Electrical Characteristics of CuO Added-$ZnFe_2O_4$ 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-$ZnFe_2O_4$ thick film ceramic has been performed. In this pleliminary work, a paste was prepared from fine powder of Fe_2O_3, ZnO and CuO (0 and 10 mole %). The paste was screen printed on alumina substrates to form films. The films were fired at 1000^oC 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 $ZnFe_2O_4$ 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-$ZnFe_2O_4$ ceramic is smaller than that of the $ZnFe_2O_4$ ceramic.

***Key words**: $ZnFe_2O_4$, 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 $ZnFe_2O_4$ 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 $ZnFe_2O_4$ it is known that many kinds of material can be applied as gas sensor such as $CdFe_2O_4$[3], SnO_2[4] , WO_3[5], $NiFe_2O_4$[6] and $CuFe_2O_4$[7]. The electrical characteristics of the $ZnFe_2O_4$ 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 $ZnFe_2O_4$ such as electrical resistance. The addition of CuO may decrease the resistance of the $ZnFe_2O_4$ ceramic.

In this work, the thick film ceramics for ethanol gas sensor were fabricated from powder of Fe_2O_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 $ZnFe_2O_4$ thick film ceramics in air and ethanol gas. Hypothetically, the addition of CuO may change the microstructure of the $ZnFe_2O_4$. The $ZnFe_2O_4$ 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_2O_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_2O_3 paste. The Fe_2O_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 %.

No.	Fe_2O_3	ZnO	CuO
1.	50	50	0
2.	45	45	10

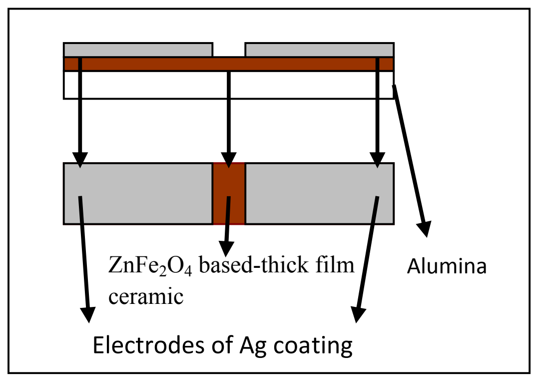

Fig.1. A schematic view of a thick film ceramic sensor [4].

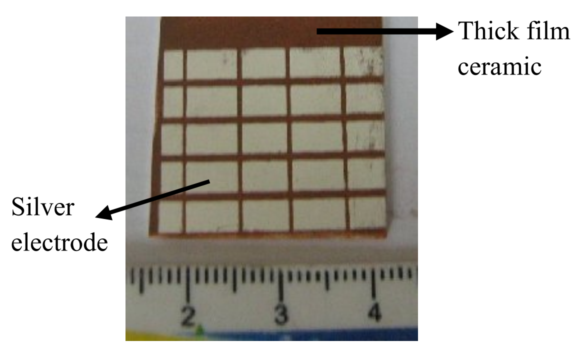

Fig.2. Appearance of the $ZnFe_2O_4$ thick film ceramic before cutting.

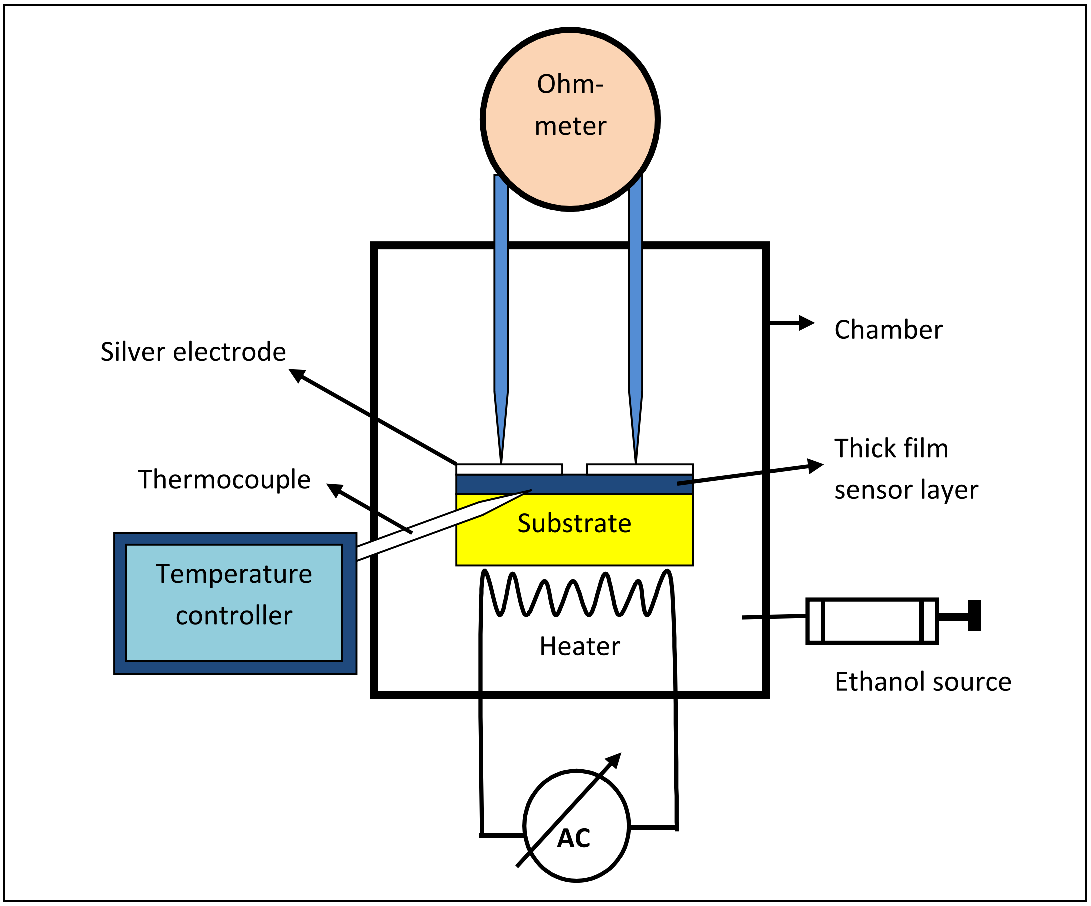

Fig.3. Schematic figure of electrical characterization.

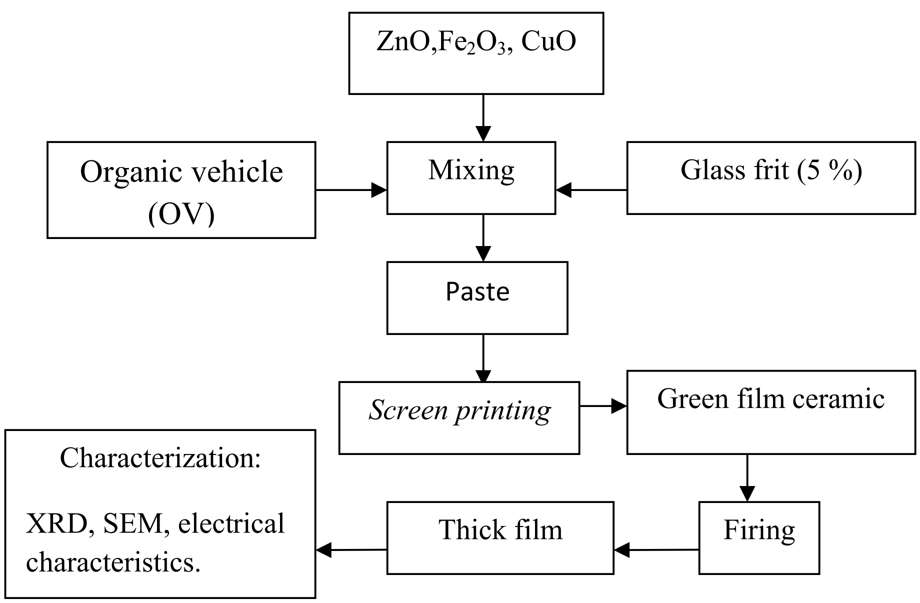

Fig.4. Flow diagram of the experiment procedure.

III. RESULTS AND DISCUSSION

XRD analyses

XRD profiles of $ZnFe_2O_4$ and 10 mole % CuO added-$ZnFe_2O_4$ films are shown in Fig.5 and Fig. 6. Most of major peaks fit the XRD standard profile of spinel $ZnFe_2O_4$ 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 $ZnFe_2O_4$. Lattice constant of $ZnFe_2O_4$ and CuO added-$ZnFe_2O_4$ thick film ceramic is nearly the same as can be seen in Table 2.

Table 2. Lattice constant of $ZnFe_2O_4$ and CuO added-$ZnFe_2O_4$ thick film ceramic.

Concentration of CuO (%)	Lattice constant (Angstrom)
0	8.461± 0.078
10	8.434± 0.018

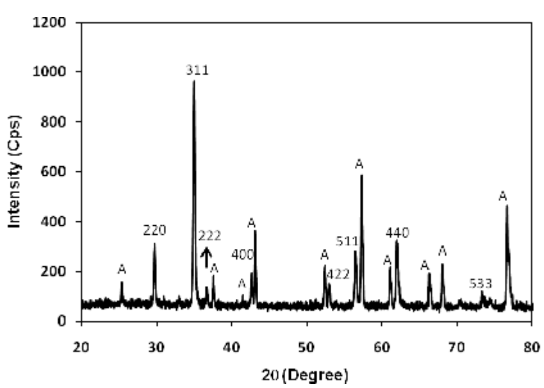

Fig. 5. Diffraction profile of $ZnFe_2O_4$ thick film.

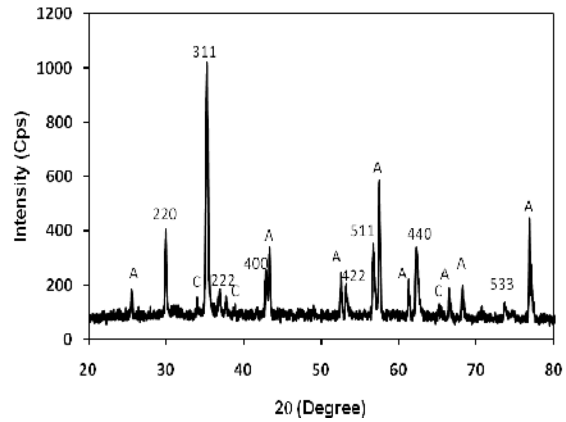

Fig. 6. Diffraction profile of CuO added-$ZnFe_2O_4$ thick film. C is peak from CuO.

Microstructure

Microstructure of $ZnFe_2O_4$ and CuO added-$ZnFe_2O_4$ thick film ceramics is shown in Fig. 7 and Fig. 8. As can be seen in Fig.7, the $ZnFe_2O_4$ ceramic contains small grains and many pores. This microstructure is quite different than that of the CuO added-$ZnFe_2O_4$ ceramic. In the microstructure of the CuO added-$ZnFe_2O_4$ 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 $ZnFe_2O_4$ ceramic during firing. The grain size of $ZnFe_2O_4$ ceramic is about 200 nm whereas the grain size of the CuO added-$ZnFe_2O_4$ ceramic is about 2000 nm (Calculated using the intercept method).

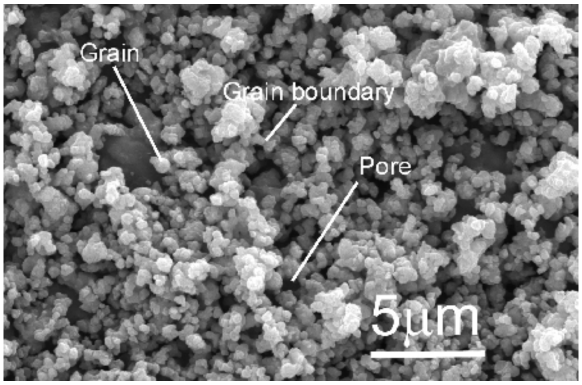

Fig. 7. Microstructure of $ZnFe_2O_4$ thick film.

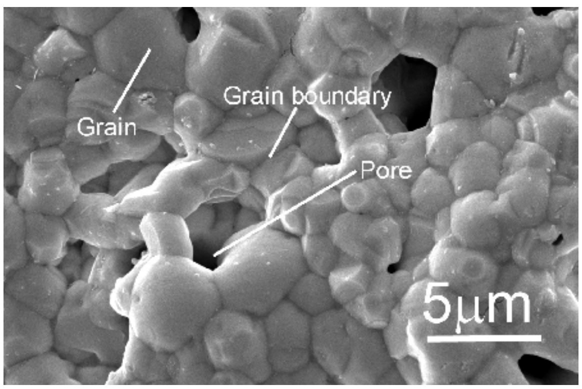

Fig.8. Microstructure of $ZnFe_2O_4$:CuO 10 mole % thick film.

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 $ZnFe_2O_4$ and CuO added-$ZnFe_2O_4$ 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 $ZnFe_2O_4$ is 200-350^{o}C and that for CuO added-$ZnFe_2O_4$ according to Fig. 10 is 60-130^{o}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].

$O_2(gas) \rightarrow O_2(Adsorbed)$ .... (1)

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

$O_2^- + e^- \rightarrow 2O^-$ ....(3)

$C_2H_5OH_{gas} + O^- \rightarrow CH_3CHO + H_2O + e^-$ ……(4)

where Vo^{2-} is a doubly charged oxygen vacancy. 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.

By taking a working temperature of 290^{o}C for the $ZnFe_2O_4$ thick film ceramic and 120^{o}C for the CuO added-$ZnFe_2O_4$ 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-$ZnFe_2O_4$ is lower than that of the $ZnFe_2O_4$, however, the sensitivity of the CuO added-$ZnFe_2O_4$ (0.0048 Mohm/ppm) is little bit lower also compared to the sensitivity of the $ZnFe_2O_4$ ceramic (0.0070 Mohm/ppm).

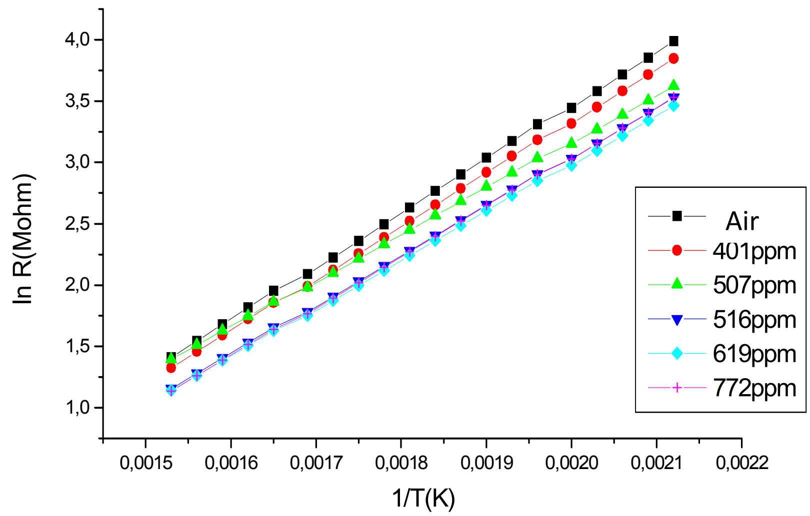

Fig. 9. ln R versus 1/T for $ZnFe_2O_4$ thick film ceramic in air and ethanol gas.

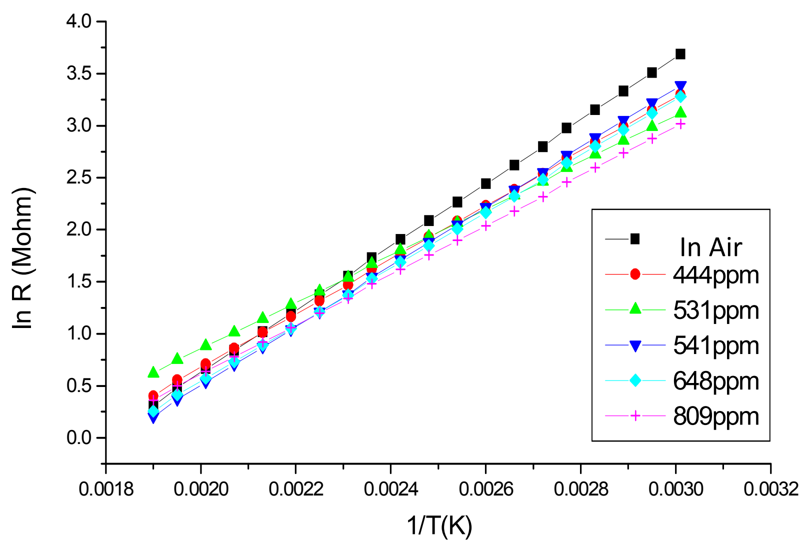

Fig. 10. ln R versus 1/T for CuO added-$ZnFe_2O_4$ thick film ceramic in air and ethanol gas.

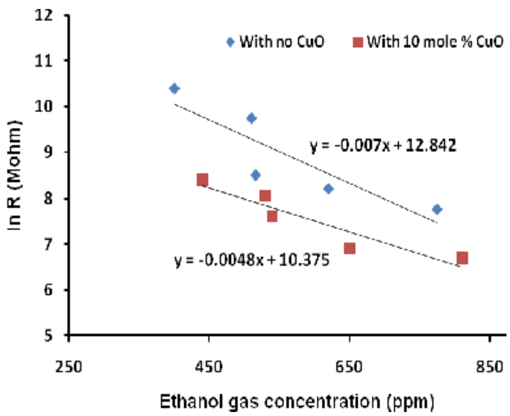

Fig. 11. Resistance (R) as a function of ethanol gas concentration of $ZnFe_2O_4$ thick film ceramic for measurement temperature of 290^0C and of CuO added-$ZnFe_2O_4$ thick film ceramic for measurement temperature of 120^0C.

IV. CONCLUSION

Thick film ceramics of $ZnFe_2O_4$ and CuO added-$ZnFe_2O_4$ can be well produced at firing temperature of 1000^oC. All of the thick films crystallizes in spinel cubic. The addition of 10 mole % CuO decreases the electrical resistance of the $ZnFe_2O_4$ 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

1. K.Arshak, I.Gaidan, Gas sensing properties of $ZnFe_2O_4$/ZnO screen-printed thick films, Sensors and Actuators, B111-112, 58-62(2005).
2. D. K. Kusnaeni, D. G. Syarif, Synthesis of $ZnFe_2O_4$-based thick film ceramics and its characterization in air and ethanol gas, Proceeding of the International Seminar on Chemistry, UNPAD, Jatinangor, Sumedang, 2008.
3. Zhang Tianshu, P. Hing, Zhang Jiancheng, Kong Lingbing, Ethanol-sensing characteristics of cadmium ferrite prepared by chemical coprecipitation, Materials Chemistry and Physics 61, 192-198 (1999).
4. Sanju Rani, Somnath C. Roy, M.C.Bhatnagar, Effect of Ge doping on the gas sensing properties of nano-cryslline SnO2 thin film, Sensors and Actuators B 122, 204-210 (2007).
5. R.S. Khadayate, R.B.Wagulde, M.G.Wankhede, J.V. Sali, P.P. Patil, Ethanol vapor sensing properties of screen printed WO_3 thick film, Bull.Mater.Sci. 30(2), 129-133 (2007).
6. I.Satyanarayana, K.Madhusu and Rhedy, Sunkara V. Manoroma, Nanosized spinel $NiFe_2O_4$:A novel material for detection of liquefied petroleum gas in air, Mater. Cem. Phys. 82, 21-26 (2003).
7. Shanwen Tao, Feng Gao, Xingqin Liu, Ole Toft Sorensen, Preparation and gas sensing properties of $CuFe_2O_4$ at reduced temperature, Mater.Sci.Eng. B77, 172-176 (2000).