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Sn Doped ZnO Thin Film For Formaldehyde Detection

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Abstract. In this work, sol-gel with spin coating technique was applied in order to produce undoped and Sn doped ZnO thin film with different doping concentration of 0.5 at%, 1.0at% and 1.5at%. The starter material used was zinc acetate dehydrate ($Zn(CH_3COO)_22H_2O$). The thin film was deposited on an interdigitated electrodes (IDE) for 5 hours and annealed at the temperatue of 500°C. The crystallite size of the film decreased when dopant was introduced, as well as the surface roughness of the thin film. XRD was used to identify the crystallinity, crystallographic orientation and phase evaluation of undoped and Sn doped ZnO. From the XRD pattern, it was observed that the peaks and diffraction correspond to the wurtzite-structured of ZnO. Sensing results indicate that the gas sensing response increase from undoped to doped ZnO thin film as a function of operating temperature where the maximum response for formaldehyde detection was at 130°C (~95%) for doping concentration of 1.5at%. The response time for 0.4ppm of formaldehyde was 17sec followed with 16sec, 12sec and 13 sec for 0.6ppm, 0.8ppm and 1.0ppm respectively

INTRODUCTION

Formaldehyde is an organic compound that is colorless and soluble in water, alcohol and ether [1]. It is typically produced from automobile, industries that burn fossil fuels, and open burning [2]. In addition, formaldehyde can also be found in rain water and ocean, due to its water solubility [1]. Toxicity and carcinogenicity of formaldehyde has caused concern in community as highlighted by International Agency for Research on Cancer (IARC) [3]. It is reported that most people spend 80% of their time indoor, where the concentration of formaldehyde indoor is 2-10 times higher compared to the concentration of formaldehyde found outdoor which is in the range of tens ppb [4]. The effect of exposure to formaldehyde varies as it depends on the concentration level of formaldehyde. At the concentration of 0.5-2 ppm, formaldehyde could cause irritation and pain on the nose, throat and eyes. Meanwhile, exposure to formaldehyde at the concentration of 3-5ppm could induce breathing difficulty, coughing, teary eyes and blazing nose and throat [5]. Due to these factors, the highest amount of allowed formaldehyde as endorsed by the World Health Organization (WHO) is 0.08 ppm.

Thus, it is imperative to monitor and control the presence of formaldehyde in the environment. There are several existing methods of formaldehyde detection such as optical detection device and gas chromatography-mass spectrometry (GC-MS) [6]. GC-MS method is the combination of gas-liquid chromatography and mass spectrometry. Even though this method has better sensitivity, however high cost and heavy weight equipment is not preferred for in-field measurement [7]. Meanwhile, optical sensor tends to be bulky and enlarged when used even though it is less time consuming [8].

Gas sensors based on metal oxides such as SnO_2,[9] TiO_2 [10] and ZnO [11-12] have played an increasing role in this field because they have good responses and it is possible to modify their electrical characteristics. In particular, gas sensor based on thin film Zinc Oxide (ZnO) has been preferred for sensing applications because of its tuneable surface morphology, very large surface-to-volume ratio, and superior stability due to better crystallinity. The mechanism of gas detection is by means of surface reaction, where the absorption of gas by ZnO thin film will affect its conductivity, hence reducing its electrical properties.

There are various methods that can be used to prepare ZnO thin film namely sol gel [10], magnetron sputtering [11], electron beam evaporation [12] and spray pyrolysis [13]. Sol gel offers many advantages, such as

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easily controlled chemical component used, has high surface morphology even at low temperature and often required low cost equipment [14]. In addition, sol-gel method has an ability to distribute the precursor uniformly [15-16].

In this paper, we introduce Sn doped ZnO gas sensor for formaldehyde detection at low temperature using sol gel method. The doping concentration of Sn are varied at 0.5 at%, 1.0 at% and 1.5 at%. Then, the doped IDE structure is used as a sensing device to detect formaldehyde at operating temperature of 150°C. Sn is chosen as the dopant because it has two more frees electron after Sn become Sn^{4+} when replaced with Zn^{2+} in ZnO structure [17]. This is crucial for electron conduction purpose. According to Yung [18], doping play a crucial role in optical properties, and this proved that doping can alter the behaviour of ZnO thin film by affecting the grain size and vibrational structure of the thin film. Apart from that, the radius difference between Sn^{4+} and Zn^{2+} is at about 30% (Zn^{2+} = 0.74Å and Sn^{4+} = 0.69Å), and this allow for a limited solid solution to be formed. This sensing device consists of glass substrate (22.8x7.6mm) with gold interdigitated electrode purchased from DropSens. The purpose of using IDE was due to the fact that a better electrical conductivity can be obtained when the formaldehyde was in contact with the device. In addition, IDE technology with various gap sizes has been proven to be sensitive, can be working in low volume of sample, avoiding tedious polishing of solid electrodes, can enhance detection limit and fast response for sensor application as presented by other authors [19-20]. Similar work using the IDE technology for formaldehyde detection also has been done [21-22]. Based on [22], SnO_2 thin film was coated on Al-IDE electrode with 8 fingers in total. It has been reported that the lowest detection was 11ppm for formaldehyde at 200°C. Apart from that, other metal oxide semiconductor, ZnO was deposited on an IDE that consists of Al and SiO_2 with 37 fingers in total [22]. From the paper, the lowest detection for formaldehyde was 1.5ppm. Moreover, the device showed a good selectivity response of formaldehyde compare to DI water. However, based on the previous works [21-22], both used a few 'fingers' of IDE only, meanwhile in this work, 250 fingers of IDE were used and according to [23], the sensing area can be increased when the number of 'fingers' were also increased. In addition, the material used in both previous works [19-20] is different type of dopant contrary to this work.

MATERIALS AND METHOD

Sol gel with spin coating method was used for preparation of undoped and Sn doped ZnO solution. Zinc acetate dehydrate and tin chloride pentahydrate ($SnCl_45H_2O$) were dissolved in 2-methoxyethanol ($C_3H_8\ O_2$). These solution were mixed with different concentration of $SnCl_45H_2O$ which were 0.5 at%, 1.0 at% and 1.5 at%. Then, magnetic stirrer was used to stir the precursor at 80°C for 1 hour and during that time, ethanolamine as a stabilizer was added little by little until the precursor becomes homogeneous and colourless. Then the prepared solution are left for 24 hours. After that, the precursor was deposited on the IDE and rotated at 1500 rpm for 40 seconds by spin coating. Then, the sample was placed on the hot plate (soft bake) for 10 minutes at 150°C, so that the solvent evaporated and any organic residue can be removed. Lastly, the samples were annealed in a furnace for five hours at 500°C.

The layer structure of the sample was identified and studied by using XRD. Bruker Diffract.Suite Eva with CuK$\propto$ (λ = 1.54056Å) radiation with scanning range set between 25° to 80° was used to record the result. The morphological of the structure was studied by using SEM and AFM. Meanwhile the resistance of the thin film was measured using Agilent (E4980A). The sensing device consists of a glass substrate (22.8x7.6mm) deposited with gold interdigitated electrode (DropSens). As shown in Figure 1, the IDE consists of 125x2 fingers with 10µm gap size. The length of each finger is 6760µm. The purpose of using IDE is due to the fact that a better electrical conductivity can be obtained when the formaldehyde is in contact with the device. In addition, the use of IDE could avoid tedious polishing of solid electrodes and can enhance sensitivity and detection limit. The schematic of the test chamber for formaldehyde detection is shown in Figure 2.

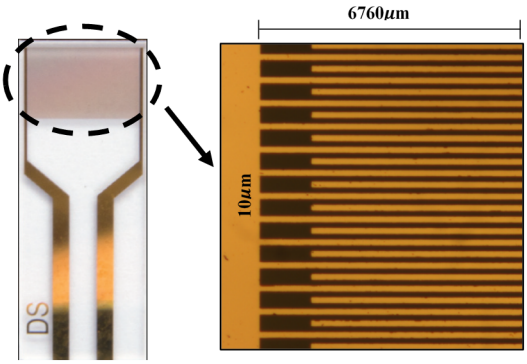

FIGURE 1. IDE Sensing electrode structure

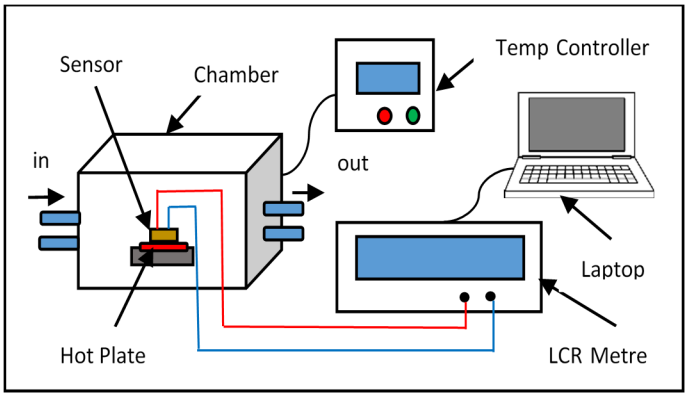

FIGURE 2. Formaldehyde measurement setup

RESULTS AND DISCUSSION

XRD is used to identify the crystallinity, crystallographic orientation and phase evaluation of undoped and Sn doped ZnO. From the XRD pattern shown in Figure 3, the peaks and diffraction correspond to the wurtzite-structured of ZnO indexed with JCPDS No.: 05-0664 [13]. The patterns have a strong (002) peak. However, for doped ZnO samples, there is also peak at (102) and (112). This behavior is similar as obtained by [24-25] using sol gel method.

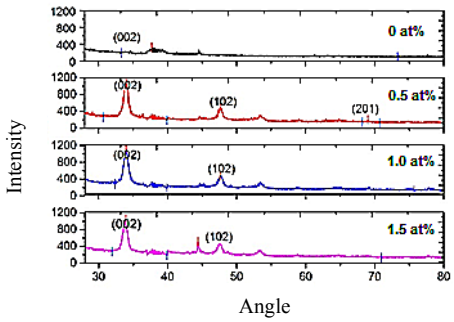

FIGURE 3. Image of XRD spectrum for Sn doped ZnO thin film

Based on Table 1, the intensities peak of ZnO thin film decrease at (002) as the Sn concentration increase from 0.5at% to 1.5at%. The destruction of undoped thin film's growth orientation is the reason why the peak intensity decrease [26-27]. The crystallite size increase from undoped thin film to 0.5at%, and this may happen because of agglomeration. This is proven from the lattice parameter c which decrease from 5.2769 to 4.3001 due to the replacement of tin into the lattice. However, the crystallite size decrease again when doping concentration is increased as the density of the nucleation centre gets higher with the film growth [15].

TABLE 1. XRD analysis for undoped and doped ZnO thin film

ZnO Thin Film	Position (2θ)	d spacing observed (Å)	hkl	Crystalline Size (nm)	a=b (Å) (average)	c (Å) (average)	Average Grain Size (nm)	Average Surface Roughness (nm)
Undoped	34.5	2.592	002	10.09	2.993	5.276	34.33	3.442
0.5 at%	33.9	2.634	002	33.36	2.271	4.300	9.28	2.266
	47.6	1.905	102	10.29				
	69.1	1.356	201	24.79				
1.0 at%	33.7	2.650	002	8.736	2.630	4.556	7.5	1.780
	47.6	1.905	102	9.138				
1.5 at%	33.7	2.650	002	9.31	2.635	4.564	5.49	1.602
	47.4	1.913	102	22.6				

According to results shown in Table 1, it can be seen that the grain size are affected by the dopant concentration. The trend shows that the average grain size decreases as the dopant concentration increases. This is similar as reported by [28] where there is a reduction in grain size with the growth in Sn concentration. The film thickness is approximately 150nm to 160nm. When the thickness of the film is below 200nm, the in-plane grain size does not differ much, and only small part of the grain changed. The structural and morphological properties of the undoped and Sn doped ZnO thin film was determined by using AFM and SEM, as reported in our previous work [29].

The measurement of the resistivity of the doped and undoped ZnO films are conducted using a dc-two probe method. Figure 4 shows the resistance value as a function of temperature in the range of 130 to 190°C. It can be seen that the resistivity decreases as the dopant concentration is increased. The conductivity characteristics of n-type ZnO semiconductor is due to the electron vacancies from O^{2-} and Zn^{2+} atom. In order for dopant to be incorporated, the difference between the ionic radii and the lattice of the dopants should be less than 15%. For this work, the value of Zn^{2+} ionic radii and Sn^{4+} is 0.74Å and 0.69Å respectively, thus, the substitution of these dopants with Zn^{2+} is possible in the film matrix [13]. The contribution of ions from Sn^{4+} on site of Zn^{2+} ions causes the conductivity of Sn doped ZnO to be higher compared to undoped ZnO thin film, thus reducing its resistance [30]. When the temperature is increased, there are two processes that occur simultaneously, which are thermal excitation of electron and the adsorption of electrons. For undoped ZnO thin film, it is hypothesized that the thermal action of electrons are influenced by the oxygen adsorption as the resistance increases up to 170°C. However, when the temperature keep increasing, the thermal excitation of electron dominate oxygen adsorption of the thin film on the surface, hence decreasing the resistance value [13]. This situation also happen when the temperature is beyond 180°C as all films resistance tend to decrease, and the trend is similar as reported by [31-32]. In order to obtain a good and stable sensor, optimal temperature must be identified as electrical conductivity does not only depends on the gas atmosphere. Apart from that, in dominance oxygen adsorption case, it will form ionic atom such as O^{2-}, O^{-}, and $O^{-}_{2,}$ in which the electron is obtained from the conduction band [13].

The response characteristic of the ZnO thin films toward formaldehyde were investigated at different operating temperature from 130 to 190°C. Formaldehyde concentration was varied from 0.4 ppm to 1.0 ppm. Figure 5 shows the gas response of 0.4 ppm based on varying operating temperature for different dopant concentration. The response of the sensor to formaldehyde is calculated by using the following equation:

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

where S is the formaldehyde sensitivity response, R_a is the thin film resistance before being introduced to formaldehyde, and R_g is the film resistance after being exposed to formaldehyde.

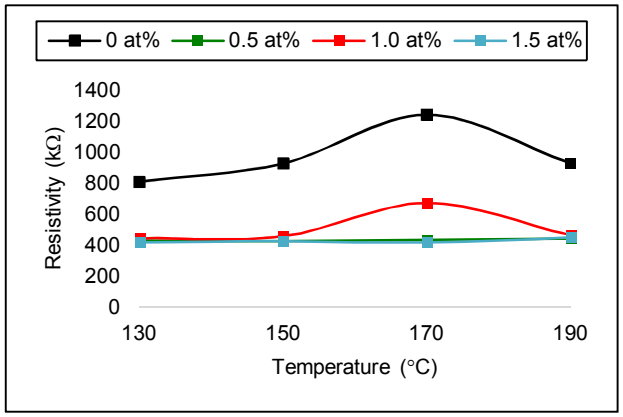

FIGURE 4. Electrical resistance as a function of temperature

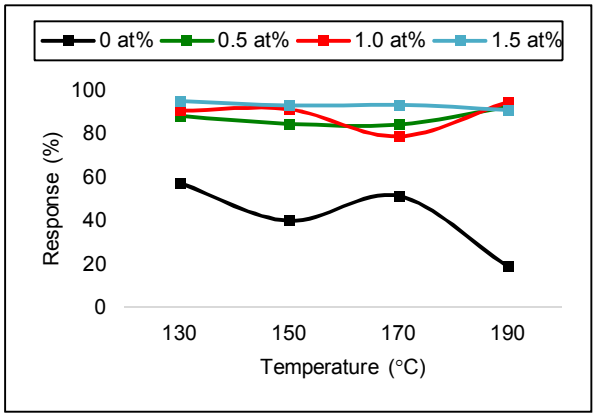

FIGURE 5. The influence of operating temperature on the response of formaldehyde at 0.4 ppm

Based on the results obtained, the response increase from undoped to doped ZnO thin film as a function of temperature. The response increase as the surface desorption of oxygen higher along with the temperature. However, among all the doped thin film, the maximum response for formaldehyde detection is at 130°C (~95%) for 1.5at% Sn doped ZnO thin film. For 0.5at%, the response decreases compared to 1.0at%, but it is still higher than undoped ZnO thin film. The results obtained are similar to the gas response result as reported by [33]. This may happen because of the higher surface roughness and smaller crystallite size of the film as stated in Table 1 from the AFM and XRD analysis. Higher surface roughness may lead to higher absorption of oxygen and create more sensing sites. The decrease response when the temperature increases maybe due to the absent of sufficient adsorbed oxygen species. The formaldehyde response changes because of electron concentration in the material [31-32].

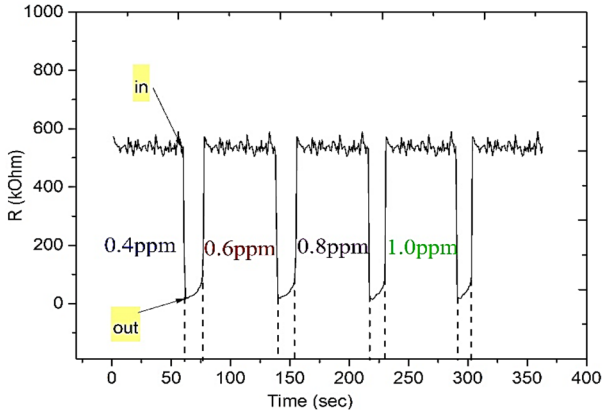

FIGURE 6. Resistance for the response and recovery time of 1.5at% Sn doped ZnO thin film for different formaldehyde concentration at 130°C.

Figure 6 shows the response characteristic of the gas sensor for 1.5at% Sn doped ZnO thin film at 130°C, where the film shows the highest response at this particular temperature. The response characteristics are the relationship between the time taken for changes in gas concentration and the resistance. The response time for 0.4ppm of formaldehyde is 17sec followed with 16sec, 12sec and 13 sec for 0.6ppm, 0.8ppm and 1.0ppm respectively. The response time is imperative as it determine the applicability of the sensor. A good sensor has a quick response and recovery time with low operating temperature.

CONCLUSION

In conclusion, sol gel technique can be used to prepare Sn doped ZnO thin film and possess hexagonal wurtzite structure. The XRD data revealed that Sn doping affects the peak intensity of the ZnO thin film. The crystallite size of the film decrease as there is doping whereas the surface roughness increase. This means that, the presence of Sn dopant can modified the surface roughness and it is crucial as it can favour the adsorption of oxygen, hence the sensing response can be increased. Based on the result, 1.5at% doped ZnO thin film shows a good gas response which is more than 90% for all temperature, but works the best at the temperature of 130°C. The resistance value decreases from 800 kΩ to 400 kΩ as doping is present. Oxygen adsorption, excitation of electron and oxygen desorption explained the change in film resistance.

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