Preliminary studies of $Mn(x)Zn(2-x)FeO_4$ ($x = 0$ dan $0.1$) thick film semiconductors as an ethanol gas sensor

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Abstract. Preliminary studies about fabrication of $Mn_0Zn_{2.0}FeO_4$ ($x = 0$ dan $0.1$) had been done to identify the effect of adding $Mn_2O_3$ 10%mol towards gas sensor sensitivity. Gas sensor ceramics that fabricated through local nature mineral-based is Yarosite mineral. The fabrication of $Mn_0Zn_{2.0}FeO_4$ thick film semiconductor by using Screen Printing method and firing at temperature $800 \degree C$ for 2 hours. Through electrical properties test it is known that the adding of $Mn_2O_3$ materials made semiconductor thick film faster to response ethanol gases rather than without $Mn_2O_3$ materials. Thick film $Mn_{0.1}Zn_{1.9}FeO_4$ has lower operating temperature and higher conductivity than $Zn_{2}FeO_4$ thick film. Electrical resistance test indicated that by adding $Mn_2O_3$ 10%mol, it is sufficiently effective to obtain new properties of $Mn_{0.1}Zn_{1.9}FeO_4$ thick film and it can be used as ethanol gas sensor.

1. Introduction

The Islamic world needs a sensor/detector device for testing contained alcoholic matter in the consumption ingredients, include food and drinks. As clarified in fatwa MUI No. 11, 2009 Year, that consumption items contained within alcohol is Haram in Islam [1]. Where the detector are now it is still imported and its price is very expensive. So, need a effort to makes local detector from Indonesia local materials, like as Yarosite mineral most contained $Fe_2O_3$.

The efforts of making device as the gas sensor from local materials-based is need long phase by experimental variations through resulting a products accepted on the market. On the other hand, the research about this Preliminary Studies of $Mn(x)Zn(2-x)FeO_4$ ($x = 0$ dan $0.1$) is going to be a beginning that need to be developed in the future.

Gas sensor is an electronic device that has principle as changing chemical interaction to be electrical signal [2; 3]. Materials used in the fabrication of gas sensor had semiconductor properties. One of the more often used materials is Metal Oxide Semiconductor (MOS), its advantage is a large surface area [2; 4]. Many MOS material that used as gas sensor material, such as ZnO, CuO, SnO2, ZrO2, Fe2O3 [5; 6; 7; 8; 9; 10]. The research of gas sensor has been done by many researchers [11; 12; 13; 14], generally...
they were obtaining high operating temperature and low stability. Instead, the sensitivity, responses and recovery times were good enough. It is a challenge for us to fabricate gas sensor MOS-based successfully which has low operating temperature and high sensitivity. In recent research, MnO (Mangan [II] oxide)-doped to Fe$_2$O$_3$ and then temperature was known at 150-200 °C, but its tendency to sensitivity was random [15]. Therefore, in this research the addition of ZnO and Mn$_2$O$_3$ was done to gas sensor material Fe$_2$O$_3$-based. Researchers reported that adding ZnO was used to improve the surface area of sensor affected to the velocity of response and recovery times to the gas target [16; 13; 17]. Whereas adding Mn$_2$O$_3$ expected to obtain the result in substituting Fe$^{3+}$ and being host. So that low operating temperature and high sensitivity gas sensor was obtained.

In this research, Fe$_2$O$_3$ powder obtained from purifying Yarosit mineral and Mn$_2$O$_3$ from Manganite minerals. Both of them synthesized by using precipitation method. Fe$_2$O$_3$, ZnO and Mn$_2$O$_3$ powders were mixed and made thick film through 2 variations. Thick film fabricated by screen printing method with firing temperature at 800 oC. The aims in this research were knowing the effect of Mn$_2$O$_3$ by response of Mn$_{1-x}$Zn$_{x}$Fe$_3$O$_4$ (x = 0 dan 0.1) semiconductor of thick film. The thick film was characterized by PWX (electrical properties tester) to know its electrical properties.

2. Experiment

2.1. Synthesis of materials
Fe$_2$O$_3$ powder was obtained by purifying yarosite mineral from Kuningan, Jawa Barat. Yarosite minerals was dissolved with HCl 5M and precipitated with NH$_4$OH. Then, it was filtered and washed by using water. It was dried at 100°C and calcined at temperature 600 °C for 3 hours. Mn$_2$O$_3$ powder was obtained by purifying Manganite minerals from Garut, Jawa Barat. The procedure of purifying Mn$_2$O$_3$ powder is same as the purifying Fe$_2$O$_3$ powder from Mineral yarosite, but it was adding HNO$_3$ solution for Mn$_2$O$_3$. Zinc Oxid (ZnO) powder used E merck commercial. The powder of Fe$_2$O$_3$, ZnO and Mn$_2$O$_3$ was dissolved with HCl respectively until consistently uniform and mixed to be 2 various solutions by mol ratio 2 : 1 : 0 and 1 : 1 : 9 : 0.1 respectively. The solutions were precipitated with NH$_4$OH and the results was dried at 100 oC and then calcined at temperature 800 °C temperature for 3 hours. So that we get Zn$_3$FeO$_4$ (ZF) and Mn$_{0.1}$Zn$_{0.9}$FeO$_4$ (MZF) powder.

2.2. Fabrication and characterization of thick film
ZF dan MZF powder mixed with Organic Vehicle (OV) respectively (OV made of mixture 90% Terpineol alpha dan 10% Etil selulose). The ratio of the powder and OV used is 70 : 30. The mixture is mixed until paste forms. Before the paste of ZF and MZF coated on the alumina substrate, the substrate was coated silver electrode and puried at 600 °C for 10 minutes. And then the substrate was coated with ZF and MZF by using screen printing method (225 mesh screen size) respectively. Design of thick film was shown as figure 1 (figure 1.a) shows that alumina substrate is used as media for coating silver electrode and ceramics. Figure 1.b) shows alumina substrate which coated silver electrode by measure 4.75 mm from alumina substrate tip point respectively, and emptied 0.5 mm on middle of substrate. Figure 1.c) shows that substrate is coated with ceramic by 5 x 5 mm area. And then thick film fired at 800 °C for 2 hours. Thick film were fabricated and characterized by using PWX to know the sample electrical properties in the air and ethanol gas atmosphere on rank 25 – 400 °C.
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Figure 1. Design of thick film. (a) Substrat alumina, (b) Alumina Substrate coated silver electrode, (c) Alumina Substrate coated silver electrode and ceramic.

The electrical data of thick film measuring was made up changed electrical resistance in line with increasing temperature of heater on PWX. This condition is for identifying the response of thick film to the gas target in which using ethanol gas. Gas responded and measured proportional to the Eq. 1 and 2 [18; 19]. Moreover, it was obtaining the enstivity value $\alpha$ constant and activate energy on such as of the samples.

\[ R_{N-type} = \frac{R_o - R_g}{R_o} \times 100\% \]  
\[ R_{P-type} = \frac{R_g - R_o}{R_o} \times 100\% \]  

Where, $R_{N-type}$ is response of N-type sensor material, $R_{P-type}$ is response of P-type sensor material, $R_o$ is electrical resistance in air (non target gas) and $R_g$ is target gas atmosphere.

3. Result and discussions

Figure 2 shows the change in electrical resistance to the temperature in the ZF sample. Increased temperature is accompanied by a decrease in the resistance value of the sample. Physically, this decrease in the resistance value is caused by excited electrons from the valence band to the conduction band. The higher of temperature caused the more of the excited electrons. The excitation process will leave a hole in the valence band and the electrons in the conduction band become free electrons. Therefore, the material becomes conductive if higher temperatures [20].

Figure 2. The changes of resistance to the temperature at the sample:(a) ZF and (b) MZF.
Figure 2(a) shows the response of ZF thick film in the air and ethanol gas. The Resistance value of ZF thick film in the ethanol gas is lower than when there are in the air. The higher the concentration of ethanol, then the value of the electrical resistor is lower. This showed that the sample of ZF thick film is the n-type semiconductor [21]. The decrease in resistance value is caused by the surface that adsorbs oxygen in the air and then the oxygen ionized becomes O-. This process will form a potential barrier and then when treated with a reducing gas (ethanol), electrons bound with oxygen will be reduced by the ceramics in the conduction band. Therefore the conductance value will be increased and the resistance value will be decreased [9; 14; 22]. The adsorption reaction of oxygen by the ceramic surface, following eq. 3-5:

\[ O_2(g) + e^- \rightarrow O_{2(adg)}^- \] \hspace{1cm} (3)

\[ O_{2(adg)}^- + e^- \rightarrow 2O_{(adg)}^2- \] \hspace{1cm} (4)

\[ O_{(adg)}^2- + e^- \rightarrow O^{2-} \] \hspace{1cm} (5)

The reaction when the ceramic interacts with ethanol gas, following eq. 6-8 [23], [14]:

\[ C_2H_5OH_{(g)} + 3O_{2(adg)}^- \rightarrow 3CO_2 + 3H_2O + 3e^{-} \] \hspace{1cm} (6)

\[ C_2H_5OH_{(g)} + 6O_{2(adg)}^- \rightarrow 2CO_2 + 3H_2O + 6e^- \] \hspace{1cm} (7)

\[ C_2H_5OH_{(g)} + 6O_{2(adg)}^- \rightarrow 2CO_2 + 3H_2O + 12e^- \] \hspace{1cm} (8)

The response of MZF thick film in the air and ethanol gas shown at Figure 2(b). The Resistance value of MZF thick film in the ethanol gas is higher than when there are in the air. This showed that the sample of ZF thick film is the n-type semiconductor unlike n-type, ionized oxygen by ceramics on p-type reacted with ethanol gas. The electron-bound of oxygen will return to the ceramic and recombine with the hole in the conducting band. Electron recombination from the conduction band to the valence band causes a decrease in the number of holes and the depletion of the depletion region. Thus causing the conductance decreases or the resistance increases [24; 4]. In addition, the method to find the type of material is look response of sensor at the gas feed. If the resistance is greater than when it's ambient condition, then the material is p-type. But if it is smaller than the ambient condition, the sensor material is n-type [25; 2]. Because of ethanol includes the reducing gas [26], obtained the ZF film is n-type ceramic and the MZF film is p-type ceramic.

The Both semiconductors have a response at different temperatures. The MZF films are able to respond to gases at 205 °C temperatures in both ambient and ethanol condition. The ZF film responds when temperatures reach 260 °C (ambient) and 225 °C in the ethanol condition. At the one temperature value, the MZF films have a smaller electrical resistance value compared to ZF film. This indicates that MZF is more conductive.

Figure 3 shows the sensitivity of ZF and MZF film. Figure 3 (a) shows the optimum temperature for all concentrations of ethanol gas feed (100-300 ppm) in the range 285 - 300 °C. Where the maximum point is at a temperature of 290 °C. This indicates that the adsorption process is best located at that point. Figure 3 (b) shows that the optimum temperature of MZF ceramics for 100 ppm ethanol concentration is in the range of 205 - 305 °C with the maximum point being 270 °C. As for the ethanol concentration of 200-300 ppm the optimum temperature is in the range 225-280 °C with the maximum point is at 235 °C. This operating temperature is lower when compared to ceramics without doping Mn3O4 [11]. This indicates that the addition of Mn3O4 lowers the operating temperature. So that power consumption on Fe-based gas sensor, Zn, Mn does not require high power.
The alpha constant of ZF thick film is $\alpha_{(280)} = 0.0704$ shown by figure 4(a). The alpha constant of MZF thick film is $\alpha_{235} = 0.4287$ shown by figure 4(b). The alpha constant reveals the sensor’s ability to detect the target gas. These are often used in commercial sensors in detecting at a certain gas concentration.

![Figure 3. The sensitivity of thick film (a) ZF and (b) MZF.](image)

**Figure 4** (a) The alpha constants of ZF, (b) The alpha constants of MZF.

**Table 1.** The activation energy of thick film

| Sample          | 100 ppm | 200 ppm | 300 ppm |
|-----------------|---------|---------|---------|
| ZnFe$_2$O$_4$   | 0.566   | 0.626   | 0.654   |
| Mn$_{0.1}$Zn$_{0.9}$FeO$_4$ | 0.59     | 0.622   | 0.624   |

The activation energy was obtained from plotting of $\ln R$ to $1 / T$ (K) using eq. 5:

$$\ln R = \frac{E_a}{T} K_B - \ln C$$

The R is resistance in certain circumstances, $E_a$ is activation energy (eV), T is temperature in units of Kelvin, $K_B$ is Boltzman constant [8,617 x 105 (eV / K)]. Table 1 shows the activation energy in each of ethanol concentration. The data suggest that MZF ceramics are consecutive in various concentrations of ethanol having less activation energy than ZF. Referring to Eq. 5 shows that the activation energy is proportional to $\ln R$, where R is inversely proportional to conductivity. This indicates that Energy activation has a relationship with the conductivity of a material. So the sensor material that has small
activation energy has high conductivity. Therefore, the MZF thick film has higher conductivity than the ZF thick film.

4. Conclusions
In summary, \( Mn_{(x)}Zn_{(2-x)}FeO_4 \) \( (x = 0 \) dan \( 0.1) \) thick film had been fabricated by using screen printing method. The adding \( Mn_2O_3 \) 10%mol sufficiently effective to obtain new properties of MZF thick film. Electrical resistance value at same temperature the MZF thick film was lower than ZF. It was indicated that MZF higher conductivity than ZF. Gas Response obtained of the sample ZF 63% and MZF 47% at operating temperature 290 °C and 235 °C respectively. Low operating temperature need on fabrication of gas sensor because it need low energy. Therefore, \( Mn_{0.1}Zn_{0.9}FeO_3 \) thick film and it can be used as ethanol gas sensor.

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