Effects of Molar Ratio of Zn:Sn on the Properties of ZnO/SnO_2 Humidity Sensor

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***Abstract* - In this research ZnO thin films prepared by rf magnetron sputtering and ZnO/SnO_2 cubic structure thin films developed by immersion method are reported. The effects of molar ratio Zn/Sn that varies from (1:10, 2:10, 3:10, 4:10) on the ZnO/SnO_2 thin films were characterized by using 2 probe I-V measurement (Keithley 2400) inside a humidity chamber (ESPEC SH-261) for electrical properties. The surface morphology of ZnO/SnO_2 thin films were characterized by using Field Emission Scanning Electron Microscopy (FESEM) (JEOL JSM 6701F). The parameter of molar ratio 4:10 shows high sensitivity and therefore is suitable for humidity sensor application. The size of cubic structure thin films decrease as the molar ratio of Zn/Sn increase.**

***Keywords* – ZnO; ZnO/SnO_2; immersion method; molar ratio; electrical properties; cubic structure.**

I. INTRODUCTION

Nanotechnology is the research and technology development at the molecular or macromolecular levels on the nanometer length scale (1-100 nm). Nanotechnology provides a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and system that have novel properties and functions because of their small or intermediate size [1]. The development of humidity sensor is increasingly in demand for research and application in technologies for environmental monitoring in both living and manufacturing spaces [2]. The criteria for a desirable humidity sensor include high sensitivity, long-term durability, fast response, low cost, and operation over a wide range of humidity and temperature [3]. So, the selection of a material should be based on certain conditions, in order to assure the satisfactory operation of the humidity sensor [4]. One of the popular materials that had been used is semiconducting oxides because of certain advantages include low cost, simple construction, small size and ease of placing the sensor in the operating environment [5].

Composite sensor may improve the reliability since it contains many hetero-contacts produced by the sintering of each phase. Some composites have the unique properties not observed in each component [6]. Among the semiconducting oxides, SnO_2 and ZnO are the most commonly used materials and have been widely studied due to their range of conductance variability and their response towards both oxidative and reductive gases [7]. Various deposition methods have been applied to deposit transparent and conducting ZnO, SnO_2 and zinc stannate thin films, including spray pyrolysis, vacuum evaporation, magnetron sputtering, molecular beam epitaxy (MBE), reactive ion assisted deposition and filtered vacuum arc deposition (FVAD) [8]. It is well known that SnO_2-based sensors containing smaller particles show high sensitivity [9].

However, they still have problems such as long-term instability and sensitivity to ambient humidity. Poor selectivity is another problem caused by the surface-controlled reaction [6]. Zinc oxide (ZnO) is a semiconducting II-VI metal oxide [9]. ZnO is an important material in many applications such as varistors, gas sensors, etc [9, 10]. Dipak Bauskar et al. reported on humidity sensing properties of $ZnSnO_3$ cubic crystallites synthesized by a hydrothermal method. The sensor exhibits excellent humidity sensing characteristics such as fast response time, rapid recovery, linearity, excellent repeatability, good stability and broad range of operation [11]. Vaezi et al. examined the sensing properties of SnO_2/TiO_2 core shell nanocomposite that was prepared by sol gel processing. The sensors based on SnO_2/TiO_2 core shell nanocomposite show improvements in sensing behaviour [12].

The objectives of this research to study the effect of molar ratio Zn/Sn on the electrical properties and surface morphology for humidity sensor application characteristics of ZnO/SnO_2 cubic structure thin films.

II. METHODOLOGY

A. Cleaning Process

Firstly, the glass substrates had been cut by using diamond cutter into a size of 2cm x 2cm. The substrates were immersed inside acetone. Then, the substrates were sonicated by using ultrasonic cleaner for 10 minutes at 50°C. After that, DI was used to wash the substrates. Next, the above steps had been repeated by replacing acetone with methanol. Then, the substrates were immersed inside water bath with DI water inside. Lastly, the substrates were drying by using nitrogen gas. The cleaning process is needed in order to remove organics residues which appear on glass surfaces.

B. Preparation of Nanostructured Zinc Oxide Thin Films

ZnO thin films were deposited on glass substrates by radio frequency (RF) magnetron sputtering using SNTEK model. ZnO with high purity (99.999%) was used as target. The sputter was pump at $5x10^{-4}$ Pa using a molecular pump and the chamber was filled with pure Ar gas (99.99%) at 45sccm and O_2 at 5sccm. The deposition was carried out for 60min at 500°C and the pressure of the system was maintained at 7mTorr.

C. Preparation of ZnO/SnO_2 Sol-Gel Solution

Experiment procedures were as follows: First, $SnCl_4.5H_2O$ (3mmol) and NaOH (20mmol) was dissolved in 50mL distilled water for each, respectively. Then, both solutions were under magnetic stirring at 2rpm for 10minutes at 50°C. Then, $SnCl_4$ solution was taken and slowly dropped into NaOH solution under magnetic stirring with the same condition as before. Next, $ZnCl_2$ (0.3mmol) solution was introduced to the solutions under stirring. Then, the solution was sonicated by ultrasonic for 10 minutes at 50°C to obtain white slurry. Lastly, the white slurry was transferred into a container contain the sample of ZnO thin film. Then, the container was immersing inside the water bath with 95°C DI water inside. The thin films were washed in distilled water and dried sample at 100°C for 10minutes after deposition. Finally, the samples were annealed in the furnace at 500°C for 1hour. The experiment was repeated with different amount of $ZnCl_2$.

D. Metal Contact Deposition

The metal contacts were deposited on the SnO_2 for I-V measurement purpose using thermal evaporator and sputter coater method. The metal contact is use to attract or transmit the signal efficiently from the thin film to external circuit at humidity atmosphere.

E. Characterization of Humidity Sensor

Sensor performance was measured using 2 probe I-V measurement (Keithley 2400) to study sensitivity, responsistivity and stability inside a humidity chamber (ESPEC SH-261). The temperature was set at room temperature (25°C) while relative humidity (RH %) is varied in the range 40 to 90 RH%. The humidity sensitivity measurement was conducted for the fabricated device with Au as the metal contact. The FESEM (JEOL JSM 6701F) used to characterize surface morphology ZnO/SnO_2 thin film deposited on the substrates. Figure 1 shows the flowchart of overall experimental procedures in this project and Figure 2 shows the device structure that had been characterized.

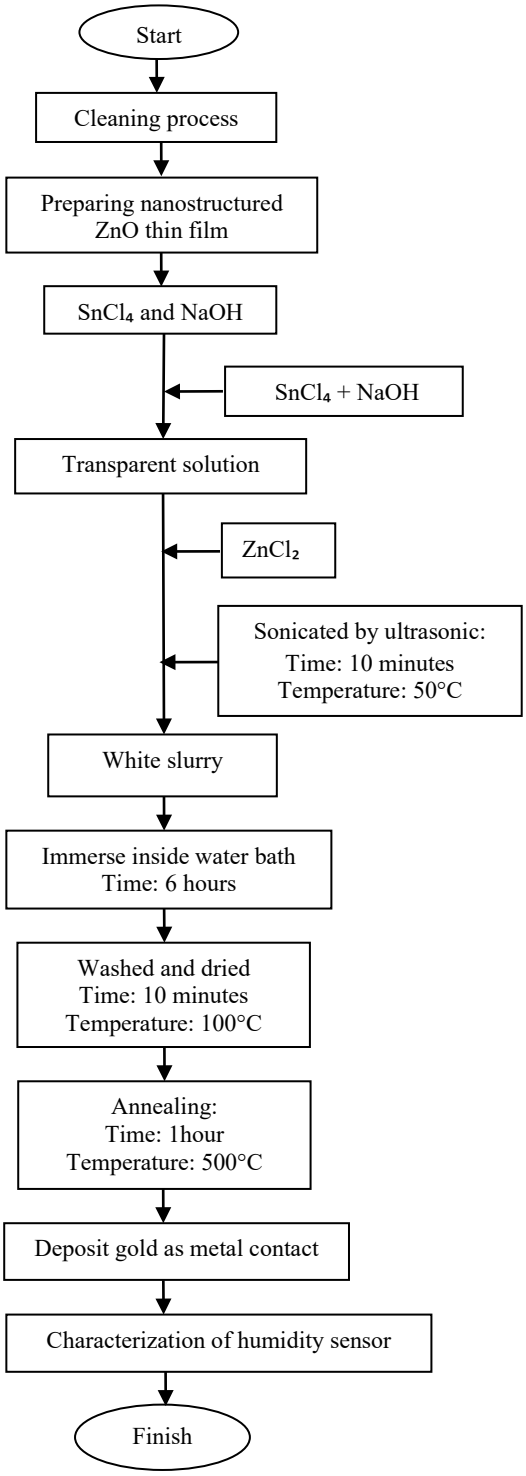

Figure 1: Flowchart of the methodology for the project

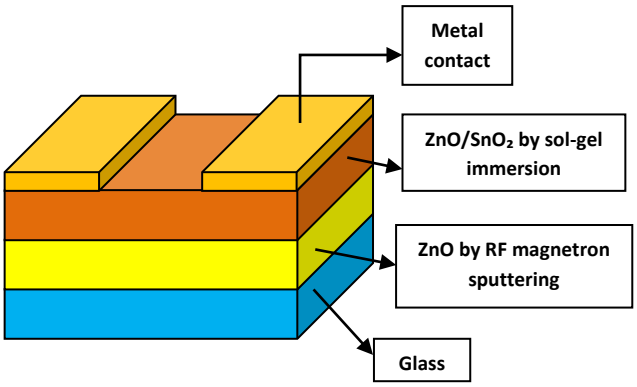

Figure 2: Diagram of the device configuration that had been characterized

III. RESULT AND DISCUSSION

A. Electrical Properties

Current and voltage was measured using 2 probe I-V measurement (Keithley 2400). Figure 3 show the I-V graph for zinc thin film by RF sputtering at different relative humidity (40-90RH%). Figure 4, 5, 6 and 7 shows current versus voltage graph of ZnO/SnO_2 thin films for molar ratio 1:10, 2:10, 3:10 and 4:10 for different relative humidity (40-90RH %) at 25°C temperature. It can be seen that the current increase with the increasing of relative humidity. This happen due to the condition where the structures of ZnO/SnO_2 thin films absorbed the water vapour. The current flow with less resistance due to the existence of the water vapour thus more current can pass through the sample as the relative humidity increase. This shows that ZnO/SnO_2 materials have the ability to absorb water vapour from the surroundings. It can be prove that the ZnO/SnO_2 thin films can increase the sensitivity of the humidity sensor [13].

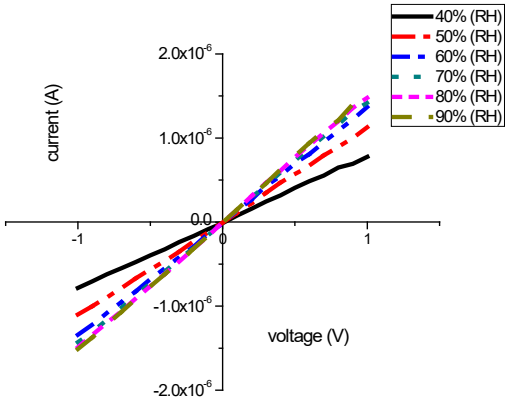

Figure 3: I-V graph for zinc thin film by RF sputtering at different RH%

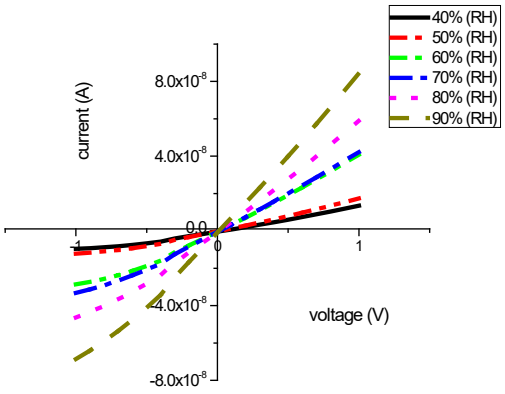

Figure 4: I-V graph for molar ratio 1:10 Zn/Sn at different RH%

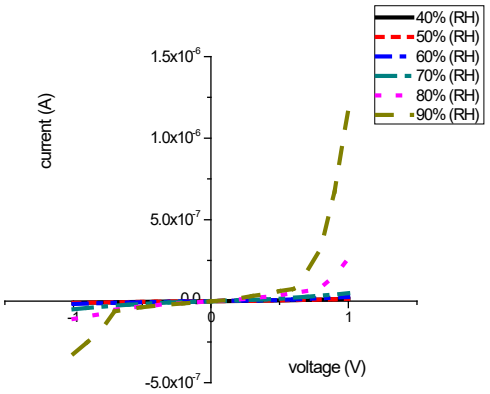

Figure 5: I-V graph for molar ratio 2:10 Zn/Sn at different RH%

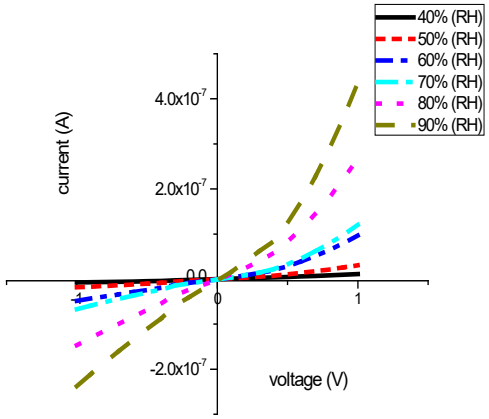

Figure 6: I-V graph for molar ratio 3:10 Zn/Sn at different RH%

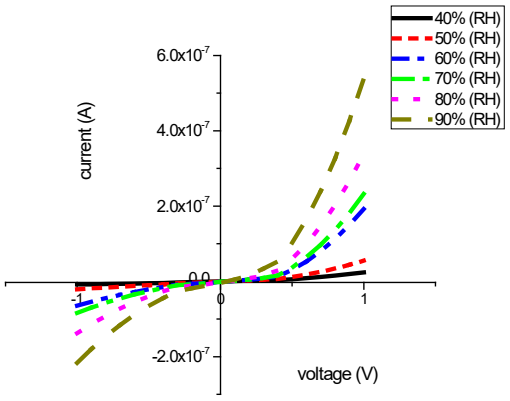

Figure 7: I-V graph for molar ratio 4:10 Zn/Sn at different RH%

More information on the most important parameters for a sensing device which are sensitivity, response and recovery time, and repeatability were provided by carried out further dynamic testing procedures. Figure 8 shows the current versus relative humidity graph. Generally, it can be seen that the current increase with an increasing of the relative humidity. The sample with molar ratio 4:10 has a higher sensitivity than the other samples. These results indicate that the water vapour in air gives a strong impact on the current of the ZnO/SnO_2 cubic structure thin films. In general, water molecule acts as donor contributing electrons to the semiconducting oxides materials. At 80RH%, the current of the sample of molar ratio 2:10 tend to increase dramatically. It might be because at high humidity, liquid water starts to condense in the pores between the cubes, leading to the limited surface diffusion of water molecules. Then the electrolytic conduction between cubes takes place along with protonic transport. These phenomena interpret the nonlinear behavior of the sensitivity fluctuated at high humidity [14].

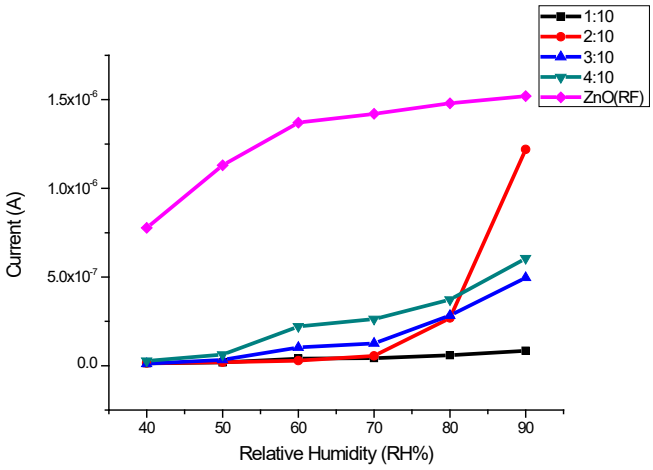

Figure 8: Current versus Relative Humidity, RH%

Figure 9, 10, 11 and 12 show the response and recovery time of 1:10, 2:10, 3:10 and 4:10 Zn:Sn. It is known that the response and recovery behavior are the important characteristics for evaluating the performance of humidity sensor [5]. For calculation of response time, the humidity in the chamber has been switched over from 0RH% (low humidity) to 90RH% (high humidity) and for calculation of recovery time the humidity in the chamber has been brought down from 90RH% (high humidity) to 0RH% (low humidity) [15]. The response time defined here as the time it takes for the current of ZnO/SnO_2 cubic structure thin films to increase to 90% of the maximum current when relative humidity is created inside the chamber. The recovery time is the time required for 90% decrement in current when relative humidity is turned off [5].The response and recovery times of ZnO/SnO_2 humidity sensor are shown in Table 1. Adsorption and desorption of the water molecules take place at different energy levels. Adsorption is an exothermic process, where as desorption needs external energy for water molecules to depart from the metal oxide surface. Since desorption is an endothermic process, it takes a longer time to desorb the water vapor; therefore, the recovery time is always greater than the response time [15].

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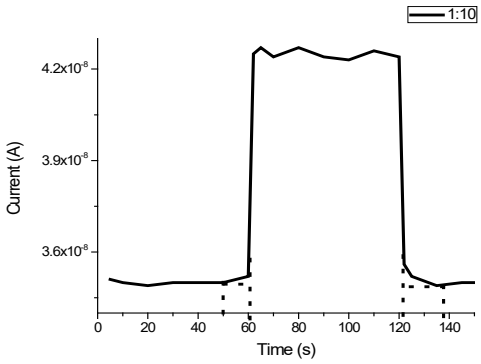


Figure 9: Response and recovery time for molar ratio 1:10

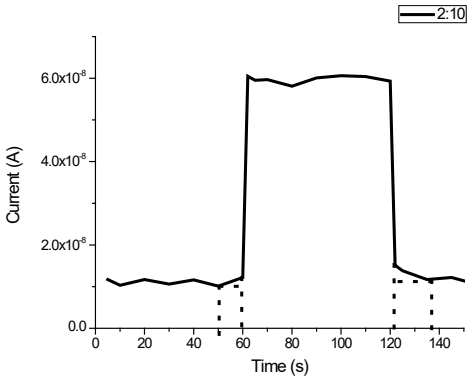


Figure 10: Response and recovery time for molar ratio 2:10

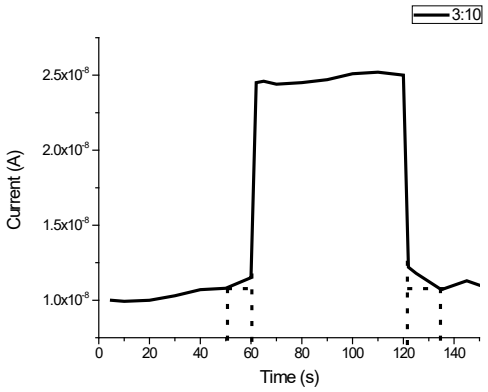


Figure 11: Response and recovery time for molar ratio 3:10

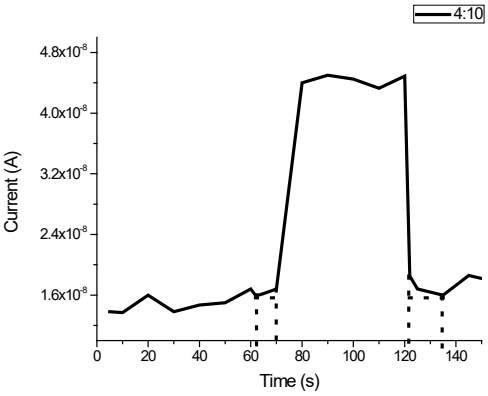


Figure 12: Response and recovery time for molar ratio 4:10

TABLE 1: RESPONSE AND RECOVERY TIME OF ZnO/SnO_2 HUMIDITY SENSOR

Molar Ratio (Zn/Sn)	Response Time (second)	Recovery Time (second)
1:10	11	16
2:10	10	15
3:10	9	14
4:10	8	13

Figure 13 shows a series of current response of the ZnO/SnO_2 cubic structure thin films. To estimate the repeatability the ZnO/SnO_2 cubic structure thin films was exposed from 0 RH% to 90RH% for 4 cycles at 25°C inside humidity chamber. When the ZnO/SnO_2 cubic structure thin films was exposed to the moist air of 90RH%, the current of the ZnO/SnO_2 cubic structure thin films rapidly increased and then gradually reached a relatively stable value. When the ZnO/SnO_2 cubic structure thin films was switched to dry air again, the current abruptly decreased and rapidly reached a relatively stable value [14].

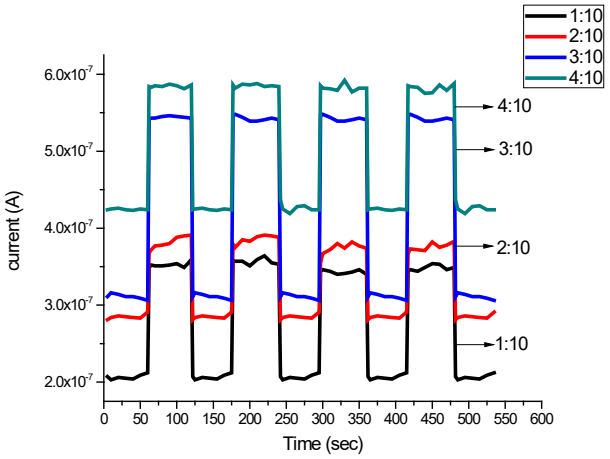


Figure 13: Repeatability graph of ZnO/SnO_2 humidity sensor performance

The resistance variations with time for ZnO thin film by RF samples of the ZnO/SnO_2 cubic structure thin films are shown in Figure 14. To study the stability, all samples were exposed to 90RH% at 25°C for 10 hours. The measurements were repeated every 2 hours. Slight variation in resistance is observed over time. It shows that the resistance of the samples is relatively stable to the exposure to water in air [16].

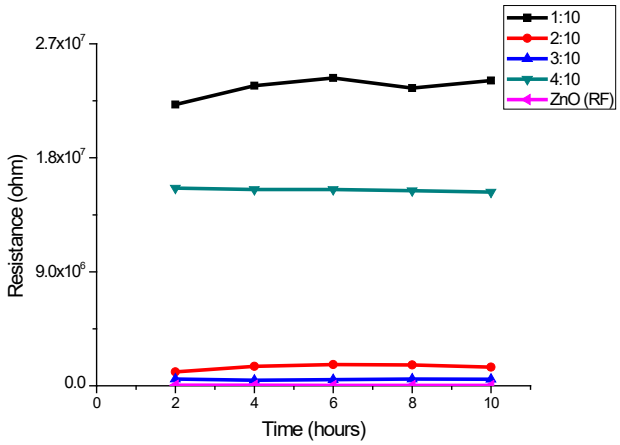


Figure 14: Resistance variations with time for samples ZnO, 1:10, 2:10, 3:10 and 4:10 Zn:Sn

B. Surface Morphology

The surface morphology of ZnO/SnO_2 thin films was measured by using Field Scanning Electron Microscopy (FESEM). Figure 15 shows the FESEM image of ZnO thin film by RF. Figure 16 show FESEM images ZnO/SnO_2 thin films with different molar ratio of Zn: Sn at (a) 1:10, (b) 2:10, (c) 3:10, (d) 4:10. All images were taken at 5kV with 30K and the inset images show the measurement of cubic size. It can be seen that the size of cubic size decrease as molar ratio of Zn:Sn increase with the size of 1:10 (270nm), 2:10 (139nm),

3:10 (117nm) and 4:10 (78.2nm). This might be due to the segregation of a ZnO/SnO_2 phase at the grain boundaries, which might decrease the grain boundary mobility leading to a decrease in the grain size [17].

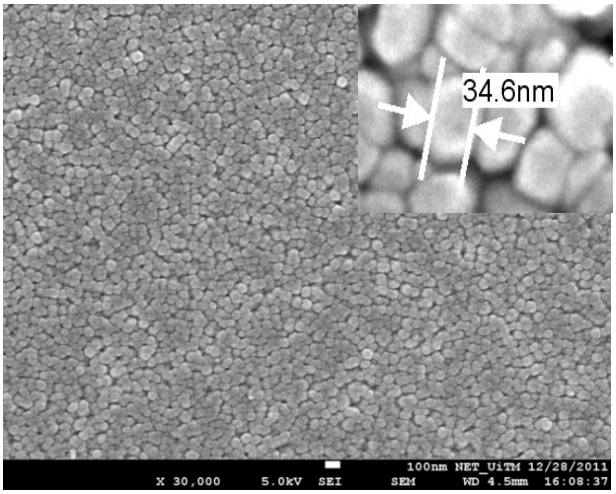
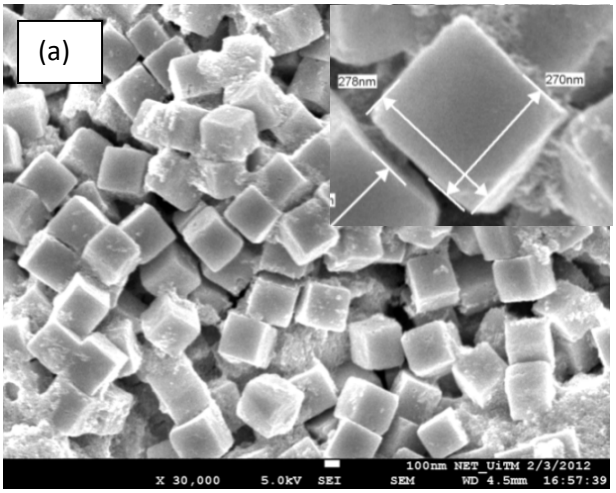
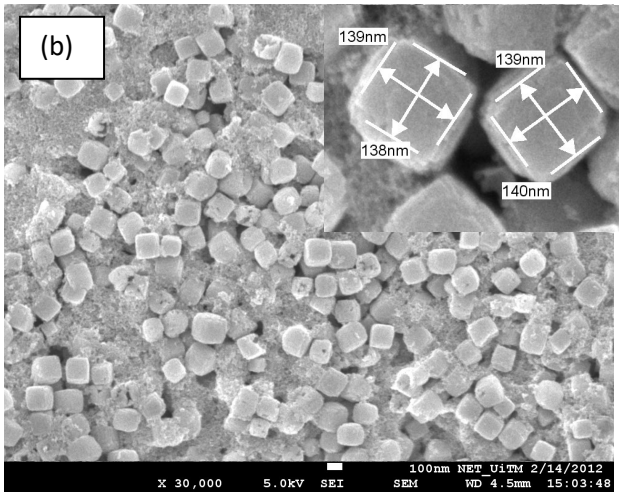
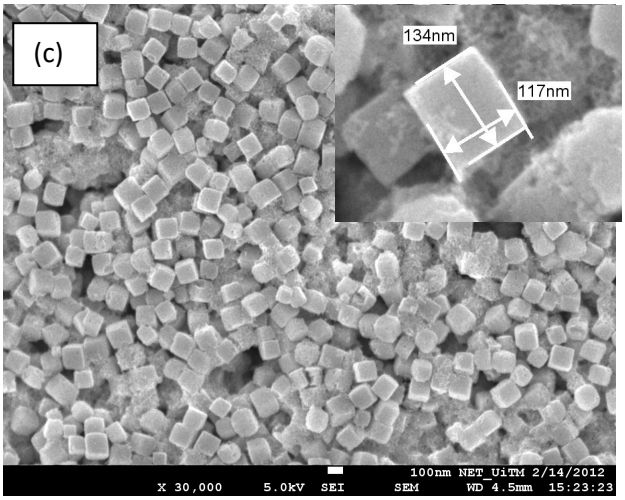


Figure 15: FESEM images of ZnO thin film by RF sputtering







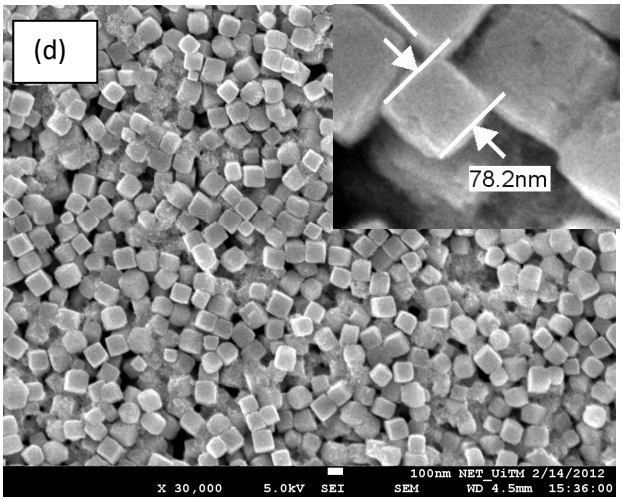


Figure 16: FESEM images of SnO_2/ZnO thin films at molar ratio (a) 1:10, (b) 2:10, (c) 3:10, (d) 4:10

IV. CONCLUSION

ZnO/SnO_2 thin films have been successfully deposited by using sol-gel immersion method. The I-V graph shows the current increase proportionally with humidity due to the changes of resistance. The current versus relative humidity (RH%) graph show the highest sensitivity is at molar ratio 4:10 of Zn:Sn. It also show good characteristic of repeatability, high stability and high response and recovery time. Therefore, the sample with molar ratio 4:10 is suitable for humidity sensor. This result was support by surface morphology of thin film. Based on FESEM the sizing of the particle size of ZnO/SnO_2 cubic structure thin films at molar ratio 4:10 is small compared to other parameters. For future works, it is recommended to investigate other parameters in order to further reduced particle size. This will increase the surface area which increases sensor performance/sensitivity.

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