Recent developments on the detection and monitoring of gases with semiconducting metal oxide gas sensors: A Review

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Abstract: The boom of industries has demanded the necessity of the gas sensing devices. This catches the attention of researchers towards the gas sensing materials. Semiconducting metal oxides hold the property of changing its electrical or optical parameters in adsorption/desorption of gases, which can play a crucial role in the detection of gases. To augment the properties of mixed metal oxides are used, as they tend to be complementary in their properties. This paper critically reviewed the metal oxide gas sensors and the supremacy of the heterojunction gas sensor over single metal oxide gas sensor and the sensing mechanism of metal oxide gas sensors.

Keywords: Metal oxide, heterojunction, gas sensor, sensing mechanism.

1. INTRODUCTION

Monitoring and control of toxic gases in industries and laboratories are essential, where it is used as a process gas or generated as a by product. Recently, increasing interest has been taken in semiconducting metal oxides. Various mixed metal oxide semiconductors are synthesized and characterized by the researchers [1, 2]. Semiconducting metal oxide gas sensors works on the principle of a change in electrical conductance on exposure to the gas which is to be detected [3].The main advantage of these sensors are their high sensitivity, small size, low power consumption and low price [4]. Followed by the simple metal oxides like ZnO, SnO_2, TiO_2, In_2O_3, etc coupling two semiconductors were studied more intensively during the last decades to improve physical and chemical properties of simple oxide systems [5]. The presence of heterojunction in the mixed metal oxides improves the gas sensing properties like sensitivity, selectivity, response and recovery time etc.

2. SINGLE METAL OXIDE SEMICONDUCTOR GAS SENSORS

Chethana *et al.* [6] synthesised CuO nanoparticles of ~ 25–30 nm sized spherical particles. They reported that the prepared nanoparticles showed a good sensing response towards NO_2 in the temperature range of 200 °C – 300 °C.

Chougule *et al.* [7] fabricated Nanocrystalline zinc oxide (ZnO) thin films were deposited onto glass substrates by a spin coating method with the hexagonal crystal structure oriented along (1 0 1) plane. The film showed good selectivity towards NO_2 and achieved a maximum gas response of 37.2% with 78% stability at 200 °C operating temperature.

Porous SnO_2 thin films were prepared by a colloidal template method by Xu *et al.* [8]. The oxygen vacancies found in the films played a vital role in the sensing of triethylamine (TEA) with an ultrahigh response at room temperature. In addition they stated that the porous SnO_2 film with rich oxygen vacancies exhibits a high response of 150.5 to 10 ppm TEA, relatively short response-recovery time (53 and 120 s), excellent selectivity and stability, as well as ultralow LOD of 110 ppb at RT.

Wang *et al.* [9] prepared SnO_2 nanoparticles of orthorhombic and tetragonal mixed phases and tetragonal single phase by calcining a novel Metal-Organic Frameworks material. The mixed phase SnO_2 exhibited good performance toward 100 ppm ethanol than that of tetragonal phase SnO_2 with a higher response of 1134 and a lower optimum operating temperature of 170 °C.

Kakati *et al.* [10] fabricated thin films of ZnO by sol-gel method and studied the effect of thickness of films in its physical and chemical properties. They reported that the surface morphology like surface roughness and grain size increases as the film thickness increases and the sensitivity of the thin film sensors towards the acetone vapour depends on surface morphology as well as gas concentration. The film showed a meaningful response to acetone gas at an operating temperature of 200 °C. In their report they concluded that a low temperature ZnO thin film gas sensor can be fabricated by the controlling of surface morphology of the film.

Nano-bitter gourd like structured CuO material was synthesized by Nakate *et al.* [11] by chemical route method. The prepared material showed a remarkable high gas response of 175% towards 100 ppm hydrogen (H_2) at the operating temperature 200 °C with response time 150 s. The lowest detection of H_2 was observed at 2 ppm concentration with the gas response of 5%.

Samarasekara *et al.* [12] deposited CuO thin films by reactive DC sputtering. The film quickly responded to CO_2 with a response time of 3 s. The film showed a good selectivity towards CO_2 than N_2.

Karunagaran *et al.* [13] showed that TiO_2 films prepared by DC magnetron sputtering experience an increase in conductance upon exposure to ammonia. They proposed that the reduction of surface oxygen is the dominant mechanism for the increase in conductance in TiO_2 sensing films upon exposure to ammonia.

Tungsten oxide films with different preferred orientations deposited by Liu *et al.* [14] using reactive magnetron sputtering with glancing angle deposition showed an enhanced NO_2 sensing performance.

Cao *et al.* [15] synthesised TiO_2 with different crystal phases via one-step hydrothermal process and showed gas sensors based on rutile TiO_2 nanorods exhibited excellent repeatability under six cycles and good selectivity to acetone.

3. MIXED METAL OXIDE SEMICONDUCTOR GAS SENSORS

Cynthia *et al.* [16] developed thin films of Zn_2SnO_4–SnO_2 composite by radio frequency (RF) magnetron sputtering on quartz substrate with the sputtering power of 50, 100, and 150 W and stated that the films showed an excellent sensing toward NH_3 gas at room temperature with highest sensing response of 1897.

Darko *et al.* [17] synthesised In_2O_3/ZnO nanostructures with mixed heterostructures showed a good response to response to H_2S gas.

Zheng *et al.* [18] synthesized n-ZnO/n-SnO_2 nano-heterostructures. The sensor with the ZnO–SnO_2 nano-heterostructure nanoparticles presents a much higher response (230.52) to Cl_2 (upgrade to 50 times) than that of the sensor with the pure SnO_2 nanoparticles.

Vuong *et al.* [19] developed CuO-decorated ZnO semiconducting hierarchical nanostructures observed to promote sensitivity for H_2S gas higher than 30 times at low working temperature (200 °C) compared with that in the nondecorated hierarchical structure.

Zhu *et al.* [20] developed heterostructured p-CuO/n-SnO_2 core-shell nanowires through a sequential process combining a solution processing and atomic layer deposition. The well-structured p-CuO/n-SnO2 core-shell NWs achieved excellent selectivity for HCHO from commonly occurred reducing gases.

Cynthia *et al.* [21] prepared thin films of CuO:SnO_2 (1:1) by radio frequency magnetron sputtering technique at room temperature on quartz glass substrates. The CuO:SnO_2 film exhibited a highest sensing response of 3838 for 125 ppm of NH_3 gas at room temperature.

Kaneti *et al.* [22] synthesised ternary α-Fe2O3–ZnO–Au nanocomposites. The ternary α-Fe_2O_3–ZnO–Au nanocomposites showed higher sensitivity/responses of 113 and 57 toward 100-ppm n-butanol and acetone, respectively.

Su *et al.* [23] fabricated Pd/SnO_2/RGO ternary nanocomposite by one-pot route. The sensor based on a Pd/SnO_2/RGO ternary nanocomposite film responded strongly to low concentrations of NH_3 gas at room temperature.

Gawli *et al.* [24] synthesised $NiMn_2O_4$ nanoparticles and reported that the nanoparticles exhibit excellent humidity sensing property.

Cynthia *et al.* [25] ternary CuO:SnO_2:ZnO (1:1:1) thin films by radio frequency magnetron sputtering and reported that the ternary CuO:SnO_2:ZnO (1:1:1) films showed an excellent sensitivity towards ammonia (NH_3) at room temperature.

Table 1 shows the comparison of the gas sensitivity of single metal oxide with the mixed metal oxide gas sensor. All the mixed metal oxides showed enhanced gas sensitivity compared to the single metal oxide semiconductor. The formation of heterojunction in the mixed metal oxide claims the response for the enhancement in the sensitivity towards different gases.

Table 1. A comparison on the gas sensitivity of single metal oxide gas sensor with mixed metal oxide gas sensor

S. No	Target Gas	Single metal oxide	Sensitivity	Mixed metal oxides	Sensitivity
1	Ethanol (600 ppm)	MoO_3	14.0	MoO_3 – WO_3	53 [26]
		WO_3	7.0		
2	Acetone	α-Fe2O_3	9.1	α-Fe2O_3-ZnO	28 [22]
				α-Fe_2O_3–ZnO–Au	57 [22]
3	Formaldehyde (100 pm)	SnO_2	10.6	5% NiO-SnO_2	39.2 [27]
4	NO_2	V_2O_5	1.46	Al_2O_3 - V_2O_5	2.71 [28]
5	Formaldehyde (100 pm)	ZnO	9.6	NiO-3/ZnO	26.2 [29]

4. GAS SENSING MECHANISM IN METALOXIDES

When a metal oxide is exposed to target gases the gases adsorbed on the surface of the metal oxide react with ionic oxygen species by attracting electrons (oxidizing gases) or by donating electrons (reducing gases). Thus there will be a variation in the resistance of the metal oxides. For an n- type metal oxide semiconductor (MOS) the resistance of the MOS decreases on exposure of the reducing gases by donating electrons to the surface of the MOS. On the other hand the resistance of the MOS increases on exposure of the oxidising gas by attracting electrons from the surface of the MOS as shown in the Figure (1). In contrast p-type MOS shows an increase in resistance on exposure of the reducing gases and decrease in resistance on exposure of the oxidising gas [30, 31] as shown in Figure (2).

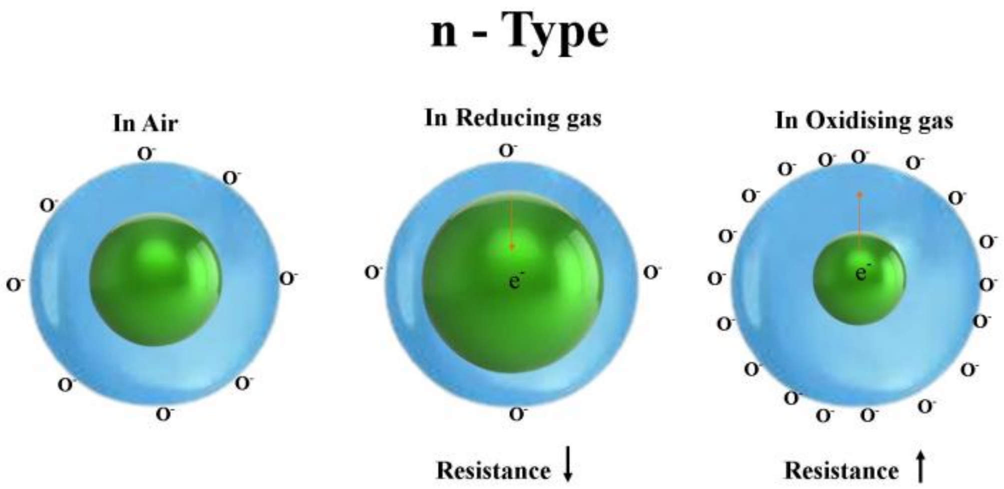

Fig. 1. Schematic presentation of gas sensing reaction of n-type metal oxide semiconductor

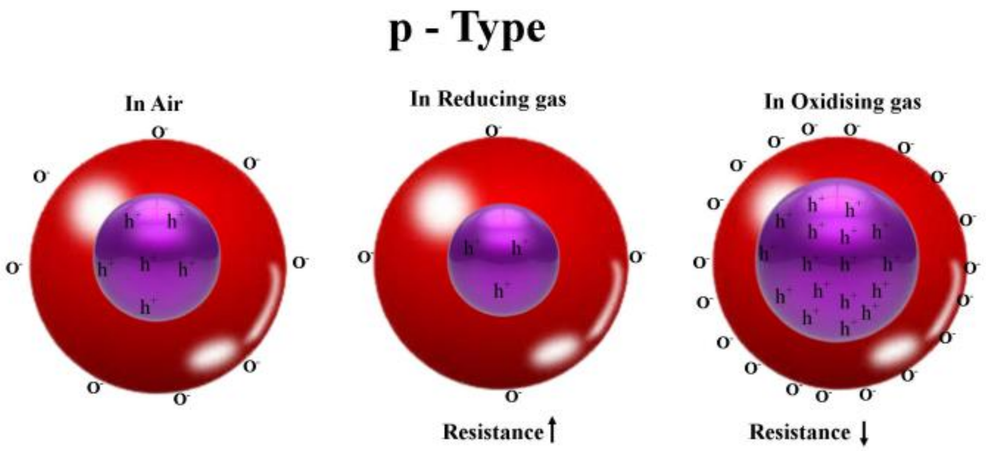

Fig. 2. Schematic presentation of gas sensing reaction of p-type metal oxide semiconductor

5. ENHANCED GAS SENSING MECHANISM OF MIXED METAL OXIDES

The reports discussed above made clear that the mixed metal oxides can effectively enhance the gas sensing properties of the metal oxides. The formation of n-n or n-p or p-p heterojunctions at the interfaces of the mixed semiconducting metal oxides takes away the due credit. It was reported that in the n-n heterojunctions the variation in the Fermi level leads to the band bending of the mixed semiconductors, which results in the formation of depletion layer at the interface of the mixed semiconductors. This can induce an elevated potential barrier in air due to the adsorption of oxygen molecules. The potential barrier always acts as an obstacle to the transportation of electrons in the sensing materials, resulting in the high resistance of the mixed metaloxides [32]. The improvement in the gas sensing behaviours of the sensors based on n-p or p-p heterojunctions can be attributed to variations in the thicknesses of the accumulation layers in the junctions [33].

6. CONCLUSION

In this report the recent developments on the metal oxide gas sensors were survived and also comparisons of single and mixed metal oxides were done. Further the sensing mechanism of the metal oxides was discussed in detail. The reason for enhanced sensing in heterojunction metal oxides is also detailed. To conclude heterojunction metal oxide semiconductors can be considered as a potential sensor for gas sensors.

REFERENCES

1. **S R Cynthia., R Sivakumar., C Sanjeeviraja., S Ponmudi,** Characterization of ZnO:SnO_2 (50:50) thin film deposited by RF magnetron sputtering technique *AIP Conference Proceedings* 1728 (2016) 020567.
2. **S R Cynthia.,** Characterization of ZnO doped SnO_2 thin films deposited by RF magnetron sputtering *European Chemical Bulletin* 12 2023: pp. 382 – 387.
3. **J C Sohn., S E Kim., Z W Kim., Y S Yu.,** H_2S gas sensing properties of SnO_2:CuO thin film sensors prepared by E-beam Evaporation *Transcations on Electrical and Electronic Materials* 10 2009: pp. 135 – 139.
4. **S Pawar., M Chougule., S patil., B Raut., D Dalvi., P Patil., S Sen., P Joshi., V Patil.,** Fabrication of nanocrystalline TiO_2 thin film ammonia vapour sensor *Journal of Sensor Technology* 1 2011: pp. 9 – 16.
5. **S J Lee., C S Hwang., J E Pi., M K Ryu., H Oh., S H Cho., J H Yang., S H K Park., H Y Chu.,** Characterization of ZnO–SnO_2 nanocomposite thin films deposited by pulsed laser ablation and their field effect electronic properties *Material Letters* 122 2014: pp. 94 – 97.
6. **D.M. Chethana., T.C. Thanuja., H.M. Mahesh., M.S. Kiruba., A.S. Jose., H.C. Barshilia., J Manjaan.,** Synthesis, structural, magnetic and NO_2 gas sensing property of CuO nanoparticles *Ceramics International* 47 2021: pp. 10381 – 10387.
7. **M.A. Chougule., Shashwati Sen., V.B. Patil.,** Fabrication of nanostructured ZnO thin film sensor for NO_2 monitoring *Ceramics International* 38 2012: pp. 2685 – 2692.
8. **Y Xu., L Zheng., C Yang., W Zheng., X Liua., Jun Zhanga.,** Oxygen Vacancies Enabled Porous SnO_2 Thin Films for Highly Sensitive Detection of Triethylamine at Room Temperature *ACS Applied Materials and Interfaces* 12 2020: pp. 20704 – 20713.
9. **B J Wang., S Y Ma.,** High response ethanol gas sensor based on orthorhombic and tetragonal SnO_2 *Vacuum* 177 2020: 109428.
10. **N Kakati., S H Jee., S H Kim., J Y Oh., Y S Yoon.,** Thickness dependency of sol-gel derived ZnO thin films on gas sensing behaviours *Thin Solid Films* 519 2010: pp. 494 - 498.
11. **U T Nakate., G H Lee., R Ahmad., P Patil., Y B Hahn., Y T Yu., E K Suh.,** Nano-bitter gourd like structured CuO for enhanced hydrogen gas sensor application *International Journal of Hydrogen Energy* 43 2018: pp. 22705 - 22714.
12. **P Samarasekara., N T R N Kumara., N U S Yapa.,** Sputtered copper oxide (CuO) thinfilms for gas sensor devices *Journal of Physics Condensed Matter* 18 2006: pp. 2417 - 2420.
13. **B.Karunagaran., P Uthirakumar, S.J. Chung, S. Velumani., E K Suh.,** TiO_2 thin film gas for monitoring ammonia *Materials Characterization* 58 2007: pp. 680 - 684.
14. **H Liu., Y Xu., X Zhang., F We.i,** Influence of structural orientation of tungsten oxide films on gas sensing properties *Sensors and Actuators A: Physical* 349 2023: 114021.
15. **S Cao., N Sui., P Zhang., T Zhou, J Tu., T Zhang.,** TiO_2 nanostructures with different crystal phases for sensitive acetone gas sensors *Journal of Colloid and Interface Science* 607 2022: pp. 357 - 366.

16. **S R Cynthia., R Sivakumar., C Sanjeeviraja., C Gopalakrishnan., K Jeyadheepan .,** Sputtering Power and Annealing Effects on the Properties of Zn_2SnO_4–SnO_2 Composite Thin Film for Pungent Smelling Gas(NH_3) Detection *Physica status solidi (a)* 217 2020: 2000512.
17. **J N O A Darko., S Hussain., X Zhang., A A Alothman., M Ouladsmane., M Nazir., G Qiao., G Liu.,** Metal-organic frameworks-derived In_2O_3/ZnO porous hollow nanocages for highly sensitive H_2S gas sensor *Chemosphere* 314 2023: 137670.
18. **X Zheng., H Fana., H Wan.g, B Yan., J Ma., W Wang., A K Yadav., W Dong., S Wang.,** , ZnO–SnO_2 nano-heterostructures with high-energy facets for high selective and sensitive chlorine gas sensor *Ceramics International* 46 2020: pp. 27499– 27507.
19. **N M Vuong., N D Chinh., B T Huy., Y I Lee.,** CuO-Decorated ZnO Hierarchical Nanostructures as Efficient and Established Sensing Materials for H_2S Gas *Science Report* 6 2016: 26736.
20. **L Y Zhu., K Yuana., J G Yang, H P Ma., T Wang., X M Ji., J J Feng., A Devi., H L Lu.,** Fabrication of heterostructured p-CuO/n-SnO_2 core-shell nanowires for enhanced sensitive and selective formaldehyde detection, *Sensors & Actuators: B. Chemical* 290 2019: pp. 233-241.
21. **S. R. Cynthia., R. Sivakumar., C. Sanjeeviraja., C. Gopalakrishnan., K. Jeyadheepan.,** Room temperature ammonia gas sensing characteristics of copper oxide-tin oxide composite thin films prepared by radio frequency magnetron sputtering technique *Journal of Materials Science: Materials in Electronics* 31 2020: pp. 18018–18036.
22. **Y V Kaneti., J Moriceau., M Liu., Y Yuan, Q Zakaria., X Jiang., Aibing Yu.,** Hydrothermal synthesis of ternary α-Fe_2O_3–ZnO–Au nanocomposites with high gas-sensing performance, *Sensors and Actuators B: Chemical* 209 2015: pp.889 – 897.
23. **P G Su., LY Yang.,** NH_3 gas sensor based on Pd/SnO_2/RGO ternary composite operated at room-temperature, *Sensors and Actuators B: Chemica*l 223 2016: pp. 202 -208.
24. **Y Gawli., S Badadhe., A Basu., D Guin., M V Shelke., S Ogale.,** Evaluation of n-type ternary metal oxide $NiMn_2O_4$ nanomaterial for humidity sensing, *Sensors and Actuators B: Chemical* 191 2014: pp. 837-843.
25. **S.R. Cynthia., R. Sivakumar., C. Sanjeeviraja.,** Ternary CuO:SnO_2:ZnO (1:1:1) composite thin film for room temperature gas sensor application, *Optik* 234 2021: 166615.
26. **K. Galatsis., Y.X. Li., W. Wlodarski, E. Comini., G. Sberveglieri., C. Cantalini., S.Santucci., M. Passacantando.,** Comparison of single and binary oxide MoO_3, TiO_2 and WO_3 sol–gel gas sensors, *Sensors and Actuators B* 83 2002: pp. 276 -280.
27. **D Meng., D Liu., G Wang., Y Shen, X San., M Li, F Meng.,** Low-temperature formaldehyde gas sensors based on NiO-SnO2 heterojunction microflowers assembled by thin porous nanosheets, *Sensors and Actuators B: Chemical* 273 2018: pp. 418-428.
28. **T Ishihara., K Shiokawa., K Eguchi., H Arai.,** The Mixed Oxide AlO_3-V_2O_5, as a Semiconductor Gas Sensor for NO and NO_2, *Sensors and Actuators*, 19 1989: pp. 269 – 265.
29. M San., M Li., D Liu., G Wang., Y Shen., D Meng., F Meng., A facile one-step hydrothermal synthesis of NiO/ZnO heterojunction microflowers for the enhanced formaldehyde sensing properties, *Journal of Alloys and Compounds* 739 2018: pp 260-269.
30. L Liu., Y Wang., Y Liu., S Wang., T Li., S Feng., S Qin., T Zhang., Heteronanostructural metal oxide-based gas microsensors. *Microsyst Nanoeng* 8 2022: pp. 85.
31. **S M Majhi., G K Naik., H J Lee., H G Song, C R Lee., I H Lee., Y T Yu.,** Au@NiO core-shell nanoparticles as a p-type gas sensor: Novel synthesis, characterization, and

their gas sensing properties with sensing mechanism, *Sensors and Actuators B: Chemical*, 268 2018: pp. 223 – 231.

32. **Xun H., Zhang Z., Yu A; Yi J.,** Remarkably enhanced hydrogen sensing of highly ordered SnO_2 -decorated TiO_2 nanotubes. *Sensors and Actuators B: Chemical* 273 2018: pp. 983-990.
33. **S Yang., G Lei., H Xu., Z Lan., Z Wang., H Gu.,** Metal Oxide Based Heterojunctions for Gas Sensors: A Review *Nanomaterials* 11 2021: 1026.