

Semiconductor Metal Oxide Nanoparticles: A Review for the Potential of H₂S Gas Sensor Application

Zaid Hameed Mahmoud, Omar Dhaa Abdalstar and Noor Sabah

Department of Chemistry, College of Sciences, Diyala University, Iraq

Abstract

In modern world, gas sensors play important role in many fields of technology used for air pollution, breath analysis, public safety and many others. Gas sensor based semiconductor metal oxide is mostly used in these applications because of low cost, ease-to-use, high sensitivity and lower power consumption. This paper gives an overview about the semiconductor metal oxide and reviews why using it as sensing of gases in electrical applications and then it addresses to the work mechanism of a sensor to sensing H_2S gas.

Abbreviations

- MOS Metal Oxide Semiconductor
- NPs Nanoparticles
- MO Metal oxide
- ZnO Zinc oxide
- H₂S Hydrogen sulphide

1. Introduction

The applications based on gas sensor technology play an important role in our life, such as the detection of toxic gas, the quality of air and control of environmental [1-8]. Received: July 17, 2020; Accepted: August 3, 2020

Keywords and phrases: gas sensor, MOS, nanoparticles, H₂S.

Copyright © 2020 Zaid Hameed Mahmoud et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Many types of sensors have been used to detection of gas but the type that based on resistivity is most used because the low cost prepared and ease operation [9-16]. The first commercial oxide-based gas sensor was used in 1963 by Taguchi to detection H₂S gas using ZnO. After that, many efforts were made to improve of properties such as the selectivity, stability and sensitivity. Semiconducting (MO) - based gas sensor has attracted the researchers comparing with the conventional techniques because it advantages such as low cost and sensitivity and fast responsible and detection. Because of the electronic unique properties of semiconductor metal oxide nanoparticles, it used in various applications such as gas sensor, lithium battery and solar cell. Many semiconductor metal oxides were used as gas sensor because have electric properties such as In₂O₃, TiO₂ and SnO₂. In spite of advantages, there are many disadvantages that (MOS) appear like higher energy consumption. The appearance of nanotechnology allowed great progress that has been made in the field of sensing because of the unique properties that nanomaterial has such as high surface area to volume, surface active site and very high surface reactivity [17, 18]. This review aimed to study the mechanisms of gas sensing using semiconductor metal oxide (MOS) and appear the effect of temperature and role of particle size in efficiency of sensing.

2. System of Gas Sensor and Mechanism

The gas sensor contains sensing film which changes the resistance upon exposure of gas, two conducting electrodes that measure the resistance and heater to control and to get optimum working temperature as shown in Figure 1. The electric conductivity of sensor changes upon explore to gas while the receptor and transducer functions depend on the interaction between the gas and solid gas sensor and the structure of metal oxide respectively. The mechanism of gas sensing realized by changing the resistance as results from interaction the target gas with sensor, number of surface active sites and adsorption the species of O_2 that increase the active sites of the surface [19]. Many factors play important role on the affectivity of surface conductivity specially the surface stoichiometry due to the vacancies of O_2 increased the conductivity while the adsorbed ions less or decreased it. At MO vacancies, O_2 or NO₂ adsorbed and this causes the flow out of the electrons of conduction band and decrease the surface conductivity while H₂ or CO in atmosphere react with adsorbed O_2 and release electron and increasing the conductance.



Figure 1. Conductometric gas sensing device [19].

3. Detection of H₂S Gas by MO

The mechanism in conductometric for sensing gas is based on the resistance as a result of interaction between target gas and sensor. In air, large electronegativity is found back to oxygen that adsorbed on the surface of semiconductor gas sensor and abstract electron from conduction band of metal oxide and formed on the surface oxygen ions O_2^- , O^- . This trapping of electron causes increasing the resistance in n-type of gas sensor and decreasing in p-type [20]. The abstraction of electrons from the outer surface of metal oxide results accumulation layer in p-type and electron-depleted layer in the n-type [21]. The electron concentration in depleting layer low and this causes decreasing the resistance in layer compared with core layer in n-type MO while, the resistance is lower in accumulation layer in p-type comparing with core layer due to the holes are in the majority in this type. When exposed the sensor of MO with target gas, the gas reacts with oxygen ions absorbed on the surface and causes to release of electrons and back to MO and the processes can be expressed by the equation:

 $H_2S + 3O^- \longrightarrow SO_2 + 3e$

The releasing of electrons to MO decreasing the width of depleting and accumulation layers and this causes increasing and decreasing of the resistance of p- and n-type, respectively. X-ray photoelectron microscopy (XPS) used as a characterizing tool to understand the mechanism of sensing H_2S on the sensor. Many researchers used this tool

to characterize or demonstrate the interaction between the target gas and the surface of sensor. Vishal reported a large shift in the position of peak for O 1s after exposing to H_2S gas and this indicates occurring interaction between oxygen site and target gas as well as, two bending energy appear at (160eV) and (165.3 eV) back to sulfide and sulfite respectively, characterize to conversion of Fe₂O₃ to Fe₂S₃ then decomposition of FeS and FeS₂.

4. The Effect of Temperature

The absorption reaction and change in the temperature of sensor continuously work on the changing of conductance. Thereby the optimum temperatures are directly related to release of electrons to conduction band and increasing the conductance [22]. To control the reaction rate, heating gas sensor used [23]. At low temperature, the response of sensor is controlled by the chemical reaction speed while the speed of molecules diffusion plays the main role at high temperature. These two processes become equal or equilibrium at optimum temperature. The heating in conductometric sensor is direct or indirect but the indirect heating is preferable to prevent or lack of interference with sensor layer. The system of MOS-based gas sensing works at high temperature with range 100-400C and this causes to reduce the stability, life time and sensitive of sensing because the growth of metal oxide grains [24-27]. Some sensors fabricate using semiconductor polymer work it at room temperature but it affects by humidity and also causes the poor sensitive [28]. The strategies were ongoing to improve the efficiency and selective of sensor by making composite sensor or functionalization the surface by heterogeneous oxide. In spite of all these efforts but remain the high temperature and humidity are the main problems. For this, the challenge in my field is to prepare sensor work at room temperature with humidity and high selective and response for sensing gas.

Materials	Structure	Gas	Conc.	Sensitivity	Response time
SnO ₂	Nanocrystalline tubes	NO ₂	9.7ppb	16.1	20s
SnO ₂	Nanowire	СО	20ppm	4	
CuO	Nanosheet	H_2S	200ppb	5.01	400s
NiO	nanowire	NH ₃	50ppm	0.19	36s
LaFeO ₃	nanocube	NO ₂	1ppm	0.29	24s
CuO/SnO ₂	nanorode	H_2S	30ppm	4.8	2.5s

Table 1. Shows the using many metal oxides with different size and forms working at room temperature.

5. Role of Particle Size

As a general base, decreasing the size of grain and particles causes increasing the surface area of oxide [29-42] for adsorbing the gas molecules and this leads to higher response of the sensor. As well as decreasing of grain exposes the surface to depletion of electrons during exposing the sensor for air. Additionally, as shown in Figure 2, the size of particles plays main role in the sensing capability of heterogeneous MO depending on the number of n-p junctions. With small particles the number are increased and this causes increase the total resistance compared with large particles and as a result increasing the capability of sensor.



Figure 2. Effect of injection number on sensing capability.

6. Conclusion

This paper summarized and demonstrated the importance of using semiconductor metal oxide nanoparticles as a gas sensor specially H_2S because of the intrinsic properties that back to high surface reaction activity and low cost for using at room temperature. The general mechanism of sensing depended on the number of O_2 vacancies and absorption ions on the surface of sensor. The XPS results for detection H_2S by using Fe_2O_3 as sensing showed new energy band during sensing assigned to Fe_2S_3 and FeS_2 and this causes the activity of metal oxide for sensor H_2S gas. The studies in review appear a great role for increasing or decreasing temperature in activity for sensing. Thereby the optimum temperatures are directly related to release electrons to conduction band and increasing the conductance.

Acknowledgment

I would like to extend my sincere thanks and gratitude to Dr. Zahraa Al-Karawi for her continuous follow-up during writing this review.

References

- K. Dieter, Function and applications of gas sensors, J. Phys. D Appl. Phys. 34(19) (2001), R125.
- [2] G. F. Fine, L. M. Cavanagh, A. Afonja and R. Binions, Metal oxide semi-conductor gas sensors in environmental monitoring, *Sensors* 10(6) (2010), 5469-5502. https://doi.org/10.3390/s100605469
- [3] J. Zhang, Z. Qin, D. Zeng and C. Xie, Metal-oxide semiconductor based gas sensors: screening, preparation, and integration, *Phys. Chem. Chem. Phys.* 19(9) (2017), 6313-6329. https://doi.org/10.1039/c6cp07799d
- [4] S. S. Varghese, S. Lonkar, K. K. Singh, S. Swaminathan and A. Abdala, Recent advances in graphene based gas sensors, *Sensors Actuators B Chem.* 218(Supplement C) (2015), 160-183. https://doi.org/10.1016/j.snb.2015.04.062
- [5] A. Gusain, N. J. Joshi, P. V. Varde and D. K. Aswal, Flexible NO gas sensor based on conducting polymer poly[N-9-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2,1,3benzothiadiazole)] (PCDTBT), *Sensors Actuators B Chem.* 239 (2017), 734-745. https://doi.org/10.1016/j.snb.2016.07.176

- [6] N. Joshi, V. Saxena, A. Singh, S. P. Koiry, A. K. Debnath, M. M. Chehimi and D. K. Aswal, SK Gupta Flexible H2S sensor based on gold modified polycarbazole films, *Sensors Actuators B Chem.* 200(Supplement C) (2014), 227-234. https://doi.org/10.1016/j.snb.2014.041
- [7] S. Yoriya, H. E. Prakasam, O. K. Varghese, K. Shankar, M. Paulose, G. K. Mor, T. J. Latempa and C. A. Grimes, Initial studies on the hydrogen gas sensing properties of highly-ordered high aspect ratio TiO₂ nanotube-arrays 20μm to 222μm in length, *Sens. Lett.* 4(3) (2006), 334-339. https://doi.org/10.1166/sl.2006.042
- [8] A. Singh, A. Kumar, A. Kumar, S. Samanta, N. Joshi, V. Balouria, A. K. Debnath, R. Prasad, Z. Salmi, M. M. Chehimi, D. K. Aswal and S. K. Gupta, Bending stress induced improved chemiresistive gas sensing characteristics of flexible cobalt-phthalocyanine thin films, *Appl. Phys. Lett.* 102(13) (2013), 132107. https://doi.org/10.1063/1.4800446
- [9] N. Ramgir, N. Datta, M. Kaur, S. Kailasaganapathi, A. K. Debnath, D. K. Aswal and S. K. Gupta, Metal oxide nanowires for chemiresistive gas sensors: Issues, challenges and prospects, *Colloids Surf. A Physicochem. Eng. Asp.* 439 (2013), 101-116. https://doi.org/10.1016/j.colsurfa.2013.02.029
- [10] M. Shaik, V. K. Rao, M. Gupta, K. S. R. C. Murthy and R. Jain Chemiresistive gas sensor for the sensitive detection of nitrogen dioxide based on nitrogen doped grapheme nanosheets, *RSC Adv.* 6(2) (2016), 1527-1534. https://doi.org/10.1039/c5ra21184k
- [11] K. A. Mirica, J. M. Azzarelli, J. G. Weis, J. M. Schnorr and T. M. Swager, Rapid prototyping of carbon-based chemiresistive gas sensors on paper, *Proc. Natl. Acad. Sci.* 110(35) (2013), E3265-E3270. https://doi.org/10.1073/pnas.1307251110
- [12] N. Joshi, L. F. da Silva, H. Jadhav, J.-C. M'Peko, B. B. Millan Torres, K. Aguir, V. R. Mastelaro and O. N. Oliveira, Jr., One-step approach for preparing ozone gas sensors based on hierarchical NiCo₂O₄ structures, *RSC Adv.* 6(95) (2016), 92655-92662. https://doi.org/10.1039/c6ra18384k
- [13] A. Kumar, N. Joshi, S. Samanta, A. Singh, A.K. Debnath, A.K. Chauhan, M. Roy, R. Prasad, K. Roy, M.M. Chehimi, D.K. Aswal, S.K. Gupta, Room temperature detection of H₂S by flexible gold–cobalt phthalocyanine heterojunction thin films, *Sensors Actuators B Chem.* 206(Supplement C) (2015), 653-662. https://doi.org/10.1016/j.snb.2014.09.074
- [14] V. Balouria, S. Samanta, A. Singh, A. K. Debnath, A. Mahajan, R. K. Bedi, D. K. Aswal and S. K. Gupta, Chemiresistive gas sensing properties of nanocrystalline Co₃O₄ thin films, *Sensors Actuators B Chem.* 176(Supplement C) (2013), 38-45. https://doi.org/10.1016/j.snb.2012.08.064

- [15] N. Joshi, F. M. Shimizu, I. T. Awan, J. C. M'Peko, V. R. Mastelaro, O. N. Oliveira and L. F. da Silva, Ozone sensing properties of nickel phthalocyanine: ZnO nanorod heterostructures, 2016 IEEE Sensors, Orlando, USA, 2016, pp. 1-3. https://doi.org/10.1109/ICSENS.2016.7808407
- [16] T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani A new detector for gaseous components using semiconductive thin films, *Anal. Chem.* 34(11) (1962), 1502-1503. https://doi.org/10.1021/ac60191a001
- [17] X. Liu, J. Zhang, S. Wu, D. Yang, P. Liu, H. Zhang, S. Wang, X. Yao, G. Zhu and H. Zhao, Single crystal α-Fe₂O₃ with exposed 104 facets for high performance gas sensor applications, *RSC Adv.* 2 (2012), 6178-6184.
- [18] X. Li, W. Wei, S. Wang, L. Kuai and B. Geng, Single-crystalline α-Fe₂O₃ oblique nanoparallelepipeds: High-yield synthesis, growth mechanism and structure enhanced gas-sensing properties, *Nanoscale* 3 (2011), 718-724. https://doi.org/10.1039/C0NR00617C.
- [19] A. I. Ayesh, A. F. S. Abu-Hani, S. T. Mahmoud and Y. Haik, Selective H₂S sensor based on CuO nanoparticles embedded in organic membranes, *Sens. Actuators B Chem.* 231 (2016), 593-600. https://doi.org/10.1016/j.snb.2016.03.078
- [20] M. E. Franke, T. J. Koplin and U. Simon, Metal and metal oxide nanoparticles in chemiresistors: does the nanoscale matter?, *Small* 2 (2006), 36-50. https://doi.org/10.1002/smll.200500261
- [21] N. Barsan, M. Schweizer-Berberich and W. Göpel, Fundamental and practical aspects in the design of nanoscaled SnO₂ gas sensors: a status report, *Fresenius J. Anal. Chem.* 365 (1999), 287-304. https://doi.org/10.1007/s002160051490
- [22] F. H. Saboor, T. Ueda, K. Kamada, T. Hyodo, Y. Mortazavi, A. A. Khodadadi and Y. Shimizu, Enhanced NO₂ gas sensing performance of bare and Pd-loaded SnO₂ thick film sensors under UV-light irradiation at room temperature, *Sensors Actuators B Chem.* 223(Supplement C) (2016), 429-439. https://doi.org/10.1016/j.snb.2015.09.075
- [23] T. Ueda, H. Abe, K. Kamada, S. R. Bishop, H. L. Tuller, T. Hyodo and Y. Shimizu, Enhanced sensing response of solid-electrolyte gas sensors to toluene: Role of composite Au/metal oxide sensing electrode, *Sensors Actuators B Chem.* 252(Supplement C) (2017), 268-276. https://doi.org/10.1016/j.snb.2017.05.172
- [24] A. Ponzoni, C. Baratto, N. Cattabiani, M. Falasconi, V. Galstyan, E. Nunez-Carmona, F. Rigoni, V. Sberveglieri, G. Zambotti, D. Zappa, Metal oxide gas sensors, a survey of

selectivity issues addressed at the SENSOR Lab, Brescia (Italy), Sensors 17(4) (2017), 714. https://doi.org/10.3390/s17040714

- [25] T. Gessner, K. Gottfried, R. Hoffmann, C. Kaufmann, U. Weiss, E. Charetdinov, P. Hauptmann, R. Lucklum, B. Zimmermann, U. Dietel, G. Springer and M. Vogel, Metal oxide gas sensor for high temperature application, *Microsyst. Technol.* 6(5) (2000), 169-174. https://doi.org/10.1007/s005420000048
- [26] C. Wang, L. Yin, L. Zhang, D. Xiang and R. Gao, Metal oxide gas sensors: sensitivity and influencing factors, *Sensors* 10(3) (2010), 2088-2106. https://doi.org/10.3390/s100302088
- [27] A. Arbab, A. Spetz and I. Lundström, Gas sensors for high temperature operation based on metal oxide silicon carbide (MOSiC) devices, *Sensors Actuators B Chem.* 15(1) (1993), 19-23. https://doi.org/10.1016/0925-4005(93)85022-3
- [28] H. Yoon, Current trends in sensors based on conducting polymer nanomaterials, Nanomaterials 3(3) (2013), 524-549. https://doi.org/10.3390/nano3030524
- [29] Zaid Hamid Mahmoud, Omaima Emad Khalaf and Mohammed Alwan Farhan, Novel photosynthesis of CeO2 nanoparticles from its salt with structural and spectral study, *Egyptian Journal of Chemistry* 62(1) (2019), 141-148.
- [30] Zaid Hamid Mahmoud and Aklas Ahmed Abdalkareem, Removal of Pb+2 ions from water by magnetic iron oxide nanoparticles that prepared via ECD, *European Journal of Scientific Research* 145(4) (2017), 354-365.
- [31] A. F. Mohammed, H. M. Zaid and S. F. Marwa, Syntheses and characterization of TiO2/Au nanocomposite using UV-irradiation method and its photocatalytic activity to degradation of methylene blue, *Asian J. Chem.* 30 (2018), 1142-1146. https://doi.org/10.14233/ajchem.2018.21256
- [32] H. M. Zaid, The magnetic properties of alpha phase for iron oxide NPs that prepared from its salt by novel photolysis method, *Journal of Chemical and Pharmaceutical Research* 9(8) (2017), 29-33.
- [33] H. M. Zaid, Effect of Au doping on the magnetic properties of Fe3O4 NPs prepared via photolysis and co-precipitation methods, *Diyala Journal for Pure Science* 14 (2018), 137-147. http://dx.doi.org/10.24237/djps.1403.426A
- [34] Zaid Hamid, Synthesis of bismuth oxide nano powders via electrolysis method and study the effect of change voltage on the size for it, *Aust. J. Basic & Appl. Sci.* 11(7) (2017), 97-101.

- [35] Z. H. Mahmoud and R. F. Khudeer, Spectroscopy and structural study of oxidative degradation Congo Red Dye under sunlight using TiO2/Cr2O3-CdS nanocomposite, *International Journal of ChemTech Research* 12(3) (2019), 64-71. https://doi.org/10.20902/IJCTR.2019.120311
- [36] Zaid Hamid Mahmoud, Marwa Sabbar Falih, Omaima Emad Khalaf, Mohammed Alwan Farhan and Farah Kefah Ali, Photosynthesis of AgBr Doping TiO2 Nanoparticles and degradation of reactive red 120 dye, *J. Adv. Pharm. Edu. Res.* 8(4) (2018), 51-55.
- [37] Zaid Hamid Mahmoud, Marwah Hashim and Farah Kefah Ali, Low temperature photosynthesis of Bi2O3 nano powder, *Earthline Journal of Chemical Sciences* 2(2) (2019), 303-307. https://doi.org/10.34198/ejcs.2219.303307
- [38] Nuha Abdul Jaleel Omran, Zaid Hamid Mahmoud, Noor Kadhum Ahmed and Farah Kefah Ali, Low-temperature synthesis of α-Fe2O3/MWCNTS as photo-catalyst for degradation of organic pollutants, *Orient J. Chem.* 35(1) (2019), 332-336. https://doi.org/10.13005/ojc/350140
- [39] Wijdan Amer Ibrahim and Zaid Hamid Mahmoud, Synthesis and characterization of new Fe-complex and its nanoparticle oxide using the novel photolysis method, *International Journal of Pharmaceutical and Phytopharmacological Research* 8 (2018), 57-61.
- [40] Noor Sabah Al-Obaidi, Zaid Hamid Mahmoud, Ahlam Ahmed Frayyih Anfal S. Ali and Farah K. Ali, Evaluating the electric properties of poly aniline with doping ZnO and α -Fe₂O₃ nanoparticles, *Pharmacophore* 9(5) (2018), 61-67
- [41] H. M. Zaid, F. A. Nuha and A. A. Aklas, Effect of solvents on the size of copper oxide particles fabricated using photolysis method, *Asian J. Chem.* 30 (2018), 223-225. https://doi.org/10.14233/ajchem.2018.21047
- [42] N. A. Ahmed and H. M. Zaid, Synthesis of α-Fe₂O₃ nano powders by novel UV irradiation method, *Diyala Journal for Pure Science* 14 (2018), 57-67. http://dx.doi.org/10.24237/djps.1401.330B