p-ISSN: 1693-1246
e-ISSN: 2355-3812
July 2016

Jurnal Pendidikan Fisika Indonesia 12 (2) (2016) 142-147
DOI: 10.15294/jpfi.v12i2.4621

http://journal.unnes.ac.id/nju/index.php/jpfi

THIN FILM-BASED SENSOR FOR MOTOR VEHICLE EXHAUST GAS, NH_3, AND CO DETECTION

Sujarwata*, P. Marwoto, L. Handayani

Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Indonesia

Received: 21 April 2016. Accepted: 12 June 2016 . Published: July 2016

ABSTRACT

A *copper phthalocyanine* (CuPc) thin film based gas sensor with FET structure and channel length 100 µm has been prepared by VE method and lithography technique to detect NH_3, motor cycle exhaust gases and CO. CuPc material layer was deposited on SiO_2 by the vacuum evaporator (VE) method at room temperature and pressure of 8 $x10^{-4}$ Pa. The stages of manufacturing gas sensor were Si/SiO_2 substrate blenching with ethanol in an ultrasonic cleaner, source, and drain electrodes deposition on the substrate by using a vacuum evaporator, thin film deposition between the source/drain and gate deposition. The sensor response times to NH_3, motorcycle exhaust gases and CO were 75 s, 135 s, and 150, respectively. The recovery times were 90 s, 150 s and 225, respectively. It is concluded that the CuPc thin film-based gas sensor with FET structure is the best sensor to detect the NH_3 gas.

ABSTRAK

Sensor gas berbasis film tipis *copper phthalocyanine* (CuPc) berstruktur FET dengan panjang *channel* 100 µm telah dibuatdengan metode *VE* dan teknik *lithography* untuk mendeteksi NH_3 gas buang kendaraan bermotor dan CO. Lapisan bahan CuPc dideposisikan pada permukaan silikon dioksida (SiO_2) dengan metode vacuum evaporator (VE) pada temperatur ruang dengan tekanan 8 $x10^{-4}$ Pa. Tahapan pembuatan sensor gas adalah pencucian substrat Si/SiO_2 dengan *etanol* dalam *ultrasonic cleaner*, deposisi elektroda *source* dan *drain* di atas substrat dengan metode *vacuum evaporator,* deposisi film tipis diantara *source/drain* dan deposisi *gate.* Waktu tanggap sensor terhadap NH_3, gas buang kendaraan bermotor dan CO berturut-turut adalah 75 s, 135 s,dan 150 s. Waktu pemulihan berturut-turut adalah 90 s, 150 s,dan 225 s. Disimpulkan bahwa sensor gas berstruktur FET berbasis film tipis CuPc merupakan sensor paling baik untuk mendeteksi adanya gas NH_3.

Keywords: OFET; thin film; response time; recovery time; lithography

INTRODUCTION

Technology development does not only bring progress for human life, but also to a negative impact on the environment. This is apparent in the decrease in air quality posed by pollution of motor vehicle exhaust gas emissions, such as the presence of carbon monoxide gas (CO) and carbon dioxide (CO_2). Besides, the waste generated by the industry also causes air pollution. The presence of various types of gas at a certain level causes more worry for the survival of living things. Related to this phenomenon, there is a need of an effort through research to produce technologies that can be used for early detection of toxic gases.

CO gas which reacts with the blood hemoglobin would forms a compound of carboxy haemoglobin (HbCO) which can not carry O_2 in the blood circulation. CO gas binding ability of hemoglobin is 210 times stronger than those between O_2 and Hb resulting in loose of O_2.

Someone who has been poisoned by CO will experience symptoms of health problems, among others: the headache, mental dullness, dizzy, nausea, vomiting, loss of control of the muscles, followed by a decrease in pulse and breathing frequency, fainting, and may even die. Cases of fainting or even death will happen

***Correspondence Address:**
Kampus Sekaran, Gunungpati, Semarang 50229
E-mail: sjarwot@yahoo.co.id

if the Hb-CO levels in the blood reach 60% of total hemoglobin.

NH_3 gas that smells and pungent is harmful to human health. Short term effects cause irritation of respiratory tract, nose, throat and eyes. Contact with the eyes generates irritation until total blindness, whereas contact with the skin causes burns (frostbite). Long-term effects of continuous NH_3 gas inhalation with high concentrations cause damage of the lungs and of death (Christopel, 2009).

In connection with the danger posed by NH_3, there is a need of a tool that can be used to detect the presence of the NH_3 gas (Muliadi, 2006).Gas detection devices that have sensitivity to gas is a gas sensor made of a semiconductor material (Min, 2003).

Phthalocyanine semiconductor materials and alloys have commercial potential aspects and offer a superior application compared to silicon. Phthalocyanine shows high sensitivity to electron acceptor gas and thin film surface absorption followed by charge transfer reaction (Zhou et al, 1996). This reaction affects the charge carrier and an increase in conductivity. Research conducted by Mirwa, Friedrich & Hofman (1995) indicated that phthalocyanine is a complex metal suitable to be used as a gas sensor instrument and to detect NO_2 gas.

Recent studies show that organic substances of phthalocyanine material in the form of a thin film are used as the active layer of the gas sensor. The electronic properties of thin films of phthalocyanine metal (MPc) are influenced by foreign gas (Toshihiro et al, 2003). MPc is an organic semiconductor material that has a high sensitivity toward NO_2 gas. The most widely used method of MPc thin film deposition is the high vacuum evaporation (Maggioni et al, 2005).The sensitivity of the CuPc thin film is very high when detecting NO_2 gas, but its response time is slow. Time to reach 90% saturation value with a concentration of 500 ppm at room temperature is 6 minutes (Chakane, Datir & Ghole, 2012).

Sensitivity of gas sensor with NO_2 doping and cooling temperature of 770 K in liquid nitrogen, has been studied for room temperature operation (Roto, Triyana & Sudirman, 2000). Pretreatment with NO_2 showed an increase of sensor sensitivity with two changes of magnitude conductivity and increase of recovery time.

The weakness of this study is the difficulty to control the NO_2 doping, causing damage to the edge of the thin film surface and change of the dynamic conductivity. The CuPc thin film gas sensor has high sensitivity at a substrate temperature of 170 ^{0}C and 475 ^{0}C with a thin film thickness of 50 nm. This condition was found when detection carried out with gas concentration of 0.18 ppm Cl (Toshihiro et al, 2003).

Detection of toxic chemicals in the environment are more effective when using simple techniques and tools that are easy to be used. The tool has the ability to monitor the environment, such as work environment, factories and homes, so that it can report pollution level. One form of such a tool is a gas sensor (Brunet et al, 2001). There are many amonia gas sensors, one of which uses an organic semiconductor material of CuPc.

Today's research on thin film became one of the areas that are very interesting and useful for human life. Thin films are used as optical devices, opto-electronics, ferromagnetic materials, superconductors and micro-acoustics materials. Various attempts have been made to expand the use of a thin film as a gas sensor application. With the increase of technology development, material needs are also increasing. Gas sensors can also be applied to test the oxygen levels issued by the hydrocarbon-fueled engine (Moseley, 1992).

In addition the gas sensor is also used by the industry to detect harmful gases resulted from the production process. Gas sensors can also be integrated into the electronic nose (e-nose) for the detection of a variety of scent as did by Abe et al. (1987).The study mainly aimed to find new semiconductor materials that can be used as thin film-based gas sensors (Brunet et al, 2005).

At this time the development of thin film as a more practical sensor has been carried out, one of which is a thin film semiconductors which can work at room temperature and detect a variety of toxic gas.

The thin film will be used as a sensor of motor vehicle exhaust gas: NH_3 and CO which are highly reactive and harmful to living things if those are undetected. The problem is how electrical properties of thin films of organic semiconductors resulted from evaporation. Can the thin film be used optimally in its function as a gas sensor element to be operating at room temperature (Lee, Sheu, Hsiao, 2004).

The main reason to use CuPc because some results of previous studies showed that CuPc is very sensitive (1 ppb - 200 ppm) to the gas. On the other hand, CuPc is a semiconduc-

tor having high conductivity and can be used as an active ingredient gas sensor (Zhou, et al., 1996).

In this research, the thin film has been deposited on CuPc semiconductor. Deposition was done by vacuum evaporation method (Maggioni et al., 2005). Manufacture of FET structured gas sensors was performed by using gold as a toxic gas sensor (Joseph and Menon, 2002). Gas sensor performance testing was conducted to detect toxic gas.

METHOD

This study used CuPc material (copper phthalocyanine) as the FET active layer. The active layer was deposited on SiO_2 with vacuum evaporation method (Model JEOL JEE-4X) at room temperature. The FET (Field Effect Transistor) fabrication used bottom contact structure with the drain (D) electrode distance to the source (S) was defined as L and the width of each drain and source was W

In this research, gas sensor was fabricated in bottom-contact structure and based on thin film. At the beginning of the process, Si/SiO_2 substrate was blenched with ethanol in an ultrasonic cleaner. After that, source (S) and drain (D) electrodes were deposited on the substrate by using a vacuum evaporator at room temperature and pressure of 8 $x10^{-4}$ Pa. It was, then, followed by thin film deposition between the source/drain, and finally, the gate was deposited.

The lithigraphy technique and vacuum evaporation (VE) method were used in the deposition at room temperature.The bottom contact structure of the gas sensor (FET) is shown in Figure 1.

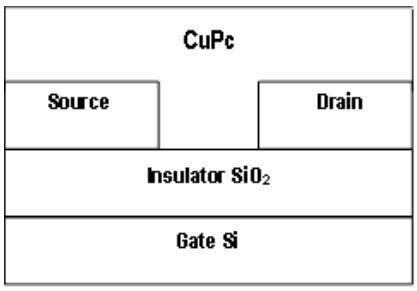

Figure 1. CuPc thin film based FET scheme

Distance between drain electrode (D) and source electrode (S) is defined as L (channel length) and the length of the drain/source is the channel width (W). The design of mask for the manufacture of gas sensor is shown Figure 2, with a length *L* of 100 µm, the channel width of 1 mm, the electrode length of 1 mm and the contact length of 1 mm.

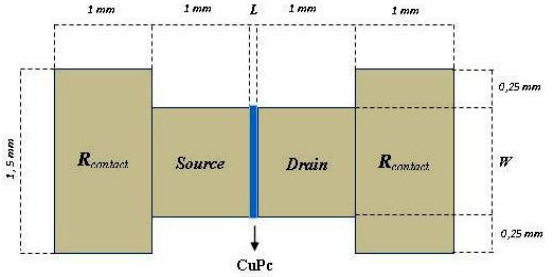

Figure 2. Gas sensor mask.

Lithography process in the manufacture of gas sensor is an important part, where the device geometry was determined at the wafer surface of SiO_2/Si. Device manufacture of the sensor consisted of repeatedly lithography processes, such as gate opening step for diffusion and oxidation.

Ways to characterize and measure the charge carrier mobility of the FET with bottom-contact structure were as follows: Electrodes of source was connected to a grounded, while the electrodes gate and drain respectively were connected to the backward bias. To determine the characteristics of the FET chart, then the measurement of currents (I_D) derived from the source to the drain (I_D) was done by varying the drain voltage (V_D) for each value of gate voltage (V_G).

In order to determine mobility the data required were $I_{DS,}$ V_{DS}, V_T, Ci, V_{GS}, L and W. After the complete data gathered, they were then applied to the equation:

$$I_D = \frac{C_i W}{L} \mu \left[(V_G - V_T) - \frac{V_D}{2} \right] V_D$$

where *L* and W were length and width of the channel.

Ci = was the capacitance per unit insulator area.

μ = charge carrier mobility

V_T = threshold voltage

Characterization of thin film based gas sensor was done in such a way as follows: gate voltageswere made in varied items, namely: -3 V; -1.5 V; 0 V; 1.5 V and 3 V, while that apply to source voltage ('s) and drain (D) was 3 V.

The feasibility testing of the gas sensor was determinedon response and recovery time. The ways of testing were as follows: gas

sensors and FET structure were placed in a glass chamber and closed with the metal and protected with varnish to avoid gas leakage. Test gas at a certain flow rate of glass was flowed into the chamber. It was then continued by measuring the I_{DS} and V_{DS} with a certain time interval.

RESULTS AND DISCUSSION

Results of fabrication FET (Field Effect Transistor) for gas sensor applications at room temperature are shown in Figure 3. The FET structured and thin film-based gas sensors on were placed on the PCB using a gold wire and silver paste for ease of experiment.

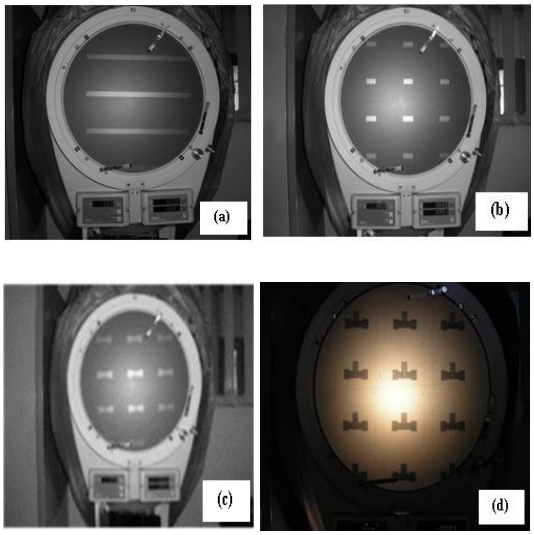

Figure 3. Gas sensor fabrication processes: (a) Au deposition on SiO_2 substrate, (b) source/drain electrode, (c) patterned source and drain electrode, (d) patterned source, drain and gate electrode.

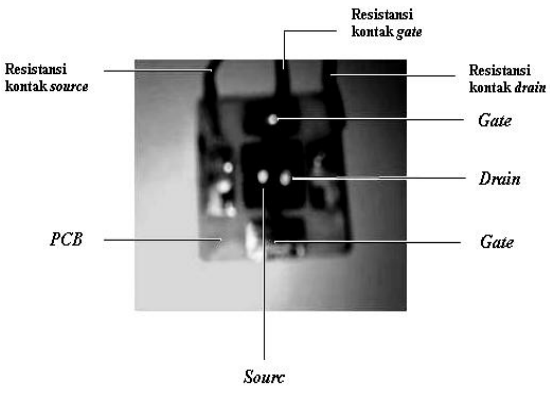

Figure 4. FET fabrication result on PCB

Figure 4 shows results of gas sensor fabrication with channel length of 100 µm for motor vehicle exhaust gases, NH_3 and CO detection. FET components were composed of two contact resistance (source/drain) and coated with gas-sensitive semiconductor. Gate was printed on Si/SiO_2 at the bottom (bottom gate). Gas sensors did not require heating for motor vehicle exhaust gases, NH_3 and CO detection, because it operated at room temperature.

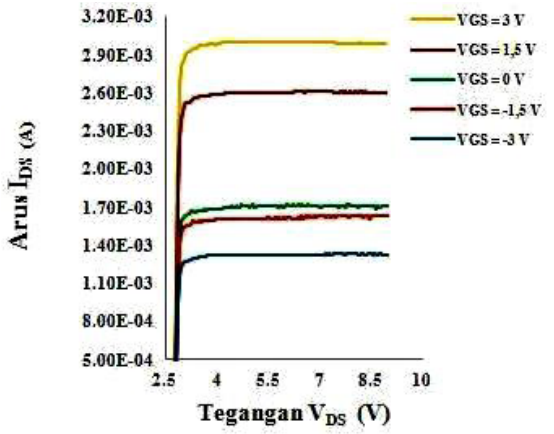

Figure 5. FET Characteristics.

The FET characteristics shown in Figure 5 represent the active voltage *drain* (V_D) is 2.79 V - 3.43 V and drain current (I_D) is 0.00095 A - 0.00109 A. FET has a voltage *drain* V_D in the saturation region is 3.43 - 9 V and this area is called as *cut off.* FET operates optimally in the voltage of 2.80 - 3.42 V. The increase of voltage V_{DS} causes the increase of I_D current up to the transistor saturated point.

The increase in the value of V_D will cause the increase in current I_D up to the saturation point of the transistor. If V_D depletion region is increasing, there will be a cut-off voltage conditions (V_P). The V_{DS} voltage that causes the cut off is called cut-off failure, despite an increase in the value of V_D. The FET drain current (I_D) at that time is a maximum drain current (I_D), which is achieved when $V_G = 0$ V and $V_D > |V_P|$. At the cut off area I_D has a fixed value, so FET can not respond to gas. The FET detects gas in the active area, in which the I_D current change will alter V_D.

Gas sensor (Field Effect Transistor) will exhibit certain properties when it is subjected to gas or when the gas sensor is kept out of gas. Sensor resistance will decrease rapidly when the sensor is subjected to the gas and when it is kept out from the gas, the resistance will back to its original value. An event of a decrease in resistance of gas sensor subjected to gas is called a response time and an event

when the resistance is back to the original value is called a recovery time.

Response time is required by the sensor to recognize a detected gas, while the recovery time is the time taken by the sensor to return to the normal position. The response time is the time to reach 80% of the maximum current and the recovery time is the time to release 80% of the maximum current (Liu, Hsieh & Ju, 1996). The feasibility testing of the gas sensor was determinedon response time and recovery time.

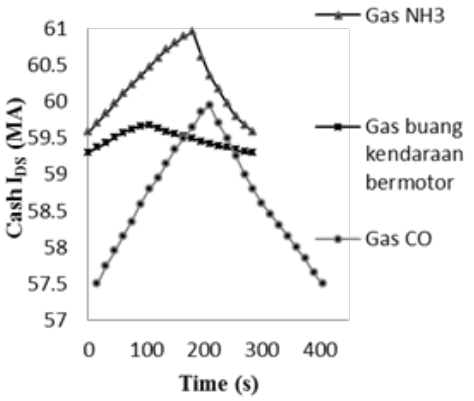

Figure 6. Graph of time Vs current I_{DS} for NH_3, motor vehicle exhaust emissions and CO

The response graph (Figure 6) of thin films-based gas sensors with of NH_3, motor vehicle exhaust gas and CO test gases indicates that the response times are 75 s, 135 s, and 150 s, respectively. Meanwhile there covery time the same gases are 90 s, 150 s, and 225 s, respectively.

The data in Table 1 shows that the type of test gas affects the FET gas sensor response. The best response of gas sensor is in detecting a test gas of ammonia (NH_3), whereas the FET gas sensor to detect CO test gas has the lowest response times, due to the slow decreasing of gas sensor resistance when subjected to gas. Therefore, the FET gas sensor is best to be applied to detect the presence of ammonia gas.

Table 1. Response time and recovery time of gas sensor

Kind of gas	Response time (s)	Recovery time (s)
NH_3	75	90
motor vehicle exhaust	135	150
CO	150	225

The relation between conductivity and the sorts of test gas was observed by studying the change in resistance of thin film. The conductivity of the material is determined by the charge carrier mobility, while the charge carrier mobility is determined by the distance between electrodes of thin layers used.

Different kinds of gases cause the tendency of increase length of depletion layer and potential barrier. Kinds of gas can hamper FET charge carrier mobility and reduce the gas sensor response. The increase ofthe FET charge carrier mobility causes an increase of the response time of the sensor.

CONCLUSIONS

CuPc based thin film FET has been made by implementing a vacuum evaporation method at room temperature and pressure of 8×10^{-4} Pa having an active region of 2.80 V - 3.42 V. The charge carrier mobility FET of liner and saturation regions are 0.10121664 $cm^2\ V^{-1}\ s^{-1}$ and 0.05468465 $cm^2\ V^{-1}\ s^{-1}$, respectively.

The FET size is 6.15 mm^2 and the distance between source and drain is 100 μm. The FET response times to test of NH_3, motor vehicle exhaust gas and CO are 75 s, 135 s and 150 s, respectively. Where as the recovery times are 90 s, 150 s, and 225 s, respectively. The CuPc thin film based gas sensor is best to detect NH_3 gas.

ACKNOWLEDGMENTS

Doctoral Dissertation Research Program Dikti Depdiknas on the research fund granted in 2015.

REFERENCES

Abe, H., Yoshimura, T., Kanaya, S., Takahashi, Y., Miyashita, Y., & Sasaki, S. (1987). Automated Odor-sensing System Based on Plural Semiconductor Gas Sensors and Computerized Pattern Recognition Techniques*, Anal. Chim. Acta.;* 194, 1-9.

Brunet, J., Talazac, L., Battut,V., Pauly, A Blanc, J.P., Germain, J.P., Pellier, S., & Soulier, C. (2001). Evaluation of atmospheric pollution by two semiconductor gas sensors*, Thin Solid Films* 391(2), 308-313.

Brunet, J., Paulya, A., Mazet, L., Germain, J.P., Bouvet, M., & Malezieux, B. (2005). Improvement in real time detection and selectivity of phthalocyanine gas sensors dedicated to oxidizing pollutants evaluation, *Thin Solid Films* 490(1), 28-35.

Chakane, S.D., Datir, A.M., Ghole, V.S., (2012). Nitrogen Dioxide Sensing Characteristics of Spin Coated Unsubstituted Copper Phthalocyanine Films, IMCS 2012-The 14th International Meeting on Chemical Sensors.

Christopel, D. P. (2009), Pembuatandankarakterisasi sensor gas ammonia berbasis polianilin. *Skripsi*. Bogor: FMIPA, Institut Pertanian Bogor.

Joseph, C. M. & Menon, C. S. (2002). Device preparation and characteristics of CuPc transistor. *Materials Letters,* 52(3), 220-222.

Lee, Y.L., Sheu, C.Y., & Hsiao, R. H. (2004). Gas sensing characteristics of copper phthalocyanine films: effects of film thickness and sensing temperature. *Sensors and Actuators B,* 99(2), 281–287.

Liu, C. J., Hsieh, J. C., & Ju, Y. H. (1996). Response characteristics of lead phthalocyanine gas sensor: effect of operating temperature and postdeposition annealing. *Journal of Vacuum Science & Technology A*, 14(3), 753-756.

Maggioni, G., Quaranta, A., Carturan, S., Patelli, A., Tonezzer, M., Ceccato, R., & Della Mea, G. (2005). Deposition of copper phthalocyanine films by glow-discharge-induced sublimation. *Chemistry of materials*, 17(7), 1895-1904.

Mirwa, A., Friedrich, M, & Hofman, A. (1995). Sensors and Actuator B24 -25,596

Min, Y. (2003). *Properties and Sensor Performance of Zinc Oxide Thin Film*, Massachusetts Institute of Technology.

Moseley, P. T. (1992). Materials selection for semiconductor gas sensors. *Sensors and Actuators B: Chemica*l, 6(1-3), 149-156.

Muliadi, L., O. (2006). Pembuatan sensor fiber optik dengan cladding polianilin untuk mengukur gas amonia. *Skripsi*. Bogor: Fakultas Matematika dan Ilmu Pengetahuan Alam, Institut Pertanian Bogor.

Roto, Triyana, K. & R. Sudirman. (2000) Pengaruh konsentrasi pembawa muatan pada laju tanggap polianilin sebagai dasar sensor gas, Laporan penelitian Fundamental Nomor: 16/P2IPD/DPPM/VI/1999.

Toshihro, M., Kawaguchi, S., Ishii, M., & Minami, T. (2003). High sensitivity chlorine gas sensors using Cu–phthalocyanine thin films. *Thin Solid Films*, 425(1), 255-259.

Zhou, R., Josse, F., Göpel, W., Öztürk, Z. Z., & Bekaroğlu, Ö. (1996). Phthalocyanines as sensitive materials for chemical sensors. *Applied Organometallic Chemistry*, 10(8), 557-577.