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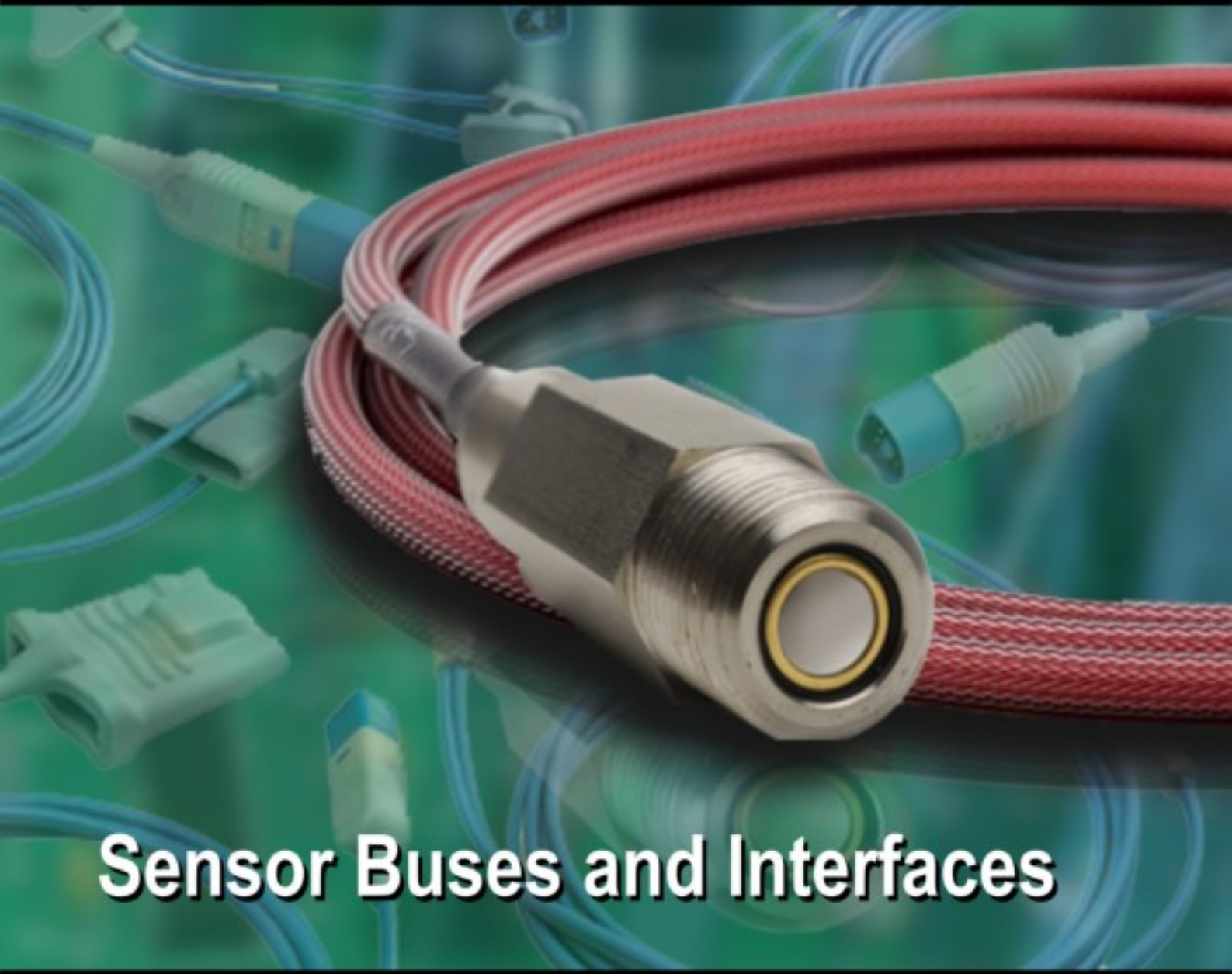

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Study of Room Temperature H_2S Gas Sensing Behavior of CuO-modified BSST Thick Film Resistors

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Abstract: Thick films of $(Ba_{0.1}Sr_{0.9})(Sn_{0.5}Ti_{0.5})O_3$ referred as BSST, were prepared by screen-printing technique. The preparation, characterization and gas sensing properties of pure and CuO-BSST mixed oxide semiconductors have been investigated. The mixed oxides were obtained by dipping the pure BSST thick films into 0.01 M aqueous solution of $CuCl_2$, for different intervals of time. Pure BSST was observed to be less sensitive to H_2S gas. However, mixed oxides of CuO and BSST were observed to be highly sensitive to H_2S gas. Upon exposure to H_2S gas, the barrier height of CuO-BSST intergranular regions decreases markedly due to the chemical transformation of CuO into well conducting CuS leading to a drastic decrease in resistance. The crucial gas response was found to H_2S gas at room temperature and no cross sensitivity was observed to other hazardous and polluting gases. The effects of microstructure and doping concentration on the gas response, selectivity, response and recovery of the sensor in the presence of H_2S gas were studied and discussed. *Copyright © 2008 IFSA.*

Keywords: BSST, CuO, Mixed oxide, Cross sensitivity, Thick film resistor and H_2S gas sensor

1. Introduction

Environmental pollution is a burning global issue; pollution has raised its ugly head high in the global environment. Various polluting and toxic gases result in crucial pollution. Hydrogen sulphide is one of the most polluting gases. It can cause serious health hazards. Combustions of petroleum and coal [1] are the predominant sources of the gases containing sulfur. The gases containing sulfur can result in undesirable disastrous deformations such as infection to respiratory track and lung cancer [1, 2]. Infection to respiratory track causes difficult breathing or breathing under pressure. Therefore,

monitoring of traces of such gases has become extremely important. Materials like SnO_2, ZnO, Fe_2O_3, $BaTiO_3$, $SnTiO_3$, etc. [3-6] have been known to detect the toxic gases. The gas sensing characteristics of the materials can be improved by incorporating some additives [7] into the oxide films. Among the various additives tested, CuO is an outstanding promoter in enhancing the catalytic activity and gas sensing properties of BSST for H_2S detection. The most general adsorption-desorption gas sensing mechanism of semiconductor gas sensors is the simple resistivity change, due to the desorption of surface oxygen adsorbates via reactions with reducing gases such as H_2S, CO and H_2. In the present article, dipping them into a Cu precursor for a particular time interval, followed by firing, modifies the surfaces of BSST thick films. This process is referred to as surface CuO-modification or cuprication. Efforts are made to develop the BSST based H_2S gas sensors.

2. Experimental

2.1. Thick Film Preparation

The $(Ba_{0.1}Sr_{0.9})(Sn_{0.5}Ti_{0.5})O_3$ powder was prepared by mechanochemical method. The AR grade powders of [$Ba(OH)_2.8H_2O$ and $Sr(OH)_2$] and [SnO_2 and TiO_2] in the desired proportions were ball milled to mix thoroughly, followed by sintering at 800^0C for 12 h. This results the BSST powder. The thixotropic paste was formulated as explained elsewhere [3-6]. The films prepared were fired at 550^0C for 30 min. These films were surface modified by dipping them into a 0.01 M aqueous solution of cupric chloride ($CuCl_2$) for different intervals of time. The $CuCl_2$ dispersed on the film surface was oxidized to CuO in firing process, and sensor elements with different mass % of CuO were obtained. Silver contacts were made by vacuum evaporation for electrical measurements.

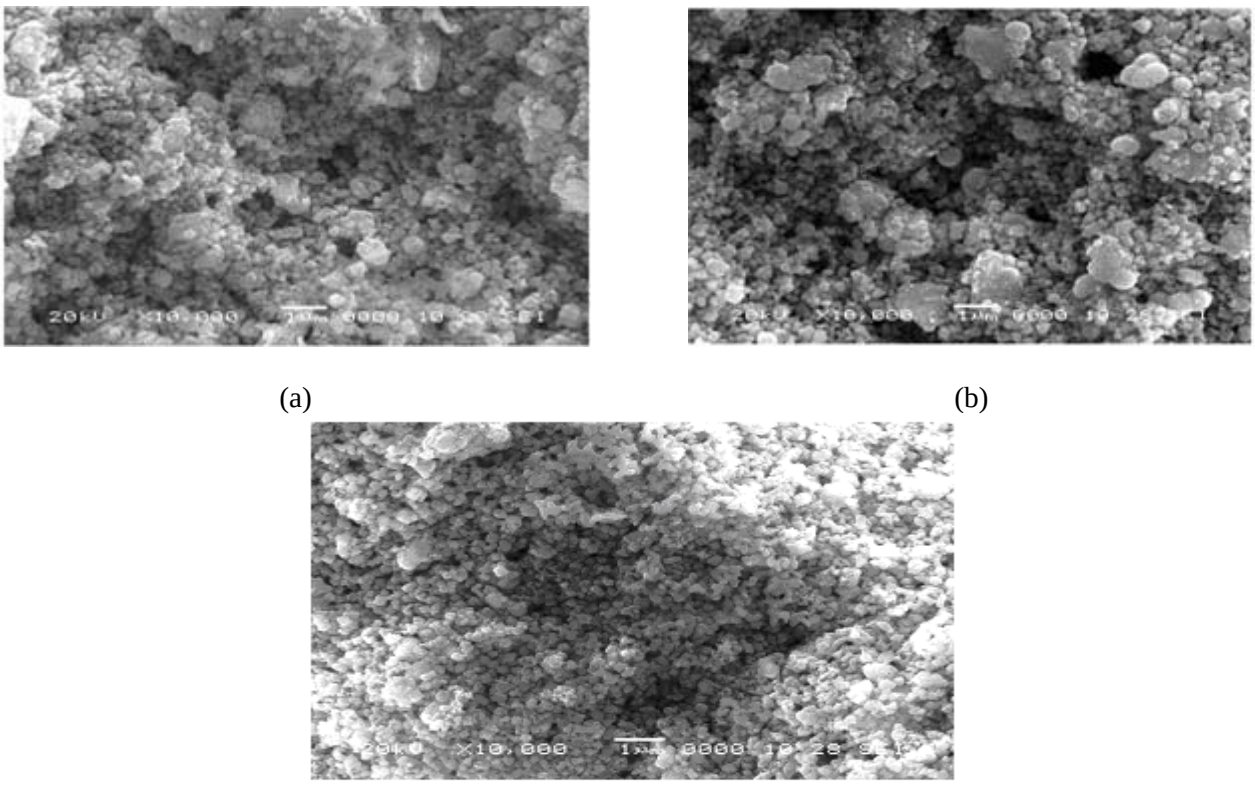
2.2. Characterizations

The microstructure and chemical composition of the films were analyzed using a scanning electron microscope (JOEL JED 2300) coupled with an energy dispersive spectrometer (6360 LA). Thickness measurements were carried out using a Taylor- Hobson (Talystep, UK) system. Electrical and gas sensing characteristics were measured using a static gas sensing system.

3. Materials Characterizations

3.1. Microstructure-SEM

Fig. 1 depicts the SEM images of pure BSST and CuO-modified BSST thick films. Unmodified BSST film (Fig. 1(a)) consists of randomly distributed grains with smaller size and shape distribution. Fig. 1 (b) depicts the microstructure of a most sensitive CuO-modified BSST film consisting of large number of grains of Cu-species associated with the grains of BSST. This film shows more porosity, giving largest effective surface area. This enables larger surface for the gas to react giving more response. Fig. 1 (c) consists of large number of grains of Cu-species associated with BSST grains as compared to the grains associated with Fig. 1 (b). The CuO grains are distributed randomly with BSST grains. The grains of BSST are entirely covered with the grains of Cu-species. The decreased porosity in Fig. 1 (c) tends to reduce the gas response.



(a) (b)

(c)

Fig. 1. Micrographs of (a) Pure BSST, (b) CuO-BSST (30 min dipped), (c) CuO-BSST (60 min dipped) thick film samples.

3.2. Thickness Measurement

The thicknesses of the films were observed to be in the range from 35 to 45 μm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

4. Electrical Properties

4.1. I-V Characteristics

Fig. 2 depicts the I-V characteristics of the CuO-modified BSST thick films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film were ohmic in nature.

4.2. Electrical Conductivity

Fig. 3 shows the variation of log (conductivity) with operating temperature of CuO-modified BSST (30 min) thick films. The conductance values of all samples increase with operating temperature. They are nearly linear from 150^0C to 250^0C. The increase in conductance with increasing temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of the CuO-modified BSST. Pure BSST has only one kind of grains arranged uniformly. The modified films cause the formation of heterogeneous intergrain boundaries of CuO-BSST. Thus increased barrier height of the intergranular region of modified BSST may be responsible to decrease the conductance.

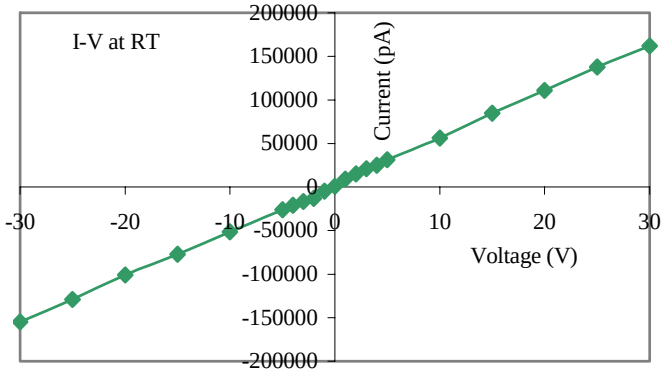


Fig. 2. I-V characteristics.

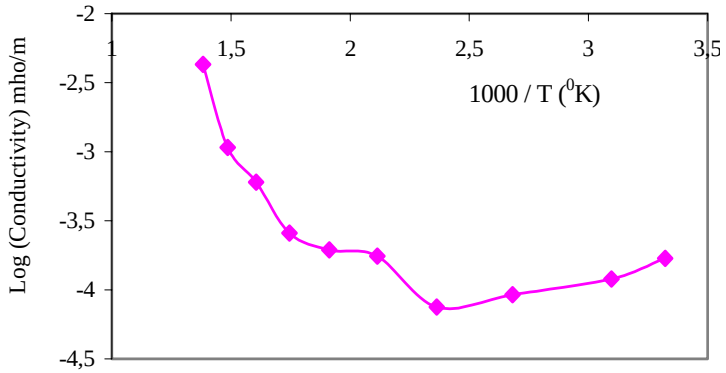


Fig. 3. Conductance-temperature profiles of CuO-modified BSST samples in air.

5. Sensing Performance

5.1. Sensing Characteristics

The relative response (S) to a target gas is defined as the ratio of the change in conductance of a sample upon exposure of the gas to the conductance in air. The gas response can be written as:

$$\text{Gas Response (S)} = \frac{G_g - G_a}{G_a} = \frac{\Delta G}{G_a},$$

where G_a = conductance in air and G_g = conductance in a sample gas.

Specificity or selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of different gases. Response time (RST) was defined as the time required for a sensor to attain the 90 % of the maximum increase in conductance after the exposure of test gas on the sensor surface, while recovery time (RCT) is the time taken to get back 90 % of the maximum conductance in air.

5.2. Response of Unmodified BSST Films

Fig. 4 shows the variation of gas response of unmodified BSST to 1000 ppm H_2S gas with operating temperature. The response was observed to increase with temperature up to 150^0C and then decrease with a further increase in temperature. The response of unmodified BSST was very poor to H_2S gas at 150^0C.

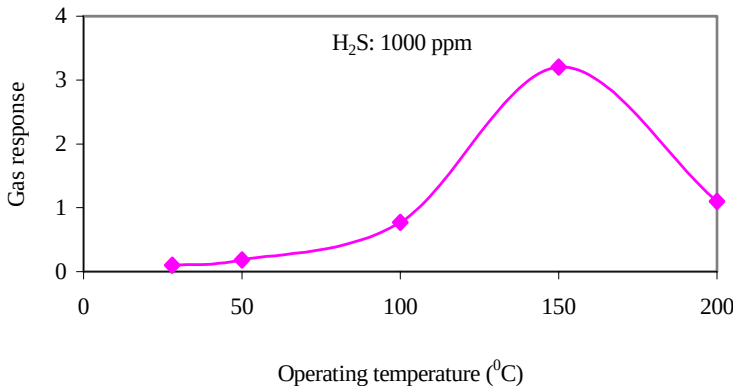


Fig. 4. Variation of gas response of pure BSST with operating temperature.

5.3. Gas Response of CuO-modified BSST

5.3.1. Gas Response and H_2S Gas Concentration

The variation of gas response of CuO-modified (30 min) BSST sample with H_2S gas concentration is represented in Fig. 5. It is clear from the figure that the gas response goes on increasing with gas concentration up to 50 ppm at room temperature. The rate of increase in gas response was relatively larger up to 50 ppm and smaller beyond 50 ppm. Thus, the active region of the sensor would be up to 50 ppm.

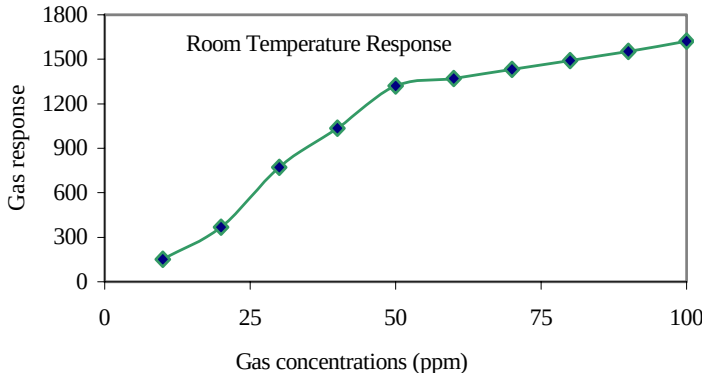


Fig. 5. Variation in gas response of modified BSST with H_2S gas concentration.

5.3.2. Response and Operating Temperature

The response to 50-ppm H_2S of CuO-modified films, as a function of operating temperature is shown in Fig. 6. The sample, with CuO-modified BSST (dipped for 30 min), was observed to be the most sensitive of all. It showed the larger response to 50 ppm H_2S at 50^0C. It also responds to H_2S gas at

room temperature. The response could be attributed to the heterojunction type gas sensing mechanism [3]. The higher response of this sample as compared to other modified samples may be due to the optimum porosity and largest effective surface area available to react the gas.

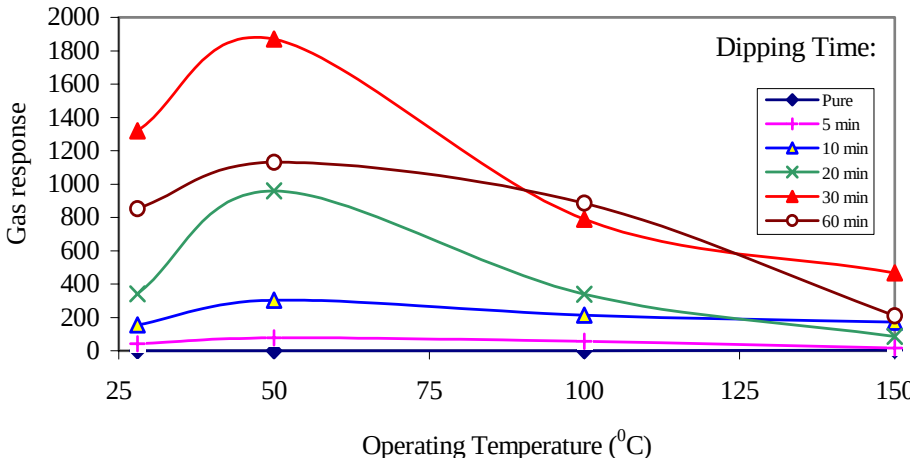


Fig. 6. Variation of gas response with operating temperature.

5.3.3. Response and Dipping Time

Fig. 7 is the histogram indicating the H_2S gas (50 ppm) response as a function of dipping time. The sensor with 30 min dipped in $CuCl_2$ was observed to be most sensitive at room temperature.

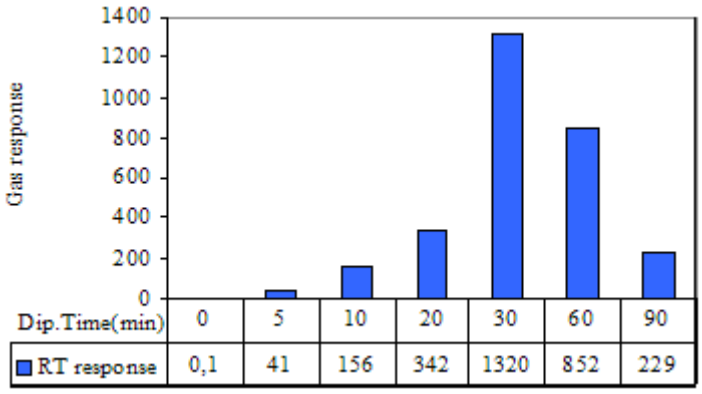


Fig. 7. Response values of different CuO-modified samples.

5.3.4. Selectivity for H_2S against Various Gases

Fig. 8 depicts the selectivity of CuO-modified BSST sensor for H_2S (50 ppm) gas at room temperature. The sensor showed high selectivity for H_2S and could distinguish the H_2S among all the gases, such as LPG, CO_2, C_2H_5OH, NH_3, H_2 and Cl_2.

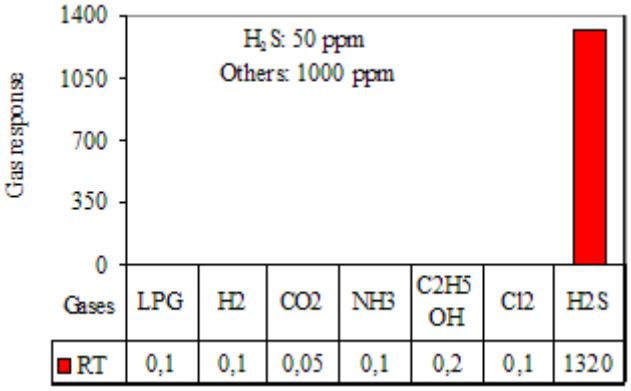


Fig. 8. Selectivity of H_2S gas from mixture of gases.

6. Discussion

Instead of using the mechanism of adsorption-desorption of oxygen for the detection of H_2S gas, the principle of formation of heterojunction barriers [3] in air ambient and their disruption on exposure to H_2S gas was employed. The total resistance of the surface CuO-modified BSST thick film can be looked upon as the resultant of two resistances connected in parallel: (i) the resistance of the bulk portion of n-BSST (R_b) and (ii) the surface resistance of (n-BSST/p-CuO) heterojunctions (R_j). The total resistance (R) of the CuO-modified film was observed to be very high (~10^9 Ω) in air. Therefore, the values of the bulk resistance R_b and the junction resistance R_j would also be very high. It is well known that the resultant of two very high resistances connected in parallel is also high. On exposure to H_2S containing atmosphere, due to sulfurization, CuO would be converted into well conducting Cu_2S. This can be expressed by the following reaction:

$$4H_2S + 6CuO \rightarrow 3Cu_2S + SO_2\uparrow + 4\,H_2O$$

This transformation of highly resistive p-CuO (n-BSST/p-CuO) into well conducting Cu_2S (n-BSST/Cu_2S) leads to a drastic decrease of the electrical resistance. The total resistance of the CuO-modified film was observed to be very low. Therefore, the value of the bulk resistance R_b would remain as it was in case of air ambient and the surface resistance R_s would be very low. It is well known that the resultant of a very high resistance connected in parallel with a very low resistance is very low. The extremely high response of the order of 10^3 was obtained to 50 ppm H_2S gas. The high response (to ppm level of gas), high selectivity from mixed gases, quick response, fast recovery time and the room temperature operation of the sensor are the main features achieved in the present investigation.

7. Summary

From the results, following statements can be made for the sensing performance of CuO-modified BSST sensors.

1. Pure BSST thick films are observed to be less sensitive to H_2S gas.
2. CuO-modified BSST sensors showed high response to 50 ppm H_2S gas at room temperature.
3. Doping CuO in BSST conveniently customized the bulk properties of pure BSST.
4. The sensor was highly selective to a trace amount (50 ppm) of H_2S gas from other toxic gases of higher concentrations.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Sensor instrumentation;
- Virtual instruments;
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