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Effect of Surface Modification on $SrTiO_3$ Thick films: Room Temperature H_2S Gas Sensor

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Abstract: Strontium Titanate ($SrTiO_3$, (ST)) was prepared mechanochemically from $Sr(OH)_2$ and TiO_2. XRD confirms the perovskite phase of material. Thick films of ST were prepared by screen-printing technique. The gas sensing performances of thick films were tested for various gases. It showed maximum sensitivity to CO gas at 350 ^oC for 100 ppm gas concentration. To improve the sensitivity and selectivity of the film towards a particular gas, ST thick films were surface modified by dipping them into the solution of nano copper for different intervals of time. These films were found to be sensitive towards 1 ppm of H_2S at Room Temperature. The response was reproducible and the films were stable for operation over three months. The detection mechanism of the sensors was investigated and it was found that the Cu would be transformed upon firing into copper oxide. The p-type CuO grains around n-type ST grains would form n-ST/p-CuO hetero-junction. Upon exposure to H_2S gas, the barrier height of n-ST/p-CuO hetero-junctions decreases markedly due to the chemical transformation of p-CuO into well conducting CuS leading to drastic change in resistance. The efforts have, therefore, been made to develop the Room Temperature H_2S gas sensor based on strontium titanate surface modified with nano Cu. The gas response, selectivity, stability of sensor, response and recovery time of the sensor in the presence of H_2S gas were studied.

Keywords: $SrTiO_3$ thick films, Surface modification, Room temperature H_2S gas sensor, Selectivity.

1. Introduction

In recent years, the global climate change has emerged as one of the most immediate challenges to the mankind; as it is well known that, this phenomenon is mainly caused by the emission of CO, CO_2, and H_2S to the atmosphere by combustion engines and industrial processes. It is inevitable to have a continuous control of these hazardous gases in the atmosphere. The gases such as CO, H_2, C_2H_5OH, CO_2, NO_x, O_2, CH_4, NH_3, H_2S, C_2H_2, C_2H_4, C_3H_6, LPG etc. have to be controlled for the betterment of living beings.

Fuels are widely consumed for transport services all over the world. During combustion, various polluting and toxic gases are released resulting in environmental pollution which can cause serious health hazards. Upon burning, toxic hydrogen sulfide gas is oxidized to sulfur dioxide by atomic oxygen, molecular oxygen or ozone [1]. Combustions of petroleum and coal are the predominant sources of the gases containing sulfur [2]. The gases containing sulfur can result in undesirable disastrous deformations such as infection to respiratory track and lung cancer [2, 3]. Thus H_2S is harmful to human body and the environment. According to the safety standards established by American conference of Government Industrial Hygienists, the threshold limit value (TLV) for H_2S is 10 ppm. Even at low concentration its effect on the nervous system is severe [4].

The emission of H_2S and release of sulfur needs effective monitoring which can allow one to control its free release to environment. Currently there are a number of materials being used for such sensoric applications but these are often not so effective and suffer from various drawbacks, such as low sensitivity, poor selectivity, and slow response and recovery times. Therefore there is a need for low cost and more effective H_2S sensor operable in sub-ppm range. In addition, concentration of H_2S varied from the types of oil or natural gas used. The concentration of H_2S gas is different for different source of oil or natural gases mines. Therefore, the detection and monitoring of H_2S should be considered of high importance for both resource exploitations and human health. Similarly, carbon mono oxide is a deadly gas that is released due to combustion of the fuels in automobiles.

In the recent years, a number of semiconductor sensors have been found to be suitable for H_2S gas e.g. SnO_2, WO_3, In_2O_3, ZnO and a few perovskite-type materials like $NdFeO_3$ and $NiFeO_4$ [5 -12]. Generally these sensors are fabricated by thick film technology or by deposition of a film by chemical bath deposition method etc. However, metal oxides have been used nearly for four decades for gas sensing applications [13] but application of these conventional semiconductor gas sensors is limited by some disadvantages, for instance poor selectivity, long response time high operating temperatures (typically in the range 200-500 ^{0}C), which implies that power is required. Obviously it would be desirable for many applications if the sensor could operate at room temperature, and a reduction of the power consumption is a key goal for battery-operated gas sensors. Recently it has been reported that ZrO_2-SnO_2 [14] and ZnO [15] sensors can be used to detect H_2S and NH_3 at room temperature, respectively but their sensitivity was low. Solis et al reported H_2S sensing properties at room temperature but it need short heating pulses of 523 K for stable operation [16].

A different approach to make selective metal-oxide gas sensor is by using metals or additives that enhance the chemisorptions of specific gases. It is well known that perovskite oxides are used as gas-sensing materials because they possess good properties such as chemical and thermal stability, environmental adaptability and wide range of working temperature. The perovskite oxide ceramics promoted interest in chemical sensors over the last decade. Furthermore, some composite systems such as (Ba,Sr)TiO_3 and (Ba, Pb)TiO_3 ceramics have been studied to broaden the application of $BaTiO_3$ -based thermistors for wider temperature range [17, 18]. Recently, $SrTiO_3$ and $BaTiO_3$-based sensors have received much attention because of their multi-sensing properties, such as humidity, thermal and photosensitivities [19, 20].

As an alternative, hetero-junction-based sensors have been constructed. Usually, a hetero-junction gas sensor consists of two semiconducting oxides in contact, with enhanced sensing behaviour occurring at the interface between the two materials. Gases that are adsorbed onto the sensor surface on either side of the hetero-junction modify its charge-transfer characteristics by changing the structure of the interfacial barrier [21]. This process gives rise to a gas detection mechanism distinct from that of semiconductor metal oxide sensors. Hetero-junction based humidity sensors were first proposed in 1979 [22]. The responses of different hetero-junction-based sensors to a range of gases including CO, H_2, H_2O, NO_2 and C_2H_5OH have been investigated [21, 23]. Several rectifying junctions formed between p- and n-type semiconducting ceramics include CuO (p)/ZnO(n), [24, 25] La_2CuO_4(p)/ZnO(n) [23] and $SmCoO_3$(p)/MO_x(n), where M = Fe, Zn, In, Sn [26]. In addition, n-type semiconductor hetero-junction ceramics with slightly different band energies have also been reported [27, 28].

The present work describes the technique to form an n-ST/p-CuO hetero-junction with a good rectification ratio. The n-ST/p-CuO hetero-junction in thick film form has been fabricated using simple screen-printing technique followed by surface modification of the thick films.

2. Experimental

2.1. Mechanochemical Preparation of $SrTiO_3$

The AR grade powders of $Sr(OH)_2$ and TiO_2 were milled for 2 h using planetary ball mill to obtain fine grained powder. Then hot water is added with constant stirring, followed by slow heating up to dryness. The powder was calcined at 1000 ^oC for 6 h. The XRD pattern of so-prepared powder confirmed the sub-microcrystalline perovskite phase. The sub micron size powder was then used to formulate the paste for screen-printing.

2.2. Sensor Fabrication

The screen-printing technique was used to manufacture the sensors. In this process, a thixotopic paste is pressed through a screen on to the substrate using a rubber squeeze. The thixotropic paste of sensor material suitable for screen-printing was formulated by adding 75 wt.% of the fine powder of ST to 25 wt.% of the organic binder (solution of ethyl cellulose in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol etc.) The binder was used to provide the necessary viscosity for the screen-printing process. After mixing the powder with the organic binder, the paste was milled in a planetary ball mill in order to homogenize the mixture. This thixotropic paste then used for screen-printing of thick films on glass substrate in the desired pattern [29, 30]. The thickness of films was measured by using Taylor-Hobson (Talystep, UK) system. The thicknesses of the films were observed in the range from 65-75 μm. The reproducibility in the thickness of the films was possible by maintaining proper rheology and thixotropy of the paste. The films were dried at 80-100 ^oC for 0.5 h. Sintering of the dried films was carried out by heating at temperature 550 ^oC in the furnace for 30 min.

2.3. Surface Modification of Thick Films

The nano Cu activated $SrTiO_3$ thick films were obtained by dipping them in a 0.02 % aqueous solution of nano copper at different intervals of dipping time: 1, 5, 10, 20 and 25 min as explained elsewhere [31]. These films were dried at 80 ^oC, followed by firing at 550 ^oC for 30 min. The films so prepared are termed as ‘surface modified ST’ films. The silver contacts were made for electrical measurements.

3. Characterization

3.1. Structural Analysis

The structural properties of the powder were studied by using a Rigaku Model DMAX-2500 X-ray diffractogram (XRD) with CuKα radiation, having λ = 1.5406 Å. The XRD pattern of the synthesized $SrTiO_3$ powder at 1000°C is shown in Fig. 1. From the XRD peaks the average grain size was calculated using Scherrer equation of $B = \lambda\zeta/(d_c \cos\theta)$ [32] (considering broadening error due to the instrument itself), where B in radians is the broadening of the diffraction peak due purely to crystalline size measured at half of its maximum intensity; λ, wavelength of radiation; θ, Bragg angle; d_c, diameter of crystalline size; and ζ, constant. The constant ζ depends mainly on the crystalline shape indices. It has a value of about 0.9.

The XRD revealed that the material is in sub-microcrystalline perovskite phase. The observed peaks in the XRD pattern are matching with the ASTM data book (28 of B-123). The average grain size was determined by using Scherrer formula and was estimated to be 229 nm.

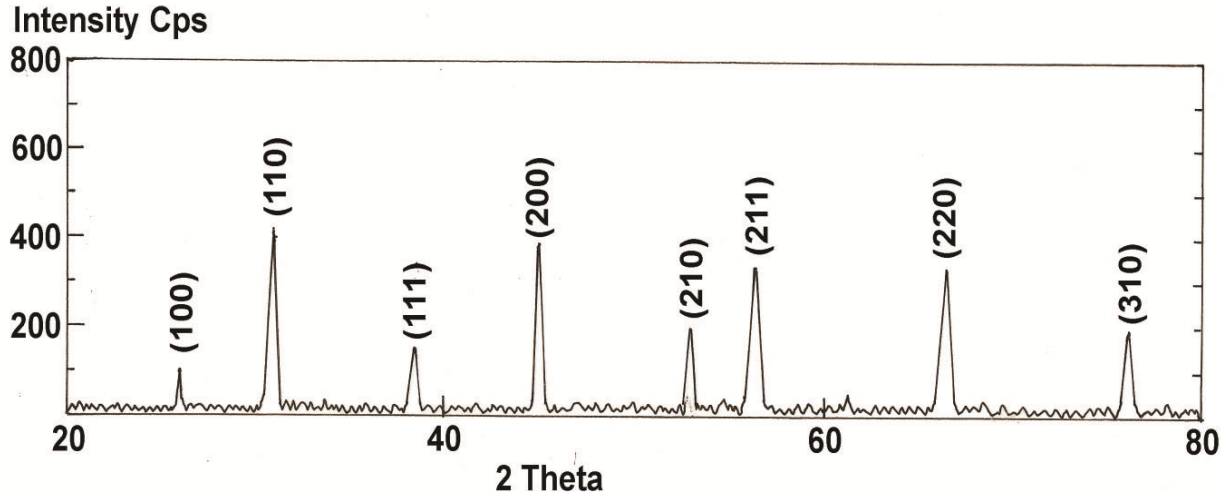
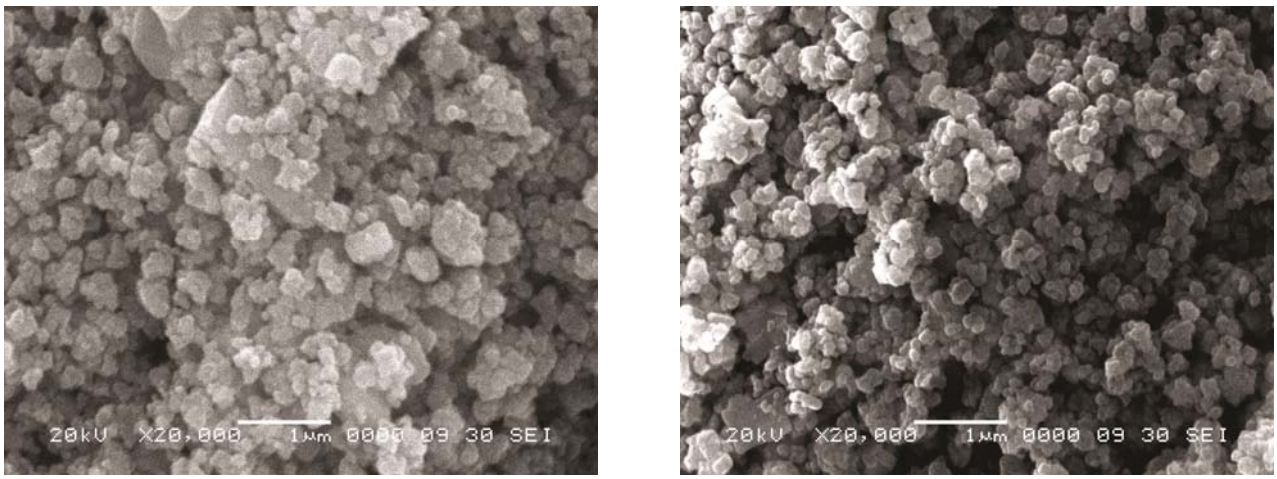


Fig. 1. X-ray diffractogram of the ST thick films.

3.2. Micro Structural Analysis

The micro structure and chemical composition of the films were analyzed by using a scanning electron microscope (SEM, JEOL JED 6300) coupled with an energy dispersive spectrometer (EDS, JEOL JED2300LA). The thicknesses of the thick films were measured using a Taylor-Hobson (Talystep, UK) system. Fig. 2 (a, b) depicts the SEM images of unmodified and surface modified ST thick films (20 min) fired at 550 °C. The unmodified film consists of large number of grains ranging from 0.1 μm to 1 μm in size, leading to high porosity and large effective surface area available for the adsorption of oxygen species. While the surface modified ST film shows a number of small particles distributed uniformly between the larger grains around the ST, which may be attributed to the presence of nano copper. The grain size range of ST was observed to be from 0.1 μm to 0.3 μm.



(a) (b)

Fig. 2. SEM images: (a) unmodified and (b) surface modified ST thick film (20 min).

3.3. Quantitative Elemental Analysis of Unmodified and Surface Modified ST Film

The quantitative elemental compositions of surface modified films are presented in Table 1. Stochiometrically (theoretically) expected wt % of cations (Sr, Ti) and anions (O) are 67.28 and 32.72 respectively. The wt % of constituent cations and anions in as prepared ST and nano Cu surface activated ST were not as per the stoichiometric proportion and all samples were observed to be oxygen deficient, leading to semiconducting nature of ST. It is clear from table 1 that the weight percentage of nano copper went on increasing with dipping time. The film with dipping time of 20 min is observed to be more oxygen deficient (29.92 wt %). This oxygen deficiency would promote the adsorption of relatively larger amount of oxygen species favorable for higher gas response.

Table 1. Elemental analysis of unmodified and surface modified ST films.

Elements (wt %)	**Dipping Time (min)**					
	0	**1**	**5**	**10**	**20**	**25**
(Sr + Ti)	68.86	67.69	66.94	66.38	66.08	66.83
Cu	0.00	0.63	1.15	1.30	2.70	0.68
O	31.14	30.98	30.96	30.88	29.92	32.29
ST	100.00	99.30	99.05	98.56	98.70	99.80

3.4. Electrical Properties

Fig. 3 shows the dependence of conductivity of unmodified and surface modified ST films in air ambience. The conductivity of these films goes on increasing with the increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films.

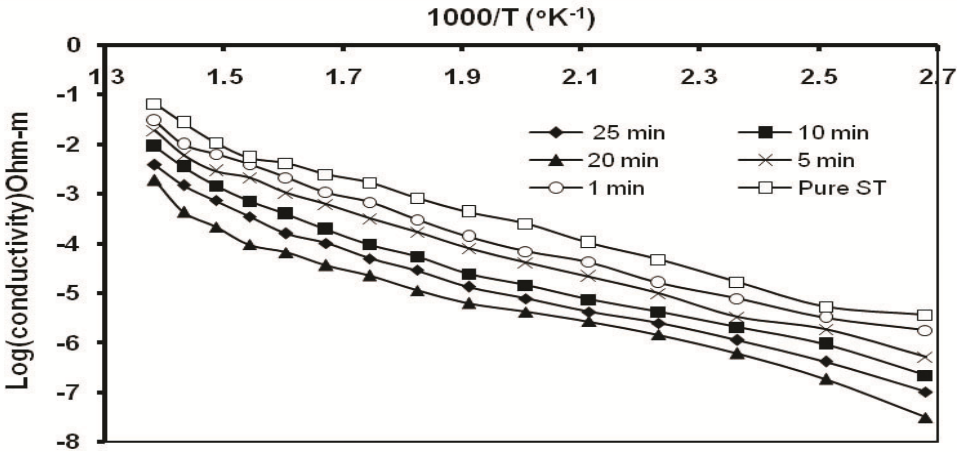


Fig. 3. Electrical profile of pure and surface modified ST thick films.

4. Result and Discussion

4.1. Gas Sensing Properties of Unmodified ST Films

4.1.1. Gas Response with Temperature

Gas response of a sensor was defined as the ratio of the change in conductance of a sample on exposure to the test gas to the conductance in air.

$$\text{Gas Response} = \left|\frac{Gg - Ga}{Ga}\right| = \left|\frac{\Delta G}{Ga}\right|, \quad (1)$$

where Gg & Ga are conductance of a sample in the presence and absence of a test gas respectively, and ΔG is the change in conductance.

Fig. 4 presents the variation in the sensitivity to CO gas (100 ppm) with operating temperatures ranging from 100° to 450 °C. It is noted from the graph that response increases with the increasing temperature, attains a maximum at 350°C, and decreases with further increase in operating temperature.

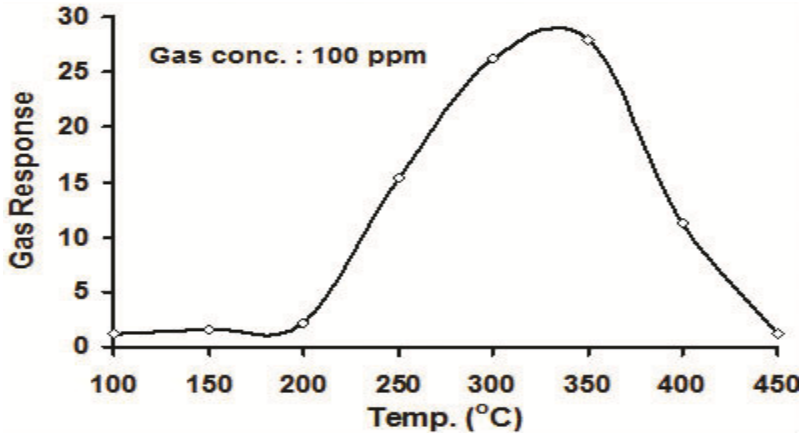


Fig. 4. Variation of CO gas response of pure ST film with operating temperature.

4.1.2. Selectivity of Pure ST Film

The ability of a sensor to respond to a certain gas in presence of other gases is known as selectivity. A good sensor will discern a particular signal by allowing adsorption of the desired gas while remaining insensitive to others. Fig. 5 presents the bar diagram indicating selectivity of unmodified ST film at 350^{o}C to CO gas against the other gases. The sensor is the most selective to CO gas against the other gases except NH_3.

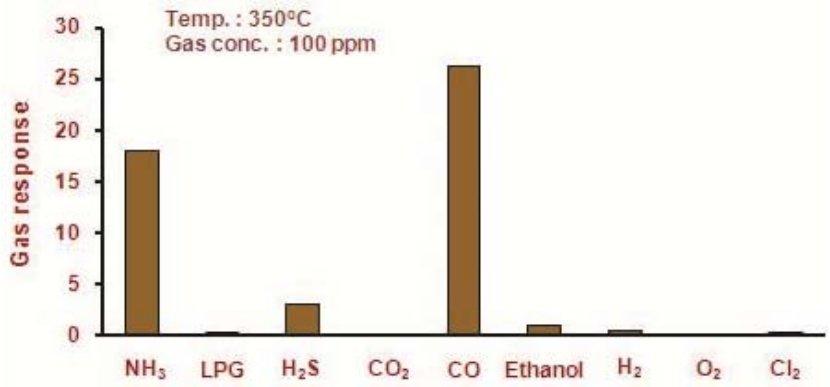


Fig. 5. Selectivity of pure ST thick film.

4.1.3. Response and Recovery Time of Pure ST Film

Response and recovery times are two important parameters of a gas sensor since their values determine the applicability of the sensor. In gas detection, response time is usually defined as the time taken to achieve 90 % of the final change in conductance of the sensor in a given gas concentration [33].

Recovery time is the time taken to return from the conductance in a given gas concentration to 90 % of initial conductance of the sensor [33]. However, figures are often quoted to 50 % or 70 % of the changes, particularly for semiconductor sensors. This is because the shape of the response curve is such that the lower figures may be a better indication of the response [34]. The response and recovery time of unmodified ST film was 6s and 20 s respectively.

4.2. Gas Sensing Properties of Surface Modified ST Films

4.2.1. Gas Response with Operating Temperature

Fig. 6 presents the variation in the sensitivity of unmodified and surface modified ST films to H_2S gas (1 ppm) with operating temperatures ranging from room temperature to 450 ^{o}C. It is noted from the graph that sensing response increases with dipping time and attains maximum sensitivity for dipping time of 20 min and subsequently decreases on further increase in dipping time. The pure films show the highest response to CO, while modified films show to H_2S gas.

4.2.2. Selectivity of Unmodified and Surface Modified ST Films

Fig. 7 presents the bar diagram indicating selectivity of surface modified ST film dipped for 20 min at Room temperature (30 ^{0}C) to H_2S gas against the other gases. The sensor is the most selective to H_2S gas against the other gases except NH_3.

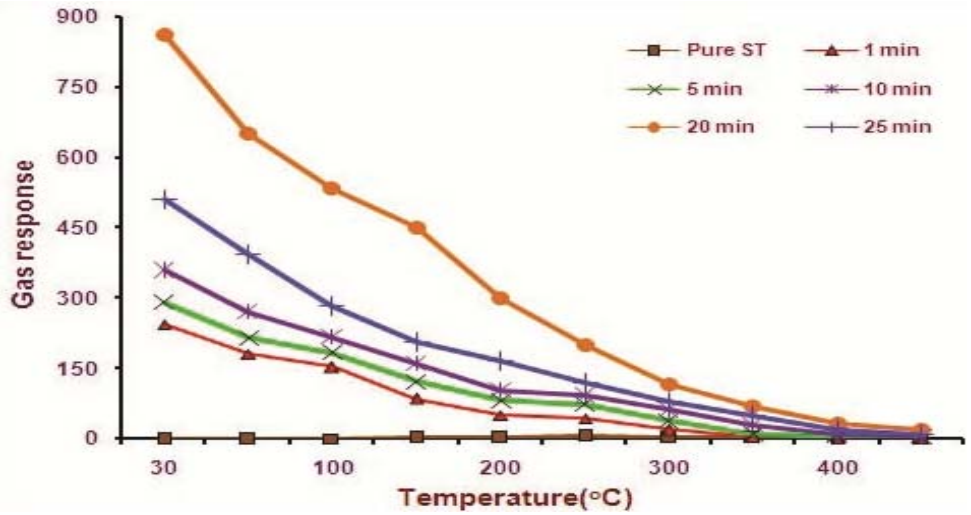
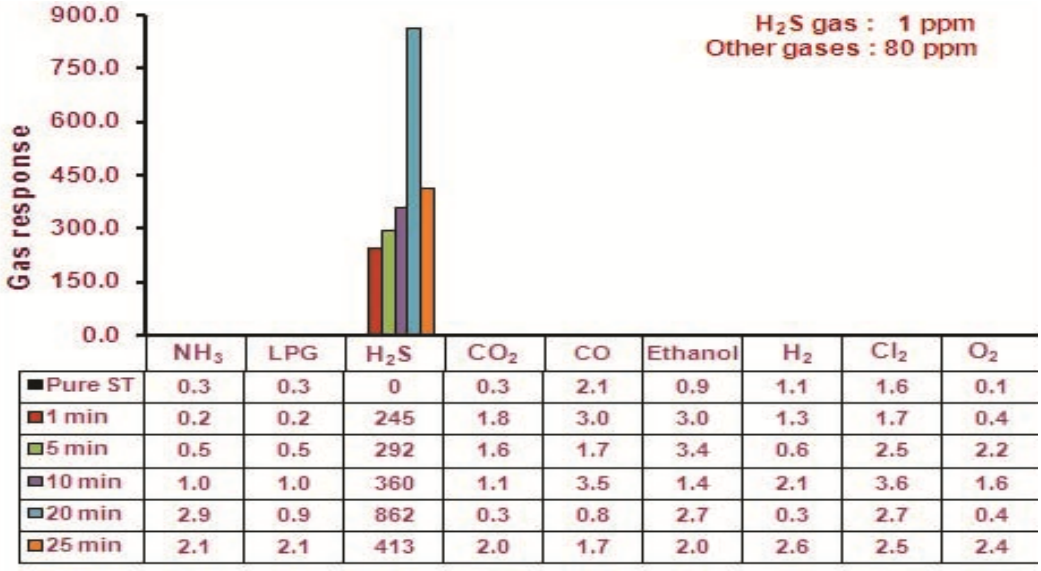


Fig. 6. Variation of H_2S gas response to pure and surface modified ST films with temperature.



	NH_3	LPG	H_2S	CO_2	CO	Ethanol	H_2	Cl_2	O_2
Pure ST	0.3	0.3	0	0.3	2.1	0.9	1.1	1.6	0.1
1 min	0.2	0.2	245	1.8	3.0	3.0	1.3	1.7	0.4
5 min	0.5	0.5	292	1.6	1.7	3.4	0.6	2.5	2.2
10 min	1.0	1.0	360	1.1	3.5	1.4	2.1	3.6	1.6
20 min	2.9	0.9	862	0.3	0.8	2.7	0.3	2.7	0.4
25 min	2.1	2.1	413	2.0	1.7	2.0	2.6	2.5	2.4

Fig. 7. Selectivity of modified ST film to H_2S gas with other gases.

4.2.3. Response and Recovery Time of Surface Modified ST Film

Fig. 8 represents the response and recovery time of surface modified ST film (20 min). It has been found that the response and recovery time was 6 s and 16 s respectively. The recovery time was found to be larger compared to unmodified ST film.

4.2.4. Stability of the Surface Modified ST Films

The surface modified films were evaluated for their long term stability by recording their gas response for a period of over three months. The films were used for this study and these were repeatedly exposed to 1 ppm of gas. The Fig. 9 shows the response of the film for a period of 3 months. It can be seen that sensitivity remains stable within a range of ± 5 %. These films, thus are suitable for gas sensor applications.

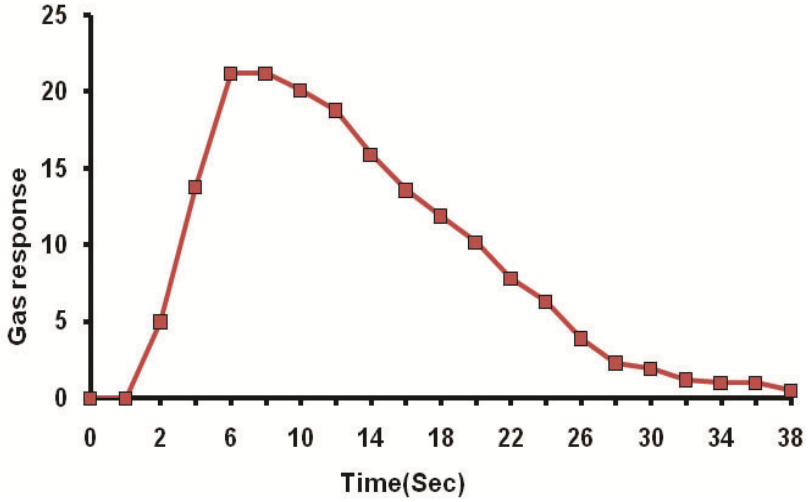


Fig. 8. Response and recovery time of unmodified and surface modified ST films.

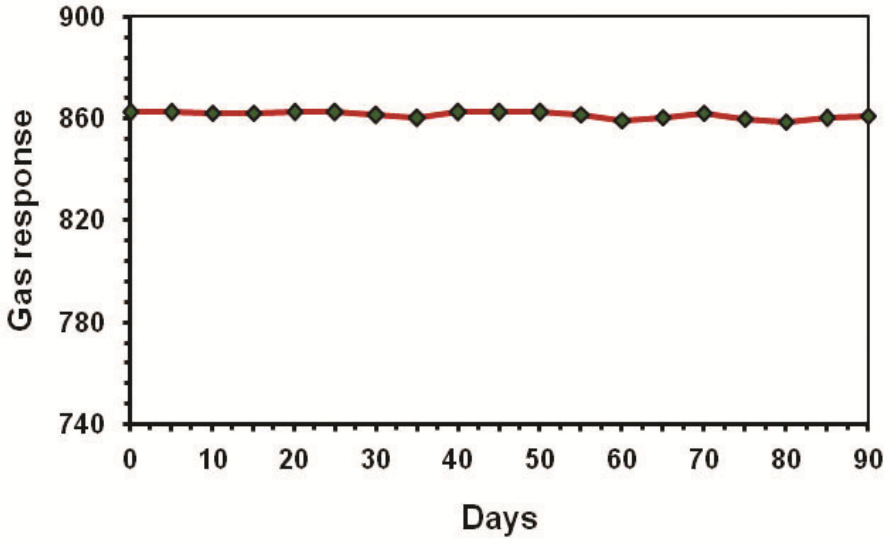


Fig. 9. Response of surface modified ST film for a period of three months.

5. Discussion

5.1. Surface Modified ST Film as H_2S Gas Sensor

Instead of using the mechanism of adsorption–desorption of oxygen for the detection of H_2S gas, the principle of formation of hetero-junction barriers in air ambient and their disruption on exposure to H_2S gas was employed. The total resistance of the CuO-modified ST thick film surface can be looked upon as the resultant of two resistances connected in parallel: (i) the resistance of the bulk portion of p-CuO/n-ST (Rb) and (ii) the surface resistance of (p-CuO/n-ST) hetero-junctions (Rs). The total resistance of the CuO-modified film was observed to be very high (~109 Ω) in air. Therefore, the values of the bulk resistance Rb and the surface hetero-junction resistance Rs would also be very high. It is well known that the resultant of two very high resistances connected in parallel is also high. Fig. 10 represents an equivalent resistance model for the CuO modified ST thick film in air and H_2S gas ambient.

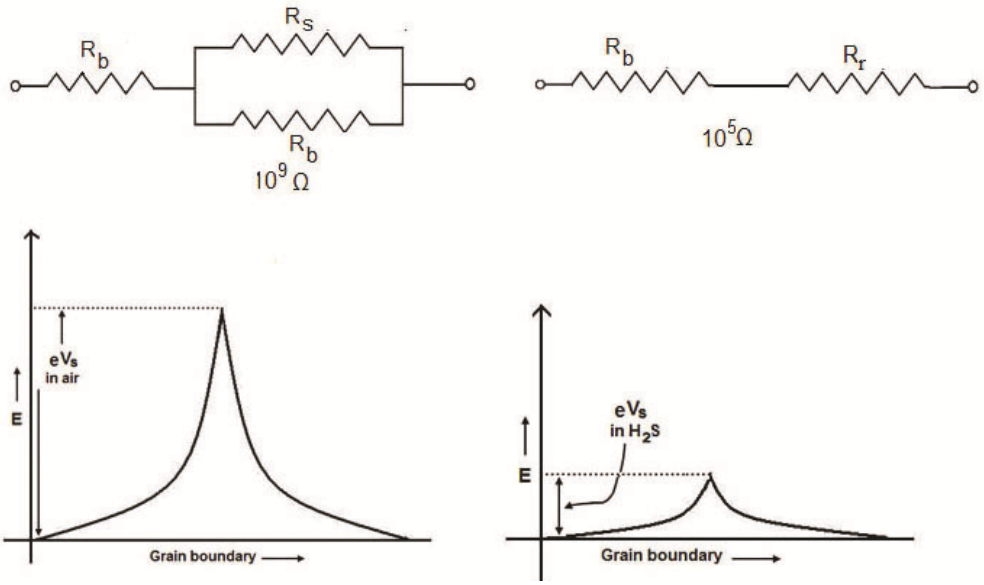


Fig. 10. Resistance model for the CuO modified ST thick film in air and H_2S gas ambient.

On exposure to the H_2S containing atmosphere, due to sulfurization, CuO would be converted into well conducting CuS [35]. This can be expressed by the following reaction:

$$CuO + H_2S \rightarrow CuS + H_2O \tag{2}$$

As can be seen CuS or Cu_2S are the product of the reaction and being a metallic will destroy the hetero-junction as well as the potential barrier, and new type of n-ST/metallic-CuS/Cu_2S (Rr) hetero-junction will be formed. The destruction of potential barrier results in sharp decrease in the electrical resistance.

This transformation of highly resistive p-CuO (p-CuO/n-ST) into well conducting Cu_2S (n-ST/Cu_2S/CuS) 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 Rb would remain as it was in case of air ambient and the surface resistance Rs would be very low in presence of the gas. It is well known that the resultant of a very high resistance connected in parallel with a very low resistance is very low.

When the sensor is brought back in the air ambient conditions, the CuS reacts with the oxygen via following reaction.

$$2CuS + 3O_2 \xrightarrow{Heat} 2CuO + 2SO_2 \uparrow \tag{3}$$

The extremely high response of the order of 10^4 was observed to 1 ppm H_2S. The high response (to ppm level of gas), high selectivity from mixed gases, fast response, moderate recovery time and the room temperature operation of the sensor are the main features achieved in the present investigation.

6. Summary

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

i. The H_2S gas sensors fabricated in this investigation were hetero-junction type.
ii. The room temperature sensing of H_2S gas was possible due to the heterocontact type of sensing mechanism.
iii. The optimum dipping time obtained for surface modification of the ST thick film is 20 min.
iv. The barrier height of n-ST/p-CuO hetero-junctions decreased markedly due to the chemical transformation of highly resistive p-CuO into well conducting CuS or Cu_2S, leading to a drastic decrease in resistance.
v. The sensors showed extremely high response toH_2S gas. The response was of the order of 10^4 to 1 ppm H_2S gas at room temperature.
vi. Surface properties of the films could be conveniently customized (without affecting bulk properties) by the surface CuO-modification method.
vii. The sensor was highly selective to a trace amount (1 ppm) of H_2S gas from thousand times concentrations of the other toxic gases.
viii. The sensor showed very rapid response (6 s) and recovery time (28 s) to H_2S gas.

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