# Fabrication of Humidity Sensor Deposited by Sol-Gel Immersion Method of Nano-Cubic Structured Znsno$_3$/Zno Based Thin Film

N.D. Md Sin, M.H. Mamat, Abdul Aziz. A and M. Rusop

***Abstract*— Nano-cubic Zinc Stannate ($ZnSnO_3$) was synthesis by sol-gel immersion method growth on zinc oxide (ZnO) template prepared by RF magnetron sputtering. Using field emission scanning electron microscopy (FESEM) it was noted that the distribution of nanocubic $ZnSnO_3$ growth on ZnO template ($ZnSnO_3$/ZnO) increase as the precursor solution volume increase. The photoluminescent spectra of $ZnSnO_3$/ZnO reveal emission at 417 nm and 644 nm. The measured humidity sensor has been exhibited in good agreement with the performance by using a nano-cubic ZnSnO3/ZnO with a sensitivity ratio of about 209. The response and recovery times nano-cubic $ZnSnO_3$/ZnO were about 409s and 9s respectively. The sensor shows a good repeatability characteristic after had been radiated towards humidity at 4 cycles.**

**Index Terms— nano-cubic; $ZnSnO_3$; immersion method; humidity sensor**

## I. Introduction

RECENTLY, many researchers have given much attention to develop three dimensional (3D) nanostructures such as nanocubic, nanosphere and nanoflower, due to high specific area and highly functional for sensor application. The sensitive material of 3D nanostructures are promote for the diffusion of gas molecules which is important to improve the sensor performance [1-3]. The crucial issue to enhance the humidity sensor performance including increasing sensitivity, fast response and recovery times, reproducibility, good in stability, and wide range operation are directly required. Due to that, selecting a good material as a medium sensing, providing high surface area and high porosity are the recommended. Zinc stannate ($ZnSnO_3$) is well known material, has received extensive investigation for the capability in performing excellence device in nanotechnology. It has been studied widely for gas sensor application but less for humidity sensor. $ZnSnO_3$ has attracted attention for sensor application for having high electron mobility[4], low visible absorption and high chemical sensitivity[5]. Many technique such as thermal evaporation[6], low temperature ion exchange[7], co-precipitation[8], sputtering [9] and hydrothermal [3, 10-11] have been used to engineer different type of $ZnSnO_3$ nanostructures. The hydrothermal process is simple wet chemical processes that used low processing temperature and provide large-scale production. Various type of $ZnSnO_3$ nanostructure has been reported such as sphere[3], hexagon[2] , cubic[12] and rods[13].

The chemicophysical parameter such as temperature, reaction duration time, concentration and surfactant plays significant role to control of the energy in the nucleation and crystal growth[14]. These factors are favourable to enhance sensing performance. Wang et al[15] reported on the synthesis of ZnSnO3 cubic structures for formaldehyde (HCHO) sensor by controlling the reaction time, temperature,

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perform high sensitivity, fast response and recovery times to detect HCHO gas. Aarthy et al [16] reported the preparation of zinc stannate microcubic growth on ZnO nanorod for Liquefied Petroleum Gas (LPG) sensing and found that the surface modification of

ZnO nanorods using Zinc Stannate microcubes thus increase the sensing performance. Dipak et al [17] synthesized ZnSnO3 microcubes via spin coating process deposited on alumina substrate exhibit excellent humidity sensing properties. This paper focus on the effect of precursor volume solution on the nano-cubic structured ZnSnO3 that has been deposited using ultrasonic sol-gel immersion method on a ZnO template prepared by RF magnetron sputtering. The template favourable to enhanced sites for water vapour molecular adsorption and lowers the activations energy required for the sensing reaction to take places. The sensitivity of as-prepared sample towards humidity was investigated of humidity sensor properties. To the best our knowledge, there is no report on nano-cubic structured ZnSnO3/ZnO prepared using ultrasonic sol-gel and immersion method at different precursor volume solution.

## II. METHODOLOGY

### A. Material preparation

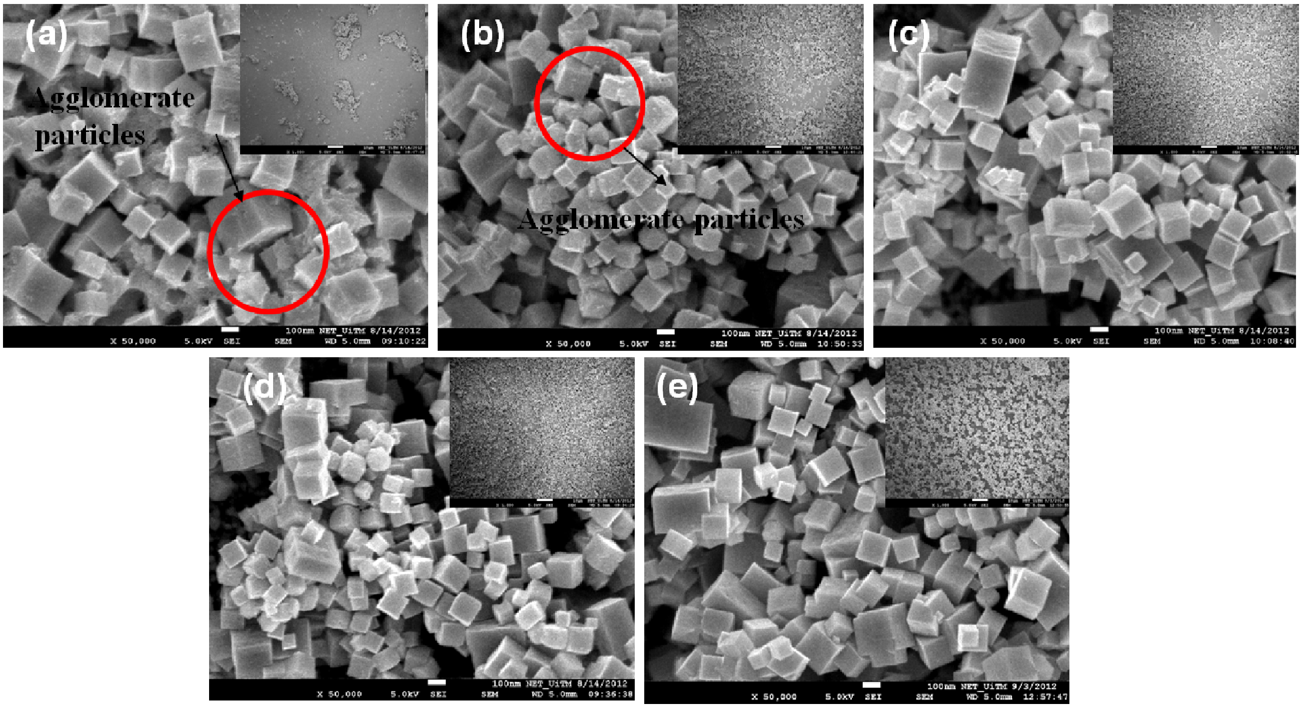
The immersion process were carried out with preparation of aqueous sol-gel solution with ZnO deposited on glass substrate by sputtering system which act as the template for nano-cubic structured ZnSnO3 to growth. Firstly, ZnO with high purity (99.999%) thin film were deposited by RF magnetron sputtering on cleaned glass substrate. The sputtering system was pumped at 5x10-4 Pa using a molecular pump. The argon to oxygen flow rate ratio (45:5) sccm inside the chamber. The RF sputtering system power was at 200 watt and the pressure was maintained at 7 mTorr. The deposition time of ZnO thin film on glass substrate was 1hour with heated temperature at 500°C followed with annealing process for 1 hour. Second, the preparation of ultrasonic sol-gel solution 0.02M tin(IV) Chloride Pentahydrate (SnCl4.H2O) and NaOH, (0.2mol) Sodium Hydroxide were dissolved in 40 ml DI water respectively. Both solutions were mixed together under stirring. Then, 0.02M $ZnCl_2$ solution were dropped slowly and there were whitish solution appear. The whitish solutions were sonicated using ultrasonic (Hwasin Technology Powersonic 405, 40 kHz) for 5 minutes at 50°C. The ZnO templates have been place at the bottom of each container and were immersed in different volume of final solution 100, 200, 300, 500 and 1000 ml. Then the containers were placed inside a water bath with the condition 95°C for 30 minutes. After deposition, the samples were washed with DI water to remove the residual particles. Finally the samples were annealed for 1 hour at 500°C.

### *B. Characterization*

Field Emission Scanning Electron Microscopy (FESEM; model: JEOL JSM-7600F) was used to examine the morphology and the distribution of the nanorods with accelerating voltage of 5 kV. Photoluminescence spectrometer (model: Horiba Jobin Yvon) with He:Cd emitting at 325 nm as laser source was used to measure the PL spectra for characterization of the optical properties.

### *C. Sensor Measurement*

The sensitivity, response and recovery time, repeatability and stability of the sensor were tested in a humidity chamber (ESPEC SH-261) using 2 probe I-V measurement (Keithley 2400). The humidity sensor measurement was conducted for the fabricated device with Au as the metal contact. The temperature was set at room temperature (25°C) while relative humidity (RH %) is varied in the range 40 to 90 RH%.




Fig, 1. FESEM images of nano-cubic structured $ZnSnO_3$/ZnO thin film with the inert image with difference volume of solution. (a) 100, (b) 200, (c) 300, (d) 500 and (e) 1000 ml.

## III. RESULTS AND DISCUSSIONS

### A. *Structural Properties*

The surface morphology of prepared product was observed by FESEM. Fig.s 1(a) 100ml, (b) 200ml, (c) 300ml, (d) 500 ml and (e) 1000ml presented the images of nano-cubic structured $ZnSnO_3$ thin film deposited on top of ZnO thin films with difference volume of solution respectively. The inert image of Fig.s 1 (a~e) show the surface morphology difference volume of solution at 1000 magnification. This show that the distribution uniformity of nano-cubic structured $ZnSnO_3$ cubic structures growth on top of ZnO thin films at different precursor volume solution. The distribution of nano-cubic structured $ZnSnO_3$ were increase as the volume of solution increase. At 100ml volume solution, there was agglomerate particles growth at the nano-cubic structured $ZnSnO_3$/ZnO as shown in Fig. 2b. The size of cubic is around 100~250 nm. The size of nano-cubic structured $ZnSnO_3$/ZnO were almost the same for at 200, 300, 500 and 1000ml volume solution around 70~250 nm. The agglomerate particles reduced as the volume solution increased to 200 ml as shown in Fig. 1(b). As the volume solution increased to 300, 500 and 1000 ml, the agglomerates particles were slightly less as shown in Fig.s 1(c), (d) and (e) respectively. It remarkable that the $ZnSnO_3$ precursor volume solutions was effect the contribution of uniformity cubic structured $ZnSnO_3$ growth on top ZnO thin film. The size of cubic structured $ZnSnO_3$/ZnO for 100 ml volume solution was bigger than other volume solution might due to sonic process which the ions particles $Zn^{2+}$ and $Sn^{4+}$ of 100 ml volume solution had started to combines with each other to form a structured. The thicknesses of nano-cubic structured $ZnSnO_3$ for all samples were almost the same with an average thickness 3.1µm. The element of Zn, Sn and oxygen that contained in nano-cubic structured $ZnSnO_3$/ZnO for 1000 ml volume solution detected using energy dispersive X-ray spectrum (EDS) as shown in Fig.s 2. This was to ensure the element of Zn, Sn and oxygen in thin film. The atomic ratio of Zn:Sn:O were 17.85:17.78:60.72.

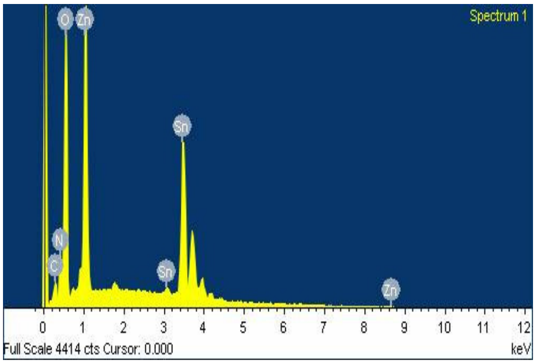



Fig. 2. EDS spectra nano-cubic structured $ZnSnO_3/ZnO$ thin film at 1000 ml volume solution.

*B. Optical Properties*

The PL spectrum was measured at room temperature as shown in Fig. 3 for $ZnSnO_3$ cubic structures for 1000 ml volume solution. Two peaks was obtained when the sample were excited with helium-cadmium (He-Cd) excitation laser at 325 nm. The first peaks shows at UV emission 417 nm which attributed to the recombination of free excitons energy. A strong orange-yellow emission at 644 nm was corresponding to defect in nano-cubic structured $ZnSnO_3/ZnO$. The defects happen due to the formation of oxygen vacancies where cause of insufficient oxygen or residual strain induced during the deposition process[18]. In this experiment, the cubic structured were formed at low temperature which resulting more oxygen vacancies exist in our product.

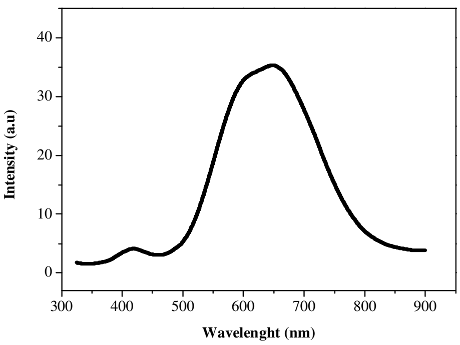



Fig. 3. Photoluminescence spectra of nano-cubic structured $ZnSnO_3/ZnO$ thin film at 1000 ml precursor volume solution.

*C. Humidity Sensor Measurement*

Fig. 4 show the device configuration of humidity sensor. The nano-cubic structure of $ZnSnO_3$ was the active layer to sense the humidity. Au electrode was as the metal contact deposited on top of nano-cubic structured $ZnSnO_3/ZnO$. The active layer was the nano-cubic structured $ZnSnO_3$ to sense the humidity environment. The ZnO thin films was the template of nano-cubic structured $ZnSnO_3$ to growth.

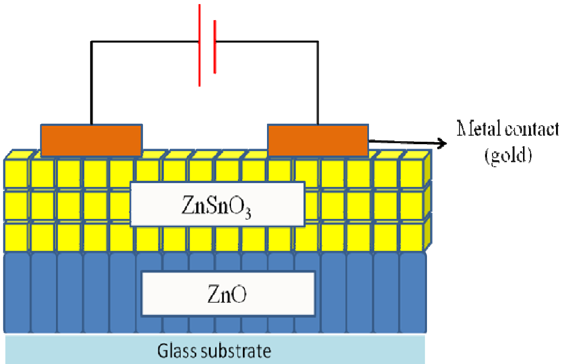



Fig. 4. Device configuration for humidity sensor application

The fabricated sensor was tested using I-V measurement with supplied from -5V to 5V. The humidity chamber was controlled at constant temperature (25°C) at different RH% during the investigation process. The current-voltage curve nano-cubic structure of $ZnSnO_3/ZnO$ of 1000 ml volume solution was shown in Fig. 5 (a). The graph show ohmic behavior. The current densities increase the water vapor increase. These occur due to the reaction of water with nano-cubic $ZnSnO_3/ZnO$. 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.

The value sensitivity was calculated by using following equation (1)[1]:

$$S = \frac{I_{RH}}{I_A} \tag{1}$$

$S$ is sensitivity, $I_A$ is resistance of the sensor in air, and $I_{RH}$ is resistance in the different RH. This shows that nano-cubic structure of $ZnSnO_3/ZnO$ materials have the ability to absorb water vapour from the surroundings. The changes values of resistance measurement as a function of relative humidity for $ZnSnO_3$/ZnO cubic structure of 1000 ml volume solution is shown in Fig. 2.The response and recovery time of $ZnSnO_3$/ZnO cubic structure of 1000 ml volume solution were approximate 409s and 9 s respectively is shown in Fig. 5 (c) .The repeatability of $ZnSnO_3$/ZnO cubic structure of 1000 ml volume solution were tested for 4 cycles with changing from 40%RH to 90%RH as shown in Fig. 5(d). It shows that the sensor have potential to perform the switching characteristic. The sensor show the repeatability characteristics which they have the ability to reproduce the initial current during the humidity was low.

Fig. 6 below shows the mechanism of humidity sensing of volume solution nano-cubic structure of $ZnSnO_3$ were discussed. The resistance changes during the adsorption and desorption process. At low humidity, the water molecules chemisorbed and the protons hopping to available site that possible to conduct thus the resistance of nano-cubic structure of $ZnSnO_3$ was high[19-21]. As the humidity increase, the amount of water vapor increase. The water molecules react with the cubic structured nano-cubic structure of $ZnSnO_3$ layer which physically absorbed. At this condition, $Zn^{2+}$ and $Sn^{4+}$ from the bond absorb the $OH^-$ of H2O and $H^+$ ions release. As the $H^+$ ions move freely together with the water , the resistance of film decreasing due to conduction occur[22]. The Grotthuss transport mechanism prompts the protons conductions occur.

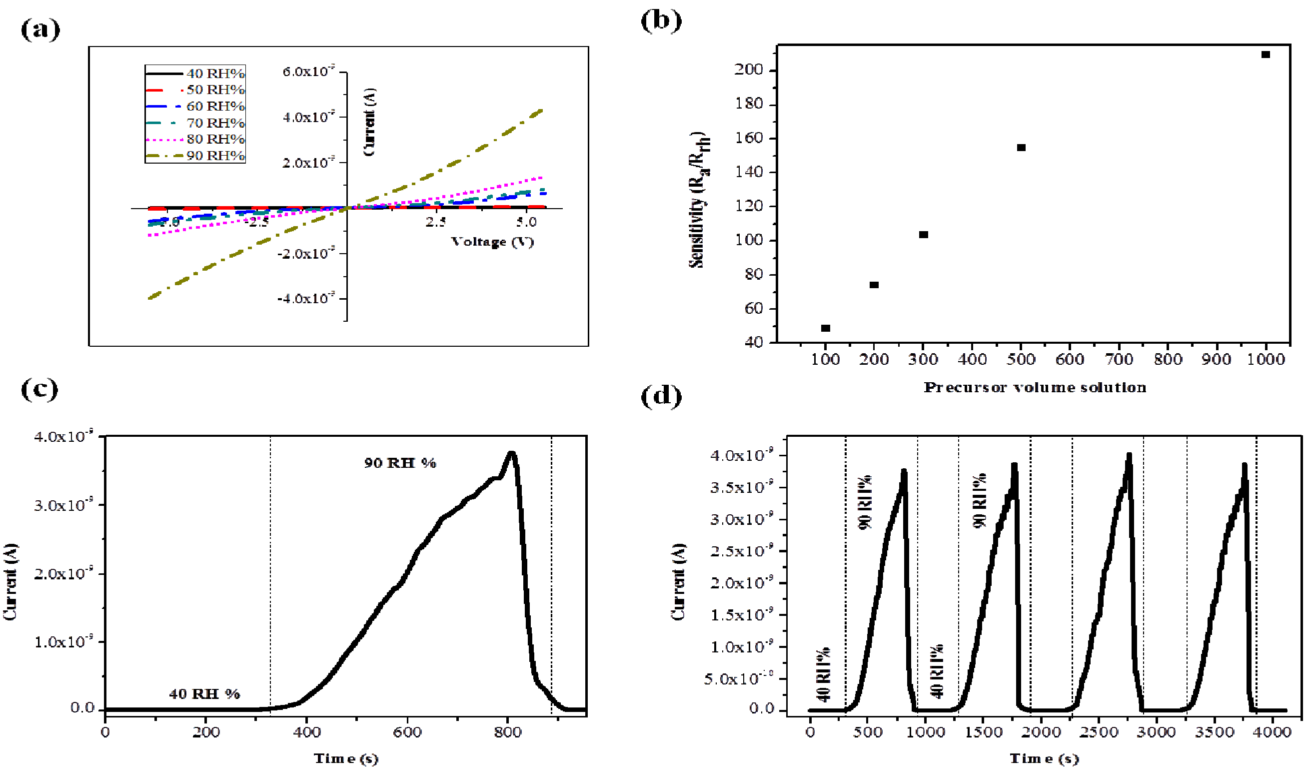



Fig. 5. (a) I-V measurement of nano-cubic structured $ZnSnO_3$/ZnO thin film at 1000 ml precursor volume solution. (b) The calculated sensitivity for all samples at different volume solution. (c) Response and recovery times for 1000 ml volume solution. (d) Reproducibility properties of nano-cubic structured $ZnSnO_3$/ZnO thin film at 1000 ml volume solution with supplied bia 5V for 4 cycle tested.

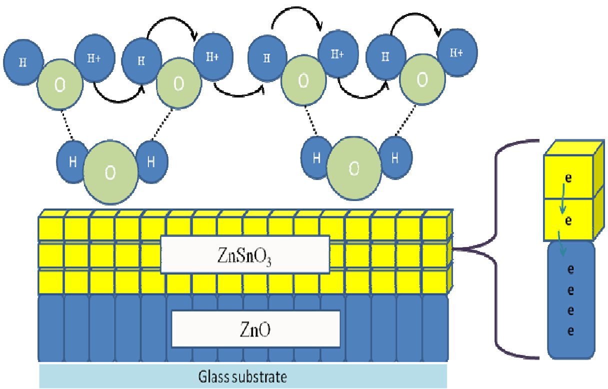



Fig. 6. Mechanism of Humidity Sensor.

## IV. CONCLUSION

In summary, nano-cubic structure of $ZnSnO_3$ has preparation based of the structural and optical properties of sol–gel ZnO thin films have been found to be influenced by the volume solution. The PL spectra depict that cubic structured ZnO-$SnO_2$ had low intensity at UV emission region at around 417 nm and broad emission was dominant in the visible region at around 644 nm. The sensor of volume solution of nano-cubic structure of $ZnSnO_3$ demonstrate 409s response times and recovery 9s times. In addition, this sensor also shows repeatability characteristics. Thus, nano-cubic structure of $ZnSnO_3$ has great potential for humidity sensor application.

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