Improvement of Nanocomposited Zno/SnO_2 towards Humidity Sensor Application

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Abstract— **This technical paper investigates the improvement of nanocomposite ZnO/SnO_2 that has been prepared on ZnO coated glass using thermal chemical vapor deposition (CVD). The sensor properties were characterized by using current-voltage (I-V) measurement (Keithley 2400). The results analyzed were for ZnO nanoparticle, SnO_2 nanorod and ZnO/SnO_2 nanoflower like structure. The structural properties have been characterized using field emission scanning electron microscopy (FESEM) (JEOL JSM 6701F). The thins films were tested using two point probe and the sensor were characterized using I-V measurement (Keithley 2400) in a clean humidity chamber (ESPEC SH-261) and the chamber has been set at same room temperature (25 °C) with percent relative humidity (RH %) varied in the range of 40% to 90% RH. ZnO/SnO_2 nanoflower like structure performed highest sensitivity with 15 ratio compared to the ZnO nanoparticle and SnO2 nanorod. The response and recovery time for ZnO/SnO_2 nanoflower like structure were 156s and 54 s respectively.**

Keywords- ZnO nanoparticle; SnO_2 nanorod; Zn/SnO_2 nanoflower like structure; CVD; Humidity Sensor.

I. INTRODUCTION

Humidity sensors have been important for the precise control and reliable estimate of water vapors content in atmospheres from industrial processes to the general improvement in the quality of life [1, 2]. Generally a humidity sensor has to possess fast response and recovery time, high sensitivity, good in stability, negligible hysteresis over periods of usage and possibly a large operating range for both humidity and temperature [3]. As an n-type wide band gap semiconductor (Eg = 3.6 eV) tin dioxide (SnO_2) nanostructures having rutile structure attracted great interest in recent years. SnO2 has good characteristics in optical, electrical, chemical and thermal stability [4].

ZnO is one of the most important group II-VI semiconductor materials. It is an n-type and a wide band gap material with a direct band gap (3.37 eV) and large excitation binding energy of 60 MeV. ZnO also come from Wurtzite- structured semiconductor that can help to mix with SnO2 [5]. Zinc and tin compounds have recently appealed considerable attention because they display technological properties [6], such as high capacity anode material, which can also be used to oxygen separation acting as a photo catalyst under the visible light, humidity and gas sensors action [7, 8]. Doping is an attractive and effective method for manipulating various applications of semiconductors.

Using single materials can cause low sensitivity of sensor [9] due to the insufficient exposing surface area and low electron transportation due to the surface morphology. This is because nanogenerators, sensors, and piezoelectric tubes based on nanostructures will strongly depend on the strength and stiffness of the materials [10]. By combining ZnO and SnO2 on thin film can produce high sensitivity due to the heterogeneous interfaces between them.

Sensitivity, selectivity, response time, recovery time and stability can be improved by combining different additives to SnO_2 [11]. Composite type sensors were suggested to improve thermal reliability because they contain many heterogeneous boundaries between different phases [12, 13]. For example ZnO/CuO, SnO_2/CuO, SnO_2/ZnO composites showed increases sensitivities in comparison to single phase materials [14, 15]. Composites are beneficial because the combination of materials tend to be more porous. Especially SnO_2 can be made more porous with small amount of ZnO addition [16]. This porosity may play an imperative role in the humidity sensing because the pores of the materials serve as adsorption sites. The sensitivity of the sensor directly depends on these pores size.

In this paper, we introduce the technique of chemical vapor deposition method to prepare ZnO/SnO_2 nanoflower like structure thin film on a glass substrates cover with ZnO thin film for humidity sensor applications. This technical paper investigates the effect of nanocomposited ZnO/SnO_2 nanoflower like structure on the surface morphology and humidity sensor application.

II. METHODOLOGY

The experiment was conducted by following the flow chart in Figure 1 below. Glass is a material which used as substrate in this project. The glasses were cleaned with acetone, methanol and deionized water in the ultrasonic device using several steps before the experiment began.

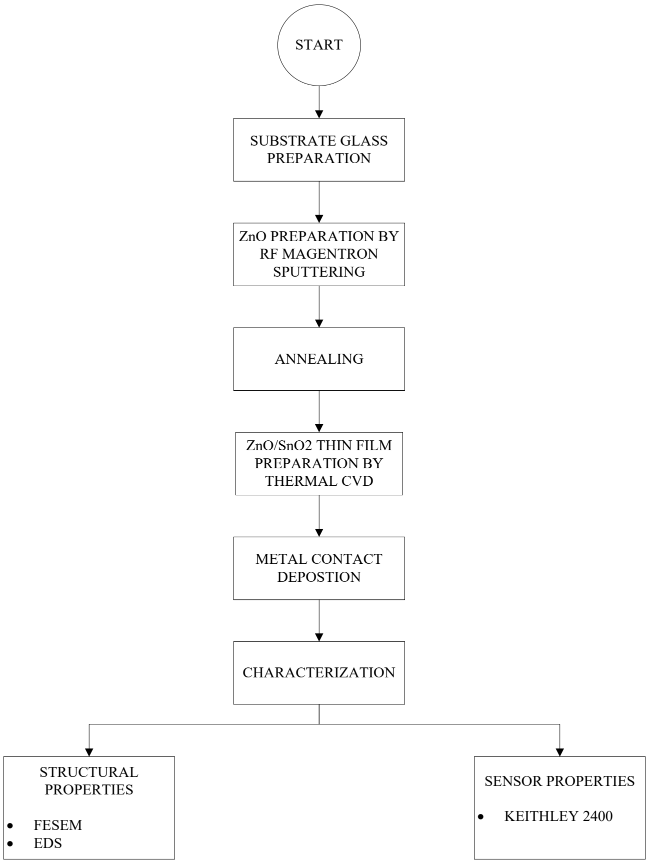


Figure 1: Flow chart of the project.

At first, ZnO thin film was deposited on glass substrates using the RF magnetron sputtering method. At second process, these ZnO films act as the template for ZnO/SnO_2 nanoflower like structure deposition. Two furnaces were used to grow doped ZnO/SnO_2 nanoflower like structure thin film as shown in Figure 2 below. Furnace 1 was used to place precursor and Furnace 2 was used to place ZnO coated glass. Both precursor and glasses use a single Quarzt tube. Zinc nitrate and tin chloride as the precursor, Argon (Ar) as the carrier gas and oxygen (O_2) act as the reactor gas. The flow rates of the gases were 20 sccm for Ar and 5 sccm for O_2. Both precursors were measured with 3g. The substrate temperature was deposited at 500°C and the deposition time was set to 1 hour.

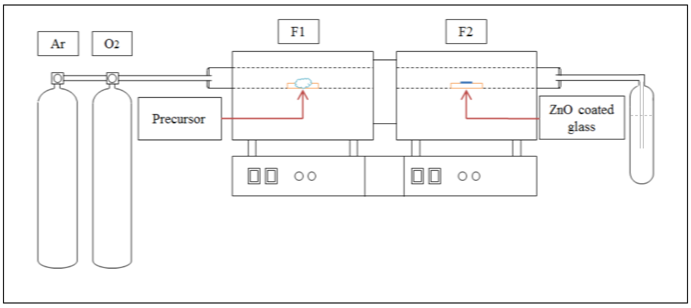


Figure 2: CVD process.

The humidity sensor measurement was conducted on Au metal contact deposited on the thin film as the electrode by using thermal evaporation. The thin films were tested using two point probe and the sensor was characterized using I-V measurement system (Keithley 2400) in a clean humidity chamber (ESPEC SH-261) and the chamber had been set at same room temperature (25 °C) with percent relative humidity (RH%) varied in the range of 40% to 90% RH. Structural properties were characterized using FESEM (JEOL JSM 6701F). Then the I-V was plot by using Leios TMXpert software. The configuration of the device structure was like Figure 3 below.

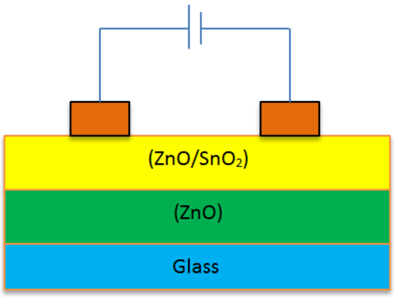


Figure 3: Configuration of device structure.

III. RESULT AND DISCUSSION

A. Structural properties

Figure 4 show FESEM image of nanoparticle of ZnO catalyst thin film at magnification 30,000 times magnification. The size of nanoparticle is in range 75 to 85 nm. This ZnO catalyst is act as a holder for ion zinc doping in thermal CVD method. This zn ion will act as the template during the growth process of ZnO, SnO_2 and ZnO/SnO_2 nanoflower like structure substrate.

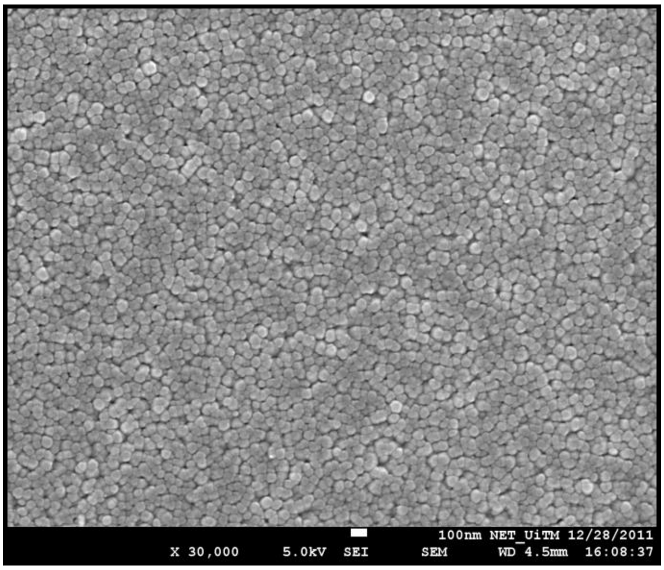


Figure 4: FESEM image for ZnO catalyst.

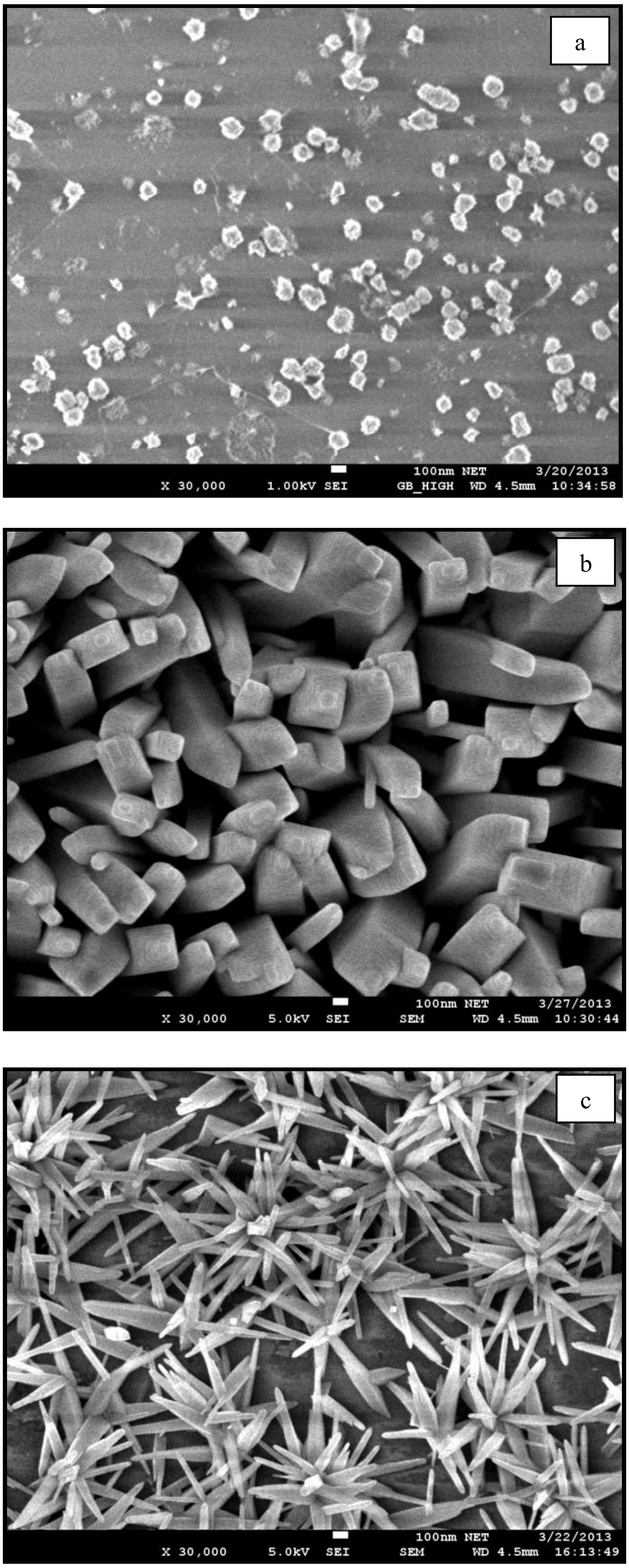


Figure 5: FESEM images for (a) ZnO nanoparticle, (b) SnO_2 nanorod and (c) ZnO /SnO_2 nanoflower like structure thin film at magnification 30kx.

The FESEM above shows that the nanostructured of ZnO nanoparticle, SnO_2 nanorod and the nanocomposited of ZnO/SnO_2 nanoflower like structure thin films shown in Figure 5 for (a) ZnO, (b) SnO_2 and (c) ZnO/SnO_2 that deposited with ZnO catalyst with 30,000 times magnification. For ZnO, the image show nanoparticle with size in range between 90 to 150 nm. For SnO_2 thin film, the image shows the uniform of nanorod. The diameter of the tip of this nanarod is about 100 to 200nm. The composite of ZnO/SnO_2 show nanoflower like structure with size in range between 70 to 90 nm. The results show that the growth of ZnO/SnO_2 nanoflower like structure has highest sensitivity to humidity compared to the other thin films due to the largest surface area that can increase the sensitivity because of larger site area to absorb the water vapor.

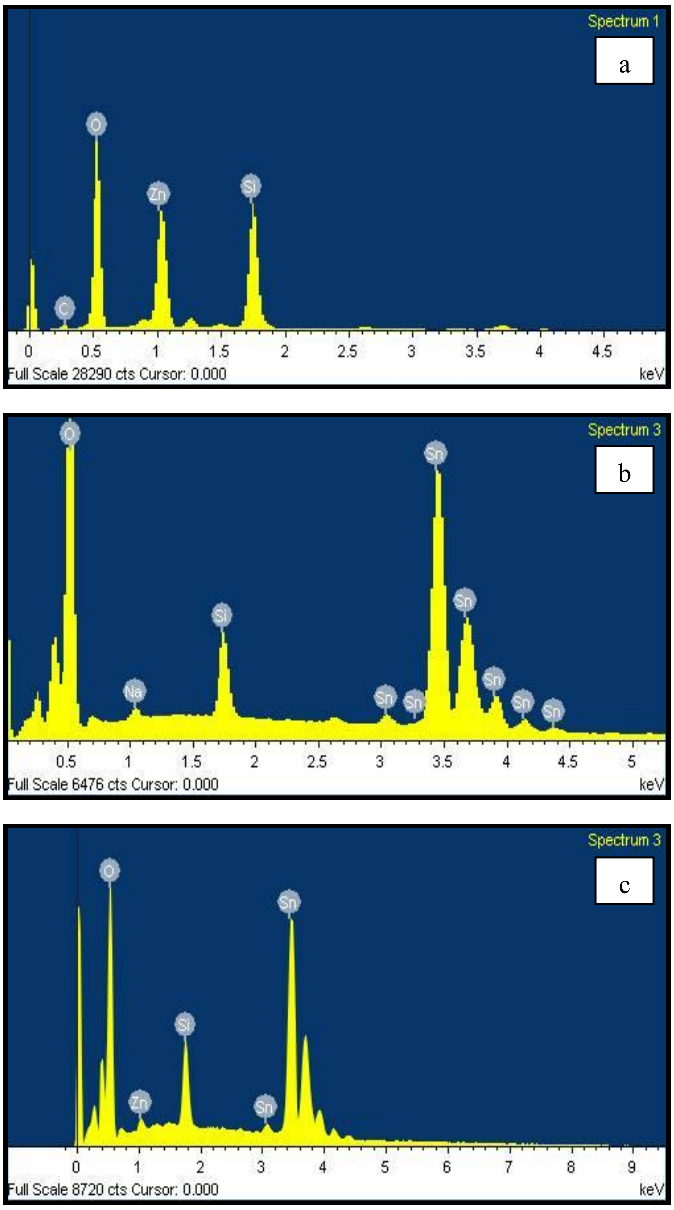


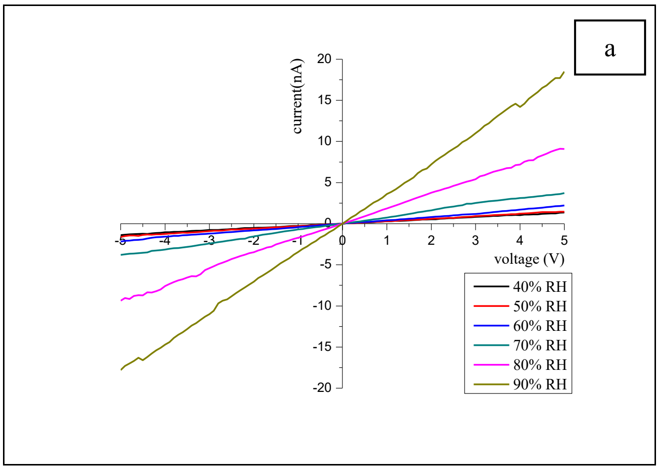
Figure 6: EDS spectrum images for (a) ZnO nanoparticle, (b) SnO_2 nanorod and (c) ZnO /SnO_2 nanoflower like structure thin film.

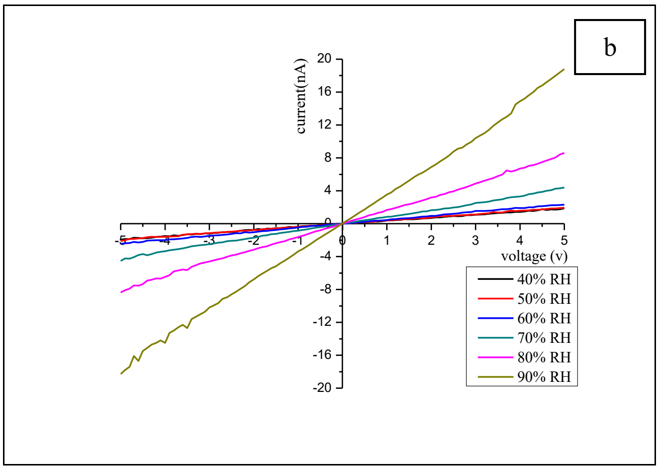
Table 1: Atomic percent of ZnO nanoparticle, SnO_2 nanorod and ZnO/SnO_2 nanoflower like structure thin films.

Atomic percent (%)	Zn	Sn	Si	O	C
ZnO	11.32	0	20.72	62.89	5.07
SnO_2	0	28.47	5.28	66.26	0
ZnO/SnO_2	0.87	71.59	3.75	23.79	0

Table 1 above show the atomic percent for the all sample refer to the EDS spectrum images in Figure 6. Table 1 and Figure 6 show the possible corresponding chemical composition. It reveals that zinc (Zn), oxygen (O), and tin (Sn) are the constituent part of ZnO/SnO_2 nanoflower like structure. The EDS measurements show that the dominant compositions for ZnO/SnO_2 nanoflower like structure thin film are Zn (0.87%), Sn (71.59%) and O (23.79%).

B. Electrical properties





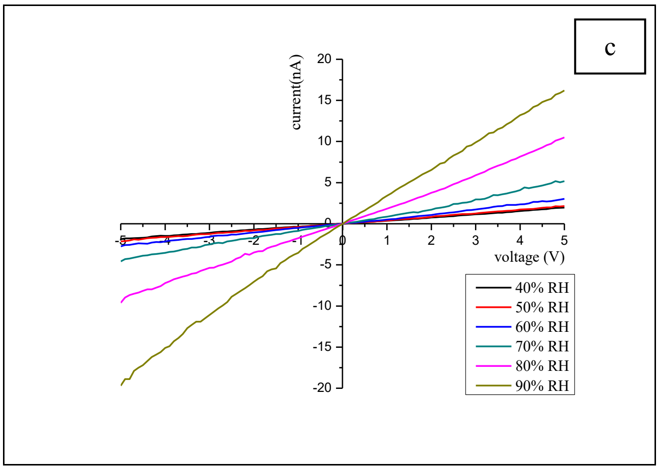


Figure 7: The I-V plots of (a) ZnO nanoparticle, (b) SnO_2 nanorod and (c) ZnO/SnO_2 nanoflower like structure.

Figure 7 (a), (b), (c) show I-V plots for thin films for ZnO nanoparticle, SnO_2 nanorod and ZnO/SnO_2 nanoflower like structure with relative humidity 40% to 90% at 25°C. The samples were given supplied voltage -5V to 5V. The current is increase when relative humidity increases so the resistance is decrease. This is because the water vapor on the surface of thin films was absorption. This water vapor can increase the flow of the current trough the thin film with less resistance. The water vapor in air has a strong influence on the conductivity of the thin films [17]. In any RH atmospheres, I-V curves of the device exhibit good linear behavior, which proves a good ohmic contact between the surfaces and Au electrodes. At low humidity, the tips and defects of the thin films present a high local charge density and a strong electrostatic field, which promote water dissociation. The dissociation provides protons as charge carriers of the hopping transport [18]. At high humidity, one or several serial water layers are formed among thin films, and electrolytic conduction between sensing materials takes place along with photonic transport and becomes dominating in the transport process [18].

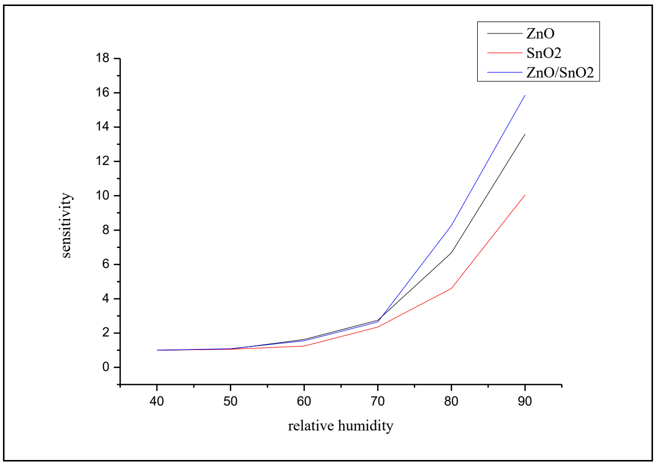


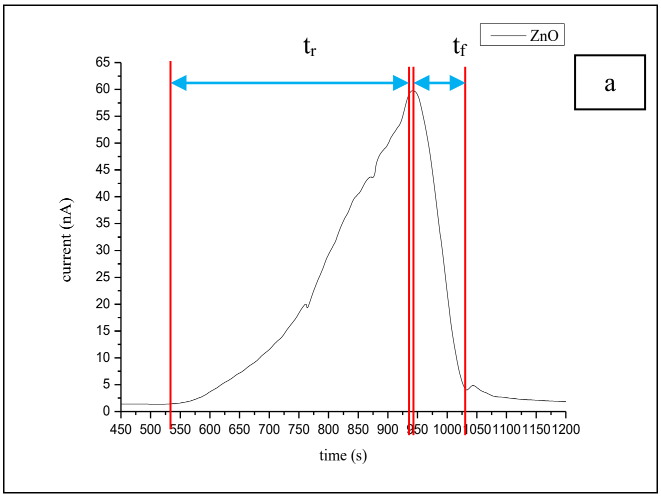
Figure 8: Sensitivity versus relative humidity all thin films

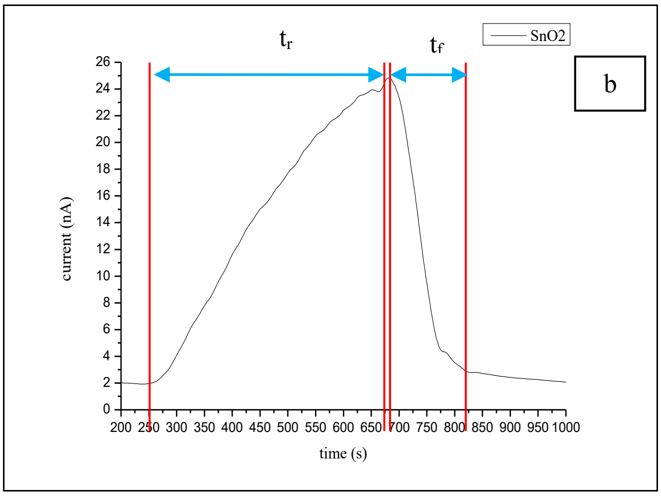
The composite ZnO/SnO_2 nanoflower like structure sensor exhibited significantly higher sensitivity than sensor constructed solely from ZnO nanoparticle or SnO_2 nanorod itself due to the heterogeneous interfaces between them and more adsorption site was created that can help more water vapor to be absorbed **[**16**]**. The graph in Figure 8 above show the sensitivity is increasing when RH increase. This phenomenon is related to the water adsorption on the thin films. At low RH, water adsorbing on the surfaces will not donate electrons to sensing layers and will significantly lower the sensitivity of thin films. The larger of the surface area, the content of water adsorbed become larger so the density of charge carrier become larger hence the sensitivity will increase [19]. The sensing mechanism is based on the absorption and desorption process between the surface structure and humidity [20].

For sensitivity, the value was calculated by using following equation (1) [21]:

$$S = \frac{R_{40\%}}{R_{90\%}}$$

Where S is sensitivity, $R_{40\%}$ is resistance of the sensor in air, and $R_{90\%}$ is resistance at 90% RH (relative humidity). Figure 8 show all thin film linearly sensitive to humidity.





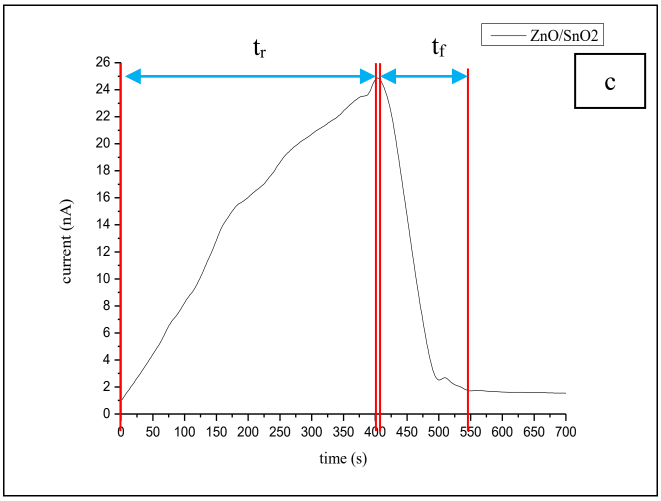


Figure 9: Response and recovery times characteristic of (a) ZnO nanoparticle, (b) SnO_2 nanorod and (c) ZnO/SnO_2 nanoflower like structure.

To perform good sensor, the sensors must have fast response and recovery time. According to the Figure 7, all thin films have fast response and recovery time while recovery time is faster than time to response. Table 2 below show the calculated of rise time and fall time. Thin film of ZnO/SnO_2 nanoflower like structure has fastest time to response and recovery with 156s and 54s respectively.

Table 2: rise time and fall time of ZnO, SnO_2 and ZnO/SnO_2

Materials	Rise time, t_r (s)	Fall time, t_f (s)
ZnO	198	83
SnO_2	177	68
ZnO/SnO_2	156	54

This response and recovery time were calculated by using this formula [22]:

1. For the response time (absorption process)

$$I(t) = I_0\left(1 - e\left(-\frac{t}{t_r}\right)\right)$$

2. For the recovery time (desorption process)

$$I(t) = I_0 e\left(-\frac{t}{t_d}\right)$$

Where I is magnitude of the current, I_0 is the saturated current, t is the time, t_r is the response time constant, t_d and is the recovery time constant.

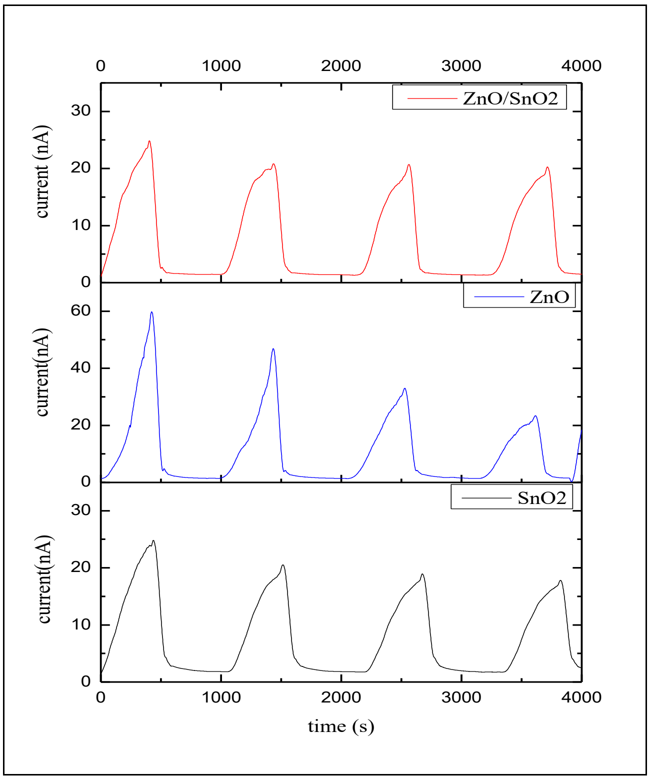


Figure 10: Repeatability performance of all sensors between 40-90 % RH

Figure 10 shows the repeatability of the thin films by applying bias voltage 5V for four cycles. When the thin films were exposed to the 90% RH, the current through the sensors increased. When the thin films switched to dry air again (40% RH), the current decreased and then reached a relative stable value. From the graph, all these thin films are suitable to be sensor because have good repeatability and stability.

IV. CONCLUSION

In this paper, ZnO/SnO_2 nanoflower like structure was successfully synthesized using thermal CVD. The ZnO nanoparticle, SnO_2 nanorod and ZnO/SnO_2 nanoflower was successfully grown on ZnO template layer. The ZnO nanoparticle and SnO_2 nanorod produce sensitivity with 13 and 9 ratios of times. The ZnO/SnO_2 nanoflower like structure gives highest sensitivity with ratio of 15 times. The response and recovery time for this ZnO/SnO_2 nanoflower like structure is the fastest among ZnO nanoparticle and SnO_2 nanorod with 156s and 54s respectively.

V. ACKNOWLEDGEMENT

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