Improvement sensitivity humidity sensor based on ZnO/SnO$_2$ cubic structure

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Abstract. ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure were prepared using sol-gel immersion method. These three structures had been growth on top sputtered ZnO thin film. The surface morphology of all thin film were characterized using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). The prepared thin films were fabricated for humidity sensor application. The composite sensor ZnO/SnO$_2$ cubic structure gave excellent sensitivity compare to ZnO nanorod and SnO$_2$ nanoparticle. The improvement sensitivities of ZnO/SnO$_2$ cubic structure were 22.5 times from ratio of $R_{40\%RH}$ to $R_{90\%RH}$ at 25°C. ZnO/SnO$_2$ cubic structure had a great potential for humidity sensor application with good in repeatability and stability.

1. Introduction

Choosing material is an important factor to enhanced behaviour of humidity sensor. The material of sensor should be conductive during the reaction with gases or humidity especially at surface component of semiconductor [1-2]. N-type material with relatively little oxygen adsorption sites available is suitable for sensing application to create potential barrier such as zinc oxide (ZnO) and tin oxide (SnO$_2$). Besides that, insertion of additives to the semiconductor material also could improve the humidity sensor performance. Mixing process is adding or combining two or more materials such as metal mixed metal oxide, metal oxide mixed metal oxide and polymers mixed metal oxide[3]. The advantages composite sensors are thermally more stable, high electron mobility, have many hetero-contacts between phase and the catalytic activity of sensing matrix are able to control [1, 4-5].

ZnO, as semiconducting II-VI metal oxide with wide band gap 3.37 eV. ZnO posses potential material for many devices applications such as gas sensor[6], solar cells[7], optoelectronic devices[8] and LED[9]. SnO$_2$ is n-type material with the band gap 3.5-3.6 eV. SnO$_2$ has been applied for various application such as solar cells[10], lithium ion batteries[11] and gas sensor[12-14]. SnO$_2$ have received attention from many researcher studied on gas sensor application for having high sensitivity and relatively low operating temperature [15]. ZnO and SnO$_2$ have unique properties due to their chemical and physical properties. Many type of deposition methods to prepare ZnO nanostructure and SnO$_2$ nanostructure such as electrochemical technique[16-17], sputtering[18-19], chemical vapour deposition[20-21] and hydrothermal[22-23]. Mixing ZnO and SnO$_2$ could form various kind of composite material such as ZnO/SnO$_2$ [24], ZnSnO$_3$ [25], Zn$_2$SnO$_4$ [26], Zn-doped SnO$_2$ [27] and Sn-doped ZnO [28]. Different type of ZnO/SnO$_2$ structured have been prepared such as nanofibers [29],
nanorod [30], nanoflowers [31] and nanoparticles [32] using various of method including electrochemical [33], hydrothermal [34], thermal evaporation [35] and sputtering [36]. In this experiment, ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure were deposited using sol-gel immersion method.

Some composites sensor that had been reported improved the humidity sensor performance. Leilei et. al reported on ZnO/TiO$_2$ composite nanorod array enhanced the sensitivity of humidity sensing [37]. Qing et. al found the preparation of composite ZnO-SiO$_2$ contribute a mesoporous that beneficial for humidity sensing properties [38].The aim of this project was to study the improvement of sensitivity towards humidity sensing for composite material ZnO/SnO$_2$ cubic structure compare to homogeneous material (ZnO nanorod and SnO$_2$ nanoparticle). To the best of my knowledge, there was no report on improvement sensitivity of humidity sensing performance for composite ZnO/SnO$_2$ cubic structure compare to single component material.

2. Methodology
   2.1. Preparation of seeded catalyst
   ZnO seeded catalyst were deposited on glass substrates by radio frequency (RF) magnetron sputtering. ZnO(99.999%) was used as target. The sputter was pump at $5 \times 10^{-4}$ Pa using a molecular pump. The chamber was injected with gas flow Ar:O$_2$ (45:5) sccm. The deposition was set up for 60 min at substrate temperature 500°C with RF power 200 watt. Then as prepared sample were anneal for 1h at 500°C.

   2.2. Preparation of sol-gel solution
   The sol-gel solutions were prepared to deposit on ZnO seeded catalyst. Firstly, the ZnO nanorod was prepared using zinc chloride (ZnCl$_2$) and 20 mmol sodium hydroxide (NaOH). ZnCl$_2$ and NaOH were dissolved in 50 mL distilled water (DI) for 10 minutes at 50°C and stirred using magnetic stirrer on a hot plate stirrer. The ZnCl$_2$ solution was slowly dropped into NaOH solution under magnetic stirring. Then the solution was sonicated by ultrasonic for 10 minutes at 50°C. As prepared solution were transfer into a container with the seed catalyst were placed at the bottom of the container. The seeded were facing up to container caps. Next, the containers were immersed inside a water bath with 95°C DI water inside. The immersion time were carried out for 6h. Then, the samples were washed with DI water and dried for 15 min at 100°C. The samples were annealed at 500°C for 1h. The same procedure was repeated for SnO$_2$ nanoparticle preparation by replacing ZnCl$_2$ to 3 mmol tin tetrachloride (SnCl$_4$·5H$_2$O). Lastly, the ZnO/SnO$_2$ cubic structure was prepared using mixture of ZnCl$_2$ solution and SnCl$_4$ solution by following the same procedure for ZnO nanorod and SnO$_2$ nanoparticle.

   2.3. Characterization
   The structural property of the thin film was characterized using FESEM (JEOL JSM 7600F) and EDX. An Au contacts were deposited on the thin film using thermal evaporator to fabricate humidity sensor. The measurements of sensor were taken using two point probe I-V measurement (Keithley 2400). The characteristic of the sensor including sensitivity, stability and reproducibility were studied. The humidity condition had been controlled using a humidity chamber (ESPEC SH-261) by varying the relative humidity percentages (RH%) from 40 RH% to 90 RH% at constant temperature 25°C.

3. Results and discussions
   3.1. Surface morphology
   Figure 1 (a), (b), (c) and (d) shows the ZnO seeded catalyst, ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure respectively. As been observed in Figure 1(a) show the ZnO seeded catalyst had columnar structured with average size 45nm. ZnO nanorod growth on ZnO seeded catalyst was shown in Figure 1(b). The average diameter of the ZnO nanorod was around 85nm. From the FESEM image, SnO$_2$ nanoparticle were form on seeded catalyst ZnO from the FESEM image as shown in Figure 1(c). As could been seen in Figure 1(d), the mixture of ZnO and SnO$_2$ resulting ZnO/SnO$_2$
cubic structure with average dimensions of cubic 120nm. The ZnO nanorod growth was based on seed layer[39]. However, SnO$_2$ nanoparticle was difficult to growth on ZnO seed layer due to lattice mismatch. There were aggregations of amorphous nanoparticles growth on ZnO/SnO$_2$ cubic structure and porosity as indicated in Figure 1(d). The formation of ZnO/SnO$_2$ cubic structure occurs when Zn$^{2+}$ and Sn$^{4+}$ particles were sonicated to let the both particles dispersed well and mix the Zn$^{2+}$ and Sn$^{4+}$ ions [39]. The combination of both particles formed cubic structure that favour from the thermal reaction during immersion process. The aggregations of amorphous nanoparticles that growth on ZnO/SnO$_2$ cubic structure might be due to Ostwald ripening law, which explained that the surface tension and surface to volume ratio [40]. Figure 2. (a), (b) and (c) shows the EDX spectrum of ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure respectively. EDX used to analyze the element of the sample. EDX spectrum of ZnO nanorod was shows in Figure 2(a) contained element of Zn and oxygen.

![Figure 1](image1.png)

**Figure 1.** (a) ZnO seeded catalyst, (b) ZnO nanorod, (c) SnO$_2$ nanoparticle and (d) ZnO/SnO$_2$ cubic structure with porosity as indicated in circle.

![Figure 2](image2.png)

**Figure 2.** EDX spectrum of (a) ZnO nanorod, (b) SnO$_2$ nanoparticle and (c) ZnO/SnO$_2$ cubic structure.

| Table 1. Atomic percentage of each element composition (%) |
|--------------------|-----|-----|--------|--------|
|                   | Zn  | Sn  | Oxygen | Carbon | Silicon |
| ZnO nanorod       | 42.02 | 52.66 | 5.32   |        |
| SnO$_2$ nanoparticle | 8.52 | 26.38 | 63.83  | 1.28   |
| ZnO/SnO$_2$ cubic structure | 16.04 | 16.55 | 61.32  | 6.09   |

Figure 2(b) shows the EDX spectrum that the presence of Zn, Sn and oxygen in the SnO$_2$ nanoparticle. The Zn element inside the SnO$_2$ nanoparticle was due to the ZnO seeded catalyst. The Zn, Sn and
oxygen element were detected in the ZnO/SnO$_2$ cubic structure as indicate in Figure 2(c). Table 1. show the list of atomic percentage of each element composition for ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure.

3.2. Humidity sensor

Figure 3 shows the sensing characteristic of fabricated sensor of ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure. Figure 3(a) shows the resistance measurement as a function of RH%. The value of resistance decreased as the RH% increased. The decrements of resistance occur due to presence of water vapour as the humidity increased. Figure 3(b) shows the sensitivity of ZnO/SnO$_2$ cubic structure show the highest with 22.5, ZnO nanorod sensitivity 7.5 and SnO$_2$ nanoparticle 2.3. The sensitivity data were calculated based from the ratio of resistance in air to resistance in humidity (at difference RH%). The highest sensitivity that produced by ZnO/SnO$_2$ cubic structure might be due to the contribution of porosity that enhanced the diffusion of water vapour [41]. Moreover, the shape of ZnO/SnO$_2$ cubic structure with three dimension (3D) favour large specific surface areas was another factor that influenced the sensitivity performance [42]. The stability of the sensor were measured at 90 RH% as indicated in Figure 3(c). The resistance were slightly the same when exposed to humidity every two hours. Figure 3(d) shows the reproducibility measurement of the ZnO/SnO$_2$ cubic structure when exposed to 40RH% and 90RH%. The current of the sensor increased steadily when the RH% increased and decreased rapidly when the RH% decreased. The sensor gave slightly same behaviour of current when it was tested for 4 cycles.

![Figure 3](image)

Figure 3. The humidity sensor characteristics of ZnO nanorod, SnO$_2$ nanoparticle and ZnO/SnO$_2$ cubic structure including (a) resistance measurement at various RH%, (b) sensitivity as function of RH% and (c) stability measurement at 90 RH%. Figure 3. (d) Repeatability measurement of ZnO/SnO$_2$ cubic structure with 1V voltage supplied tested for 4 cycles.

During high humidity, the water vapour increased and promotes the electron transport on the ZnO/SnO$_2$ cubic structure which controls the superconductivity of the thin film[43]. When the water
vapour decreased, the water vapour dissociates appearance protons as charge carrier by hoping transports on the surface of the thin film[44].

4. Conclusions
ZnO nanorod, SnO₂ nanoparticle and ZnO/SnO₂ cubic structure were successfully prepared on ZnO seeded catalyst using sol-gel immersion method. The ZnO seeded catalyst was prepared on glass substrate by RF magnetron sputtering. The sensing characteristics towards humidity indicated that ZnO/SnO₂ cubic structure give highest sensitivity compare to ZnO nanorod and SnO₂ nanoparticle. It was due to distribution of porosity on surface of ZnO/SnO₂ cubic structure and the large surface specific area for adsorption and desorption process. Besides, the stability and reproducibility performance of ZnO/SnO₂ cubic structure carry out that it’s was suitable for humidity sensor application.

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6. References
[1] Korotcenkov G 2007 Metal oxides for solid-state gas sensors: What determines our choice? Materials Science and Engineering: B 139 1-23
[2] Wang C, Yin L, Zhang L, Xiang D and Gao R 2010 Metal oxide gas sensors: Sensitivity and influencing factors Sensors 10 2088-106
[3] Singh N, Ponzoni A, Comini E and Lee P S 2012 Chemical sensing investigations on Zn–In₂O₃ nanowires Sensors and Actuators B: Chemical 171–172 244-8
[4] Yu J H and Choi G M 1999 Electrical and CO gas-sensing properties of ZnO/SnO₂ hetero-contact Sensors and Actuators B: Chemical 61 59-67
[5] Haeng Yu J and Man Choi G 1998 Electrical and CO gas sensing properties of ZnO–SnO₂ composites Sensors and Actuators B: Chemical 52 251-6
[6] Singh G, Choudhary A, Haranath D, Joshi A G, Singh N, Singh S and Pasricha R 2012 ZnO decorated luminescent graphene as a potential gas sensor at room temperature Carbon 50 385-94
[7] Chou C S, Chou F C, Ding Y G and Wu P 2012 The effect of ZnO-coating on the performance of a dye-sensitized solar cell Solar Energy
[8] Bu I Y Y and Yeh Y M 2012 Effects of sulfidation on the optoelectronic properties of hydrothermally synthesized ZnO nanowires Ceramics International
[9] Carotta M, Cervi A, Fioravanti A, Gherardi S, Giberti A, Vendemianti B, Vincenzi D and Sacerdoti M 2011 A novel ozone detection at room temperature through UV-LED-assisted ZnO thick film sensors Thin Solid Films 520 939-46
[10] Chen Z, Tian Y, Li S, Zheng H and Zhang W 2011 Electrodeposition of arborous structure nanocrystalline SnO₂ and application in flexible dye-sensitized solar cells Journal of Alloys and Compounds
[11] Wang X, Zhou X, Yao K, Zhang J and Liu Z 2011 A SnO₂ graphene composite as a high stability electrode for lithium ion batteries Carbon 49 133-9
[12] Ma X 2012 Towards Enhanced SnO2 Gas Sensor: Mini-Review Journal of Nanoengineering and Nanomanufacturing 2 143-9
[13] Choi Y J, Hwang I S, Park J G, Choi K J, Park J H and Lee J H 2008 Novel fabrication of an SnO2 nanowire gas sensor with high sensitivity Nanotechnology 19 095508
[14] Wang B, Zhu L, Yang Y, Xu N and Yang G 2008 Fabrication of a SnO₂ nanowire gas sensor and sensor performance for hydrogen The Journal of Physical Chemistry C 112 6643-7
[15] Chen A, Huang X, Tong Z, Bai S, Luo R and Liu C C 2006 Preparation, characterization and gas-sensing properties of SnO$_2$–In$_2$O$_3$ nanocomposite oxides Sensors and Actuators B: Chemical 115 316-21

[16] Elias J, Michler J, Philippe L, Lin M Y, Couteau C, Lerondel G and Lévy-Clément C 2011 ZnO Nanowires, Nanotubes, and Complex Hierarchical Structures Obtained by Electrochemical Deposition Journal of electronic materials 40 728-32

[17] Yin Y X, Xin S, Wan L J, Li C J and Guo Y G 2012 SnO$_2$ hollow spheres: Polymer bead-templated hydrothermal synthesis and their electrochemical properties for lithium storage SCIENCE CHINA Chemistry 1-5

[18] Chen L, Li C, Yin W L, Liu J, Hei L and Lu F 2011 Effect of deposition temperature and quality of free-standing diamond substrates on the properties of RF sputtering ZnO films Diamond and related materials 20 527-31

[19] Maleki M and Rozati S 2012 Structural, electrical and optical properties of transparent conducting SnO$_2$ films: effect of the oxygen flow rate Physica Scripta 86 015801

[20] Kang C G, Kang J W, Lee S K, Lee S Y, Cho C H, Hwang H J, Lee Y G, Heo J, Chung H J and Yang H 2011 Characteristics of CVD graphene nanoribbon formed by a ZnO nanowire hardmask Nanotechnology 22 292501

[21] Kwoka M, Waczyńska N, Kościelniak P, Sitarz M and Szuber J 2011 X-ray photoelectron spectroscopy and thermal desorption spectroscopy comparative studies of L-CVD SnO$_2$ ultra thin films Thin Solid Films 520 913-7

[22] Tian J H, Hu J, Li S S, Zhang F, Liu J, Shi J, Li X, Tian Z Q and Chen Y 2011 Improved seedless hydrothermal synthesis of dense and ultralong ZnO nanowires Nanotechnology 22 245601

[23] Q.T. Khuc, X. Hien Vu, D. Vuong Dang, and D. Chien Nguyen 2010 The influence of hydrothermal temperature on SnO$_2$ nanorod formation Advances in Natural Sciences: Nanoscience and Nanotechnology 1 025010

[24] Song X, Wang Z, Liu Y, Wang C and Li L 2009 A highly sensitive ethanol sensor based on mesoporous ZnO–SnO$_2$ nanofibers Nanotechnology 20 075501

[25] ND Sin, N. Khadijah, MH Mamat, M.Z. Musa, and M. Rusop 2012 Influence of Cubic Structured-ZnSnO$_3$ Immersion Time to the Performance of Humidity Sensor Nano Hybrids 2 1-11

[26] Parthibavarman M, Vallalperuman K, Sekar C, Rajarajan G and Logeswaran T 2012 Microwave synthesis, characterization and humidity sensing properties of single crystalline Zn2SnO4 nanorods Vacuum 86 1488-93

[27] Wang W, Tian Y, Li X, Wang X, He H, Xu Y and He C 2012 Enhanced ethanol sensing properties of Zn-doped SnO$_2$ porous hollow microspheres Applied Surface Science

[28] Han N, Wu X, Zhang D, Shen G, Liu H and Chen Y 2011 CdO activated Sn-doped ZnO for highly sensitive, selective and stable formaldehyde sensor Sensors and Actuators B: Chemical 152 324-9

[29] Zhang Z, Shao C, Li X, Zhang L, Xue H, Wang C and Liu Y 2010 Electros spun Nanofibers of ZnO–SnO$_2$ Heterojunction with High Photocatalytic Activity The Journal of Physical Chemistry C 114 7920-5

[30] Tu Y F, Fu Q M, Sang J P and Zou X W 2012 Synthesis and photoluminescence properties of the ZnO(â)SnO$_2$ core–shell nanorod arrays Journal of materials science 47 1541-5

[31] Liu Z Q, Ding L X, Wang Z L, Mao Y C, Xie S L, Zhang Y M, Li G R and Tong Y X 2012 ZnO/SnO$_2$ hierarchical and flower-like nanostructures: facile synthesis, formation mechanism, and optical and magnetic properties CrystEngComm 14 2289-95

[32] Ji H, Liu X, Wang X, Liang S, Ge X and Li Y 2011 Self-assembly of disk-like multiring ZnO–SnO$_2$ colloidal nanoparticles Journal of Colloid and Interface Science 356 412-5

[33] Wu R, Chen X and Hu J 2012 Synthesis, characterization, and biosensing application of ZnO/SnO$_2$ heterostructured nanomaterials Journal of Solid State Electrochemistry 1-8

[34] Kowsari E and Ghezelbash M R 2012 Ionic liquid-assisted, facile synthesis of ZnO/SnO$_2$ nanocomposites, and investigation of their photocatalytic activity Materials Letters 68 17-20
Yu L M, Fan X H, Shui J Y, Cao L and Yan W 2012 Fabrication of SnO$_2$/Zn$_2$SnO$_4$/ZnO Nanocables through Thermal Oxidation of Zn and Sn Mixture Powders Advanced Materials Research 532 70-3

Choi S W, Park J Y and Kim S S 2009 Synthesis of SnO$_2$–ZnO core–shell nanofibers via a novel two-step process and their gas sensing properties Nanotechnology 20 465603

L. Gu, K. Zheng, Y. Zhou, J. Li, X. Mo, G.R. Patzke, and G. Chen 2011 Humidity sensors based on ZnO/TiO$_2$ core/shell nanorod arrays with enhanced sensitivity Sensors and Actuators B: Chemical 159 1-7

Yuan Q, Li N, Tu J, Li X, Wang R, Zhang T and Shao C 2010 Preparation and humidity sensitive property of mesoporous ZnO–SiO$_2$ composite Sensors and Actuators B: Chemical 149 413-9

Mamat M H, Khusaimi Z, Zahidi M M, Bakar S A, Siran Y M, Rejab S A M, Asis A J, Tahiruddin S, Abdullah S and Mahmood M R 2011 Controllable Growth of Vertically Aligned Aluminum-Doped Zinc Oxide Nanorod Arrays by Sonicated Sol–Gel Immersion Method depending on Precursor Solution Volumes Japanese Journal of Applied Physics 50

Tcholakova S, Mitrinova Z, Golemanov K, Denkov N D, Vethamuthu M and Ananthapadmanabhan K 2011 Control of Ostwald Ripening by Using Surfactants with High Surface Modulus Langmuir 27 14807-19

Huang J, Xu X, Gu C, Wang W, Geng B, Sun Y and Liu J 2012 Size-controlled synthesis of porous ZnSnO$_3$ cubes and their gas-sensing and photocatalysis properties Sensors and Actuators B: Chemical 171–172 572-9

Huang J, Yu K, Gu C, Zhai M, Wu Y, Yang M and Liu J 2010 Preparation of porous flower-shaped SnO$_2$ nanostructures and their gas-sensing property Sensors and Actuators B: Chemical 147 467-74

Bauskar D, Kale B B and Patil P 2012 Synthesis and humidity sensing properties of ZnSnO$_3$ cubic crystallites Sensors and Actuators B: Chemical 161 396-400

Jamil H, Batool S S, Imran Z, Usman M, Rafiq M A, Willander M and Hassan M M 2012 Electrospun titanium dioxide nanofiber humidity sensors with high sensitivity Ceramics International 38 2437-41