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Semiconductor Ceramic $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 from Natural Minerals as Ethanol Gas Sensors

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Abstract. In this research, Mn and Fe-based ceramic gas sensing were fabricated and characterized. This research used natural mineral which is widely available in Indonesia and intended to observe the characteristics of Mn and Fe-based semiconducting material. Fabricating process of the thick films started by synthesizing the ceramic powder of $Fe(OH)_3$ and Mn oxide material using the precipitation method. The deposition from precipitation method previously was calcined at a temperature of 800 ºC to produce nanoparticle powder. Nanoparticle powder that contains Mn and Fe oxide was mixed with an organic vehicle (OV) to produce a paste. Then, the paste was layered on the alumina substrate by using the screen printing method. XRD method was utilized to characterize the thick film crystal structure that has been produced. XRD spectra showed that the ceramic layer was formed from the solid $Mn_{0.5}Fe_{1.5}O_3$ (bixbyite) and Fe_2O_3. In addition, the electrical properties (resistance) examination was held in the room that contains air and ethanol to determine the sensor sensitivity of ethanol gas. The sensor resistance decreases as the ethanol gas was added, showing that the sensor was sensitive to ethanol gas and an n-type semiconductor. Gas sensor exhibit sensitive characterization of ethanol gas on the concentration of (100 to 300) ppm at a temperature of (150 to 200) ºC. This showed that the $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 ceramic semiconductor could be utilized as the ethanol gas detector.

Keywords. Bixbyite, gas sensor, jarosite minerals, nanoparticle, semiconductor ceramic, XRD.

1. Introduction

Jarosite mineral is one of the minerals that widely available in Indonesia. Jarosite mineral that contains Fe_2O_3, can be used as the main component of oxide ceramic-based semiconductor manufacturing. Several studies have been conducted to utilize the Fe_2O_3 in Jarosite mineral, including in fabrication of $CuFe_2O_4$ ceramics [1, 2], Fe_2O_3- NiO [3], Fe_2TiO_5 [4] and Fe_2TiO_5/Nb_2O_5 [5]. The gas sensor is an example of metal oxide ceramic application, especially on detection of flammable gases and hydrocarbons [6, 7]. Nowadays, alcohol gas sensor is one of the most popular necessaries. Alcohol gas sensor can be applied to detect the alcohol vapor on human's breath, foods, beverages, or alcohol vapor in the air. The oxide ceramic-based semiconductor material is sensitive to certain gases. MnO_2 is a useful dopant because of the multivalency characteristic of Mn ion [8] and can improve the sensor quality with the thermistor constant value [4]. In the present study, Fe_2O_3 ceramic is suitable for alcohol sensor application [9]. However, the sensing performance of the sensor has not been qualified for sensitivity, operating temperature and response rates. The doping technique is one way that could develop the sensor performance as a function of Mn dopant to qualify insensitivity, sensor operating temperature and response rates. Furthermore, Mn addition could produce the bixbyite solid solution that contains different particle size than Fe_2O_3 phase in composite [10–12].

2. Materials and methods

2.1. Synthesis of $Fe(OH)_3$

$Fe(OH)_3$ was synthesized by precipitation methods using Jarosite minerals from PD Kerta Pertambangan as precursors. An amount of 20 g Jarosite minerals was dissolved in HCl solution and precipitated using NH_4OH solution that was slowly dropped until the pH value 10. The solution was filtered to separate the precipitate. It was heated in an oven at 110 ºC for 31 h. Finally, it was crushed to get nanopowder.

2.2. Fabrication of Semiconductor Ceramic $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3

Ceramic powder for producing Mn and Fe oxide-based sensors was synthesized using Fe_2O_3 derived from Jarosite mineral. $Fe(OH)_3$ powder (1.391753 g) was dissolved in 30 mL distilled water and MnO powder from Aldrich with purity of 99 % (0.922777 g) was dissolved in 20 mL HCl and both were mixed until homogeneous. The mixture was added with NH_4OH until a precipitate was formed and the precipitate was calcined at a temperature of 800 °C to get nanoparticle powder that contains Mn and Fe oxides. The powders mixed with *Organic Vehicle (*composed of ethyl cellulose and terpineol alpha) in a ratio of 74.1 %: 25.9 %. The mixture was homogeneously stirred to form a paste (Figure 1).

Figure 1. $Mn_{0.5}Fe_{1.5}O_3$ – Fe_2O_3 paste

The paste was printed on a silver-coated alumina substrate using a screen. The film was heated at 800 °C for 2 h in the air.

2.3. Characterization of Semiconductor Ceramic $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3

The crystal structure of semiconductor ceramic $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 was analyzed using X-ray diffraction (XRD) from Philips X-ray PW 1710 BASED type. This instrument was equipped with Cu target, voltage source 40 kV, current source 35 mA and wavelength of 1.54056 Å. The electrical resistance of the thick film was measured at various temperatures in the air and in the atmosphere of ethanol gas. The principle of the instrument for measuring the electrical resistance is shown in Figure 2.

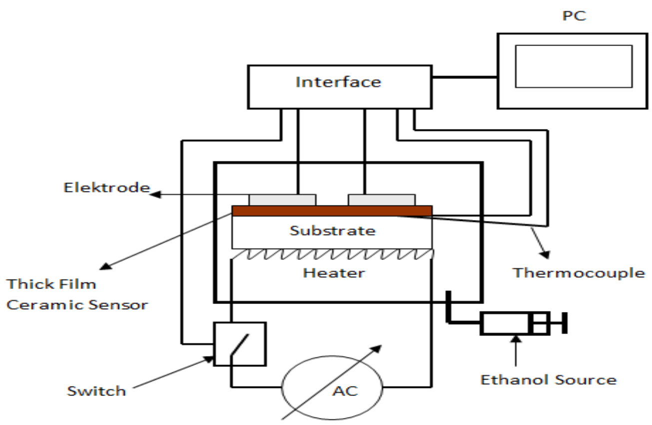

Figure 2. The instrument principle for measuring electrical resistance.

3. Results and discussion

Thick films of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 were successfully fabricated. A sample as a representative is shown in Figure 3. The thick films of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 are smooth without cracks on the ceramics surface. The XRD pattern of the $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 thick film is depicted in Figure 4.

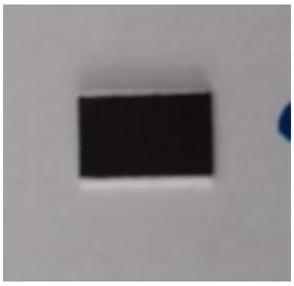

Figure 3. Representation of thick film Mn and Fe-based oxide.

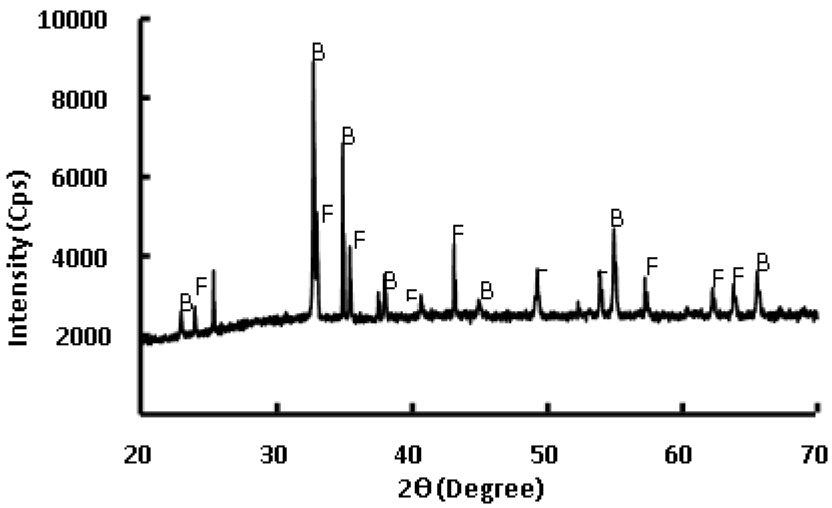

Figure 4. XRD pattern of semiconductor ceramic $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3. B is from bixbite, and F is from Fe_2O_3.

Figure 4 shows the XRD profile of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 thick film ceramics. The analysis was done by comparing the XRD pattern of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 thick film ceramics to the XRD pattern of JCPDS standard No. 41-1442 for Mn_2O_3 and JCPDS No. 33-0664 for Fe_2O_3. From the analysis it was known that the fabricated ceramic formed a ceramic composite that consists of $Mn_xFe_{2-x}O_3$-Fe_2O_3 solid solution ceramic (indicated by B) and Fe_2O_3 (indicated by F). Here x is 0.5.

The electrical resistance of the thick film ceramics of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 as a function of temperature is shown in Figure 5. Whereas Figure 6 shows the sensitivity characteristics of the film. As can be seen in Figure 5, the resistance decreases with temperature. This indicates that thick film $Mn_xFe_{2-x}O_3$-Fe_2O_3 material has a semiconducting property with n-type [13, 14]. The resistance of the samples in the ethanol-containing atmosphere (100 ppm) is smaller than that in the air. And when the ethanol concentration is increased from 100 ppm to 200 ppm and from 200 ppm to 300 ppm, the resistance decrease. This data shows that the thick film is sensitive to ethanol gas, and means that the thick film ceramic of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 has the potentiality to be ethanol gas sensor.

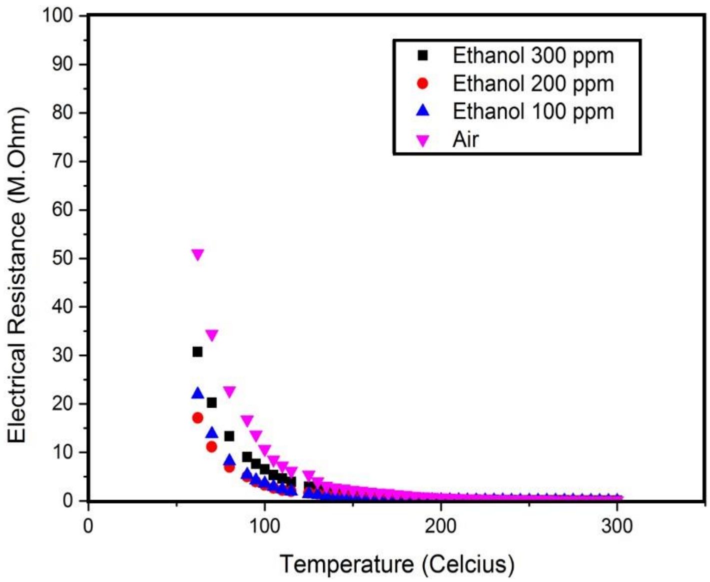

Figure 5. The electrical resistance characteristic of thick film $Mn_{0,5}Fe_{1,5}O_3$-Fe_2O_3 to temperature changes.

Figure 6 shows that the thick film of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 ceramic is sensitive to ethanol gas. Sensitivity value is calculated with Equation 1. The highest sensitivity is for ethanol gas concentration of 100 ppm. The optimum operating temperature of the sensor is between (150 to 200) ºC.

$$S = \left[\frac{R_O - R_G}{R_O} \right] \times 100\% \qquad (1)$$

Where S is the sensitivity of thick film ceramics (%), R_O is the electrical resistance of thick film ceramic in the air environment and R_G is the electrical resistance of thick film ceramic in the ethanol gas environment.

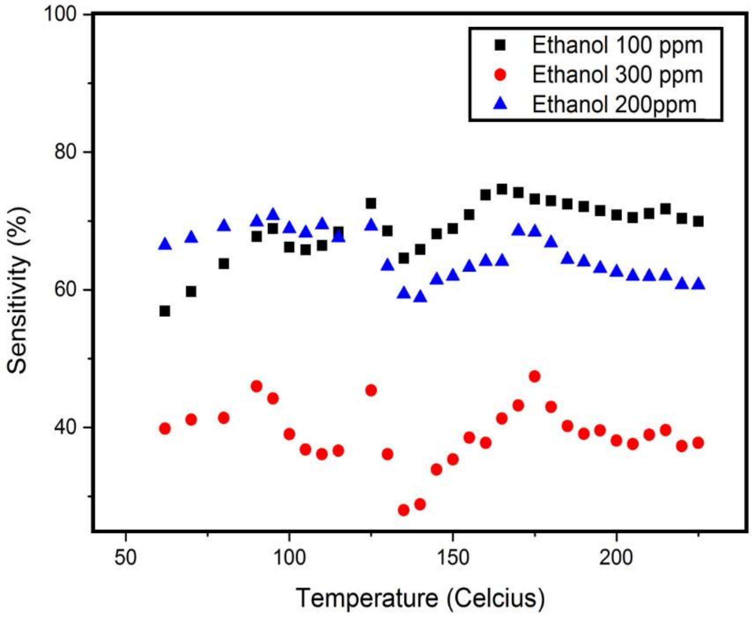

Figure 6. Interpretation of thick Film $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 sensitivity

The decreasing of the resistance of $Mn_{0.5}Fe_{1.5}O_3$-Fe_2O_3 thick film electricity is caused by several factors. One is that when the thick film is in the air environment, the thick film surface absorbs oxygen (O_2) ions and electrons in the conduction band move to oxygen, the barrier increases. When the thick film surface absorbs ethanol gas, a reaction between ethanol gas and adsorbed oxygen is formed. Due to the reaction, barrier resistance decreases. At this time the resistance decreases, increasing the conduction [15].

4. Conclusions

Ethanol gas sensor can be fabricated by using thick film technology. A thick film of $M_{0.5}Fe_{1.5}O_3$-Fe_2O_3 ceramics that is sensitive to ethanol gas has been fabricated. The sensor ceramic has n-type semiconductor characteristic. The resistance decreases with ethanol gas concentration.

Acknowledgments

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