



Ethanol sensing properties of Zn_2TiO_4 particles

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Abstract

Zn_2TiO_4 particles were prepared using the ball-milling technique in ethanol solution. Zn powder mixing with anatase- TiO_2 powder at ratio of 2:1 by mole were used as raw materials. The mixed powders were grounded in agate mortar for 2 h, subsequently transferred into the ball-milled container with 1 mm zirconia balls and, then, milled for 24 h with ball-milling speeds of 200, 300 and 400 rpm. The ratio of powders and zirconia balls was 1:20 by weight. After that, the powders were washed using distilled water for 4 times, dried at 80 °C for 24 h and calcined at 1000 °C for 6 h. Morphological characteristics, chemical compositions, phase formation and defect of the synthesized powder were examined. The SEM result showed that the particle size was reduced as increase in the ball-milling speed, while the EDS showed that the Zn/Ti ratio was about 2. The XRD indicated that the synthesized powders exhibited a face center cubic Zn_2TiO_4 phase, confirming by the Raman spectra. The Zn_2TiO_4 particles were fabricated as the thick film ethanol sensor and tested under 50 and 200 ppm ethanol concentration at 300–500 °C. Our results suggest that the Zn_2TiO_4 particles can be used for detection of ethanol vapor, and the sensor current increased with increasing of ethanol concentration. The highest sensitivity observed at 500 °C was 3.83 for 200 rpm, 1.92 for 300 rpm and 2.36 for 400 rpm samples. This implied that, the Zn_2TiO_4 sensor can be a good candidate for high temperature application.

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1. Introduction

Nowadays, semiconductor gas sensors; ZnO , TiO_2 , SnO_2 and so on; are very important sensing devices; because they can be used for detecting several toxic gases in a wide range operating temperature [1–4]. Since nanostructured semiconductors exhibit remarkably properties for gas sensing application, many synthetic techniques such as sol–gel [5], thermal oxidation [3], sputtering [6], chemical bath deposition [7] and ball-milling [8] have been investigated and proposed in order to obtain semiconducting nanostructures. Among these, ball-milling method is one of the simplest method for powder preparation technology. Moreover, it

is widely used in production lines for powders such as cement, refractory material, glass ceramics and silicates. It has also been used for producing the nanostructure materials [8–10].

Several works reported that some metals or metal oxide additives such as Ru [11], Al [12] and TiO_2 [13] could be affected the sensing properties. In our previous work, we have reported that TiO_2 additive could be used for improving the sensitivity of ZnO tetrapods sensor, lower electron concentration resulted in widening the band gap of ZnO [3,14,15]. The TiO_2 additive can be diffused to ZnO host lattice forming $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ complex structure and/or forming additional phase as Zn_2TiO_4 , having face-centered cubic structure. These resulted in the enhancement of sensor sensitivity [16].

Since the sensing properties of Zn_2TiO_4 were rarely reported, it is very interesting to investigate its sensing properties. In this work, Zn_2TiO_4 particles were prepared using the simply ball-milling

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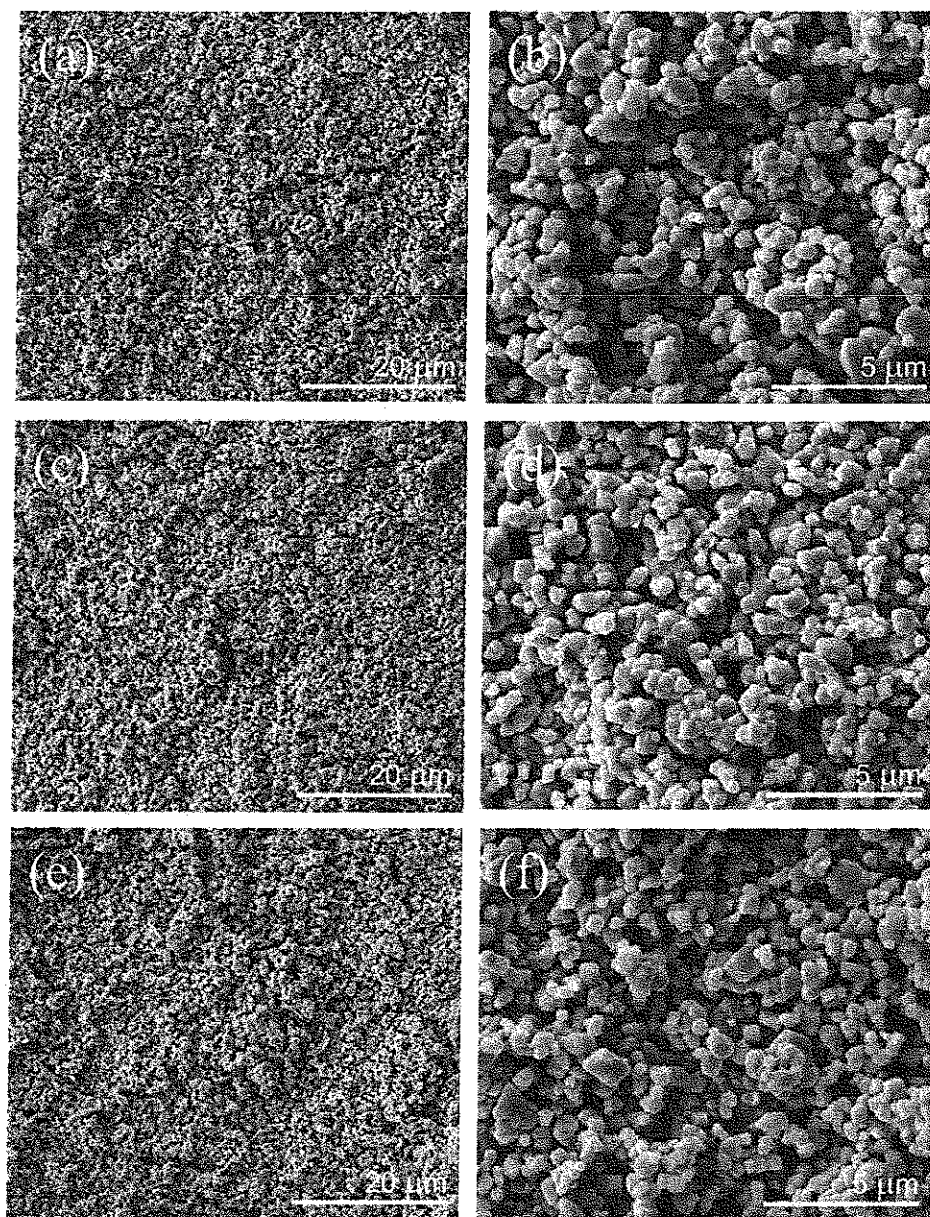


Fig. 1. SEM image of (a and b) ZTO200, (c and d) ZTO300 and (e and f) ZTO400 powders at different magnifications.

method and characterizations of Zn_2TiO_4 particles were carried out. Also, Zn_2TiO_4 particles sensing properties towards ethanol gas were investigated.

2. Experimental

Zn_2TiO_4 particles were prepared by a ball-milling technique using a mixture of Zn powder and anatase- TiO_2 powder as a raw material, with the mole ratio of 2:1. The mixture powders were grounded by hands in an agate mortar for 2 h. Then, the mixed powders were transferred into the ball-milled container with 1 mm zirconia balls and milled for 24 h in ethanol solution with ball-milling speeds of 200, 300 and 400 rpm. The ratio of mixed powders and zirconia balls was 1:20 by weight. After the milling process the powders were rinsed with

distilled water (DI) for 4 times, dried at 80 °C for 24 h and calcined at 1000 °C for 6 h. Then powders synthesized with ball-milling speed of 200, 300 and 400 rpm were denoted as ZTO200, ZTO300 and ZTO400 samples, respectively.

The properties of Zn_2TiO_4 particles were characterized by using scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDS), X-ray diffractometer (XRD) and Raman spectrophotometer (RS) for morphology, chemical compositions, phase formation and crystal defect investigation. Zn_2TiO_4 particles were assembled as thick film sensors by screened onto alumina substrate with comb-type gold interdigital electrodes. Current-voltage characteristic curve (I - V curve) of the sensors was monitored under ethanol gas condition with a concentration of 50 and 200 ppm at operating temperature of 300, 350, 400, 450 and 500 °C. The applied voltage was

varied from 0 V to 10 V using precision source unit and the sensor current was measured using high accuracy picoammeter. The sensor sensitivity was calculated from sensor current under ethanol gas divided by sensor current under normal air, at 5 V applied voltage, which was similar to our previous work [17].

3. Results and discussion

The morphology of the synthesized powders was examined by using SEM and the SEM images of the synthesized powders were shown in Fig. 1 with 5000 (Fig. 1(a, c and e)) and 20,000 (Fig. 1(b, d and f)) magnification. Fig. 1(a, b), (c, d) and (e, f) corresponded to the ZTO200, ZTO300 and ZTO400 samples, respectively. It was clearly seen that all ZTO200, ZTO300 and ZTO400 samples showed similar SEM images and the size of the synthesized particles was in the range of micrometer scale. The particle size was measured to be 0.33–1.60, 0.26–1.43 and 0.25–1.30 μm for ZTO200, ZTO300 and ZTO400 samples, respectively. It should be noted that the particle size was reduced as the increasing of the ball-milling speed since the higher ball-milling speed provides more energy impacted the powders during the milling process. The EDS analysis was performed for chemical compositions inspection. The result showed that those three samples of the synthesized products composed of Zn, Ti and O elements and the mole ratio of Zn/Ti was about 2 which closed to the Zn/Ti stoichiometry ratio of Zn_2TiO_4 compound.

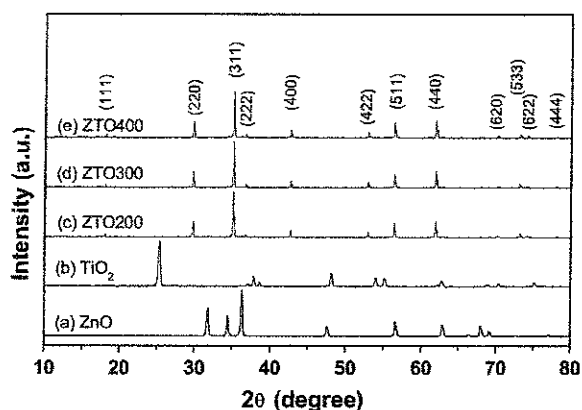


Fig. 2. XRD patterns of ZTO200, ZTO300 and ZTO400 powders in comparison with that of commercial ZnO and commercial anatase- TiO_2 powders.

Table 1

List of the vibration modes of the synthesized Zn_2TiO_4 particles in RS spectra.

Vibration modes	Wavenumber (cm^{-1})				
	ZTO200	ZTO300	ZTO400	Ref.[19]	Ref. [20]
F_{2g}	256.2	254.4	254.2	257.9	263
E_g	307.5	307.2	307.4	309.5	311
F_{2g}	354.9	354.8	356	349.6	344
F_{2g}	476.7	476.2	476.3	477.1	–
A_{1g}	714.6	714.5	714.5	722.1	–

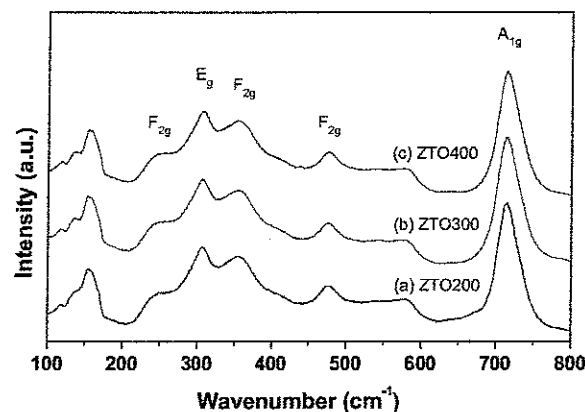


Fig. 3. The vibration modes of ZTO200, ZTO300 and ZTO400 powders in RS spectra.

Phase formation and crystal defects were carried out by XRD and RS. The XRD spectra were shown in Fig. 2 compared with commercial ZnO powder and commercial anatase- TiO_2 powder, recording in the range of 10–80°. It was observed that those three samples showed similar XRD patterns. The XRD data revealed that all synthesized powders exhibited a face-centered cubic Zn_2TiO_4 structure corresponding to JCPDs file no. 86-0155. The lattice parameter was calculated to be 8.4698, 8.4638 and 8.4684 Å corresponding to the ZTO200, ZTO300 and ZTO400 samples, respectively. The formation of the face-centered cubic Zn_2TiO_4 phase detected in XRD spectra was confirmed by RS results as shown in Fig. 3. As indicated in Fig. 3, three vibration modes so called F_{2g} (located at 254.2–256.2, 354.8–356.0 and 476.2–476.7 cm^{-1}), E_g (located at 307.2–307.5 cm^{-1}) and A_{1g} (located at 714.5–714.6 cm^{-1}) were observed in RS spectra for all those three Zn_2TiO_4 samples, in good agreement with the previous reports [18,19]. This result was also shown in Table 1. The peaks observed below 200 cm^{-1} was originated from plasma induced of the laser source, while that observed around 580 cm^{-1} was created from order–disorder of Zn and Ti ions in octahedral and tetrahedral sites inside crystal structure [19,20].

Thick film gas sensors based on Zn_2TiO_4 particles were fabricated and tested under ethanol gas concentration as described above. As indicating in Fig. 4, under testing condition at 500 °C, a linear relationship between the applied voltage and the sensor current was detected. The sensor current was improved as the increasing of ethanol concentration. In the case of ZTO200 sensor (Fig. 4a), for example, the sensor current in air was measured to be 74.6 nA and increased up to 214.9 nA in 50 ppm of ethanol gas. Similarly, as 200 ppm ethanol gas injected into test chamber, the sensor current was increased up to 275.8 nA. Similar results and the same trend were obtained for those ZTO300 (Fig. 4b) and ZTO400 (Fig. 4c) sensors. Also, a similar tendency of the I – V characteristics curve were found for other operating temperatures.

For a resistive gas sensor, the sensing mechanism is normally controlled by adsorbed oxygen species on a sensor surface. As the sensor baring to the air, O_2 molecules adsorbed onto the sensor surface by capturing electron from the conduction band of Zn_2TiO_4 forming O_2^- , O^- or O^{2-} oxygen species, which depends on temperature. This resulted in decreasing of the sensor current.

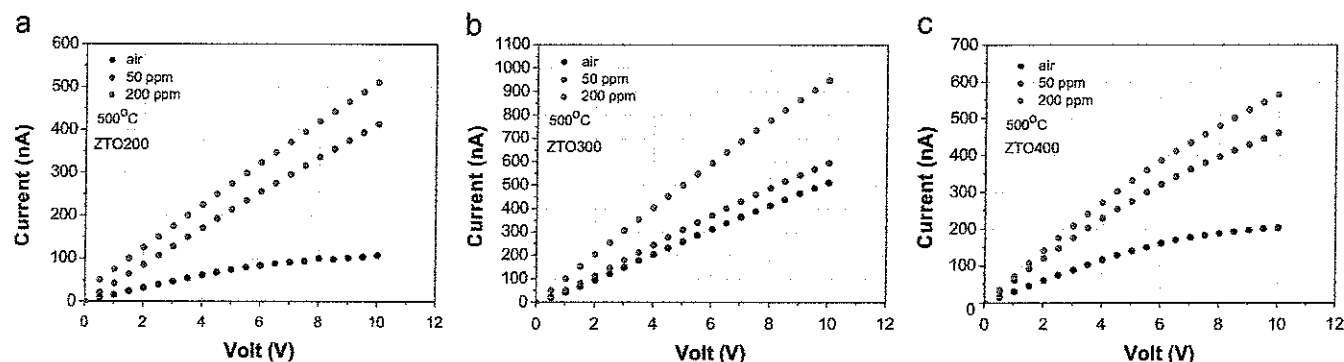


Fig. 4. The I - V characteristic curve of (a) ZTO200, (b) ZTO300 and (c) ZTO400 sensors measured at the operating temperature of 500 °C under, air atmosphere, 50 ppm and 200 ppm ethanol gas.

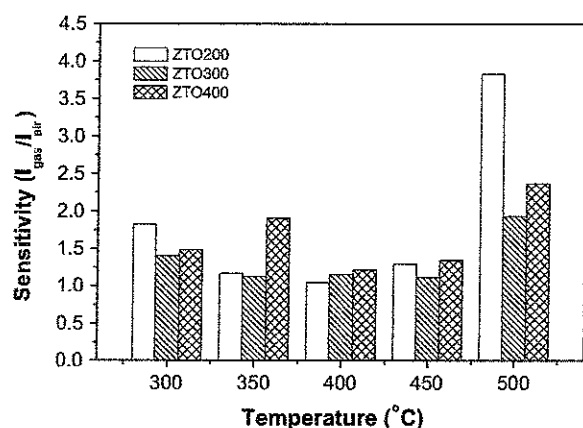


Fig. 5. Sensor sensitivity of the Zn_2TiO_4 sensors under 200 ppm ethanol gas the operating temperatures of 300, 350, 400, 450 and 500 °C.

When ethanol gas was injected into the test chamber, ethanol vapor reacted with the oxygen species and returned captured electron back to the conduction band of Zn_2TiO_4 . The sensor current, therefore, was increased. The reaction can be written as the following equation.



In this equation, R is a reaction gas, RO is product gas from reduction gas and adsorbed oxygen species and e^- is an electron. The sensor sensitivity tested under operating temperatures of 300, 350, 400, 450 and 500 °C at 200 ppm ethanol gas was plotted together as shown in Fig. 5. It was observed that those ZTO200, ZTO300 and ZTO400 sensors showed a similar tendency of sensitivity towards ethanol gas. The sensor sensitivity decreased from 300 °C to 400 °C and, then, increased at operating temperature above 400 °C. However, in case of ZTO400 sensor, the sensor sensitivity at 350 °C was higher than the sensor sensitivity at 300 °C and 400 °C. Furthermore, the highest sensitivity was found at 500 °C. It was calculated to be 3.83, 1.92 and 2.36 for ZTO200, ZTO300 and ZTO400 sensors, respectively. This result suggested that the operating temperature of 500 °C is the best suitable temperature for detecting ethanol gas, providing the activation energy for highest reaction rate between oxygen ions and ethanol molecules. As a result, the highest sensitivity was

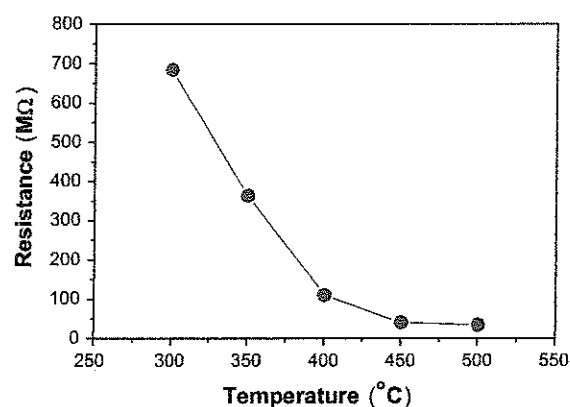


Fig. 6. Sensor resistance of ZTO400 sensor at different temperature.

detected at 500 °C. This result implies that Zn_2TiO_4 sensor is proper for operating under high temperature condition.

Previously, we have proposed a sensor response formula for the sensor based on ZnO nanostructures as the following equation [21];

$$S_g = \frac{\Gamma_r k_{\text{Eth}}(T) [O_{\text{ads}}^{\text{ion}}]^b}{n_0} C_g^b + 1, \quad (2)$$

where Γ_r is proportional constant and $k_{\text{Eth}}(T)$ is a reaction rate constant between adsorbed oxygen species and the ethanol vapor depending on the operating temperature. $O_{\text{ads}}^{\text{ion}}$ is the adsorbed oxygen species concentration and C_g^b is the ethanol concentration. While b is normally 0.5 or 1 for O^{2-} or O^- adsorbed surface oxygen species, n_0 is electron concentration of the sensor in air. It was clearly seen that the sensor sensitivity can be improved by reduced electron concentration of the sensor in air and/or enlarged a reaction rate constant, the adsorbed oxygen species concentration and the ethanol concentration.

Fig. 6 showed the sensor resistance in the air of ZTO400 sensor. It was observed that the sensor resistance was very high, indicating a very low electron concentration of the sensor in air as mention above. The sensor resistance of 684.7 MΩ measured at operating temperature of 300 °C decreased exponentially as the increasing of operating temperature. It was enormously decreased to 111.3 MΩ at 400 °C. After that, it

was slowly decreased to 41.6 MΩ at 450 °C and subsequently reached 35.4 MΩ at 500 °C.

Reported earlier in our previous work, the TiO₂ additive could improve ethanol sensitivity of ZnO tetrapods. Ti may be diffused into ZnO host lattice forming Z_{1-x}Ti_xO complex phase or forming a small fraction of Zn₂TiO₄ phase by reacts with ZnO [3,14]. Since the resistance of Zn₂TiO₄ sensor is very high, indicating in Fig. 6, the sensor resistance of ZnO tetrapods with TiO₂ additive is enriched. Subsequently, reducing of electron concentration of the sensor in air was observed and the improving of sensor sensitivity was noted. This information is considerably important and useful for theoretical study of the gas sensor technology.

4. Conclusions

The Zn₂TiO₄ particles were successfully synthesized using the ball-milling technique at different ball-milling speeds following by heat treatments at high temperature. The results showed that Zn₂TiO₄ particles exhibited good single crystal properties. The Zn₂TiO₄ particles were fabricated as the ethanol gas sensor showing an impressive sensitivity, with very high resistance in air. ZTO200 sensor exhibited the highest sensitivity. These remarkable results suggested that the Zn₂TiO₄ sensor could be used as an effective tool for the high temperature application and for theoretical study, well agreed with the previous works.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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References

- [1] C.-J. Chang, C.-Y. Lin, J.-K. Chen, M.-H. Hsu, Ce-doped ZnO nanorods based low operation temperature NO₂ gas sensors, *Ceram. Int.* 40 (2014) 10867–10875.
- [2] P.K. Kannan, R. Saraswathi, J.B.B. Rayappan, CO₂ gas sensing properties of DC reactive magnetron sputtered ZnO thin film, *Ceram. Int.* 40 (2014) 13115–13122.
- [3] T. Santhaveesuk, D. Wongratanaphisan, S. Choopun, Enhancement of sensor response by TiO₂ mixing and Au coating on ZnO tetrapod sensor, *Sens. Actuators, B* 147 (2010) 502–507.
- [4] N. Kilinc, O. Cakmak, A. Kosemen, E. Ennek, S. Ozturk, Y. Yarli, Z.Z. Ozturk, H. Urey, Fabrication of 1D ZnO nanostructures on MEMS cantilever for VOC sensor application, *Sens. Actuators, B* 202 (2014) 357–364.
- [5] X. Liu, K. Pan, W. Li, D. Hu, S. Liu, Y. Wang, Optical and gas sensing properties of Al-doped ZnO transparent conducting films prepared by sol-gel method under different heat treatments, *Ceram. Int.* 40 (2014) 9931–9939.
- [6] S. Choopun, N. Hongsih, P. Mangkornong, N. Mangkornong, Zinc oxide nanobelts by RF sputtering for ethanol sensor, *Physica E* 39 (2007) 53–56.
- [7] P. Manurung, Y. Putri, W. Simanjuntak, I.M. Low, Synthesis and characterisation of chemical bath deposited TiO₂ thin-films, *Ceram. Int.* 39 (2013) 255–259.
- [8] S. Amirkhanlou, M. Ketabchi, N. Parvin, Nanocrystalline/nanoparticle ZnO synthesized by high energy ball milling process, *Mater. Lett.* 86 (2012) 122–124.
- [9] G. Kozma, Á. Kukovecz, Z. Kónya, Spectroscopic studies on the formation kinetics of SnO₂ nanoparticles synthesized in a planetary ball mill, *J. Mol. Struct.* 834–836 (2007) 430–434.
- [10] G.R. Khayati, E. Nourafkan, G. Karimi, J. Moradgholi, Synthesis of cuprous oxide nanoparticles by mechanochemical oxidation of copper in high planetary energy ball mill, *Adv. Powder Technol.* 24 (2013) 301–305.
- [11] S.C. Navale, V. Ravi, I.S. Mulla, Investigations on Ru doped ZnO: strain calculations and gas sensing study, *Sens. Actuators, B* 139 (2009) 466–470.
- [12] Z. Yang, Y. Huang, G. Chen, Z. Guo, S. Cheng, S. Huang, Ethanol gas sensor based on Al-doped ZnO nanomaterial with many gas diffusing channels, *Sens. Actuators, B* 140 (2009) 549–556.
- [13] Y. Zeng, T. Zhang, L. Wang, M. Kang, H. Fan, R. Wang, Y. He, Enhanced toluene sensing characteristics of TiO₂-doped flowerlike ZnO nanostructures, *Sens. Actuators, B* 140 (2009) 73–78.
- [14] T. Santhaveesuk, D. Wongratanaphisan, S. Choopun, Enhancement of ethanol sensing properties by alloying TiO₂ with ZnO tetrapods, *IEEE Sens. J.* 10 (2010) 39–43.
- [15] T. Santhaveesuk, T. Chairuangsi, D. Wongratanaphisan, S. Choopun, Optical band gap of Zn_{1-x}Ti_xO tetrapods, *J. Microsc. Soc. Thai.* 23 (2009) 70–74.
- [16] B.L. Zhu, C.S. Xie, W.Y. Wang, K.J. Huang, J.H. Hu, Improvement in gas sensitivity of ZnO thick film to volatile organic compounds (VOCs) by adding TiO₂, *Mater. Lett.* 58 (2004) 624–629.
- [17] T. Santhaveesuk, S. Choopun, Ethanol sensing characteristics of Sn-doped ZnO tetrapods sensor, *Adv. Mater. Res.* 770 (2013) 185–188.
- [18] D. Wongratanaphisan, T. Santhaveesuk, S. Choopun, Raman scattering of internal dynamics in spinel Zn₂TiO₄ nanostructures, *Integr. Ferroelectr.* 142 (2013) 37–43.
- [19] Y. Yang, X.W. Sun, B.K. Tay, J.X. Wang, Z.L. Dong, H.M. Fan, Twinned Zn₂TiO₄ spinel nanowires using ZnO nanowires as a template, *Adv. Mater.* 19 (2007) 1839–1844.
- [20] Y. Yang, R. Scholz, H.J. Fan, D. Hesse, U. Gösele, M. Zacharias, Multitwinned spinel nanowires by assembly of nanobricks via oriented attachment: a case study of Zn₂TiO₄, *ACS Nano* 3 (2009) 555–562.
- [21] N. Hongsih, E. Wongrat, T. Kerdcharoen, S. Choopun, Sensor response formula for sensor based on ZnO nanostructures, *Sens. Actuators, B* 144 (2010) 67–72.