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Ethanol Sensing Property of Tetrapods Prepared by Thermal Oxidation of Zn and TiO_2 Mixture

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ABSTRACT

Tetrapods of Zn and TiO_2 mixture have been synthesized through the thermal oxidation technique. The mixed powder was placed into Al_2O_3 crucible, and then heated in furnace at 1000°C for a few minutes. The Al_2O_3 crucible was taken out from the furnace, and the white wool products were observed. The white wool products were examined by FE-SEM, EDS, and XRD for morphology, chemical composition, crystal structure, and phase formation. FE-SEM result revealed that the white wool products composed of tetrapods with single crystalline and had two different shapes, round tip and sharp tip. The round tip tetrapods had the length of 1–2 µm and the diameter of 160–280 nm, while the sharp tip tetrapods had the length of 3–13 µm and the diameter ranging from 330–470 nm. The EDS attached to the FE-SEM was performed on one leg of tetrapod and indicated Ti, O, and Zn elements. The atomic concentration of Ti was less than 1 at. %. XRD result indicated that the tetrapods exhibited hexagonal wurtzite ZnO phase (a = 3.247 Å and c = 5.175 Å) and small phase fraction of face-centered cubic Zn_2TiO_4 phase (a = 4.479 Å). The tetrapods were fabricated as the ethanol sensor and tested under the ethanol ambient of 50-1000 ppm at the various operating temperature. Our tetrapod sensors exhibited the sensitivity 20 times higher than that of pure ZnO tetrapods, prepared by the same method. The tetrapod sensors showed high resistance when exposed in air; however, its resistance dropped sharply when exposed in ethanol, indicating n-type property of metal oxide semiconductor. The sensor sensitivity was a function of the ethanol concentration and the operating temperature. The highest sensitivity was measured to be 23.6 under ethanol concentration of 1000 ppm at operating temperature of 300°C.

Keywords: Ethanol sensor, tetrapods, ZnO, thermal oxidation, crystal growth.

INTRODUCTION

One-dimensional ZnO and ZnO based nanostructures have attracted key research interest in the past few years. Nanostructures in various forms have widely been synthesized and studied; such as nanowires (Wan *et al*., 2004), nanotubes (Chen *et al*., 2008), nanobelts (Choopun *et al*., 2007; Santhaveesuk *et al*., 2008), nanorods (Li *et al*., 2008; Li *et al*., 2007), and tetrapods (Santhaveesuk *et al*., in press). ZnO nanostructures were a good promising material for humidity sensor (Zhang *et al*., 2005), field electron emission (Li *et al*., 2007), optoelectronic device

(Yang *et al*., 2008), gas sensor (Wan *et al*., 2004), and so on. Since ethanol sensor was used for food quality control and human breath detector, it became as an importance device and has been widely investigated (Wan *et al*., 2004; Li *et al*., 2007; Sadek *et al*., 2007). In order to improve the sensor sensitivity, some element, Au (Li *et al*., 2008) and Pd (Hsueh *et al*., 2007), were introduced to ZnO nanostructures, and those sensors showed higher sensitivity than that of pure ZnO nanostructures. By adding TiO_2 into ZnO nanostructures sensor, Zhu (Zhu *et al*., 2004) found that the sensor sensitivity was improved.

In this work, we reported ethanol sensing properties of tetrapod prepared by thermal oxidation of Zn and TiO_2 mixture. The improvement of sensitivity due to TiO_2 adding was demonstrated.

METHODOLOGY

Tetrapods of Zn and TiO_2 mixture have been synthesized using the thermal oxidation technique (Santhaveesuk *et al*., in press). Zn with TiO_2 powder (20 mol. % of TiO_2) were weighed, mixed, and ground in agate mortar for 2 h. The mixed powder was placed into alumina (Al_2O_3) crucible and then heated in a tubular furnace at 1000°C for a few minutes under normal atmosphere. The crucible was taken out from the furnace, and the white wool products were observed. The white wool products were examined by field emission scanning electron microscope (FE-SEM), energy dispersive x-ray spectrometry (EDS) for morphology and chemical composition. X-ray diffractometry (XRD) were performed for analyzing theirs crystal structure and phase formation.

The tetrapods were fabricated as ethanol sensors by mixing tetrapods with 5 wt.% polyvinyl alcohols in distilled water, pasted onto the alumina substrate with gold inter-digital electrode to form thick films, and then dried in air for a few hours. The thick films were annealed at 400°C under normal atmosphere for 4 h, and then cooled naturally to room temperature. The ethanol sensing response of sensor was measured by using a volt-amperometric technique at the operating temperature of 240-360°C under ethanol concentration of 50-1000 ppm. The ethanol vapor was generated from ethanol solution using alcohol simulator (GUTH laboratory Inc., Harrisburg USA). The alcohol simulator functioned to simulate alcohol concentration at conditions similar to exhaled human breath.

RESULTS AND DISCUSSION

1. Structural studied

FE-SEM images of tetrapods synthesized from Zn and TiO_2 mixture using thermal oxidation method were shown in Figure 1. It was clearly seen that there were two different sharps of tetrapods with four symmetric legs; round tip and sharp tip as shown in Figure 1(a) and Figure 1(b), respectively. Normally, the legs of tetrapods grew along [0002] direction (Li *et al*., 2007; Santhaveesuk *et al*., in press). The sharp tip tetrapods had the length of 3–13 µm and the diameter ranging from 330–470 nm, while the round tip tetrapods had the length of 1–2 µm and the diameter of 160–280 nm. The different shapes of tetrapods might be due to effect of temperature gradient of the location where the vapor was set down (Wang *et al.*, 2005). When alumina crucible (10 cm long) was loaded into the furnace, the mixing powder was suddenly vaporized due to the high temperature of 1000°C. After that, the vapor was condensed and deposited onto the top crucible at different locations. Therefore, the growth rate was likely controlled by the temperature gradient, resulted in the different shapes and sizes of the tetrapods.

The EDS spectrum performed on one leg of tetrapod was shown in Figure 2. The result indicated that the tetrapod consisted of Ti, O, and Zn elements. The atomic concentration of Ti was less than 1 at. %.

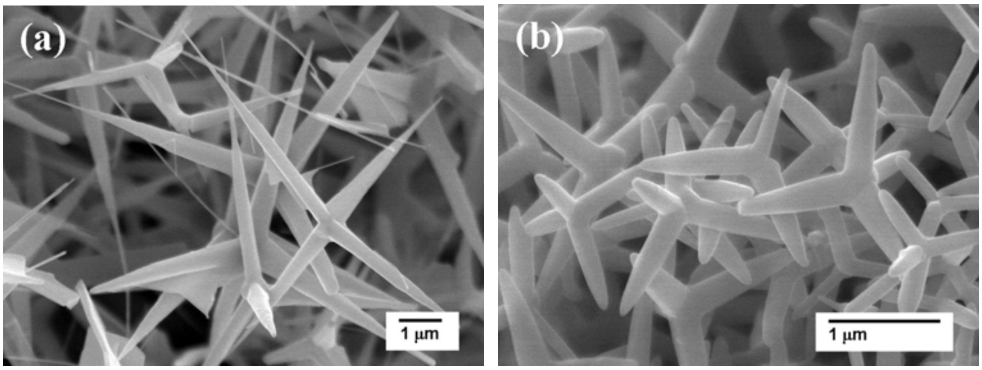

Figure 1 FE-SEM images showed two different shapes of the tetrapods, (a) sharp tip and (b) round tip.

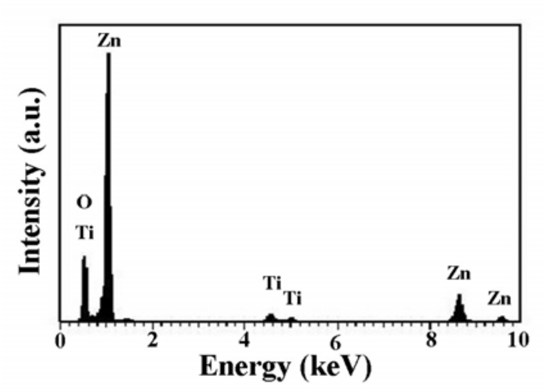

Figure 2 EDS spectrum performed on one leg of tetrapod indicated that the tetrapod consisted of Ti, O, and Zn elements.

Figure 3 showed XRD pattern of the tetrapods, scanning for 2θ in rang of 20-70°. All sharp peaks appeared in the pattern corresponded to all hexagonal ZnO signal, JCPDS file no. 36-1451 with a = 3.249 Å and c = 5.206 Å. This result was in good agreement with EDS. The sample lattice parameters a and c were calculated to be 3.247 Å and 5.175 Å, respectively. This value was lower than that of standard

JCPDS file. This may be explained by substitution of Ti^{4+} into Zn^{2+} sites since Ti^{4+} has ionic radius of 0.68 Å which smaller than that 0.74 Å of Zn^{2+}, forming $Ti_xZn_{1-x}O$ alloy (Santhaveesuk *et al.* in press; Park and Ko, 2007). Furthermore, peaks of face-centered cubic Zn_2TiO_4 phase were observed, with lattice parameter a = 4.479 Å. The Zn_2TiO_4 phase was probably formed as follows:

$$Zn + O \rightarrow ZnO,$$
$$2ZnO + TiO_2 \rightarrow Zn_2TiO_4.$$

This phase normally formed at temperature above 945°C with ZnO, for the TiO_2 content below 34 mol. % (Yang and Swisher, 1996; Dulin and Rase, 1960). Moreover, small amount of anatase-TiO_2 phase was also detected.

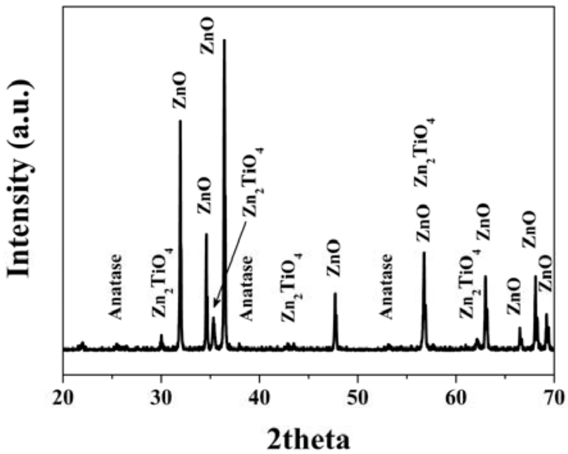

Figure 3 XRD pattern of the tetrapods scanning for 2θ in rang of 20-70°, showing ZnO phase with small amount of Zn_2TiO_4 and anatase-TiO_2 phases.

2. Ethanol sensing properties

Since both sharp tip and round tip tetrapods were formed together, the sensor fabricated from mixed tetrapods was tested under ethanol ambient of 50-1000 ppm at operating temperatures of 240-360°C. Typically, ethanol sensitivity was defined as $S = R_{air}/R_{gas}$ (Wan *et al.*, 2004; Zhu *et al.*, 2004), where R_{air} is the electrical resistance of the sensor in air, and R_{gas} is its resistance in ethanol–air mixed gas. The resistance of sensor was high when exposed to the air, and it dropped sharply when ethanol vapor was introduced. It was commonly observed for metal oxide semiconductor, indicating an n-type property of semiconductor (Wan *et al.*, 2004; Hongsith and Choopun, 2008). Typically, for most metal oxide semiconductor sensors, adsorption and adsorption of oxygen on the surface of sensor principally cause changing in sensor resistance. When sensor is exposed to air, oxygen molecule absorbs on surface of sensor by trapping an electron from conduction band and form O^{2-}, O_2^{2-} or O^- ions. Then, depletion layer is generated on sensor surface by the adsorbed molecule, resulting in enhancing the sensor resistance. When sensor is exposed to ethanol ambient, oxygen ions react with the ambient gas and release an electron back onto the surface of sensor. Then, the width of depletion layer is reduced resulting in a increasing of conductivity (Wan *et al.*, 2004; Li *et al.*, 2007; Xue *et al.*, 2006). Thus, it is likely that the same mechanism has occurred for our sensor.

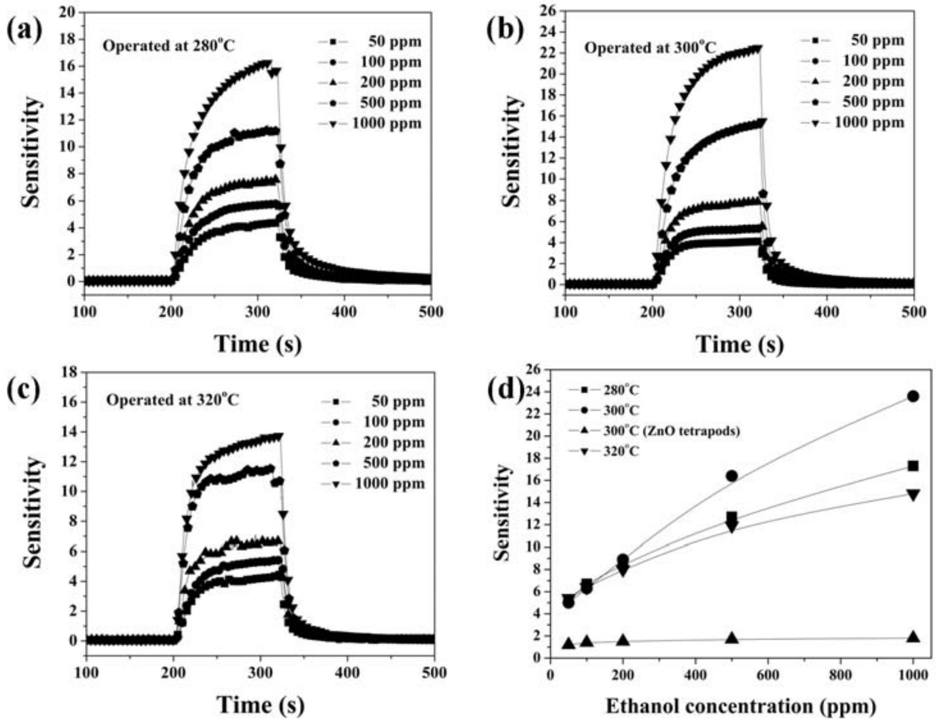

Figure 4 Sensitivities of sensor operated at (a) 280°C, (b) 300°C, (c) 320°C, and (d) the sensor sensitivity in (a-c) compared with pure ZnO tetrapods sensor.

The plots of sensitivity as a function of time were shown in Figure 4 for operating temperature of (a) 280°C, (b) 300°C, and (c) 320°C. The sensor sensitivity as a function of ethanol concentration was clearly observed. For example, the sensor sensitivity was measured to be about 5.0 and 8.9 for ethanol concentration of 50 ppm and 200 ppm at operating temperature of 300°C. Figure 4(d) displayed the sensor sensitivity operated at 280, 300, and 320°C under ethanol concentration of 50-1000 ppm compared with pure ZnO tetrapod sensor, tested at 300°C (Hongsith and Choopun, 2008). The sensor showed highest sensitivity of 23.6 at the operating temperatures of 300°C under ethanol concentration of 1000 ppm. Normally, the sensitivity of metal oxide semiconductor can be explained as in relation $S = 1 + aC^b$, (Santhaveesuk *et al.*, in press; Wan *et al.*, 2004) where C is a gas concentration, a is a constant depending on type of test gas, sensor material, and operating temperature whereas b is generally equal to 0.5 or 1 for adsorbed surface oxygen species of O^{2-} or O^{-}, respectively. Therefore, the sensor exhibited higher sensitivity at the high ethanol concentration.

For metal oxide semiconductor, its resistivity is controlled by the following equation, $\rho = \rho_0 \exp\left(E_g / 2kT\right)$, (Tilley, 2004) where ρ and ρ_0 are the resistivity and constant, E_g is energy band gap of material, k is Boltzmann's constant, and T is temperature. Exposing in air, the sensor showed a high resistivity (low conductivity) which is quite similar at 240-300°C. However, the sensor resistivity was decreased with increasing temperature. Furthermore, a sharply drop of sensor resistivity was observed when 1000 ppm of ethanol, for example, was introduced. At the same temperature as exposed in air, the resistivity different of sensor (before and after ethanol vapor was exposed) tested at 300°C was higher than that of 320°C. This implied that the sensor sensitivity tested at 300°C was higher than that of 320°C. Considering the sensor resistivity at 240-300°C, a result at 300°C is the best suitable temperature that provided the activation energy for highest reaction rate between oxygen ions and ethanol molecules. As a result, the highest sensitivity was detected at 300°C.

In order to comparison with the previous reports, the ethanol sensitivity of quasi-one-dimensional ZnO nanostructures carried out by N. Van Hieu and N. Duc Chien (Hieu and Chien, 2008) was less than 6, tested under ethanol concentration of 1000 ppm at the operating temperature of 300°C. While the sensitivity of tetrapod and multipod-shaped ZnO nanorods was about 2 tested ethanol concentration of 1000 ppm, reported by T. Gao and T.H. Wang (Gao and Wang, 2005). Also, it was clearly seen that the tetrapod sensor prepared from Zn and TiO_2 mixture exhibited higher sensitivity than that of pure ZnO tetrapods (Hongsith and Choopun, 2008) at entire ethanol concentration and also higher than that of the both previous reports. It might be the effect of the formation of $Ti_xZn_{1-x}O$ alloy by replaced Zn^{2+} site of Ti^{4+} (Santhaveesuk *et al*., in press; Park and Ko, 2007; Wan *et al*., 2004). Nonetheless, it is important to emphasize that the additional Zn_2TiO_4 phase might improve the sensor sensitivity. This result was also consistent with the previous report (Zhu *et al*., 2004). Therefore, the improvement of sensitivity due to TiO_2 adding in ZnO was observed in our work.

CONCLUSION

Tetrapods of Zn and TiO_2 mixture have been synthesized through the thermal oxidation technique and examined using FE-SEM, EDS, and XRD. The results revealed that as-synthesized product consistent with two different shapes tetrapods, round tip and sharp tip. The different sharp of tetrapods might be due to effect of temperature gradient. The EDS result indicated the tetrapods consistent with Ti, O, and Zn elements, with Ti content less than 1 at. %. XRD result revealed that ZnO phase formed together with face-centered cubic Zn_2TiO_4 phase and small amount of anatase-TiO_2. The tetrapods were fabricated as the ethanol sensor which was a function of the ethanol concentration and the operating temperature. The sensor exhibited the sensitivity about 20 times higher than that of pure ZnO tetrapods. The highest sensitivity was measured to be 23.6 under ethanol concentration of 1000 ppm at operating temperature of 300°C.

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