Electrical Characteristics of CuO Added-ZnFe\textsubscript{2}O\textsubscript{4} Ceramic Semiconductor in Air and Ethanol Gas Atmosphere

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ABSTRACT
In order to get an ethanol gas sensor ceramic with low working temperature, a study on fabrication and characterization of CuO Added-ZnFe\textsubscript{2}O\textsubscript{4} thick film ceramic has been performed. In this preliminary work, a paste was prepared from fine powder of Fe\textsubscript{3}O\textsubscript{4}, ZnO and CuO (0 and 10 mole %). The paste was screen printed on alumina substrates to form films. The films were fired at 1000°C for 1 hour in air. Electrical characterization was done by measuring electrical resistance of the thick film at various temperatures in air and ethanol gas. According to XRD analyses the produced thick film ceramics crystallized in cubic spinel. The film containing CuO formed a solid solution with cubic spinel structure. SEM images showed that the ZnFe\textsubscript{2}O\textsubscript{4} thick film ceramic was porous with relatively small grains and the film containing CuO consisted of larger grains. The electrical characteristics of all the 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 and the working temperature of the CuO added-ZnFe\textsubscript{2}O\textsubscript{4} ceramic is smaller than that of the ZnFe\textsubscript{2}O\textsubscript{4} ceramic.

Key words: ZnFe\textsubscript{2}O\textsubscript{4}, CuO, thick film, ethanol, gas sensor.

I. INTRODUCTION
In modern life people need many sophisticated products for daily life. For the people of Indonesia unfortunately many of these products are imported. One of the products required is gas sensor. The gas sensor is required in many sectors of daily life such as food industry, environment and health [1]. Now people generally need high quality food. For typical high quality food, controlling many parameters especially ethanol is necessary during storing. In this case an ethanol gas sensor is required. For the time being, the gas sensor is generally imported from the overseas.

The dependency to imported products including ethanol gas sensor has to be decreased by many efforts. A possible one is trying to self produce the product 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. In our previous work [2], a preliminary study of producing thick film ceramic based on ZnFe\textsubscript{2}O\textsubscript{4} for ethanol gas sensor has been carried out. This study was 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\textsubscript{2}O\textsubscript{4} it is known that many kinds of material
can be applied as gas sensor such as CdFe$_2$O$_4$[3], SnO$_2$[4], WO$_3$[5], NiFe$_2$O$_4$[6] and CuFe$_2$O$_4$[7]. The electrical characteristics of the ZnFe$_2$O$_4$ thick film ceramic theoretically can be changed by addition of additive such as CuO. The additive can be accommodated through solid solution formation or as inclusion. The addition may change the microstructure. The change of the microstructure may result in a change in the electrical characteristics of the ZnFe$_2$O$_4$ such as electrical resistance. The addition of CuO may decrease the resistance of the ZnFe$_2$O$_4$ ceramic.

In this work, the thick film ceramics for ethanol gas sensor were fabricated from powder of Fe$_2$O$_3$, ZnO and CuO with two different concentrations by using screen printing technique. The aim of this work is to know the effect of CuO addition on electrical characteristics of the ZnFe$_2$O$_4$ thick film ceramics in air and ethanol gas. Hypothetically, the addition of CuO may change the microstructure of the ZnFe$_2$O$_4$. The ZnFe$_2$O$_4$ ceramic with different microstructure may have different electrical characteristics. The evaluation of the thick film ceramics will be based on crystal structure and microstructure data and the data of electrical characteristics in air and ethanol media.

II. METHODOLOGY

The mixtures consisting of Fe$_2$O$_3$, ZnO and CuO with composition according to Table 1 were ground and sieved with a sieve of 38 μm (hole size of 38 μm). The sieved mixture powder with concentration of 95 mole % was mixed with 5 mole % glass frit powder. This is called as ceramic powder. The ceramic powder with concentration of 70 w/o was mixed with 30 w/o organic vehicle (OV) composed of alpha terpineol and ethyl cellulose (EC). The final mixture is called as Fe$_2$O$_3$ paste. The Fe$_2$O$_3$ paste was screen printed on alumina substrates to form thick film ceramics as shown in Fig. 1[3] and Fig.2. After being dried at room temperature, the films were then fired 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. 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. All steps of the procedure can be seen in Fig. 4.

Table 1. Composition of the mixtures in mole %.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fe$_2$O$_3$</th>
<th>ZnO</th>
<th>CuO</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>45</td>
<td>45</td>
<td>10</td>
</tr>
</tbody>
</table>

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

Fig.2. Appearance of the ZnFe$_2$O$_4$ thick film ceramic before cutting.
Fig. 3. Schematic figure of electrical characterization.

Fig. 4. Flow diagram of the experiment procedure.

ZnO, Fe₂O₃, CuO

Mixing

Organic vehicle (OV)

Paste

Screen printing

Characterization: XRD, SEM, electrical characteristics.

Green film ceramic

Firing

Thick film

Glass frit (5 %)

Chamber

Thick film sensor layer

Ethanol source

Substrate

Heater

Temperature controller

Thermocouple

Silver electrode

Chamber

Ohmmeter

AC

Temperature controller

Heater

Thermocouple

Silver electrode
III. RESULTS AND DISCUSSION

XRD analyses

XRD profiles of ZnFe$_2$O$_4$ and 10 mole % CuO added-ZnFe$_2$O$_4$ films are shown in Fig. 5 and Fig. 6. Most of major peaks fit the XRD standard profile of spinel ZnFe$_2$O$_4$ from JCPDS No. 22-1012. Some additional peaks from alumina substrate were found (indicated with A). The structure of the two ceramic is cubic spinel. Peaks from CuO (compared to the JCPDS standard for CuO No. 05-661) as the additive were observed (indicated with C) indicating that the a part of CuO did not react with ZnFe$_2$O$_4$. Lattice constant of ZnFe$_2$O$_4$ and CuO added-ZnFe$_2$O$_4$ thick film ceramic is nearly the same as can be seen in Table 2.

Table 2. Lattice constant of ZnFe$_2$O$_4$ and CuO added-ZnFe$_2$O$_4$ thick film ceramic.

<table>
<thead>
<tr>
<th>Concentration of CuO (%)</th>
<th>Lattice constant (Å)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>8.461± 0.078</td>
</tr>
<tr>
<td>10</td>
<td>8.434± 0.018</td>
</tr>
</tbody>
</table>

Fig. 5. Diffraction profile of ZnFe$_2$O$_4$ thick film.

Fig. 6. Diffraction profile of CuO added-ZnFe$_2$O$_4$ thick film. C is peak from CuO.

Microstructure

Microstructure of ZnFe$_2$O$_4$ and CuO added-ZnFe$_2$O$_4$ thick film ceramics is shown in Fig. 7 and Fig. 8. As can be seen in Fig. 7, the ZnFe$_2$O$_4$ ceramic contains small grains and many pores. This microstructure is quite different than that of the CuO added-ZnFe$_2$O$_4$ ceramic. In the microstructure of the CuO added-ZnFe$_2$O$_4$ the grains are large and just view pores observed. It is clear that this is due to the presence of CuO. The CuO has promoted the grain growth of the ZnFe$_2$O$_4$ ceramic during firing. The grain size of ZnFe$_2$O$_4$ ceramic is about 200 nm whereas the grain size of the CuO added-ZnFe$_2$O$_4$ ceramic is about 2000 nm (Calculated using the intercept method).
Electrical Characteristics

Electrical data of the thick film ceramics is shown in Fig. 9 and Fig. 10. The electrical data of Fig. 9 and Fig. 10 shows that the electrical characteristics of the ceramics follow the semiconductor characteristic where the electrical resistance decreases with the increase of temperature. The temperature for the ceramic to produce a same resistance of two kinds of ceramic namely ZnFe$_2$O$_4$ and CuO added-ZnFe$_2$O$_4$ is quite different. The working temperature difference between the two ceramic is also large. Working temperature here is defined as the temperature where the electrical resistance change due to the change of atmosphere is readable. According to Fig. 9 the working temperature range for ZnFe$_2$O$_4$ is 200-350°C and that for CuO added-ZnFe$_2$O$_4$ according to Fig. 10 is 60-130°C. This means that the addition 10 mole % CuO decreased the working temperature. This is caused by the increase of grain size due to the addition of CuO. A ceramic with larger grains has smaller number of scattering center for charge carrier making the ceramic has lower resistance. As shown in Fig. 9 and Fig. 10, the electrical resistance of the ceramics is larger when measured in air than that when measured in ethanol gas atmosphere. This means that the ethanol gas affects the electrical resistance of the ceramics. The mechanism of this phenomena is as follow. When a ceramic 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. Ethanol gas and the chemisorbed oxygen can do reactions as follow [5,7].

\[
\begin{align*}
\text{O}_2\text{(gas)} & \rightarrow \text{O}_2\text{(Adsorbed)} \quad \ldots \quad (1) \\
\text{O}_2\text{(Adsorbed)} + e^- & \rightarrow \text{O}_2^\cdot \quad \ldots \quad (2) \\
\text{O}_2^- + e^- & \rightarrow 2\text{O}^- \quad \ldots \quad (3) \\
\text{C}_2\text{H}_5\text{OH}_{\text{gas}} + \text{O}^- & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + e^- \quad \ldots \quad (4)
\end{align*}
\]

where Vo$^{2-}$ is a doubly charged oxygen vacancy. These reactions will transfer electrons into ZnFe$_2$O$_4$ based material, leading to an increase in electron concentration and a decrease in resistance of the ZnFe$_2$O$_4$ based thick film sensor.

By taking a working temperature of 290°C for the ZnFe$_2$O$_4$ thick film ceramic and 120°C for the CuO added-ZnFe$_2$O$_4$ thick film ceramic, the relation between electrical resistance and concentration of ethanol gas is evaluated. The relation is expressed in Fig. 11. As can be seen in Fig. 11, the electrical
resistance of the ceramics decreases following the increase of ethanol gas concentration. Sensitivity of the ceramic is expressed by the gradient value of the curves in Fig. 11. The working temperature of the CuO added-ZnFe$_2$O$_4$ is lower than that of the ZnFe$_2$O$_4$, however, the sensitivity of the CuO added-ZnFe$_2$O$_4$ (0.0048 Mohm/ppm) is little bit lower also compared to the sensitivity of the ZnFe$_2$O$_4$ ceramic (0.0070 Mohm/ppm).

Fig. 9. In R versus 1/T for ZnFe$_2$O$_4$ thick film ceramic in air and ethanol gas.

Fig. 10. In R versus 1/T for CuO added-ZnFe$_2$O$_4$ thick film ceramic in air and ethanol gas.
Fig. 11. Resistance (R) as a function of ethanol gas concentration of ZnFe₂O₄ thick film ceramic for measurement temperature of 290°C and of CuO added-ZnFe₂O₄ thick film ceramic for measurement temperature of 120°C.

IV. CONCLUSION

Thick film ceramics of ZnFe₂O₄ and CuO added-ZnFe₂O₄ can be well produced at firing temperature of 1000°C. All of the thick films crystallizes in spinel cubic. The addition of 10 mole % CuO decreases the electrical resistance of the ZnFe₂O₄ thick film ceramic because the addition of 10 mole % CuO changes the microstructure resulting in large grains. The addition of 10 mole % CuO also decreases the working temperature. The produced thick film ceramics have semiconductor characteristic where the resistance decreases with the increase of temperature. The resistance of the films measured in ethanol gas is lower than that of the film measured in air. The resistance of the film decreases with the increase of ethanol gas concentration. The addition of 10 mole % CuO decreases the sensitivity.

V. REFERENCES