



Review on Copper Oxide (CuO) Based H₂S Gas Sensors

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ABSTRACT

Hydrogen sulfide (H₂S) is an extremely toxic and hazardous gas. It is produced naturally or by human activities. H₂S have adverse effects on humans and the environment. Therefore it is necessary to develop rapid, sensitive, and accurate H₂S gas sensor for ensuring human, industrial and environmental safety. Various methods have been studied to detect H₂S which have some drawbacks. Metal oxide semiconductor (MOS) gas sensors have many advantages including high sensitivity, low cost, low power consumption, tunable performance, fast response speed. This paper gives review on CuO based gas sensor for detection of H₂S.

Keywords- Gas Sensors, Metal oxide semiconductor sensors, sensitivity, tunable performance , response speed

I. INTRODUCTION

With rapidly increasing industrialization and modernization there arises some environmental problems including various types of pollutions such as air pollution, water pollution , soil pollution etc. Among all these air pollution is one of the leading causes of various diseases. Carbon monoxide , nitrogen oxides, sulfur oxides, volatile organic compounds and other toxic gases are the main cause of air pollution. Hydrogen sulfide (H₂S) mainly comes from human activities, industry , paper manufacturing, oil refining, metal smelting,, rubber, dyes, pharmaceuticals and other industrial production processes and volcanic eruptions, biological decay. Hydrogen sulfide (H₂S) is a colorless, flammable, acidic, and toxic gas that smells like rotten eggs. H₂S have adverse effects on humans and the environment. Therefore it is necessary to develop rapid, sensitive, and accurate H₂S gas sensor for ensuring human, industrial and environmental safety.

Various methods have been studied to detect H₂S, including surface acoustic wave method, electrochemical method, optical analysis method and gas chromatography . Slow detection speed, complex equipments or high cost are the various limitations of these methods which restrict them to limited use in for industrial or environmental monitoring. Metal oxide semiconductor (MOS) gas sensors have many advantages including high sensitivity, low cost, low power consumption, tunable performance, fast response speed. These advantages of Metal oxide semiconductor (MOS) gas sensors attracts the attention of researchers to develop gas sensors based on metal oxides. Many n-type semiconductors and p-type semiconductors materials like ZnO,

In_2O_3 , WO_3 , TiO_2 , Fe_2O_3 , MoO_3 , SnO_2 , NiO , Co_3O_4 , Mn_3O_4 , CuO etc are used for making gas sensors. Due to its unique properties like low cost, non toxic nature and abundant availability copper oxide nanomaterials have attracted more attention in various applications. CuO (Cupric Oxide) is important oxide compound of copper. CuO is p-type semiconducting material with a narrow bandgap of 1.2 eV. High chemical stability and chemical sensitivity to gases, CuO attracted much attention as gas sensors. Nanoparticles CuO and its composite oxides have potential applications as gas sensor. The gas-sensing behavior of CuO has been studied under exposure to various gases such as NO_2 , CO_2 , H_2S , NH_3 CO and different volatile organic compounds. The CuO -based gas sensors are use in various fields, including the automotive industry, in exhaled breath analyzer environmental pollution detectors etc. Microwave assisted co-precipitation method, chemical precipitation method, sol gel combustion route, simple precipitation method, sonochemical method etc. are used for preparation of nanostructures of CuO like nanowire, nanorod, nanoneedle, nano-flower and nanoparticles.

Review of work on CuO based H_2S sensors.

Iqbal S Naji [1] prepared CuO -doped SnO_2 thin films prepared by pulsed-laser deposition. Findings shows that CuO ratio in the SnO_2 films and operation temperature affects the H_2S sensing properties of samples. It was found that 10% and 15% doped CuO is extremely sensitive to H_2S and the best operation temperature is 50°C . Fang Peng et.al. [2] worked on CuO/WO_3 composites for H_2S sensing. The response of CuO/WO_3 composites changes from p-type to n-type as the CuO content decreases. In case of CuO/WO_3 composites gas sensors different working mechanisms like CuS formation mechanism, weakening mode of n-p type, the H_2S oxidation mechanism, barrier modulation shows their combine effect on response phenomena to H_2S gas. Yempati Nagarjuna and Yu-Jen Hsiao [3] prepared CuO/ZnO Heterojunction Nanostructured Sensor Prepared on MEMS Device for Enhanced H_2S . ZnO nanostructure was prepared using hydrothermal process and CuO films were deposited on the ZnO nanostructure using RF sputtering process. CuO coated ZnO MEMS device is tested for H_2S gas at 200°C temperature. The sensor exhibited good sensitivity towards H_2S gas than other gases (SO_2 , CO , NH_3 and ethanol) at the operating temperature of 200°C . A surface acoustic wave (SAW) H_2S gas sensor based on $\text{CuO}-\text{TiO}_2$ p-n heterojunction film was designed and fabricated by Wei Wu et al [4] The sensor exhibits high sensitivity to H_2S due to the significant current response of $\text{CuO}-\text{TiO}_2$ film to H_2S gas. This SAW sensor also shows good selectivity and stability to H_2S with stable frequency shift under different humidity levels. Jianghao Wang et al [5] prepared copper oxide nanoflower/cobalt tetroxide nanofiber ($\text{CuO}/\text{Co}_3\text{O}_4$) composites by hydrothermal method and electrospinning technology for H_2S gas sensor. According to their study, the improvement of H_2S gas sensing properties of $\text{CuO}/\text{Co}_3\text{O}_4$ sensor was mainly due to the larger specific surface area brings more active sites, which promotes the adsorption of gas on the material surface. Jesse Nii Okai Amu Darko et al [6] Synthesize unique double-shelled hollow MOF based $\text{TiN}-\text{CuO}$ nanoparticles by using a two-step technique involving co-precipitating and calcination. to fabricated sensor that exhibits high selectivity and response towards H_2S gas. The related sensor had high selectivity and stability towards H_2S , and the response of $\text{TiN}/\text{CuO}-2$ is still 2.5–5 ppm H_2S .

Feng et al [7] synthesized gas sensing materials of mesoporous $\text{MoO}_3/\text{CuO}/\text{g}-\text{C}_3\text{N}_4$ by a facile hydrothermal strategy which possessed high response and ultra-low LOD to H_2S at room temperature. They found that the excellent gas sensing properties were due to the larger specific surface area that can enable more gases to be adsorbed on the material surface. The oxygen vacancy reduces the energy required to adsorb the target gas and the formed heterojunctions by $\text{MoO}_3/\text{CuO}/\text{g}-\text{C}_3\text{N}_4$ expedite carrier migration. Zhenhua Li et al [8] prepared

CuO composite ZnO nanoparticles by a novel liquid phase synthesis method. The gas sensing test conducted show that the synthesized CuO/ZnO has significantly enhanced sensing performance to H₂S which is mainly due to the formation of p-n heterojunction and the strong chemical affinity and catalytic performance of CuO for H₂S. The highest response to 10 ppm H₂S is 941 at a relatively low working temperature of 175 °C. Lili Sui et al [9] Prepared novel hierarchical CuO/NiO nanowall arrays film sensor by one-step hydrothermal route without any surfactant or template. The 2.84 at % CuO decorated NiO sensor exhibits excellent sensing properties at 133 °C. The response to 5 ppm H₂S attains 36.9, which increases as high as 5.6 times compared to the NiO one. The CuO/NiO sensor shows a wide linear range from 50 to 1000 ppb, good repeatability, selectivity and long-term stability, Sihan Li et al [10] synthesized a bamboo-like CuO/In₂O₃ heterostructure by using novel MOF-derived method for H₂S detection. It was found that The CuO/In₂O₃ (3.5 wt%) based sensor exhibits outstanding gas sensing performances toward H₂S. They also found excellent H₂S response ($R_{air}/R_{gas} = 229.3-5$ ppm), which are 8.5 times higher than that of with pristine In₂O₃. It also discloses low detection limits (200 ppb), low operating temperature (70 °C) and superior selectivity against other interfering gases. Caixuan Sun et al [11] prepared hollow-rounded cubes composed of copper oxide (CuO)-sensitized amorphous zinc stannate (zinc tin oxide (ZTO)) by a coprecipitation method combined with an impregnation treatment. They found that compared with the ZTO- and CuO-based sensors, the CuO/ZTO-based sensor exhibited excellent gas-sensing performance toward H₂S, with a maximum response value of 574–10 ppm H₂S and a low operating temperature of 160 °C. Their findings indicate that the CuO/ZTO composite is promising as an H₂S-sensing material with potential applications in the field of environmental air monitoring.

Conclusion

From the review of different papers it can be concluded that CuO nanomaterials exhibited good response to various gases, large active surface area and semiconducting nature makes it promising material to be developed for an efficient H₂S gas sensor. With the help of different chemical synthesis procedures the structural and physical properties of CuO can be modified. Particle size of the material determines the sensitivity and response time of CuO based sensors. It is also found that sensitivity of sensor enhances by using various dopants and composite materials.

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