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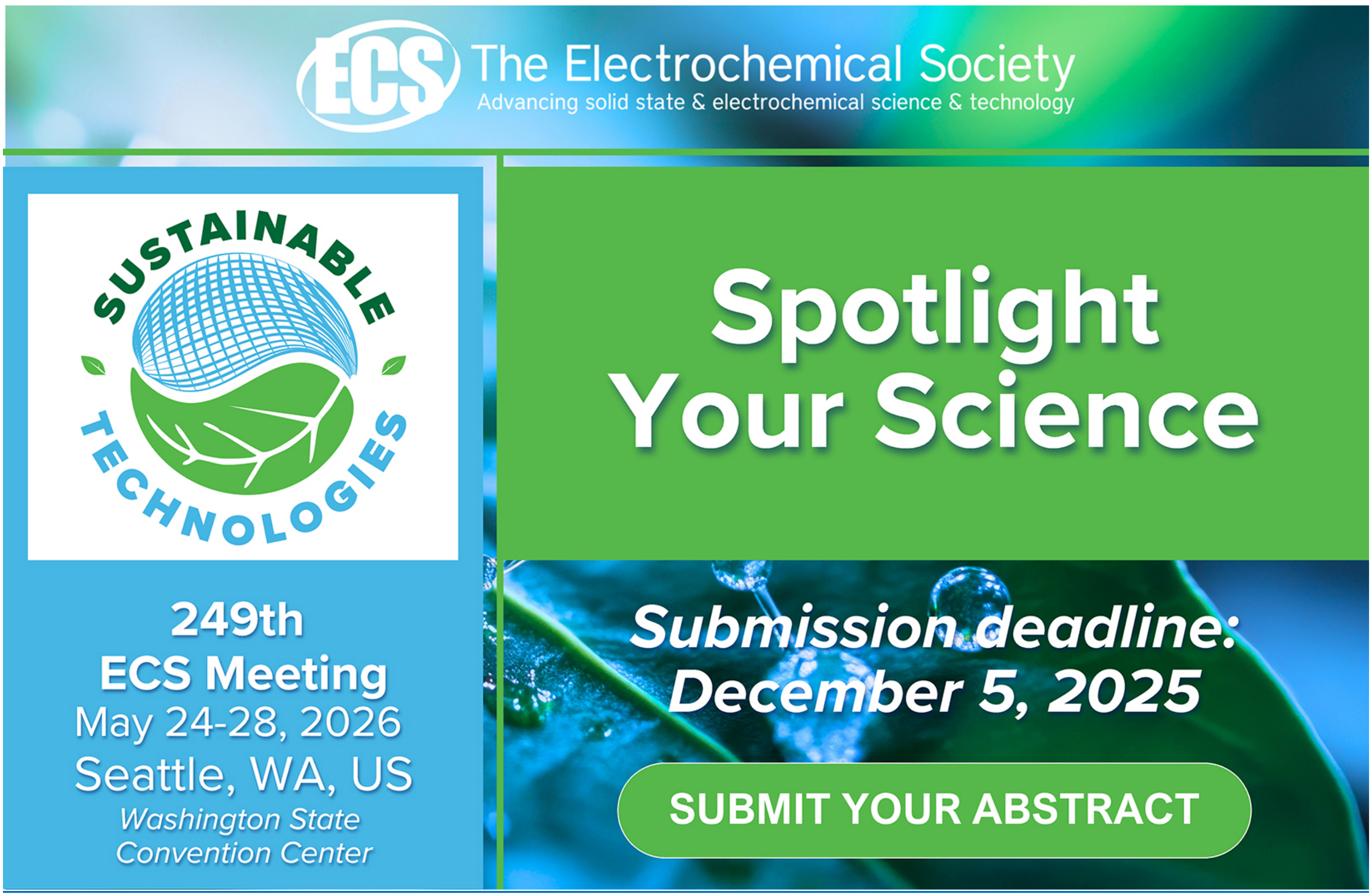

Influence of Sn dopant on ZnO Thin Film for Formaldehyde Detection

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Abstract. In this work, structural, morphological, electrical and gas sensing of ZnO and Sn doped ZnO thin film at different atomic percentage (0.5at%, 1.0at% and 1.5at%) had been studied. The precursor was prepared by sol-gel method and deposited on an IDE glass substrate by using spin coating technique. The effects of the dopant was then characterized through XRD, AFM, SEM and Agilent LCR Meter. Based on the XRD results, it was found that all films showed the highest diffraction peak intensity at (002) with crystallite size in the range of 8-33nm. Meanwhile the morphological properties from AFM and SEM showed an improvement in surface roughness from 16.7nm to 5.48nm and decrease the grain size from 45.42nm to 40.99nm in the presence of Sn dopant. Based on the image, the grains were uniformly distributed and ZnO thin film showed the hexagonal wurtzite structure, which proved the XRD result. Among all the samples, 1.0at% Sn doped showed the best result for detection of formaldehyde at 0.6ppm which up to 96% compare to undoped, 26.04% at 150°C. The response and recovery time was between 4-16 seconds. This showed that the presence of Sn can help to improve the conductivity of the ZnO thin film.

1. Introduction

Air pollution caused by volatile organic compound (VOC) has become a great interest for the researchers over the years because a lot of materials and utilities contained VOCs [1]. VOCs have a boiling point between 50 to 260°C [2]. There are many VOCs in the air, however this work is focusing on formaldehyde only. Formaldehyde is an organic compound that can be in forms of solid, liquid and gas. Formaldehyde also colorless and has a strong smelling gas even in room temperature. As formaldehyde is toxic and carcinogenic, so it can threatening human and animal life. The effect in human life is depending on the level of air concentration when exposed to the formaldehyde. When the concentration level is below than 10ppm, irritation and burning of eyes, nose, throat, difficulty in breathing and having teary eyes can happen. However, when the concentration is above 10ppm, it can cause terrible respiratory tract and lead to pneumonitis. More than 100ppm can lead to immediate danger for life and health [3]. Formaldehyde can be easily found like in wood-based product, in paper products, textiles, cleaning products, cosmetics and in insulation materials (from mineral wool or glass wool) [4]. Thus, it is important to detect the presence of formaldehyde. The detection of formaldehyde can be categorized into gas chromatography-mass spectrometry (GC-MS), optical devices [5] and metal oxide semiconductor (MOS) gas sensor [6]. Although GC-MS can give a high sensitivity and selectivity, but it is high cost, heavy and need an extra understanding before use the tool, while for optical device, the connected optical arrangement can be large and elaborate. Meanwhile, MOS gas offers great advantages like easy to use, cheap, low power consumption and can change gas concentration to electrical signal. There are a few reports focusing on using MOS for formaldehyde detection such as NiO [7], In_2O_3 [8], ZnO [9] and SnO_2 [10]. The characteristics of sensing in MOS is depend on the morphology, grain size, thickness and shape [10]. Among all MOS that have been mentioned, ZnO has always be a great attention because of high sensitivity, easy to fabricate and has widely used in gas sensor [11]. Apart from that, ZnO has a large exciton binding energy which is 60meV and band gap 3.3eV. Because of high binding energy, ZnO can be applied in various device and application like in solar cell [11], light emitting diode [12], gas and chemical sensor [13].

According to Prajapati [14], Sn doped ZnO thin film has been reported where spray pyrolysis is used for deposition method. From this work, 25ppm is the minimum detection of formaldehyde at temperature 275°C. Another reported work for formaldehyde is from Ning Han [8], where Ga doped ZnO is prepared by co-precipitation method. The operating temperature used is 400°C while the minimum concentration of formaldehyde is 2.3ppm. There are also another methods that have been done in order to prepare ZnO nanostructures such as magnetron sputtering [15], sol-gel [16], thermal evaporation [17] and spray pyrolysis [14]. In this work, sol-gel technique is chosen due to controllability of composition, simple to use, and cost effective [18]. Based on the previous work [8,14], the operating temperature used is quite high. More power consumption is needed when the temperature is high. Thus, the purpose of this work is to produce Sn doped ZnO thin film by sol-gel that can operate at temperature below than 200°C with the minimum concentration of formaldehyde.

2. Experimental Details

2.1. Sn doped ZnO Nanoparticles Synthesis

Sn doped ZnO thin film was synthesized by dissolving zinc acetate dehydrate and 0.5at% of tin chloride pentahydrate in 2-methoxyethanol. Then the solution was stirred by using a magnetic strirrer for 1 hour at 80°C. After first 10 minutes, ethanolamine was added drop by drop until the solution become homogeneous. Then the solution was aged for 24 hours. After that, the solution was drop on a prepared IDE glass substrate by using spin coating with speed 500rpm for 40seconds. The substrate then were annealed for 5 hours at 500°C to get the crystallite structure. Then, the experiment was repeated with 1.0at% and 1.5at% of tin chloride pentahydrate.

2.2. Characterization

The synthesized samples, named ZnO, 0.5at%, 1.0at% and 1.5at% Sn doped ZnO thin film were characterized by using X-ray diffraction and analyzed with CuKα radiation (λ=1.54059Å). The crystallite size was then measured by using Scherrer equation (1) [19]:

$$\mathrm{d} = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the x-ray wavelength, β is the full width at half maximum of the XRD peak (rad) and θ is the maximum Bragg diffraction peak. Meanwhile the lattice constant ‘a’ and ‘c’ of ZnO structure are determined by using equation (2) and equation (3) [19]:

$$a = \sqrt{\frac{1}{3}}\,\frac{\lambda}{\sin\theta} \tag{2}$$

$$c = \sqrt{\frac{\lambda}{\sin\theta}} \tag{3}$$

The morphological characteristics in terms of shape and surface roughness had been identified by using scanning electron microscope (SEM) operating at 10kV and atomic force microscopic (AFM).

2.3. Sensing Test

The sensing device consists of glass substrate (22.8x7.6mm) with gold interdigitated electrodes. The electrode consist of 125x2 fingers with 10 m gap size. Each length of the finger's size is 6760µm as shown in Figure 1.

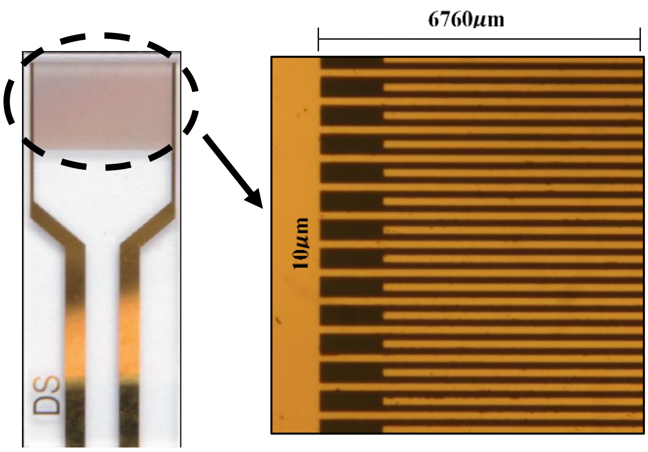

Figure 1. Structure of the interdigitated electrode.

The active sensing layer was deposited by sol-gel technique as mentioned. The device then was placed in a test chamber as shown in Figure 2 for electrical and sensing purpose. Agilent E4980 LCR Metre was used for the sensing. The device also was put on a hot plate at temperature 150°C. Once the device achieved a steady state, then the formaldehyde (10uL, 15uL, 20uL and 25uL) were injected into the chamber. The formaldehyde liquid then evaporated and vaporized by heating. The concentration of the formaldehyde (ppm) can be calculated by using the equation (4) [20]:

$$C = \left\{ \frac{V_L \times D_L \times T}{M_L \times V_A} \right\} \times 8.2\times10^4 \quad (4)$$

where T is the operating temperature (K), V_L is volume of the formaldehyde (µL), D_L is the density of the formaldehyde (g ml^{-1}), M_L is the molecular weight of the formaldehyde (g mol^{-1}) and V_A is the volume of the diluting gas which is equal to the volume of the test chamber (mL). Then, the sensitivity of the formaldehyde response was measured by using followed equation (5) [14]:

$$S\,[\%] = [(R_a - R_g) / R_a] \times 100\% \quad (5)$$

where R_a is the resistance in ambient air and R_g is when formaldehyde is introduced. Then multiply by 100 to get the response in percentage.

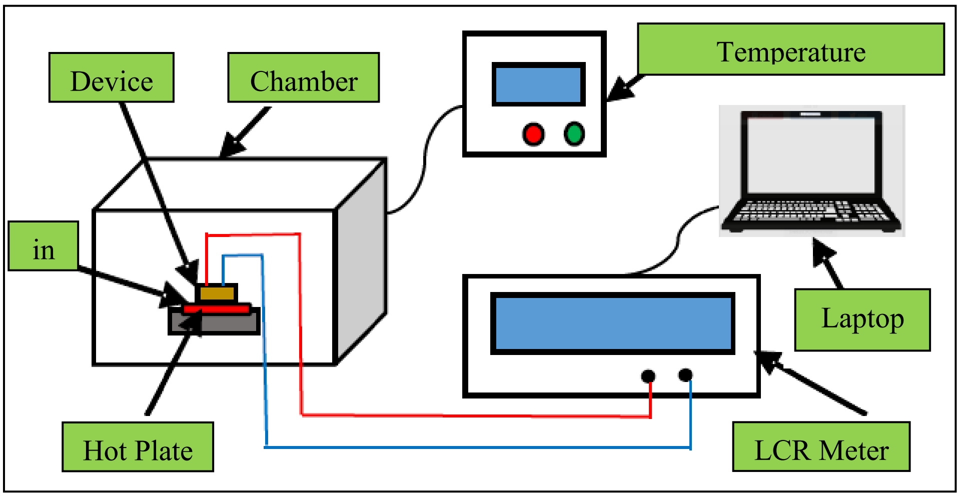

Figure 2. The schematic diagram of formaldehyde sensing.

3. Results and Discussions

3.1. Microstructure and Morphological Characteristics

X-ray diffraction spectra of ZnO and Sn doped ZnO thin film are shown in Figure 3 after annealing at 500°C for 5 hours. The intensity peak of (002) is the highest due to the replacement of Zn as Sn^{4+} (0.069nm) has smaller ionic radius than Zn^{2+} (0.074nm).

According to equation (1), the crystallite size of the grain is tabulated in the Table 1. When doping concentration increased, the crystallite size decrease. There is variation of crystallite size due to the different in density of nucleation centre, hence decrease the size when stress occur and increase the size back when undergone tensile stress. That is the reason why for 0.5at%, the size is a bit higher and decrease back when doping is keep increasing.

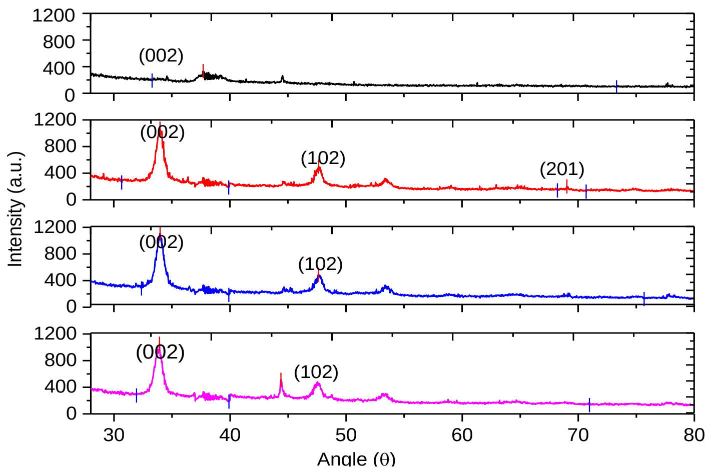

Figure 3. X-ray diffraction spectra of ZnO and Sn doped ZnO thin film.

Table 1. XRD data for ZnO and Sn doped ZnO thin film.

Thin Film	hkl	Crystalline Size,d (nm)	a=b (Å)	c (Å)
ZnO	002	10.09	2.993	5.276
0.5at% Sn doped ZnO	002	33.36	2.271	4.300
1.0at% Sn doped ZnO	002	8.736	2.630	4.556
1.5at% Sn doped ZnO	002	9.31	2.635	4.564

The lattice constant for (a=b) and c are shown in the Table by using equation (2) and equation (3). When there is Sn dopant, lattice c is decrease and this is because of incorporation of Sn into the lattice.

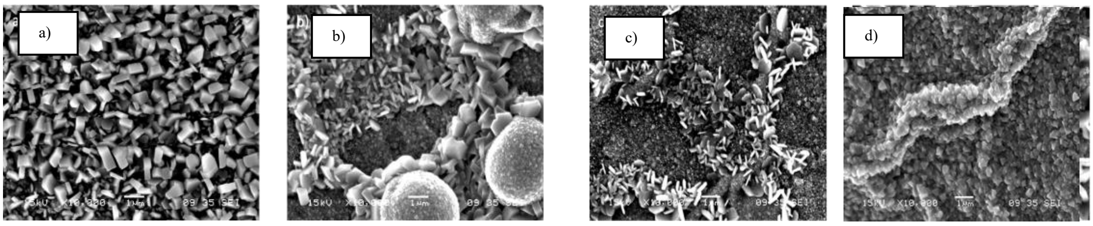

Figure 4. SEM images of (a) ZnO (b) 0.5 at% (c) 1.0at% and (d) 1.5at% Sn doped ZnO thin film.

Based on Figure 4, both ZnO and Sn doped ZnO thin film has different surfaces. This shows that the dopant strongly affects the properties of the thin film. The grain size increase along the Sn dopant. The image of Figure 4 b), c) and d) show there are two different creatures there. There is white cluster for doped ZnO thin film as Sn has high conductivity.

Meanwhile, Figure 5 show the AFM image of ZnO and Sn doped ZnO thin film. Visually, there is no significant difference between Sn doped ZnO thin film , but there is different in terms of surface roughness and grain size as shown in table 2. According to the table, the highest surface roughness is for ZnO thin film and decrease when Sn dopant is present. When the grain size decrease, the surface roughness also decrease because of substitution of Sn in ZnO thin film. However, for 0.5at% Sn doped ZnO thin film, the grain size is higher than others because the crystallite is overlap and caused agglomeration. Chemical growth of the crystallite size resulted to agglomeration [21].

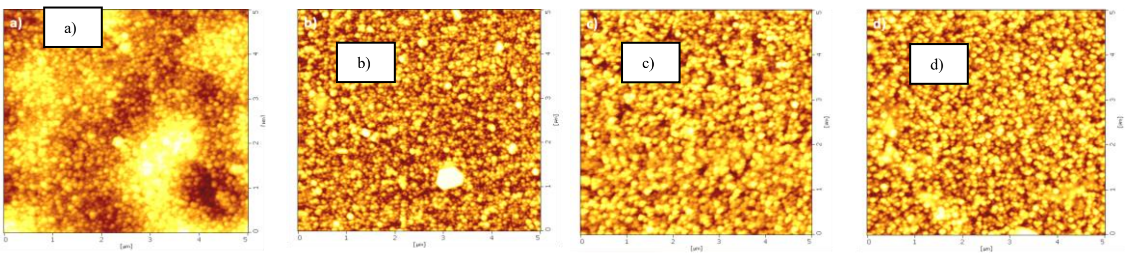

Figure 5. AFM image of a) ZnO b) 0.5at% c) 1.0at% and d) 1.5at% Sn doped ZnO thin film.

Table 2. Surface roughness (RMS), average grain size and crystallite size of ZnO and Sn doped ZnO thin film.

Type	Surface Roughness (nm)	Average Grain Size (nm)
ZnO	16.7	45.42
0.5at% Sn doped ZnO	10.19	46.31
1.0at% Sn doped ZnO	8.57	44.22
1.5at% Sn doped ZnO	5.48	40.99

3.2. Sensing Test

ZnO and Sn doped ZnO thin film were tested towards formaldehyde. In order to compare the performance of the different material and concentration, the temperature was fixed at 150°C because from previous works among 130°C, 150°C, 170°C and 190°C, 150°C shows the best sensitivity. According to the Figure 6, all sensing device are sensitive towards formaldehyde.

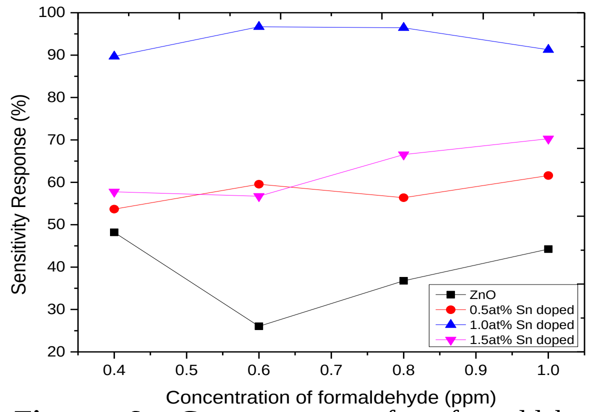

Figure 6. Gas response for formaldehyde concentration of 0.4-1.0ppm at 150°C.

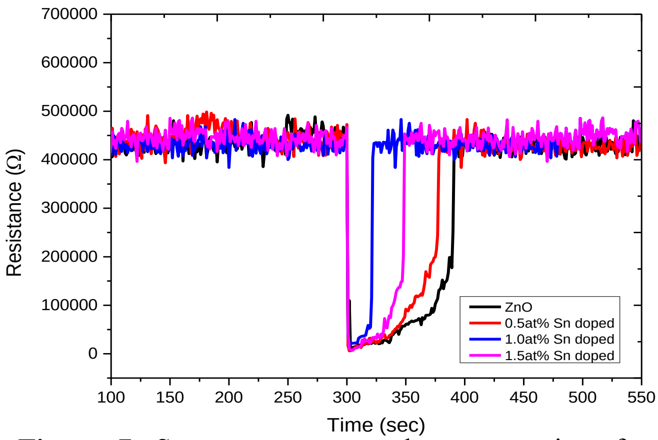

Figure 7. Sensor response and recovery time for 1.0ppm at 150°C.

Formaldehyde response between 0.4ppm to 1.0ppm is shown in Figure 6. From the figure, 1.0at% Sn doped ZnO shows the highest sensitivity compare to ZnO thin film only. The sensitivity rapidly increase when Sn dopant is present. Meanwhile Figure 7 shows the response and recovery time of the sensor towards 1.0ppm at 150°C. The resistance sharply decrease when formaldehyde was injected and back to the baseline when the formaldehyde is no longer present. The response time for ZnO, 0.5at%, 1.0at% and 1.5at% Sn doped are 5s, 6s, 4s and 5s while the recovery time are 84s, 70s, 16s and 42s respectively. The results indicate that, the shortest response and recovery time was 1.0at% Sn doped ZnO thin film and the longest response and recovery time is ZnO thin film.

In ambient air, the ZnO surface absorbed the oxygen molecules and caused the depletion region to be thick. Hence increase the resistivity and decrease conductivity. However, when formaldehyde is introduced, the conductivity of the ZnO thin film changes as it releases electron into the conduction band by reacting with the oxygen chemisorbed semiconductor surface. This situation reduce the O_2^-, O^- and O^{2-} ions, then increase the amount of electrons in the conduction band [22] and also increase the electrical conductivity. The possible reaction is shown below:

$$O_2 \text{ (air)} \leftrightarrow O_2 \text{ (ads)}$$
$$O_2 \text{ (ads)} + e^- \leftrightarrow O_2^- \text{ (ads)}$$
$$O_2^- \text{ (ads)} + e^- \leftrightarrow 2O_2^- \text{ (ads)}$$

$$HCHO + 2O^- \text{ (ads)} \quad \leftrightarrow \quad CO_2 + H_2O + 2e^-$$

The oxygen get the electron from the ZnO and form $2O^-$, hence cause the conductivity to be low. But, when formaldehyde is present, and react with $2O^-$, it will release the electron back to the conduction band, thus increase the conductivity back.

4. Conclusion
ZnO and Sn doped ZnO thin film are successfully prepared and grown by sol-gel and spin coating method. Based on the result, Sn dopant play an important role for formaldehyde sensing. This is because, when Sn dopant is present, the response and recovery time become shorter and the sensitivity also increase. The best dopant in this work is 1.0at% Sn doped ZnO thin film which give the sensitivity up to 96% for 0.6ppm of formaldehyde.

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