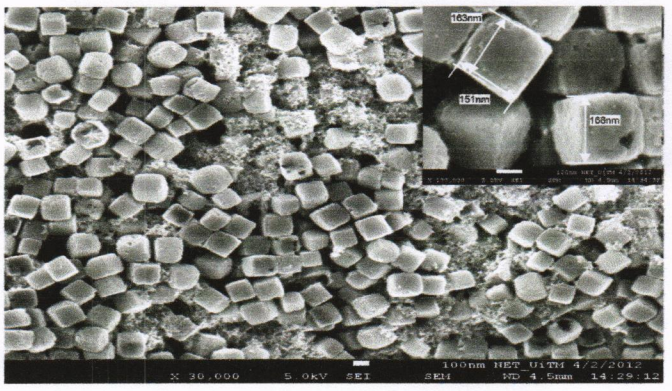

Figure 19: FESEM image of $ZnSnO_3$ thin films deposit for 6 hour

IV. CONCLUSION

In summary, $ZnSnO_3$ thin films have been successfully prepared on the glass substrate by varying the deposition time using sol-gel immersion method. The electrical properties of $ZnSnO_3$ were investigated by using I-V measurement in the humidity chamber. The sample with deposition time of 2 hour show highest sensitivity, repeatability, and stability compared to other thin films. It occurs due to the sample sensitively to oxygen and water vapor in air. The images of FESEM show that the particles size of $ZnSnO_3$ thin films increase when the deposition time increase. Furthermore a $ZnSnO_3$ thin film deposited for 2 hour also has a fast response in air and at the same time its sensitivity is linear with RH in air. Therefore, $ZnSnO_3$ thin films can effectively used for better sensing application and quite promising for the fabrication of a practical humidity sensor. For future work it is recommended to vary the molarity of zinc to decrease size of cubic to form the nanostructured or nanocubic thin films.

ACKNOWLEDGEMENT

I would like to convey my deepest gratitude and appreciation to my project supervisor, Mr Uzer Mohd Noor and Mrs Nor Diyana for invaluable suggestion, guidance, advice and discussions for the completion and success of this project. I would like to take this opportunity to express my appreciation to my family and friends for gives a lot of support until completion of my study.

REFERENCES

[1] NiZ Zifeng,Cheng Guomei, Ying Pengzhan" Synthesis and gas sensitivity of sno2 nanoparticles" *advance material research* vol 279(2011) pp-93-96

[2] M. T. Abuelma'atti, "Nanotechnolgy: Benefits, risks and ethical issues," in *GCC Conference & Exhibition*, 2009 5th IEEE, 2009, pp. 1-5.

[3] N. D. Md Sin, S. A. Kamaruddin, M. Z. Musa, and M. Rusop, "Effect of deposition time SnO_2 thin film deposited using thermal CVD for humidity sensor application," in *Industrial Electronics and Applications* (ISIEA), 2011 IEEE Symposium on, pp. 459-462.

[4] M. Parthibavarman, V. Hariharan, and C. Sekar, "High-sensitivity humidity sensor based on SnO_2 nanoparticles synthesized by microwave irradiation method," *Materials Science and Engineering*: C, vol. 31, pp. 840-844.

[5] D. Bauskar, B. B. Kale, and P. Patil, "Synthesis and humidity sensing properties of ZnSnO3 cubic crystallites," *Sensors and Actuators B: Chemical*, vol. 161, pp. 396-400.

[6] Z. Li, X. Li, X. Zhang, and Y. Qian, "Hydrothermal synthesis and characterization of novel flower-like zinc-doped SnO2 nanocrystals," *Journal of Crystal Growth*, vol. 291, pp. 258-261, 2006.

[7] N.D Md Sin, M.Z.Musa,M.Rusop " effect of R.F power to the properties of ZnO Thin Films Deposited by Magnetron Sputtering" *Advance Material Research* Vol.364 (2011) pp 119-123.

[8] Sin, N.D.M.; FuadKamel, M.; Mamat, M.H.; Mohamad, Z.; Alip, R.I.; Rusop, M.; , "A novel fabrication process for nanostructured Al-doped ZnO thin film based humidity sensors," *Electronic Devices, Systems and Applications* (ICEDSA), 2011 *International*

[9] Kandasami Asokan,JaeYoung Park,Sun-Woo Choi, and Sang Sub Kim "Nanocomposite ZnO–SnO_2 Nanofibers Synthesized by Electrospinning Method" 2010 vol 5(4) pg 747–752

[10] Qi Xiao, Rui Wang, Lei Xu "Annealing Treatment of the SnO2 Thin Film Prepared by Sol-gel Method" *Advanced Materials Research* Vol. 331 (2011) pp 194-197

[11] S. K. Tripathy, T. Sahoo, I.-H. Lee, and Y.-T. Yu, "Synthesis, characterization and photoluminescence studies of ZnOrod@SnO2 nanocomposites," *Materials Letters*, vol. 61, pp. 4690-4693, 2007.

[12] Rama Singh, Avadhesh Kumar Yadav, Chandkiram Gautam " Synthesis and Humidity Sensing Investigations of Nanostructured ZnSnO3" *Journal of Sensor Technology* vol 1 (2011) pp 116-124

[13] M. Anbia and S. E. M. Fard, "Humidity sensing properties of Ce-doped nanoporous ZnO thin film prepared by sol-gel method," *Journal of Rare Earths*, vol. 30, pp. 38-42.

[14] N. K. Pandey, K. Tiwari, and A. Roy, "Ag Doped WO3 Nanomaterials as Relative Humidity Sensor," *Sensors Journal, IEEE*, vol. 11, pp. 2911-2918.

[15] Hua Chun Zeng "Ostwald Ripening: A Synthetic Approach for Hollow Nanomaterials" *Current Nanoscience*, vol 3, pp.177-181, 2007

[16] J.Yang, L.Levina, E.D.Sargent and S.O.Kelley " Heterogeneous deposition of nobel metals on semiconductor nanoparticles in organic or aqueous solvent" *journal of materials chemistory* ,vol.16 ,pp.4025-4028