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H_2S GAS SENSING PERFORMANCES OF PURE AND COPPER DOPED CADMIUM SULPHIDE NANOMATERIALS

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Abstract

In recent years, the demand for efficient and sensitive gas sensors has significantly increased due to their crucial role in various industrial and environmental applications. This study focuses on the development and characterization of copper-doped cadmium sulfide (CdS) films as potential gas sensing materials for hydrogen sulfide (H2S) detection. The synthesis process involved a cost-effective and scalable method, aiming to enhance the sensitivity and selectivity of CdS thin films towards H2S gas. The fabricated films were systematically investigated for their structural, morphological, and gas sensing properties. The obtained results demonstrate the promising potential of copper-doped CdS films as high-performance gas sensors for H2S detection, opening avenues for further advancements in gas sensing technology.

Keywords: Copper-doped CdS film, hydrogen sulfide (H2S) gas sensor, thin film deposition, sensitivity, selectivity, semiconductor materials, environmental monitoring

1. Introduction

Gas sensors play a vital role in detecting and monitoring various harmful gases in industrial, environmental, and healthcare sectors. Among these gases, hydrogen sulfide (H2S) is a highly toxic and odorless gas that poses significant risks to human health and the environment at elevated concentrations. Consequently, the development of efficient and reliable H2S gas sensors is essential for ensuring safety and pollution control. Semiconductor metal oxides and sulfides have garnered considerable attention as gas sensing materials due to their high surface-to-volume ratio, sensitivity, and selectivity.

Cadmium sulfide (CdS) is a well-known semiconductor material with favorable properties for gas sensing applications. However, to enhance its gas sensing performance, various approaches, including doping with metal ions, have been explored. In this context, this study focuses on the synthesis and characterization of copper-doped CdS thin films. Copper doping is expected to modify the electronic structure and surface properties of CdS, leading to improved gas sensing behavior, especially towards H2S.

In this paper, a cost-effective thin film deposition technique was employed to fabricate copper-doped CdS films. The films were systematically studied using different characterization techniques to analyze their crystal structure, surface morphology, and composition. The gas sensing properties of the films, specifically their sensitivity and selectivity towards H2S gas, were thoroughly investigated under various operating conditions. The obtained results are expected to provide valuable insights into the development of highly sensitive and selective H2S gas sensors, contributing to advancements in environmental monitoring and industrial safety.

Copper-doped films of CdS have been successfully fabricated for the purpose of studying the gas sensing properties of H2S. These films were deposited onto glass and Si substrates through the process of drop casting at a temperature of 80°C [1]. Subsequent to deposition, the films were annealed at various temperatures, and an examination of their characteristics was conducted. This investigation involved the analysis of properties such as XRD, electrical properties, optical properties, and sensor properties [2]. The CdS:Cu 5%/Si heterostructures, which were annealed at a temperature of 150°C, displayed a significant response to gas, with a value of 26% when exposed to 1 ml of ethanol diffused at room temperature. Furthermore, these structures exhibited rapid response-recovery times of approximately 160 s and 183 s [3]. The gas sensing capabilities of the films were evaluated by subjecting them to various reducing gases at different temperatures and gas concentrations [4]. It was observed that the addition of 15% Cu enhanced the gas sensing properties of the ZrO2 nanostructure, resulting in higher sensitivity (43.18%), faster response (60 s), and recovery time (60 s) [5]. Through in-depth investigations into the mechanism, it was determined that the quenching response is caused by the decomposition of Au-AgNCs@GSH and the formation of Au2 S and Ag2 S in the composite film. These findings contribute to the development of a portable device for the rapid detection of H2 S gas in the air [6]. For the application of hydrogen gas sensors, both pure and Cu-doped CdO thin films were deposited on amorphous glass substrates with varying doping concentrations (ranging from 0.5 to 2 wt%) using a chemical spray pyrolysis technique [7]. A facile hydrothermal route was employed to synthesize Cu-doped ZnFe2O4 nanoparticles (Cu-ZFNPs) with a spinel structure, without the use of any surfactant [8]. The present article reveals the sensing mechanism of SnO2-CuWO4 mixed oxides through the utilization of the Pulsed Temperature Mode (PTM) for the

detection of H2S [9]. High-performance H2S gas sensors were developed using thin films of nickel-doped calcium copper titanate, which were synthesized via a sol-gel method. These sensors are capable of detecting toxic hydrogen sulfide (H2S) gas at part per million levels in the air [10].

A successful demonstration has been performed of a gas sensor for hydrogen sulfide (H2S) based on undoped zinc oxide (ZnO) and Cu-doped ZnO (CZO) nanostructures that have been synthesized hydrothermally and decorated with reduced graphene oxide (RGO) [11]. The synthesis of p-type spherical-like cobalt vanadate (CoV2O6) nanoparticles has been achieved successfully using an easy and low-cost solution-based process that relies on ethylene-glycol (EG) [12]. Scanning electron microscopy has been employed to investigate the surface characteristics of the prepared films, which were fabricated using the nano powder of both NiO-CuO, showing homogeneous, porous CuO-NiO nanoparticles with varying dimensions [13]. An important and facile approach to detect H2S at low operating temperature for practical applications has been demonstrated through the use of a facile method to prepare Pd-doped CuO nanoflowers with various doping concentrations [14]. The sensitivity of Cu-doped SnO2 thin films for gas sensors has been found to be determined by two mechanisms, and the contribution of each mechanism to the thin film sensors with various Cu/Sn ratios has been discussed [15].

2. Methodology

The structure of metal oxide gas sensor consists of electrodes mostly interdigitated type electrode on alumina substrate where the sensing layer semiconducting nano metal oxide is deposited by spin coating, sputtering, spray pyrolysis, etc., The following is the schematic representation of gas sensor.

When the Sensor is exposed to the atmosphere, the most prevalent oxygen species tends to bind to its surface. Oxygen species adsorption strongly depends on the current temperature. The operating temperature is mainly divided into three regions: (air/room temperature range, temperature range less than or equal to 100°C and temperature range greater than or equal to 300°C). In the temperature range between 0°C and 100°C, oxygen was physically adsorbed to the sensor. It released electrons (physical desorption) from the conductive metal oxide and transformed them into O^{2-}. Since the high temperature gets rid of the adsorbed, the adsorbed oxygen species, the concentration of chemisorbed oxygen would increase over time. When the operating temperature range of the sensor between100-300°C and >300°C, the oxygen species can be converted into O^{-} and O^{2-} respectively. To put it another way, the atmospheric oxygen molecules chemically adsorb to the sensor surface, thereby increasing the space charge and decreasing the amounts of electrons in the conduction band. An increase in resistance in the metal oxide and conductivity leading to a decrease in conductivity.

Synthesized Copper-doped CdSNanopowder was mixed with an organic binder alpha-terpineol 96% (Alfa Aesar) to form a thick paste. The paste was spin-coated on a glass substrate using a spin coating machine [Spin NXG P1]. The spin speed was fixed at about 5000rpm for the 30s. The coated sample was air-dried for about 15 minutes followed by sintering in a muffle furnace at 400°C for 2 hours. The prepared film was used for further studies. The H_2S gas sensitivity was measured using a static gas sensing system. The electrical contacts were made using 0.5mm diameter silver wire. The sensor was placed in a glass test chamber (volume 600cm^3). The known amount of gas was injected using a microsyringe into the gas testing chamber. The changes in impedance spectroscopy were carried out using a frequency response analyzer attached with a potentiostat (BioLogic SP240) system and software (EC-Lab V10.37). The impedance measurements were recorded by sweeping the frequency ranging from 1Hz to 1MHz. The AC sinusoidal amplitude was maintained at 20mV for all the measurements. Impedance spectra were recorded for air and films exposed to H_2S at different concentrations (2-50ppm) at room temperature without any DC bias.

3. Results and Discussions

The detection of gas sensors is extremely important, and it is essential to optimise the fundamental parameters, which include the sensor's operating temperature, selectivity, response, and recovery transient levels. As shown in the picture, the H2S gas sensing response of CdS and Cu doped CdS nanoparticles is displayed. Sensitivity was measured when 100 parts per million of hydrogen sulphide (H2S) gas was introduced into the gas sensor chamber that contained the CdS-based film. As the operating temperature of the sensor increases, it has been shown that the gas sensitivity of CdS and Cu:CdS increases. However, after reaching a temperature of 160 degrees Celsius, the gas sensitivity gradually declines. At a temperature of 140 degrees Celsius, the maximum gas sensing response was found for both films. CdS film alone does not possess the maximal detecting response towards H2S; nevertheless, the sensor that is built on Cu-doped CdSNps has this capability. During the course of our inquiry, we discovered that the ideal working temperature for CdS and Cu:CdS film is approximately 140 degrees Celsius. This temperature allows for the most effective response of gas sensitivity. Therefore, the optimised Cu:CdS film and the optimised working temperature were utilised for the purpose of conducting additional gas sensing research. According to the findings, it is abundantly obvious that the Cu dopant was a significant contributor to the enhanced gas sensitivity performance. Impedance spectroscopy was used to investigate the responses of the Cu:CdS layer that was

produced in order to determine its capacity to detect H2S. After making adjustments to the Nyquist plot, it was discovered that the impedance parameters underwent a significant transformation. A significant contribution to the sensing capability of this device is made by the composite nature of the Cu:CdSlayer and the changes that it exhibits in impedance measurements. The changes in resistance are caused by three different areas: the bulk of the grains (R1), the grain borders (R2,Q2), and the contact between the metal and the SnO2 (R3,Q3).

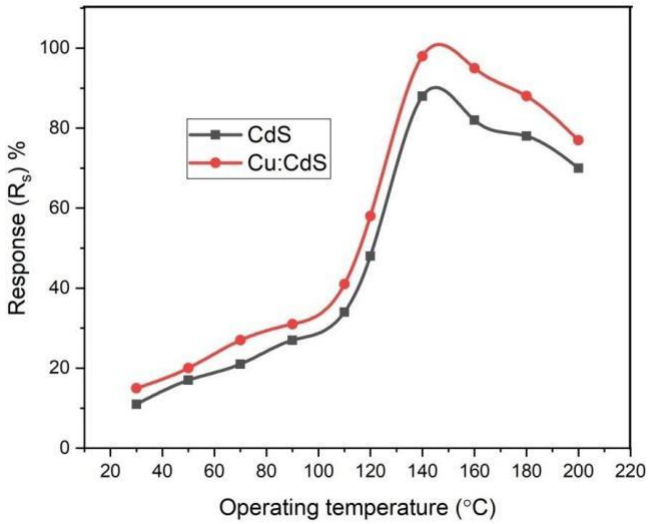

Fig. 1 H_2S Gas Sensing Response for CdS and Cu:CdS with respect to Operating Temperature

On display in Figure 2 are two incomplete semicircles that represent the Nyquist plots that were produced during exposure to Cu:CdSto H2S concentrations ranging from 2 to 50 parts per million. Lines that are solid are used to illustrate the fitted curves. As the concentration of hydrogen sulphide (H2S) increased, it was discovered that the diameter of the semicircle decreased further. In order to determine the values of resistance and capacitance, the curves are utilised. Figure 3 illustrates the imaginary portions of impedance for Cu:CdS that were obtained under a variety of H2S concentrations where the temperature was kept at room temperature. As the concentration of H2S gas increases from 2 to 50 parts per million, it is observed that the imaginary component of impedance reduces due to this phenomenon. One possible explanation for this phenomenon is that the barrier height of the grain boundary reduces as the concentration of hydrogen sulphide (H2S) increases.

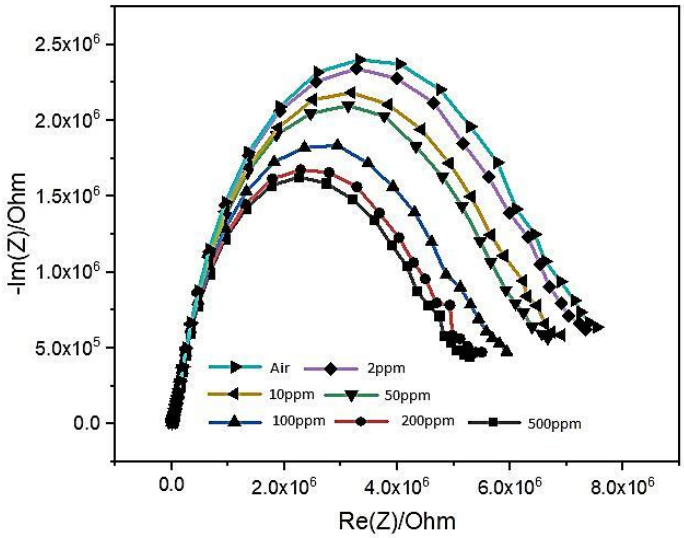

Fig. 2 Nyquist Impedance of Cu:CdS NPs Film Exposed to various Concentration of H_2S gas

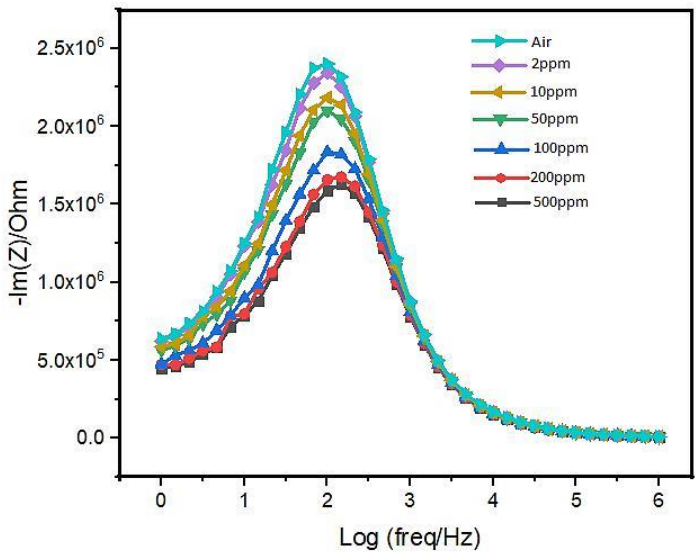

Fig. 3 Imaginary Part of Impedance Vs Log (Freq) Plot for Cu:CdS Film as a Function of H_2S Concentration

Through the utilisation of these impedance data, the mechanism may be simply clarified. A schematic representation of the gas-sensitive profile is shown in the accompanying figure. The gas response time and recovery time are indicated in the figure, which indicates when the data should be observed. Figure 4 illustrates the response and recovery curve of Cu:CdS under 2ppm H2S, with the frequency set to 1kHz. It has been noticed that the sensor has a response time of around 6 seconds and a recovery time of approximately 8 seconds.

These results provide an indication of the response and recovery capabilities of the sensor that was created in relation to H2S gas. It is possible to investigate the reaction and recovery of Cu:CdS films to varying quantities of H2S gas in order to gain an understanding of their performance under a variety of environmental situations, as was tracked and presented for you above. An investigation into the selectivity performance of Cu:CdS towards H2S was carried out in the presence of a number of different gases, including ammonia, sulphur dioxide, carbon monoxide, and acetone.

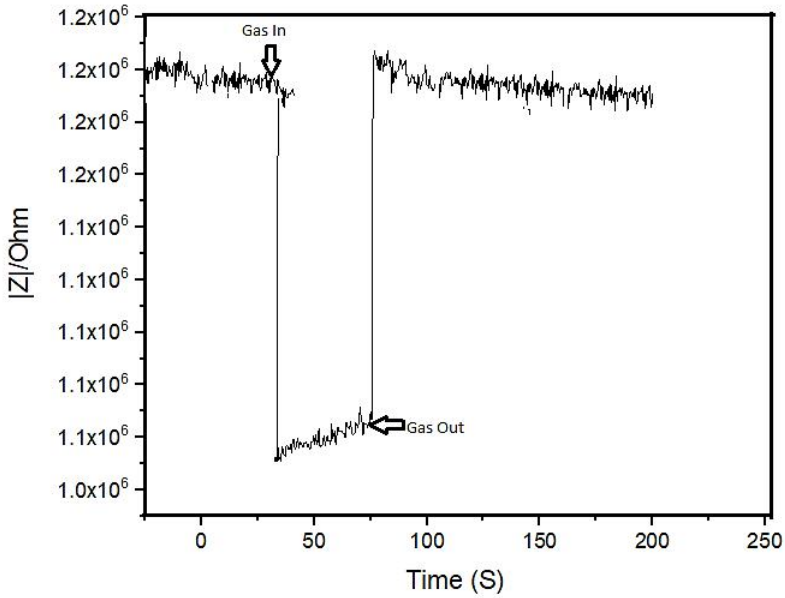

Fig.4 Response and Recovery of Cu:CdS Film exposed to 2ppm of H_2S gas Concentration

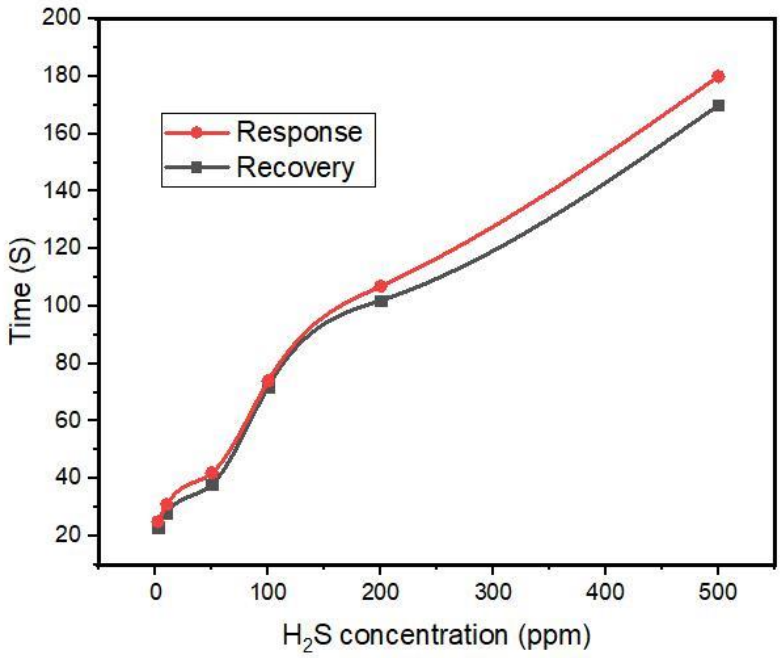

Fig. 5 Response and Recovery of Cu:CdS Film exposed to various Concentration of H_2S gas

The response and recovery of Cu:CdS films to different concentrations of H2S gas can be studied to understand their performance under various environmental conditions is traced and given above.

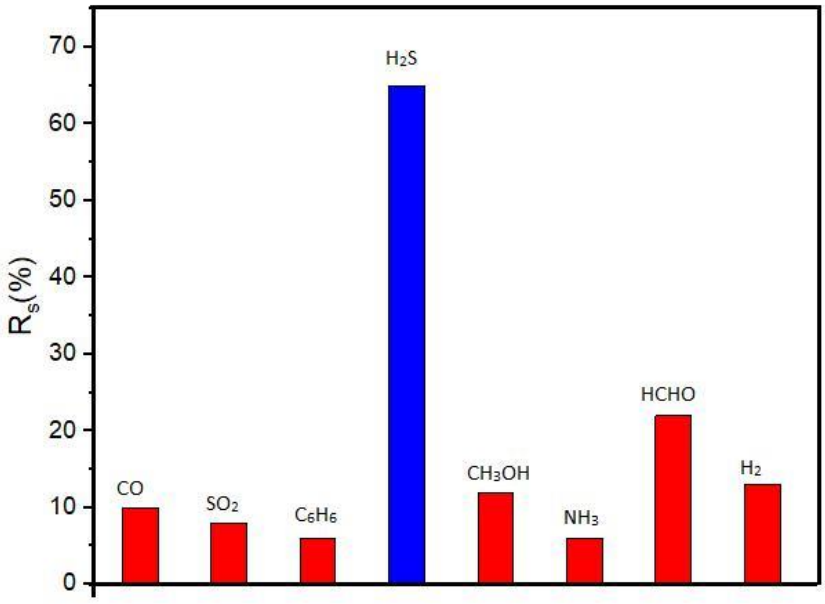

Fig. 6 Selectivity of Sensor exposed various Gases

The Selectivity Performance of Cu:CdStowards H_2S in the presence of various gases, namely ammonia, sulphur dioxide, carbon monoxide and acetone were studied and presented in Fig. 6. The gas sensitivity strongly depends on the crystal structure, grain size and defect density of the materials. The Sensor Response (Rs) is defined as given in the following equation.

$$Rs = \frac{|Z|a - |Z|b}{|Z|a} \times 100$$ …Eqn. (1)

The results of this investigation are given in Figure 6. Crystal structure, grain size, and flaw density are three material characteristics that have a significant impact on the gas sensitivity of a material. It is possible to define the Sensor Response (Rs) by using the equation that is presented below. It was discovered that the sensor that was manufactured had the highest selectivity towards H2S in comparison to the aforementioned interfering gases that are typically present.

Figure 6 provides a schematic representation of the H2S gas sensing mechanism that is exhibited by a Cu:CdS nanoparticle. When the temperature is at room temperature, the oxygen molecules are physically adsorbed on the surface of the metal oxide in the form of oxygen dioxide (O2). The presence of Cu:CdS on the surface makes the process of H2S oxidation easier by providing a significant quantity of O2− (ads) ions. Additionally, the presence of Cu:CdS removes the valence electrons from the metal oxide conduction bands, effectively facilitating the process. After that, the electrons are returned to the metal oxide conduction band since H2S is a reducing gas when it is passed via the electrochemical reaction. Therefore, there is a rise in conductance and a fall in resistance, as evidenced by the findings of impedance spectroscopic research. This cyclical process occurs without interruption. When, on the other hand, the sensor is exposed to an oxidising gas (acetone), this results in the additional extraction of electrons (trap) from the Cu:CdS host matrix, which in turn causes an increase in resistance. As a result, the findings suggest that the existence of a greater number of oxygen vacancy sites produced at the Cu:CdS structure is responsible for the improved sensor response.

4 Conclusion

During the study, we revealed that the utilisation of copper-doped CdS was capable of detecting H2S gas at room temperature at concentrations ranging from 2 to 500 portions per million. The sensor response and recovery time are around 8 seconds and 11 seconds, respectively. When contrasted with other gases that interfere with the sensor's response, the selectivity of the sensor is at its highest. As the concentration of hydrogen sulphide (H2S) increased, the grain boundary resistance values decreased. This indicates that the performance of a stable H2S gas sensor in the ppm range at room temperature was satisfactory. Additionally, the copper-doped cadmium sulphide demonstrated exceptional gas sensitivity and has the potential to be utilised in the development of harmful gas monitoring systems.

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