High selectivity Fe$_3$O$_4$ nanoparticle to volatile organic compound (VOC) for MEMS gas sensors

Yu-Jen Hsiao\textsuperscript{1}, Yempati Nagarjuna, Chun-An Tsai and Sheng-Chang Wang\textsuperscript{1}
Department of Mechanical Engineering, Southern Taiwan University of Science and Technology, Tainan 710, Taiwan
\textsuperscript{1} Authors to whom any correspondence should be addressed.
E-mail: yujen@stust.edu.tw and scwang@stust.edu.tw

Keywords: gas sensor, nanoparticle, metal oxide semiconductors

Abstract

In the current study, XRD analysis shows the polycrystalline form an inverse spinel Fe$_3$O$_4$ structure. Fe$_3$O$_4$ film is prepared by dip coating method on MEMS gas sensors to test the sensitivity on volatile organic compound (VOC) gas. VOC is being tested at 92 mW ($\sim$300 °C) power consumption with different VOC gas concentrations and also tested with different gases like NO$_2$, SO$_2$, NH$_3$ and CO gas. The results showed that the Fe$_3$O$_4$ gas sensor has better selectivity and high response with VOC 1.2 ppm concentration. Structural morphology is seen and reaction mechanism when VOC gas reacts with Fe$_3$O$_4$ material is also being discussed.

Introduction

There is an industrial impact all over the world which concerns about the quality of air in our environment. Air quality monitoring includes indoor, outdoor and local air monitoring. It all depends on the types of pollutants. Greenhouse gases are the primary concern for polluting the air but volatile organic compounds (VOC) gases like alkanes, alkenes, ketones and aldehydes causes health defects in living beings. VOC gases like methane, benzene and toluene causes breathing problems anemia and narcosis in nervous system [1, 2]. Emission of VOC gases occurs mostly by production industries, combustion, transport, agriculture, solvents and landfill [3]. So, there is a high demand for VOC gas detection in homeland security, medical and space exploration applications [4]. Volatile compounds are also used as solvents in paints, adhesives and cleaning liquids which are used in daily life and they easily evaporate causing respiratory problems [5]. In case of food market, quality and odor of the food have became primary issue due to off-odors and pungent smells. Gas sensor arrays have been suggested to detect the VOC gases that release from the plants and crops. This helps in packaging foods and off-odors detection [6].

For gas sensing applications, Metal oxide semiconductors (MOS) are most widely studied and used materials [7]. The sensing mechanism works based on the change in resistance when the gas reacts with the material. In case of VOC gas detection, there has been many research studies and used different kinds of metal oxide semiconductors like ZnO [8–10], SnO$_2$ [11], Co$_3$O$_4$ [12], Graphene composites [13] and Fe$_3$O$_4$ [14, 15]. In the current study, Fe$_3$O$_4$ is considered for the detection of VOC gas. Fe$_3$O$_4$ has one of the most unique magnetic properties such as the solubility and simplicity in synthesis in acidic media when compared to other metal oxide nano materials like SnO$_2$, TiO$_2$. So, Fe$_3$O$_4$ is one of the most researched material for gas sensing [16]. Fe$_3$O$_4$ material is also used for detecting different gases like ethanol at room temperature. Some of the other applications of Fe$_3$O$_4$ material are magnetic storage devices, biomedical filed and separation processes.

In the current study, Fe$_3$O$_4$ has been prepared in various thickness by using dip coating method and different concentrations of VOC gas is being tested. The performance of Fe$_3$O$_4$ gas sensor is being evaluated by monitoring the sensitivity of VOC gas and comparing with some other gas sensitivity like NH$_3$, SO$_3$, NO$_2$ and CO gases.
Experimental procedure

Figure 1 shows a schematic diagram of the general gas sensor MEMS structure. The structure includes a suspension, a dielectric layer, a micro heater and a sensing material. This study uses bilayer materials for the micro heater, the interdigital transducer (IDT) electrode (Ti and Au) and the sensing film (Fe3O4). Iron oxide (Fe3O4) purchased from LIWEI Nano Tech Co., Ltd at Taiwan with a particle size of about 20 nm (±15%).

A p-type 400 μm thick Si wafer was used as the substrate. A 0.6 μm thick SiO2 and 0.3 μm thick SiNx isolation layer was formed using plasma-enhanced chemical vapor deposition (PECVD). A 400 nm thick Ti layer and a 50 nm thick Au layer were then deposited on the defined pattern. The Ti and Pt layers were deposited using electron gun evaporation. A positive-type photoresist (PR) was spin-coated onto the isolation layer and then standard photolithography was used to define the bottom sensing layer area (400 μm x 400 μm). The SiO2 isolation layer was wet-etched. Finally, the structures on the reverse side were formed using SF6 plasma etching. A resistive heater operates on the metal wire thermal principle.

Different thickness of Fe3O4 sensing layer were deposited by dip coating, as shown in figure 1(b). The respective temperature of the sensing film is approximately 150 °C, 200 °C, 250 °C, 300 °C, and 350 °C when the power across the micro-heater is approximately 42 mW, 57 mW, 73 mW, 92 mW and 114 mW in figure 1(e). The power increases linearly as the temperature increases. We used the certified reference material of EPA 8260 Volatiles Calibration Mix. From Sigma-Aldrich Co. LLC. It has several numbers of VOC available, such as Methanol, Benzene, Chloromethane etc.

Experimental results and discussion

The XRD pattern shows the polycrystalline form of an inverse spinel Fe3O4 structure (JCPDS No. 65-3107) in figure 2. No diffraction peaks for notable impurities (e.g., hematite) are found. From the values of 2θ and β of the (311) peak, the grain size (D) can be estimated by Scherrer’s formula $D = \frac{0.89 \lambda}{\beta \cos \theta}$ [17], where λ is the x-ray wavelength equal to 0.1542 nm, θ is the (311) peak angle, and β is half the peak width. The average grain size of nanoparticle was about 21.5 nm.

SEM image of Fe3O4 surface structure is shown in figure 3. As the SEM image showed different sizes of Fe3O4 nanoparticles and that led to assume the size of nanoparticles can be in the rage of microns to nano. Different size particles are combined together to form a bulky structures after baking at 70 °C. The temperature is set to medium high which is 70 °C, where it helps to remove the moisture content. Since the process dispensing coating is used, there are many pores on the surface area which helps the adsorption process when the gas is
tested for sensing properties. In the figure, particles size ranges from few microns to hundreds of nanometers because of the calcination process, clusters will start to form between the particles which results in different particle sizes. Some researchers have suggested that particle agglomeration happens because the particle has relatively large surface area which corresponds to high surface area energy which results in mutual influence between surface areas.

The gas sensor is baked at 70 °C and placed inside a glass chamber for detecting the gas sensing characteristics. The temperature should be set to the working temperature and the resistance will be stabilized after some time and then the VOC gas is sent into the chamber for gas sensing. Every gas sensor has different working temperature and it is advised that the temperature is being set to required value to get better sensing results. Figure 4 shows three samples of the response graph of Fe₃O₄ nanomaterial working at different operating temperatures are considered and VOC gas concentration is taken to be 2.4 ppm. The sensing characteristics of gas sensor with different power consumption is discussed.

The response can be expressed for a particular VOC gas, is calculated using the relation,

$$ S(\%) = \frac{R_g - R_a}{R_a} \times 100 $$

where $R_g$ is the resistance of Fe₃O₄ film in presence of VOC gas, $R_a$ is the resistance in presence of the atmosphere. Until 92 mW (~300 °C), higher the power consumption, gas sensitivity is higher, but the sensitivity drops tremendously after 90 mW. Therefore, the operating temperature should be the peak value at 90 mW where the gas sensitivity is about 60%. The reason for sensitivity fall might be due to the resistance value
fluctuations of semiconductor sensor which is caused by the oxidation reaction between the surface oxygen atoms adsorption and VOC gas. At very high temperatures, the kinetic energy of the gas reduces the adsorption capacity of semiconductor sensor which causes the reduction in gas sensing capability. The oxygen atoms in Fe$_3$O$_4$ are of two kinds which are adsorbed oxygen and lattice oxygen. When VOC gas reacts with Fe$_3$O$_4$ material, CO$_2$ is produced where the oxygen atoms are adsorbed continuously, and lattice oxygen atoms are released continuously. For this phenomenon to happen, the working temperatures should be very high. According to the experimental result, the temperature is found to be 300 °C which is not high value. So, this phenomenon does not happen in this procedure since the working temperature is not high.

Different gas concentration curves of gas sensor at same temperature are discussed in figure 5. The working temperature of VOC gas sensor is set to be 300 °C and the gas concentrations tested are 0.6 ppm, 1.2 ppm, 1.8 ppm, 2.4 ppm. In figure 5, Resistance change in the VOC gas sensor is detected for various gas concentrations. The resistance changes significantly with increase in the gas concentrations. In this study, various VOC gas concentrations are introduced into the chamber from 0.6 ppm to 2.4 ppm and the recorded responses suggest that higher the gas concentration, higher the gas response to the sensor. When the gas is removed, the sensor showed good recovery response and resistance is back to the original position which shows the stability of the gas sensor. The response of an oxide semiconductor is commonly expressed as $R = A[C]^n + B$, where A and B are constants, $n$ is an exponent, and [C] is the target gas concentration. Data fitting provided the following equations for Fe$_3$O$_4$ film: $R = 21.1[C] + 6.6$. We found that when the VOC gas concentration exceeds 5 ppm, the response...
reaches a state of near saturation. At a temperature of 300 °C, for as-fabricated Fe3O4 MEMS gas sensor towards 0.6 ppm VOC gas, the response and recovery times were 6.1 s and 10.7 s, respectively.

After each testing, the readings came back to the original position which shows stable repeatability. Gas sensing analysis is done under different Fe3O4 thickness and the results show that with increase in thickness, the sensing response of the gas sensor decreases. Too much deposition of Fe3O4 layer ceases the temperature flow which makes the VOC gas difficult to capture. Different gases with different gas concentrations have been tested with Fe3O4 gas sensor and recorded the gas sensitivity response. The relation between Fe3O4 gas sensor with different gases of different concentration are shown in figure 6. The maximum response is recorded is 30% for VOC gas at 1.2 ppm concentration. The other gases like CO, SO2, NO2, NH3 are also tested with Fe3O4 sensor at a similar concentration of 1.2 ppm and all the four gases has less than 2% gas response. The increasing order of gas sensitivity response is VOC > NH3 > CO > SO2 > NO2.

The reaction mechanism characteristics for Fe3O4 gas sensor is being shown in figure 7. In the n-type semiconductor metal oxides, the surface of the film is accumulated with the oxygen molecules when the film is exposed to air. The adsorbed oxygen molecules extracts the free electrons in the conduction band and forms oxygen ion species like O2−, O− and O2−. So, electrons from the conduction band are consumed by the oxygen ions and forms a depletion layer over the surface of Fe3O4. This tends to decrease the concentration of charge carriers in the sensing layers and this results in the increased resistance and decrease in conductivity of sensor [14]. When the Fe3O4 gas sensor is exposed to VOC gas the reaction takes place on the surface of the material as shown in figure 7.
When the sensor is exposed to the VOC gas, the following reaction is expected to happen [18].

\[
\text{VOC} + \text{O}_x^- \rightarrow \text{VOCO} + \text{ne}^-
\]

(2)

The VOC gas molecules interact with the adsorbed oxygen species and release the trapped electrons which leads to decrease the depletion layer. And this reduction in the depletion layer of an n-type Fe₃O₄ causes the resistance to decrease in the presence of VOC gas [15]. However in the presence of air or humidity, the depletion layer is enlarged due to the oxygen ions accumulation and the resistance is increased [19].

Conclusion

In this study, the variables like power consumption and gas concentration are used to study the sensitivity and material properties. At 92 mW (∼300 °C) power consumption, the sensitivity increased linearly with increase in the VOC gas concentration. Gas sensitivity is tested with different gases. The gas of CO, SO₂, NO₂ and NH₃ are tested at a similar concentration of 1.2 ppm and all the four gases has less than 2% gas response. However, the maximum response is recorded is 30% for VOC gas at 1.2 ppm concentration for Fe₃O₄ MEMS gas sensor.

Acknowledgments

This work was financially supported by the Ministry of Science and Technology of Taiwan, with project numbers: MOST 107-2221-E-218-032-MY2 and MOST 107-2218-E-492-007. The authors would like to thank the Taiwan Semiconductor Research Institute (TSRI) and Ms. Hui-Jung Shih with the Instrument Center of National Cheng Kung University for supporting the use of high-resolution SEM (Hitachi SU8000).

ORCID iDs

Yu-Jen Hsiao 🐘 https://orcid.org/0000-0003-0862-6473

References

[1] Vijaya J J, Kennedy L J, Sekaran G, Bayhan M and William M A 2008 Sens. Actuators B 134 604–12
[2] Greatorex J M 2000 1–30 JTI-Institute for jordbruks-och miljoteknik, Upasala.- ISSN-401-4963 http://www.diva-portal.org/smash/get/diva2:959591/FULLTEXT01.pdf
[3] Srivastava A K 2003 Sens. Actuators B 96 24–37
[4] Li B et al 2006 Nano. Lett. 6 1588–602
[5] Kim M O, Khan M Q, Ullah A, Duy N P, Zhu C, Lee J S and Kim I S 2019 Mater. Res. Express 6 105372
[6] Park H, Lee E, Chung Y, Lee S, Ahn H and Kim D J 2015 ECS. Trans. 69 41–5
[7] Huang J and Wan Q 2009 Sensors 9 9903–24
[8] Zhu B L, Xie C S, Wang W Y, Huang K J and Hu J H 2004 Mater. Lett. 58 624–9
[9] Mascini M, Gaggiotti S, Pelle F D, Natale C D, Qakala S, Iwuoha E, Pittia P and Compagnone D 2018 Front. Chem. 6 105
[10] Al-Hardan N H, Abdullah M J, Aziz A A, Ahmad H and Low L Y 2016 Vaccum. 85 101–6
[11] Park H, Chung Y, Lee S, Lee E, Ahn H, Kim S H and Kim D J 2017 J. Electrochem. Soc. 164 B690–4
[12] Nguyen H and El-Safty S A 2013 Journal of Physical Chemistry. 115 8466–74
[13] Rattanabut C, Wongwiwiyapan W, Muangrat W, Bunjongpru W, Phonyiem M and Song Y J 2018 Jpn. J. Appl. Phys. 57 04FP10
[14] Zhai Q, Du B, Feng R, Xu W and Wei Q 2014 Anal. Methods 6 886
[15] Zhang J et al 2017 Sens. Actuators B 252 367–74
[16] Ma P, Luo Q, Chen J, Gan Y, Du J, Ding S, Xi Z and Yang X 2012 Int. J. Nanomedicine. 7 4809–18
[17] Pugazhendhi K, D’Almeida S, Kumar P N, Mary J S S, Tenkyong T, Shyla J M and Sharmila D J 2018 Mater. Res. Express 5 045053
[18] Zhang L, Wang G, Yu F, Zhang Y, Ye B C and Li Y 2017 Sens. Actuators B 258 589–96
[19] Khorsand A Z, Shirmahd H, Mohammadi S and Banhashemian S M 2020 Mater. Res. Express 7 025001