Proceeding of The International Seminar on Chemistry 2008 (pp. 164-168)
Jatinangor, 30-31 October 2008

Synthesis of $ZnFe_2O_4$-based thick film ceramics and its electrical characterization in air and ethanol gas

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Abstracts

In order to get capability in ethanol gas sensor fabrication, a study on fabrication of $ZnFe_2O_4$-based thick film ceramic and its characterization has been carried out. This study was a preliminary work that will be developed in the future by utilizing mineral abundant in Indonesia as raw material. Powder of Fe_2O_3 and ZnO with composition of (50:50) and (45:55) in mole % were crushed and sieved using a 38 micron sieve. The fine mixed powder was then mixed with 5 weight % glass frit. The powder containing glass frit was mixed with 30 weight % organic vehicle to form a paste. The paste was screen printed using screen printing technique on alumina substrates. The films were fired at 1000^{o}C for 1 hour in air. Electrical characterization was done by measuring electrical resistance of the thick film ceramic at various temperatures in air and ethanol gas with different concentrations. Microstructure and crystal structure analyses were done by using a scanning electron microscope (SEM) and an x-ray diffractometer (XRD). According to the XRD analyses the produced thick film ceramic with (50:50) concentration formed a solid solution with cubic spinel structure and that with (45:55) concentration crystallized in cubic spinel containing Fe_2O_3 second phase. The SEM image showed that the thick film ceramic with (50:50) concentration was porous with very small grains and that with (45:55) concentration contains large grains with less pores. From the electrical characteristics data, it was known that the electrical characteristics of the produced $ZnFe_2O_4$-based thick film ceramics followed a semiconductor characteristic. The thick films were responsive to ethanol gas where the resistance of the film measured in ethanol gas medium was smaller than that measured in air. The resistance of the thick film decreased with the increase of ethanol gas concentration. The sensitivity of the (50:50) ceramic is larger than that of the (55:45) ceramic.

Key words: $ZnFe_2O_4$, thick film, ethanol, gas sensor.

Introduction

There is a trend in increasing quality of life of the people in the world including Indonesia. Following this trend, so many products are required for daily life by the people of Indonesia. Unfortunately many of them are imported. So, much currency (foreign exchange) escapes to abroad. One of the products needed is gas sensor. Gas sensor is required in many sectors of daily life such as food industry, environment and health. Now people generally need high quality food. For typical high quality food, controlling many parameters especially ethanol is necessary during storing. For example to keep a typical food (meat) in fresh condition, so it will have a good taste when it is cooked, ethanol concentration should be controlled. So, in this case an ethanol gas sensor is required. The ethanol gas sensor may also be needed by the police to check driver whether drunk or not in a circumstance. For the time being, the gas sensor generally imported from the overseas.

In order to decrease the dependency to imported products including ethanol gas sensor, many efforts have to be done. A possible one is trying to self produce the products by utilizing materials abundant in Indonesia. The gas sensor especially ethanol gas sensor hypothetically may be self produced by utilizing materials abundant in Indonesia. However, in realizing this effort, a preliminary study has to be done. Here a preliminary study of producing thick film ceramic based on $ZnFe_2O_4$ for ethanol gas sensor is carried out. This study is a simulation for the future work of self producing ethanol gas sensor by utilizing mineral containing Zn and Fe abundant in Indonesia. Other than $ZnFe_2O_4$ it is known that many kinds of material can be applied as gas sensor such as SnO_2 [Misra,2002, Heule, 1973, Lou, 2007], WO_3[Heule, 1973], In_2O_3[Heule, 1973], TiO_2[Heule, 1973], and $ZnGaO_4$[Heule, 1973], $CdFe_2O_4$[Lou, 2007,Tianshu, 1999], $CoFe_2O_4$[Chu, 2006], ZnO[Cheng, 2004], $NiFe_2O_4$[Rezlescu, 2006, Rezlescu,2005], $CuFe_2O_4$[Tao, 2000] and $MgFe_2O_4$[Liu, 2005].

In this work, the thick film ceramics for ethanol gas sensor were fabricated from powder of Fe_2O_3 and ZnO with two different concentrations by using screen printing technique. The focus of this work is

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whether or not a $ZnFe_2O_4$ based-thick film ceramic can be functionalized as an ethanol gas sensor. The special case will be studied is whether the sensitivity of the sensor will change or not when the concentration of Fe_2O_3 is larger than the need for stoichiometry condition. Hypothetically, two conditions may be exist when the concentration of Fe_2O_3 is larger than the need for stoichiometry. The first, if all of Fe_2O_3 completely dissolved forming solid solution and the second, if Fe_2O_3 segregates at the grain boundaries. The ceramic having these two different microstructures may have different response to ethanol gas. The evaluation of the thick film ceramics will be based on the data of electrical characteristics in air and ethanol medium, crystal structure and microstructure.

Materials and Methods

The powders of Fe_2O_3, ZnO and glass frit were crushed and sieved with a sieve of 38 μm (hole size of 38 μm). The sieved Fe_2O_3 and ZnO were mixed with composition of (50:50) and (45:55) in mole %. Afterward, the mixed powder with composition of (50:50) and (45:55) were mixed with glass frit powders with concentration of 95 weight % (w/o) and 5 weight % (w/o), respectively. These mixed powders are called as ceramic powder. The 70 weight % (w/o) of the ceramic powder was mixed with 30 w/o organic vehicle (OV) composed of alpha terpineol and ethyl cellulose (EC). The final mixture is called as Fe_2O_3 paste. The Fe_2O_3 paste was spread on alumina substrates to form thick film ceramics as shown in Fig. 1[Syarif, 2007] and 2. After being dried at room temperature, the films were then heated at 1000°C for 60 minutes in air. Electrical characterization was performed by measuring electrical resistance of the films at various temperatures in air and ethanol gas. Sensitivity of the thick films was calculated using equation (1)[Rezlescu, 2005]. Concentrations of ethanol gas were 136 ppm and 407 ppm. The experiment principle for electrical characterization is shown in Fig. 3. Microstructure and structural analyses were carried out by using a scanning electron microscopy (SEM) and x-ray diffraction (XRD), respectively.

$$S = (Ro-Rg)/Ro \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, S is the sensitivity (with out unit), Ro is resistance of the film in air and Rg is the resistance in air containing ethanol gas.

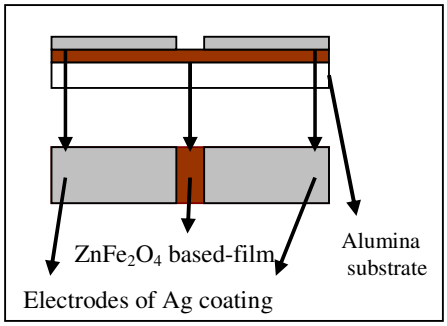

Fig.1. A schematic view of a thick film ceramic sensor [4].

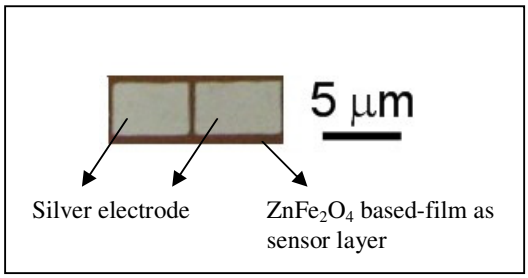

Fig.2. Appearance of a typical $ZnFe_2O_4$ based-thick film ceramic sensor.

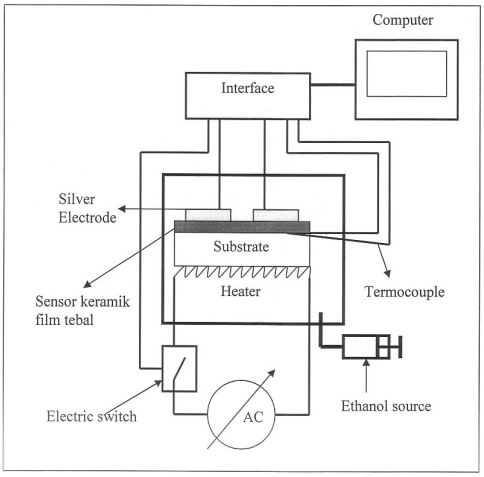

Fig.3. Schematic figure of electrical characterization.

Results and Discussion

Visual Appearance and XRD analyses

Fig. 2. shows the appearance of a typical $ZnFe_2O_4$ based-thick film sensor and Fig. 3 and Fig. 4 are the XRD profiles of the fired thick film ceramics.

The XRD profile of Fig.3 is the profile of thick film ceramic with (50:50) concentration while that of Fig. 4 is the profile of thick film ceramic with (45:55) concentration. Peaks indicated with A are from alumina substrate. As shown in Fig. 3 most of peaks fit the XRD standard profile of spinel

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$ZnFe_2O_4$ from JCPDS No.22-1012. This indicates that the structure of the thick film ceramic with (50:50) concentration is cubic spinel. Similar with Fig. 3, it is found in Fig. 4 that most of the peaks also fit the standard profile of spinel $ZnFe_2O_4$ from JCPDS No.22-1012. However, a peak of Fe_2O_3 (indicated with F) was found at around 2tetha = 33° (Compared to JCPDS No. 33-0664 for hematite Fe_2O_3). This peak is the strongest one of the Fe_2O_3. This data indicates that most of Fe_2O_3 formed $ZnFe_2O_4$ solid solution with ZnO crystallizing in cubic spinel and a part of the Fe_2O_3 was not dissolved. Since the excess Fe_2O_3 formed solid solution, the formation of solid solution in the sample with (45:55) concentration may follow equation (2) below.

$$Fe_2O_3 = 2\,Fe^{+1}{}_{Zn} + 3O_{(O)} + V^{2+}{}_{zn} \quad \text{.....(2)}$$

where, Fe_2O_3 is the excess Fe_2O_3 compared to stoichiometry concentration, $Fe^{+1}{}_{Zn}$ is the Fe ion substitutes Zn ion in the $ZnFe_2O_4$ lattice, $3O_{(O)}$ is the oxygen ion of the excess Fe_2O_3 enter oxygen sublattice and $V^{2+}{}_{zn}$ is Zn vacancy defect.

The formation of solid solution may change the value of the lattice constant of the solid solution. The radii of Zn^{2+} is 88 pm and Fe^{3+} is 69 pm [Barsoum, 1997], so when Fe^{3+} ions substitute Zn^{2+} ions according to equation (2), the lattice constant of the solid solution should be significantly smaller than that of $ZnFe_2O_4$ (stoichiometry). However, the measured lattice constants of ceramic with (50:50) and (45:55) concentrations are almost the same namely 8.4058Å and 8,4035Å respectively, only 0,027% different This data indicates that the excess of Fe_2O_3 in the (45:55) sample may be undissolved and appear as the peak indicated by F in Fig. 4.

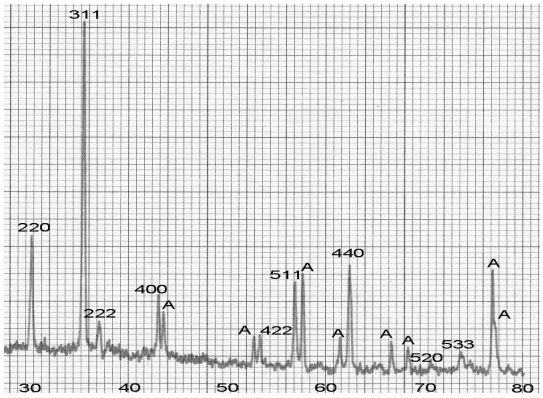

Fig. 3. XRD profile of the $ZnFe_2O_4$ (50 mole % ZnO -50 mole % Fe_2O_3) - thick film ceramic fired at 1000°C for 1 hour in air. Peaks with A indication are from alumina substrate.

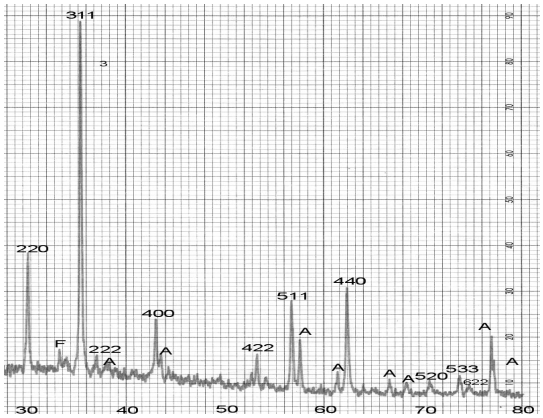

Fig. 4. XRD profile of the $ZnFe_2O_4$ based (45 mole % ZnO-55 mole % Fe_2O_3) - thick film ceramic fired at 1000°C for 1 hour in air. Peaks with A indication are from alumina substrate.

Microstructure/Nanostructure

Fig 5 and Fig. 6 are SEM images of the thick films with (50:50) and (45:55) concentrations, respectively. Fig. 5 shows the morphology of the thick film with (50:50) concentration. As can be seen from Fig. 5, the film is characterized by a typical porous structure and small grains. The average grain size is 270 nm. Fig. 6 shows the morphology of the thick film with (45:55) concentration. As depicted by Fig. 6, the film with (45:55) concentration contains large grains (with average grain size of 3500 nm) with small number of large pores. The microstructure of the film with (50:50) concentration is quite different with that of the film with (45:55) concentration. It is evident that the structure is affected by the composition. The mobility of ions in the ceramic with (45:55) concentration is larger than that in the ceramic with (50:50) concentration. Since the excess of Fe_2O_3 forms solid solution, this is a consequence of defects created in the ceramic with (45:55) concentration. According to equation (2), the defect is Zn vacancy ($V^{1-}{}_{Zn}$). During firing, the defect increases cation diffusion which then promoting grain growth. However, the presence of peak from Fe_2O_3 (indicated with F) in Fig. 4 and no change in lattice constant between the sample with (50:50) and (45:55) concentrations seems that the cause of the promoted grain growth is not the formation of cation vacancy. The cause may be related to the excess of Fe_2O_3. The excess of Fe_2O_3 activates the grain growth during firing through grain boundary activity.

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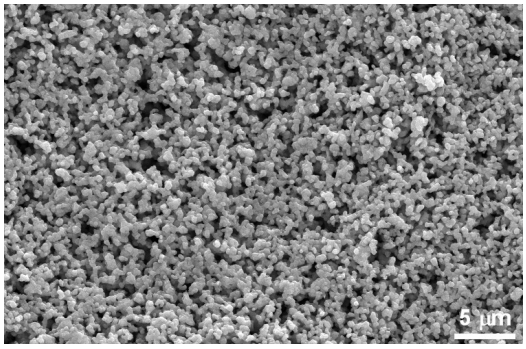

Fig. 5. The morphology of the film with (50:50) concentration fired at 1000°C in air.

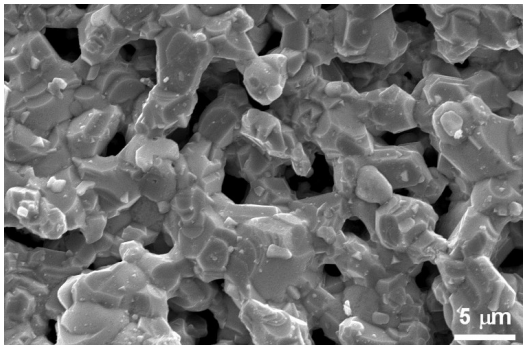

Fig. 6. The morphology of the film with (45:55) concentration fired at 1000°C in air.

Electrical Characterization

Fig. 7 and Fig. 8 are sensitivity data of the thick film ceramics with (50:50) and (45:55) concentrations, respectively. The characteristic in Fig. 7 shows that the film with (50:50) concentration responsive to ethanol gas. The best response of the film is at operating temperature of about 110°C. This operating temperature is lower than that found in literature [Misra, 2003, Lou, 2007]. It means that the gas sensor ceramic in this work is more effective. Compared to data of the film ceramic with (50:50) concentration, the ceramic with (45:55) concentration is less responsive. Fig. 8 shows that the sensitivity of the sample with (45:50) concentration is much smaller than that of the sample with (50:50) concentration. Based on the data of Fig. 5 and Fig. 6, the small sensitivity is caused by the microstructure of the sample with (45-55) concentration which is characterized by large grains and dense body containing small number of pores. The mechanism of the sensing ethanol is shown in Fig. 9 and can be explained as follow.

When a sensor is exposed to the air, O_2 was adsorbed on its surface and the adsorbed oxygen will be translated into chemisorbed oxygen at a definite temperature. In this state a depletion layer is formed and the potential barrier is high (see Fig. 9(a)). When the sensor is then exposed to ethanol gas, the ethanol gas will react with the adsorbed oxygen and transfer electron to conduction band of the $ZnFe_2O_4$ solid solution. After that, the depletion layer decreases and the potential barrier becomes low (see Fig. 9(b)).

Ethanol gas and the chemisorbed oxygen can do reactions as follow [Misra, 2003, Lou, 2007].

$O_2(gas) \rightarrow O_2(Adsorbed)$ ....(3)

$O_2(Adsorbed) + e^- \rightarrow O_2^-$ .....(4)

$O_2^- + e^- \rightarrow 2O^-$ .....(5)

$C_2H_5OH_{gas} + O^- \rightarrow CH_3CHO + H_2O + e^-$ ..... (6)

These reactions will transfer electrons into $ZnFe_2O_4$ based material, leading to an increase in electron concentration and a decrease in resistance of the $ZnFe_2O_4$ based thick film sensor.

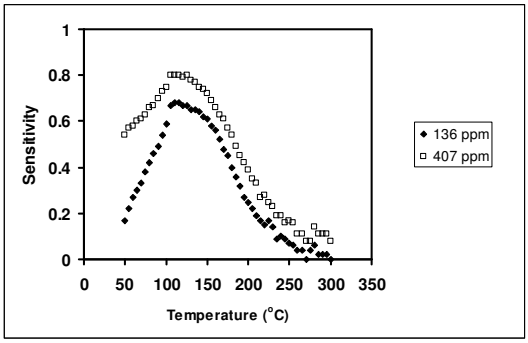

Fig. 7. Sensitivity of the film with (45:55) concentration.

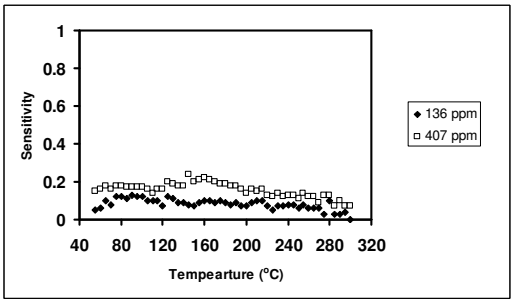

Fig. 8. Sensitivity of the film with (45:55) concentration.

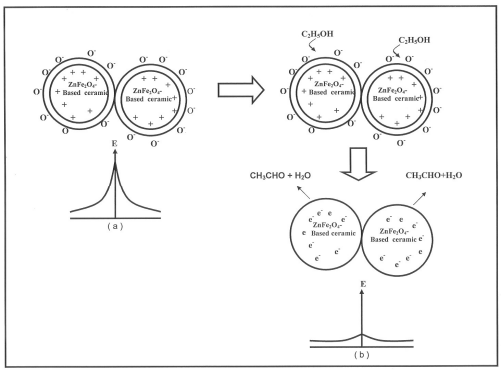

Fig. 9. Schematic principle of ethanol sensing mechanism.

Conclusions

Thick film ceramics based on $ZnFe_2O_4$ for ethanol gas sensor has been produced. All thick film ceramics crystallize in cubic spinel and responsive to ethanol gas. The thick film ceramic with (50:50) has higher sensitivity than the film ceramic with (45:55) concentration. The operating temperature of the film ceramic with (50:50) concentration is about 120^oC which is relatively lower than the operating temperature found in literature. The low sensitivity of the ceramic with (45:55) concentration is caused by the formation of the microstructure having large grains with fewer pores due to the excess of the Fe_2O_3.

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