

Ethanol Sensing Characteristics of Sn-doped ZnO Tetrapods Sensor

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Keywords: Gas sensor, Tetrapods, Zinc Oxide, Thermal Oxidation, Doping

Abstract. Sn-doped ZnO tetrapods (*T*-SnZnO) were successfully synthesized using a simple thermal oxidation reaction method. Zn powder with 20 mol% of Sn powder was used as raw material and synthesized at temperature of 1,000°C under normal atmosphere. FE-SEM images revealed that the *T*-SnZnO exhibited a four symmetry legs with the length of $1.94 \pm 0.42 \mu\text{m}$ and the width of $260 \pm 40 \text{ nm}$. EDS analysis confirmed that the tetrapods contain small amount of Sn. XRD analysis indicated that the tetrapods exhibited a wurtzite hexagonal ZnO structure corresponded to Raman results. The lattice parameters *a* and *c* were 3.2494 Å and 5.2057 Å, respectively. The *T*-SnZnO were fabricated as ethanol sensor and tested with ethanol concentration of 50, 200, and 1,000 ppm at operating temperature between 280°C-340°C by observing I-V curve of the sensors. The sensor response increased as the increasing of the operating temperature and the ethanol concentration. Moreover, the enhancement of ethanol sensor response was observed, and the highest sensor response of 30.4 was detected at 340°C. The sensor response was higher than those of ZnO tetrapods, TiO₂-ZnO tetrapods, ZnO nanowires, and TiO₂-ZnO nanowires sensors.

Introduction

Nowadays, metal oxide semiconductors have received a great attention and have extensively been investigated since they showed the great potential properties [1]. Among of these, a promising material ZnO with nanostructures have been used in widely applications such as biosensor, dye-sensitized solar cells, field effect transistor, field emission device, and gas sensor. ZnO tetrapods (*T*-ZnO) is one of the favorable materials that have been studied and used for many applications [2-5]. It was also used as the gas sensor and have been studied with several target gases [6,7].

Most researchers played their attention on improvement sensing properties of sensor by controlling architectural defects of sensing materials [1], increased reaction rate and/or a number of adsorbed oxygen species [6], and modified the electronics state of sensor surface [6,8]. As a result, the sensing properties could be improved. For example, Ti-coated ZnO nanostructures sensor showed the improvement of toluene sensor response [8]. Moreover, the enhancement of ethanol sensor response of ZnO tetrapods modified by TiO₂ additive was also reported by our group [6,9].

In this work, Sn-doped ZnO tetrapods (*T*-SnZnO) were synthesized throughout a simple thermal oxidation reaction method in normal air and fabricated as the gas sensor. The *T*-SnZnO sensor was tested with ethanol gas at several operating temperature. The *T*-SnZnO sensor exhibited a promising sensor response. Moreover, the sensor response of the *T*-SnZnO sensor was also compared with *T*-ZnO and ZnO nanowires (*NWs*-ZnO) sensors, for both with and without TiO₂.

Experimental

The *T*-SnZnO were synthesized using the simple thermal oxidation reaction method. Mixed powder of Zn with 20 mol% of Sn was put onto alumina crucible and then loaded into the center of electrical furnace at 1,000°C under normal atmosphere. A quick combustion of the mixed powder

inside the furnace was observed forming white-wool product. Then, the alumina crucible was removed from the furnace and allowed to cool down in the air for 2 hr. Subsequently, the white-wool product was collected and characterized by field emission electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), X-ray diffractometry (XRD), and Raman spectroscopy (RS) for morphology, chemical composition, phase formation, and crystal structure.

The $T\text{-SnZnO}$ was fabricated as ethanol sensor, and ethanol sensing characteristics were detected by observing current-voltage characteristic curve (I - V curve), tested with ethanol concentration of 50, 200, and 1,000 ppm at operating temperature in the range of 280°C - 340°C . The sensor response was calculated from Eq. 1 at applied voltage of 5 V. I_{gas} and I_{air} are sensor current under the ethanol gas and under the air, while R_{air} and R_{gas} are sensor resistance under the air and under the ethanol gas, respectively.

$$S = I_{\text{gas}}/I_{\text{air}} = R_{\text{air}}/R_{\text{gas}}. \quad (1)$$

Results and Discussion

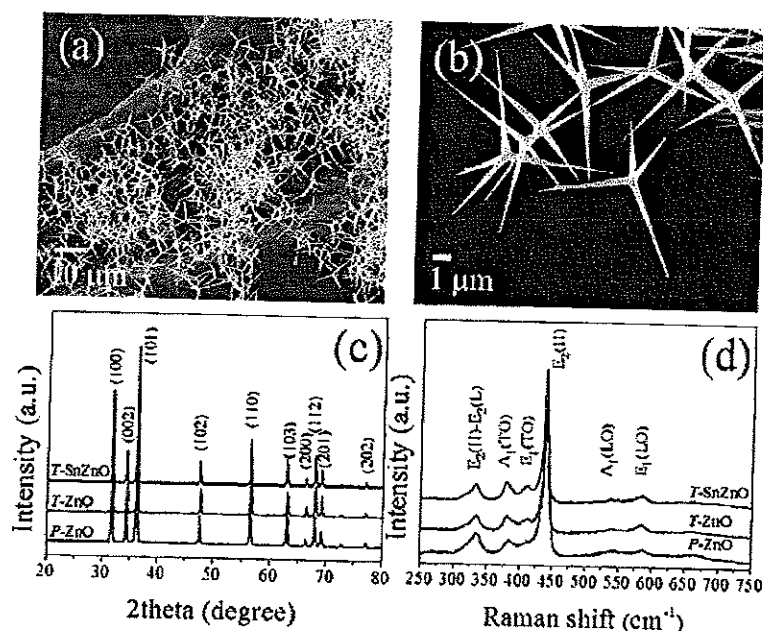


Figure 1 (a) low magnification (b) high magnification FE-SEM images of the $T\text{-SnZnO}$, (c) the typical XRD patterns, and (d) the RS spectrum of the $T\text{-SnZnO}$.

The FE-SEM images of the $T\text{-SnZnO}$ were demonstrated in Fig. 1(a) and 1(b). The large number of $T\text{-SnZnO}$ were observed exhibited a four symmetry legs with the average length of $1.94 \pm 0.42 \mu\text{m}$ and the average width of $260 \pm 40 \text{ nm}$. The chemical composition of the $T\text{-SnZnO}$ was examined using the EDS analysis (data not shown). The EDS analysis confirmed that the tetrapods contain small amount of Sn together with Zn and O. Phase formation of the $T\text{-SnZnO}$ was investigated by XRD technique. The typical XRD pattern of the $T\text{-SnZnO}$ was plotted together with ZnO powder ($P\text{-ZnO}$) and $T\text{-ZnO}$ samples as shown in Fig. 1(c). It was observed that all diffraction peaks of the $T\text{-SnZnO}$ were similar to the $P\text{-ZnO}$ and the $T\text{-ZnO}$ samples. These peaks corresponded to (100), (002), (101), (102), (110), (103), (200), (112), (201), and (202) diffraction planes of a wurtzite hexagonal ZnO structure (JCPDs no. 36-1451) [6]. The lattice parameters a and c were calculated to be $3.2494 \text{ \AA}$ and $5.2057 \text{ \AA}$, respectively.

Room temperature RS spectrum of the $T\text{-SnZnO}$ was carried out and presented in Fig. 1(d) together with the $P\text{-ZnO}$ and the $T\text{-ZnO}$, in order to investigate the crystal defect and confirmed XRD data. All peaks of RS spectrum was well agreement with the $P\text{-ZnO}$ and the $T\text{-ZnO}$, and can be attributed to the hexagonal ZnO structures [10]. This result was in good agreement with the XRD

data. Moreover, Raman peaks of the *T*-SnZnO was slightly shifted to a lower wavenumber compared to the *P*-ZnO and the *T*-ZnO. This data implied that small amount of Sn replaced into Zn sites in ZnO lattice, which corresponded to previous reports [11].

The *T*-SnZnO was fabricated as ethanol sensors and its ethanol sensing characteristics tested at 280°C was shown in Fig. 2(a), in the range of -10 V to 10 V. Sensor current in the air was lower than in the ethanol gas. The more ethanol gas that use, the more sensor current that obtain. At applied voltage of 5 V, the sensor current in the air and 50 ppm were observed to be 0.32 mA and 2.13 mA, while that of 200 ppm, and 1,000 ppm were 2.58 mA and 3.17 mA, respectively. Fig. 2(b) showed the I-V curve tested with 1,000 ppm. The sensor current increased linearly with the applied voltage and operating temperature, exhibited the ohmic contact property. Similar tendency was observed at 300°C, 320°C, and 340°C. It is noteworthy that the increasing of the sensor current with ethanol gas indicates the n-type semiconductor property of the *T*-SnZnO [6].

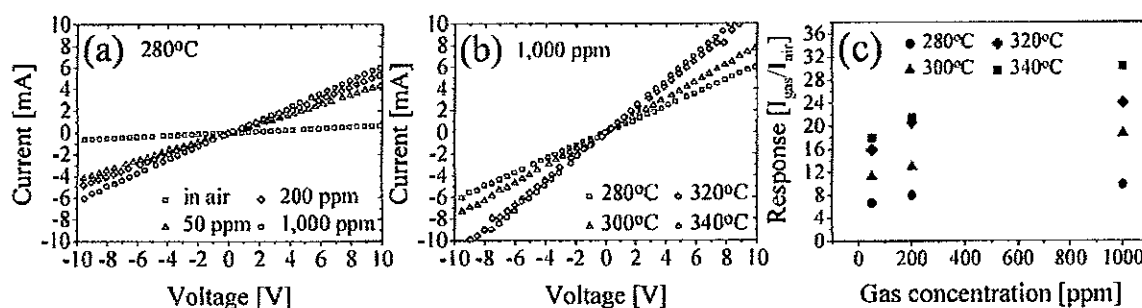


Figure 2 Ethanol I-V characteristic curve of the *T*-SnZnO sensors for (a) at 280°C and (b) 1,000 at different temperatures, (c) ethanol sensor response.

The ethanol sensor response of the *T*-SnZnO sensors was plotted in Fig. 2(c). It was found that the sensor response increased with operating temperature. For example, the sensor response was 9.8 at 280°C, and it increased to 24.0 at 320°C. The highest sensor response was 30.4 observing at 340°C. This data suggested that the *T*-SnZnO is a promising materials for a high temperature sensor application for detected the indoor volatile organic compounds (VOCs) [12]. Table 1 presented the sensor response of the *T*-SnZnO sensor, at the optimized temperature, compared with the *NWs*-ZnO, *TiO*₂-ZnO nanowires (*NWs*-*Ti*ZnO), *T*-ZnO, and *TiO*₂-ZnO tetrapods (*T*-*Ti*ZnO) sensors. Towards 1,000 ppm ethanol gas, the sensor response of the *NWs*-ZnO, *NWs*-*Ti*ZnO, *T*-ZnO, and *T*-*Ti*ZnO sensors were 1.4, 8.3, 1.8, and 23.6 which less than that of the *T*-SnZnO sensor. It is apparent that the *T*-SnZnO sensor exhibited highest sensor response. This data indicated that the Sn additive plays a crucial role for enhancing the sensor response.

Table 1 Sensor response of *T*-SnZnO sensor compared with other ZnO sensors.

Sample	Ethanol concentration [ppm]		
	50	200	1,000
ZnO nanowires (300°C) [13]	-	-	1.4
<i>TiO</i> ₂ -ZnO nanowires (340°C) [13]	-	-	8.3
ZnO tetrapods (300°C) [9]	1.2	1.5	1.8
<i>TiO</i> ₂ -ZnO tetrapods (300°C) [9]	5.0	8.9	23.6
Sn-doped ZnO tetrapods (340°C)	18.0	21.4	30.4

Summary

The *T*-SnZnO have been successfully synthesized by using the simple thermal oxidation reaction method. The *T*-SnZnO exhibited a tetrapod shape with four-symmetry legs owning the wurtzite hexagonal ZnO structure. The *T*-SnZnO sensors have been fabricated and tested with ethanol concentration of 50, 200, and 1,000 ppm. The sensor showed a promising sensor response towards ethanol gas. The highest sensor response of 30.4 was observed at 340°C tested with ethanol concentration of 1,000 ppm. Compared with the *NWs*-ZnO, *NWs*-TiZnO, *T*-ZnO, and *T*-TiZnO sensors, the *T*-SnZnO sensor showed the higher sensor response. Moreover, the sensor response of the *T*-SnZnO sensor increased with the operating temperature. This data indicated that the *T*-SnZnO could be a good candidate for high temperature sensor application, especially for detecting indoor VOCs gases.

Acknowledgment

T. Santhaveesuk would like to acknowledge National Research Council of Thailand (NRCT) and Pibulsongkram Rajabhat University for financial support.

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