Influence of Cubic Structured-ZnSnO$_3$ Immersion Time to the Performance of Humidity Sensor

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Abstract. ZnSnO$_3$ thin film was deposited at different deposition time (0.5 h, 2 h, 4 h and 6 h) using sol-gel immersion method and the electrical, optical and structural properties of this film was investigated. This research involved the preparation of nanostructured ZnO thin film by using RF magnetron sputtering, preparation of ZnSnO$_3$ sol-gel solution, metal contact deposition and characterization of humidity sensor. The thin film was characterized using current-voltage (I-V) measurement (Keithley 2400) and field emission scanning electron microscopy (FESEM) (JEOL JSM 6701F) for electrical and structural properties respectively. The sensor was characterized using I-V measurement in a humidity chamber (ESPEC SH-261) and the chamber has been set at room temperature with varied relative humidity (% RH), in the range of 40-90% RH. The film prepared with a deposition time of 2 h shows better sensitivity for humidity sensor. The FESEM investigation shows that crystal size increases with the increasing deposition time.

Introduction

Humidity sensors are commonly used as human comfort, semiconductor manufacturing and food packaging. Nowadays 1-D structured materials are commonly used in sensor fabrication. However 3-D structures still have its own advantage of performing sensor characteristics. A good sensor must perform higher sensitivity, fast response and recovery time, good in stability and reproducibility [1]. Composite zinc stannate ($ZnSnO_3$) is a mixed oxide semiconductor. This composite has the credibility to perform various device applications such as sensor [2], FET [3] and solar cell [4]. Many researchers have worked on humidity sensor using different alloy materials, such as Mg-Zn-Ti [5], SnO_2–TiO_2 [6] and ZnO-SiO_2 [7]. However, reports on zinc stannate ($ZnSnO_3$) for humidity sensor is scarce. Aarthy et al. [8] reported on microcube structured zinc stannate growth on ZnO nanorods and they have used it for gas sensor application. Here, radio frequency (RF) magnetron sputtering has been chosen for ZnO film (template) deposition, because, it can provide a uniform high quality thin film, good adhesion, high crystalline etc. [9] as compared to the ZnO template prepared using the sol-gel method.

In this study, nanostructured ZnO thin film, which acts as the seeded catalyst were prepared using RF magnetron sputtering and zinc stannate ($ZnSnO_3$) based film was prepared using sol-gel immersion method [2-4]. The effect of deposition time (0.5h, 2h, 4h and 6h) on the electrical and structural properties and also its application for the humidity sensor were investigated.

Methodology

At first, ZnO thin film was prepared on glass substrates using the RF magnetron sputtering method. These ZnO films act as the template for $ZnSnO_3$ deposition. Required amount of $SnCl_4$.$5H_2O$ and NaOH were dissolved in 400 mL of distilled water (DI). The $SnCl_4$ solution was slowly dropped into NaOH and stirred for 10 minutes at 50 °C using a magnetic stirrer, until a transparent solution was formed. The solution which contained 6 mmol $ZnCl_2$ and 200 mL DI water was introduced into this transparent solution, drop by drop with continuous stirring. Next, the solution was sonicated using an

ultrasonic bath for 10 minutes at 50 °C. The resulting whitish solution was transferred into a container with the template (ZnO thin film on glass) placed at the bottom of the container. The container was then immersed in a water bath at 95 °C for different duration (0.5 h, 2 h, 4 h and 6h). After deposition, the thin film was washed with DI water and dried for 10 minutes at 100 °C. Finally, the sample was annealed for 1 hour at 500 °C.

Metal contact was deposited on $ZnSnO_3$ film for I-V measurement by using thermal evaporation. The characterization can be divided into electrical and structural properties. For electrical properties, the measurement was conducted using 2 probe I-V measurement system (Keithley 2400). This measurement was used to study the sensitivity, responsivity and stability inside a humidity chamber (ESPEC SH -261). The temperature was set at room temperature with relative humidity (% RH) varied in the range of 40 to 90% RH. Humidity sensitivity measurement was conducted for the fabricated device with Au as the metal contact. Structural properties were characterized using FESEM (JEOL JSM 6701F) and XRD (Japan Rigaku Ultima IV).

Results and Discussions

Electrical properties. The sensing properties of cubic structured-$ZnSnO_3$ were tested in a controlled environment inside a chamber and in the voltage range of -1.0 to 1.0 V using a Keithley 2400. Fig. 1 (a), (b), (c), and (d) shows the I-V plots of $ZnSnO_3$ thin films deposited for 0.5, 2, 4, and 6 hours respectively at different % RH (40-90% RH). The current density increases as the % RH increased. This change is due to the water absorption by the cubic structured thin films. The water vapor helps more current flow through the materials with less resistance. Again, the water vapor in the air also has a strong influence on the conductivity of $ZnSnO_3$ films. The sensitivity, responsivity and reproducibility behavior are the most important characteristics for evaluating the humidity sensor [10]. Fig. 1(e) shows the current versus relative humidity for samples deposited in 0.5 h, 2 h, 4 h and 6 h. The figure also shows the variation of current with changes in relative humidity for 40-90% RH. The current increases with the increase of relative humidity. This result shows that the sample with 2

h deposition time has better sensing properties and exhibit good linearity with RH, compare to the other samples. The resistance for 2 h sample at 40 %RH ($2.42 \times 10^7 \Omega$) is higher 10.17 times than 90 %RH (2.38×10^6 Ω). This occurs mostly due to more water vapor was absorbed by the $ZnSnO_3$ sample deposited for 2h and the arrangements of the nanocubes. In general, water molecules can be absorbed by physisorption or hydrogen bonding. The sensing mechanism is based on the absorption and desorption process between the surface structure and humidity [10,11].

In order to examine the repeatability, the current of $ZnSnO_3$ film was measured for four cycles at 1.0 V of applied voltage while exposing it to the humidity off 90 %RH at 25 °C inside a humidity chamber. The corresponding current-time plots are shown in Fig. 1(f). This figure also shows the response and the recovery time. The response time is defined as the time it takes for the current of the sensor to increase to 90 % RH. The recovery time is the time required for 90 %RH decrement in current when relative humidity is turned off. The stability of the $ZnSnO_3$ thin film based humidity sensor shown in Fig. 1 (g) was exposed to measurement of the resistance once in every 2 hours which was performed at 90 %RH and at 25 °C.
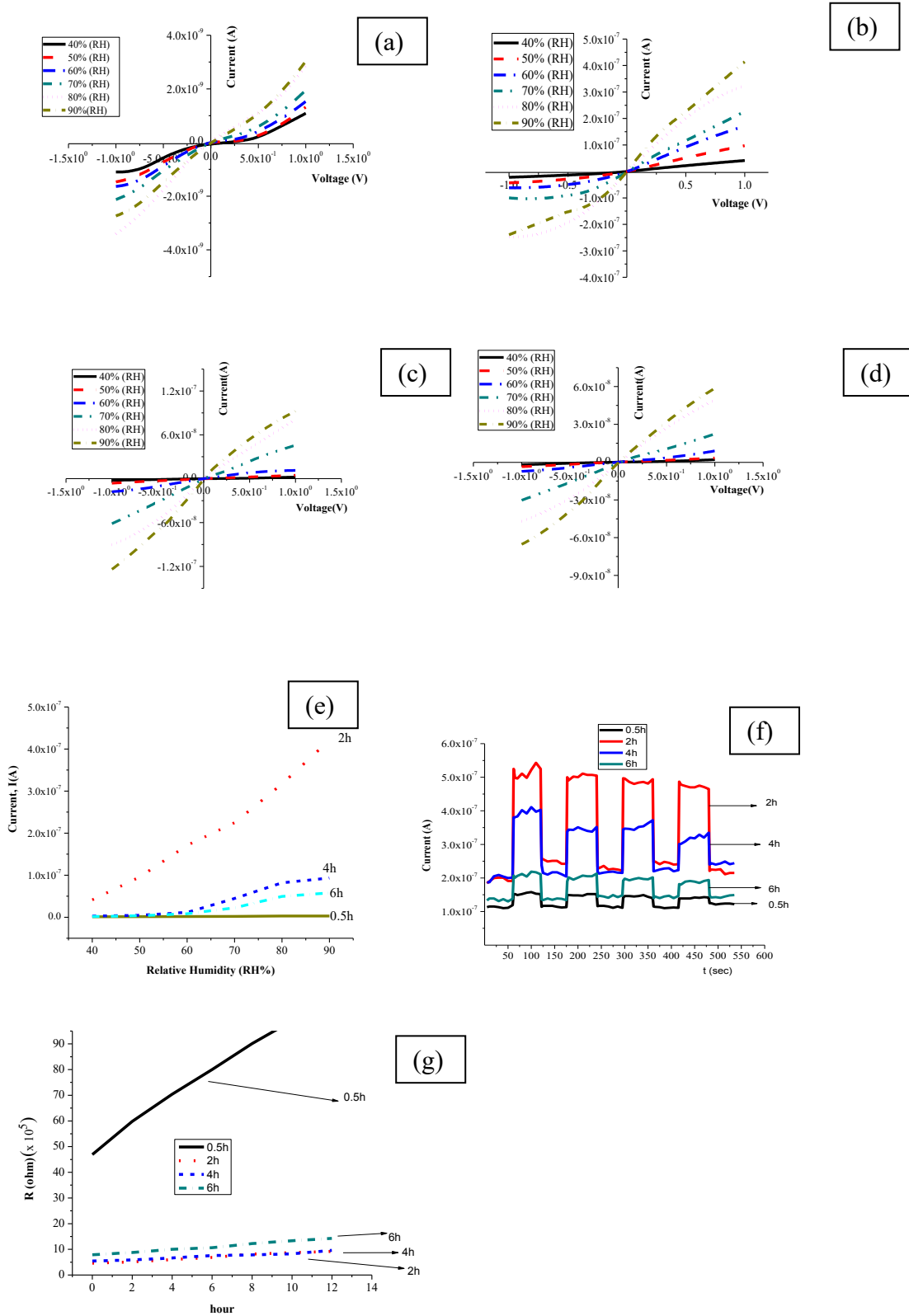
Fig. 1. Shows the I-V curve of ZnSnO$_3$ film by the deposition time of (a) 0.5 h, (b) 2 h, (c) 4 h, and (d) 6 h (e) Current versus Relative humidity for all samples (f) repeatability of the sensor for all samples measured at 90% RH with 1V applied for 4 cycles and (g) stability of the sensor for all samples measured at 90 %RH with 1V applied.

Structural properties. Three diffraction peaks were found in XRD (Fig. 2) for the film having deposition time 2 h with diffraction angle between 20° and 80°. The diffraction peaks are at 26.5°, 34.5° and 51.7° which are indexed as $ZnSnO_3$ (JCPDS card no. 00-011-0274). Fig. 3 shows the FESEM images and the energy dispersive X-ray spectroscopy (EDS) of the $ZnSnO_3$ sample prepared at 2 h deposition time. The uniform Cubic structure was observed in the FESEM image and from the EDS, the presence of Zn, Sn and oxygen have been confirmed. The Zn in sol-gel solution acts as a holder to template and cubic structure to avoid lattice mismatch.
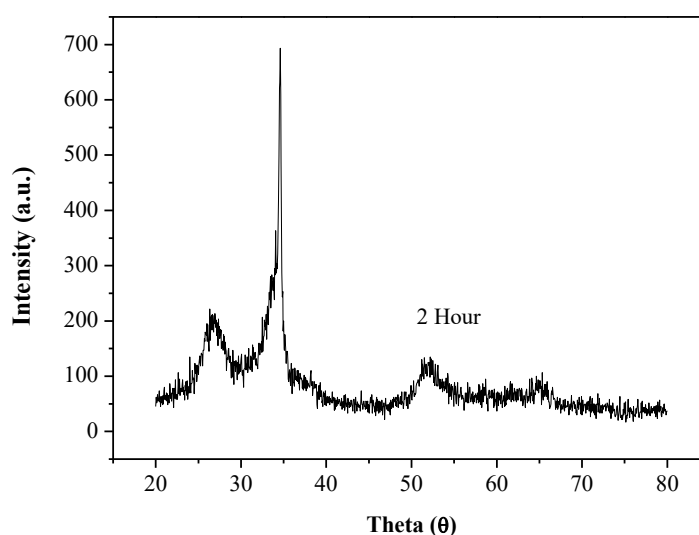
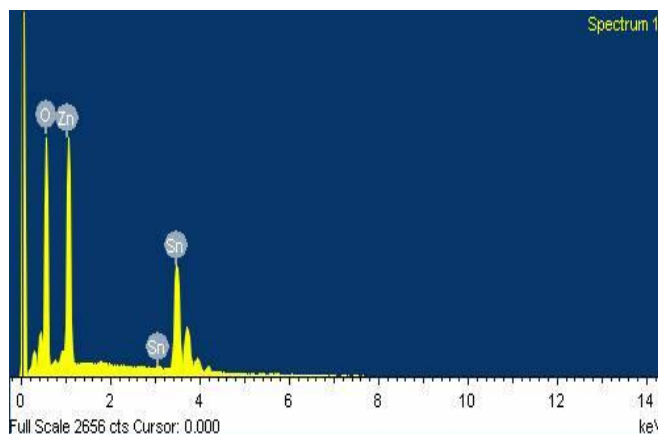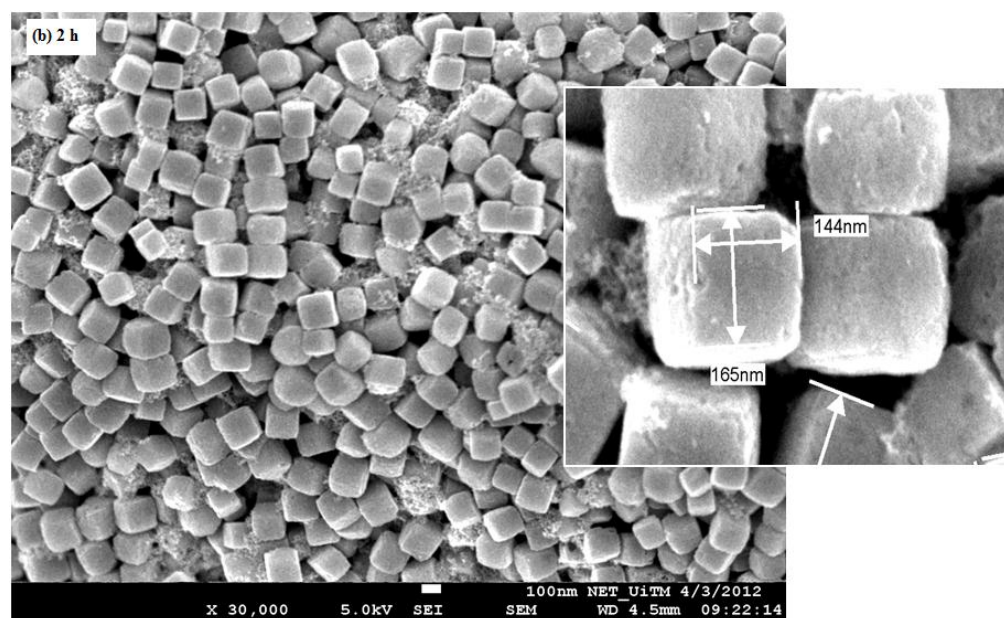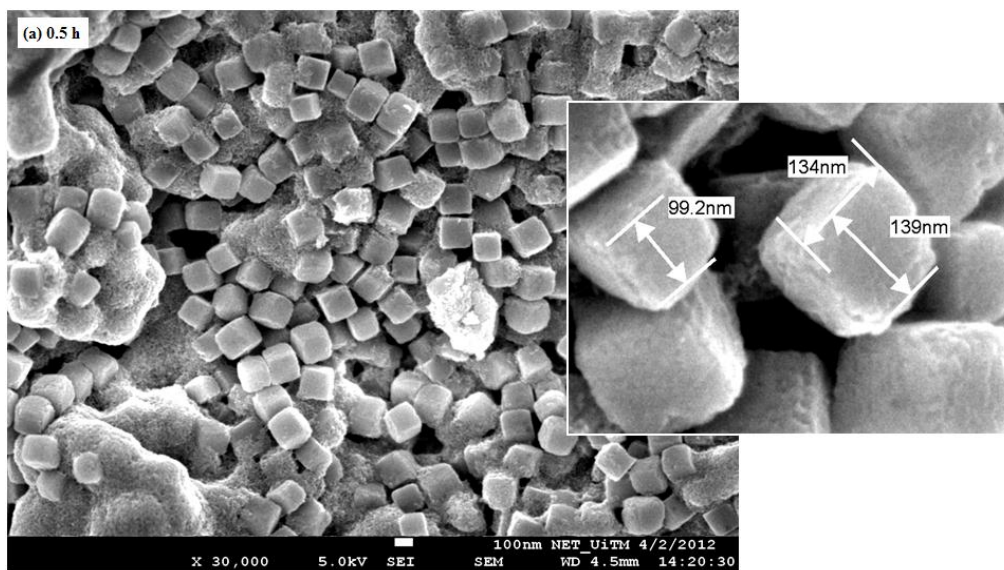**Fig. 2** XRD pattern of the sample 2 hours (JCPDS No. 00-011-0274).
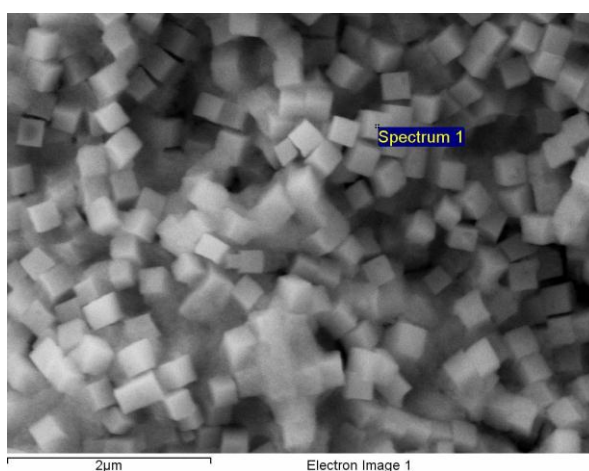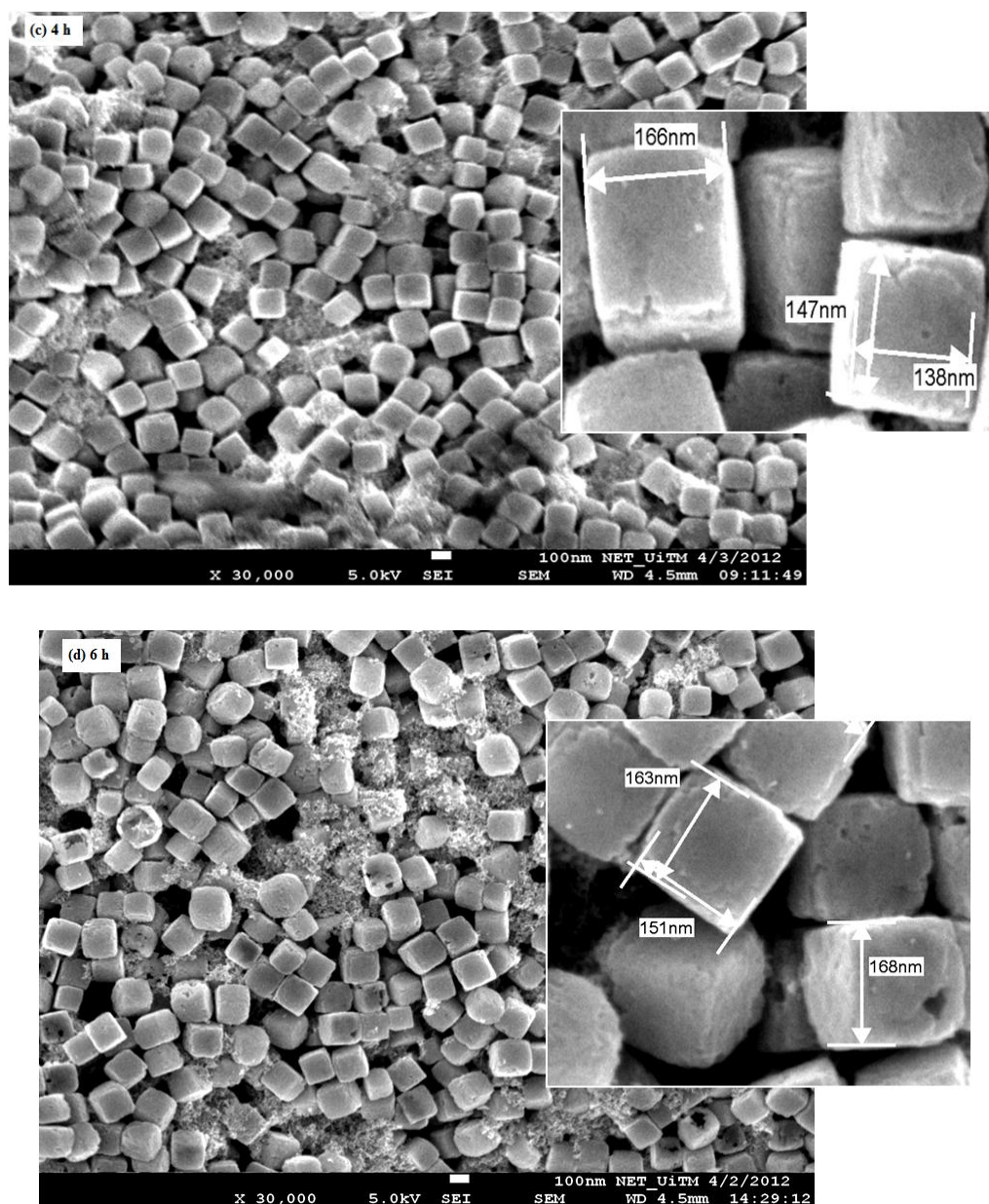
Fig. 3 EDS result of 2 h deposition time.

For further detailed structural study, Fig. 4 shows FESEM images of $ZnSnO_3$ thin films deposited for (a) 0.5 h, (b) 2 h, (c) 4 h and (d) 6 h, at higher magnification. The inset images show the measured size of cubic structured of $ZnSnO_3$ films. The average cubic size increases from 99 to 160 nm when the deposition time was increased from 0.5 to 6 h. Fig. 4(a) shows the presence of cubic structures but they were not uniformly distributed but for the film with 2 h deposition time (Fig. 4(b)) shows good uniform distribution of the cubic structure. However, for the films with deposition time 4 and 6 h (Fig. 4(c) and (d) respectively) shows an aggregation of amorphous particles. The random aggregation of amorphous particle growth on the surface of the cubic which occur due to the surface to volume ratio [12]. From the electrical study it was found that the film with 2 h deposition time showed highest sensitivity and linear behavior with the increasing %RH. It occurs due to more site area to absorb by $ZnSnO_3$ films is very sensitive to oxygen and water vapor in the air. So the uniform structural distribution plays an important role for this better characteristic properties.

(a) 0.5 h

99.2nm
134nm
139nm

100nm NET_UiTM 4/2/2012
X 30,000   5.0kV   SEI   SEM   WD 4.5mm   14:20:30

(b) 2 h

144nm
165nm

100nm NET_UiTM 4/3/2012
X 30,000   5.0kV   SEI   SEM   WD 4.5mm   09:22:14

Fig. 4. FESEM image of the $ZnSnO_3$ film immerse at difference of time (a) 0.5 h (b) 2 h (c) 4 h and (d) 6 h.

Conclusions

In summary, $ZnSnO_3$ thin films have been successfully prepared on glass substrates with different deposition time using the 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 2 hour shows better sensitivity, fast response change in the air and at the same time its response sensitivity varies linearly with RH in the air.

Overall, all the films showed good repeatability and stability. The images of cubic structured ZnSnO3 are increasing as the deposition time increase but the film with deposition time 2 h showed a better structural distribution.

Acknowledgement

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