

# Studies on H<sub>2</sub>S Gas Sensing Performance of Pure and Modified Strontium Titanate Thick Films

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**Abstract:** The AR grade powders of Sr (OH)<sub>2</sub> and TiO<sub>2</sub> precursors use to prepare the SrTiO<sub>3</sub> (STO) powder. STO powder is sintered at 800°C for 5h. The thixotropic pest is formulated for fabrication of STO thick films on glass substrate. The films were fabricated by using screen printing technique. The CuO-modified STO films were obtained by dipping technique. The STO films dipped into 0.01 molar aqueous CuCl<sub>2</sub> solutions for different time intervals. These CuO-modified films were fired again at 500°C for 30 min. The films are proposed for the characterization. The pure and modified films were tested for different gases. The CuO-modified STO thick film (dipping time 10 min) gives highest response (930) at operating temperature 300°C to H<sub>2</sub>S gas for Cu doped STO and the (155) for Pure STO. Hence the synthesized sensor could be treated as H<sub>2</sub>S gas.

**Index Terms:** STO powder, Screen printing, Dipping Technique, Cu-STO, H<sub>2</sub>S Gas Sensors.

## I. INTRODUCTION

This Gas sensors based on semiconducting metal oxides are being used to cover a wide range of applications ranging from monitoring automobile exhaust gases, to flue-gas monitoring in incinerators, from monitoring air for toxic and explosive gases to special industrial applications (Kohl C.D.,1989). Gas sensors have a simple design which makes mass production feasible, as well as having the required sensitivity, the certain materials also have a high degree of ruggedness therefore they can be used in environments containing aggressive chemicals or operated over long period of time. The use of advanced sensor film preparations has resulted in considerable progress (Sberveglieri, G., ET AL.,1992). Because of the complex surface reactions, the surface sometimes undergoes a formation process. Gas sensitivity is only obtained on completion of this process. In practice, this means that the sensors have to be operated for a certain period before full

sensitivity is reached. Metal oxides react vigorously with the moisture in the air at such low temperatures (Reti, F., et al.,1994). Therefore, one has to cope with strong effects caused by humidity variations.

Metal-oxide gas sensors are commonly used in the monitoring of toxic pollutants and can provide the necessary sensitivity, selectivity and stability required (Arshak, K., et al.,2004). Such sensors find a range of application including the monitoring of traffic pollutants or food quality in specially designed electronic noses (Pirjola, L.et al.,2004). Commonly used oxides are tin oxide, zinc oxide, titanium dioxide, iron oxide, tungsten oxide. These materials have successfully been employed to detect a range of gas vapors, particularly ethanol, methanol, ammonia, hydrogen Sulphide (Rao, B.B.,2000; Sberveglieri, G.,2000; Neri, G.,2002; Noh, W.,2002). Thick film technology is often used to fabricate sensors and possesses many advantages, such as low cost, simple construction, small size and good sensing properties (Ryeol, S., et al.,2002). In addition, this approach provides reproducible films consisting of a well-defined microstructure with grains and grain boundaries that can be studied easily.

Hydrogen sulfide (H<sub>2</sub>S) is most famous toxic gas because of bad smell can be perceived at a concentration lower than 0.1 ppm. H<sub>2</sub>S gas often produced in coal, coal oil or natural gas manufacturing. The maximum limit of safety exposure is 10 ppm, but high concentrations cannot perceive and they may cause instant paralysis. H<sub>2</sub>S has a density similar to air (Tamaki, 1998). Therefore, reliable sensors with low cost, low energy consumption having high sensitivity, selectivity and operable in sub ppm (ppb) range of H<sub>2</sub>S sensors are in high demand for environmental safety and industrial control purpose.

Research for new good gas sensing materials and the new properties of conventional materials has become an active research field. Concerning the detection of dilute H<sub>2</sub>S less than 1ppm, thick film sensors using CuO-SnO<sub>2</sub> (Yoo, D. J., et al.,1995; Jain, G. H., et al.,2006) is possible. The known H<sub>2</sub>S gas sensors BaTiO<sub>3</sub> (Jain, G. H., et al.,2006), (Ba<sub>0.87</sub> Sr<sub>0.13</sub>) TiO<sub>3</sub>-BST (Jain, G. H., et al.,2007), Cu-BST and Cr-BST (Patil, S. A., et al.,2007), have been reported to excellent performance. Heterocontact CuO modified SnO<sub>2</sub> (Patil, D. P., and Patil, L.A.,2006) and CuO-BSSST based H<sub>2</sub>S gas sensors (Jain, G. H., Patil, L. A.,2006) have been reported for the detection of ppb level of H<sub>2</sub>S gas at room temperature.

## II. EXPERIMENTAL

### A. Powder synthesis

The strontium titanate i. e. STO powder is prepared by mechanochemical process (MCP). The AR grade powders of Sr (OH)<sub>2</sub> and TiO<sub>2</sub> are ball milled to mix thoroughly, followed by sintering at 800°C for 5h. The fine-grained powder was obtained by conventional ball milling for 2h. The repeated deformation, fracturing, and cold welding of powder particles (in MCP) increases the area of contacts between the sintering the material particles due to decrease in particle size and allows the surface formed to come continually into contact. This permits the reaction to continue without the necessity for diffusion through the product layer. As a result, chemical reactions that normally need high temperature would take place at lower temperature during milling without any external heating.

### B. Thick film preparation and surface modification of films

The thixotropic paste was formulated by mixing the fine powder of STO with solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl carbitol acetate to organic part was kept 75:25 in formulating the paste. The STO films were screen printed in desired pattern on glass substrate followed by firing at 500°C for 30 min. The CuO-modified STO films were obtained by dipping technique. The STO films dipped into 0.01 molar aqueous CuCl<sub>2</sub> solutions for different time intervals. These CuO-modified films were fired again at 500°C for 30 min. The CuCl<sub>2</sub> would be converted into CuO after firing the films.

## III. MATERIAL CHARACTERIZATION

### A. Thick film preparation and surface modification of films

The structural property of the powder was studied using a Rigaku model DMAX-2500 X-ray diffractometer (XRD) with CuK $\alpha$  radiation, having  $\lambda=1.5406 \text{ \AA}$ . Fig.1 shows X-ray diffractogram of screen-printed STO thick films fired at 500°C.

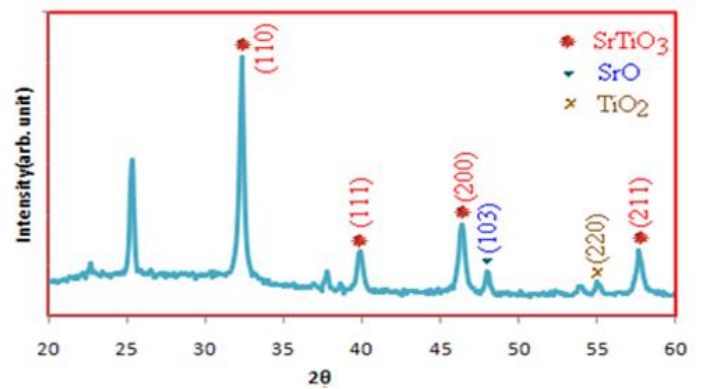


Fig.1 X-ray diffractogram of the STO thick film.

The XRD analysis revealed that the material is polycrystalline in nature with cubic perovskite phases. The peak positions (110), (111), (200), (211) corresponds to STO, (103) corresponds to SrO and (220) corresponds to TiO<sub>2</sub> (ASTM Data Manuals, pp.164,486,657). The films show presence of SrTiO<sub>3</sub>, SrO and TiO<sub>2</sub> phases. The precursor was not completely transformed into single phase STO at 800°C.

The microstructure and chemical compositions of the films were analyzed using scanning electron microscope (SEM, JEOL JED 2300LA). The sensing performance of the sensors was examined using a 'static gas sensing system' explained by (Rajendrakumar A. et al.,2017).

### B. Microstructural analysis-SEM

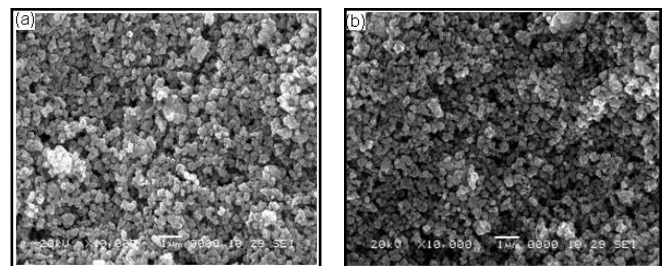


Fig.2 (a)

Fig. 2 (b)

Fig.2 SEM images of (a) pure STO (b) CuO- modified STO (10 min)

Fig 2(a) depicts SEM image of pure (unmodified) STO thick film fired at 500°C. Fig. 2(b) is the SEM image of the CuO-modified STO film dipped for 10 min. It is clear from the figure that it is comparatively less porous and grains are agglomerated. Effective surface to volume ratio would be decreased and a smaller number of oxygen ions would be adsorbed. The micrograph appears to consist of a number of small particles distributed uniformly around the large grains. The smaller particle may be attributed to the CuO grains and larger to STO. The film seems to be highly porous with a large effective area for oxygen adsorption. The smaller grain sizes have a larger specific area and as a result, high sensitivity to H<sub>2</sub>S gas. This modified film (10

min) is observed to be most sensitive and selective to H<sub>2</sub>S gas.

C. Quantitative elemental analysis of unmodified and CuO-modified STO films

Table I. Elemental analysis of unmodified and CuO-modified STO films

Element t Wt %	Dipping time (min)				
	(Pure)	10	20	30	60
Sr	29.9 6	30.9 3	31.9 4	31.8 2	32.4 0
Ti	35.4 6	34.0 9	33.8 8	35.9 6	35.9 9
O	34.5 8	34.9 4	33.9 9	31.6 9	31.0 0
Cu	---	0.04	0.19	0.53	0.61

Stoichiometric wt % of Sr, Ti and O in STO are 25.77, 60.12 and 14.11 respectively. Elemental analysis showed that, the wt % of Sr, Ti and O in STO are not as per the stoichiometric proportion, and all samples were observed to be the Ti deficient and excess in oxygen (Table 1). The film dipped for 10 min was observed to be relatively more oxygen rich than other films. Quantitative elemental analysis of unmodified and CuO-modified STO films.

D. Electrical properties

1) I-V characteristics

Fig.4 depicts the I-V characteristics of unmodified and CuO-modified STO films. It is clear from the approximately symmetrical I-V characteristics and the linearity in the graph indicates the ohmic nature of silver contacts. The resistance of 60 min is smaller in among all modified films.

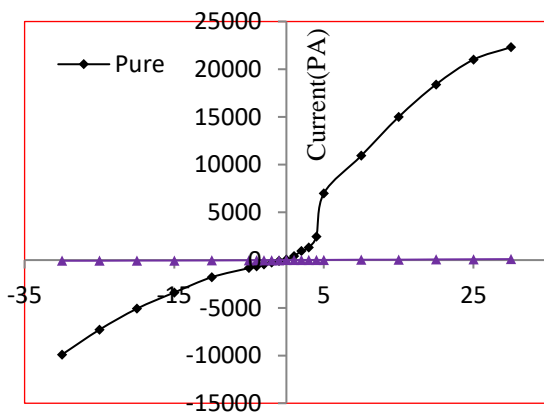


Fig. 3 I-V characteristics of pure and modified STO thick films

Fig3 depicts the I-V characteristics of unmodified and CuO-modified STO films. It is clear from the approximately symmetrical I-V characteristics and the linearity in the graph indicates the ohmic nature of silver contacts. The resistance of 10

min is smaller in among all modified films.

2) Electrical conductivity

Fig.4 represents the variation of log of conductivity ( $\sigma$ ) with temperature for the pure and modified samples. The nonlinearity of the electrical conductivity-temperature profiles of the samples reveals the semiconducting nature of pure and CuO modified STO. The conductivity of CuO modified samples is larger than pure STO film.

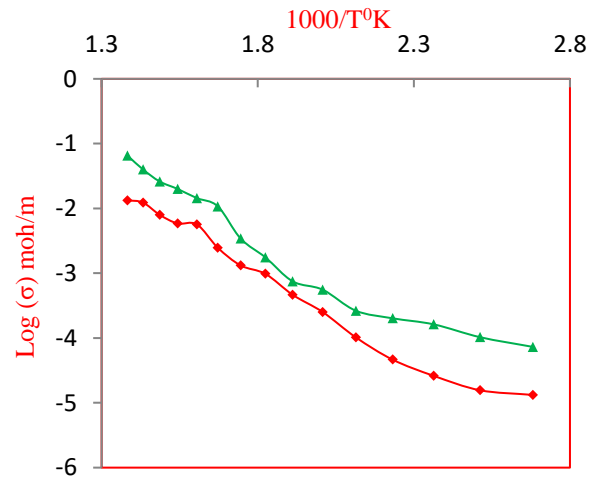


Fig.4 Conductivity- temperature profile of pure and modified STO films

The conductivity of sample modified for 10 min is largest of all in gas ambient. The semiconducting nature may be attributed to oxygen deficiencies in STO. CuO modification of STO has enhanced the electrical conductivity. This may be due to the bridging of intergranular gaps between STO particles by small particles of CuO segregated around the grain boundaries of STO.

E. Selectivity of H<sub>2</sub>S against various gases

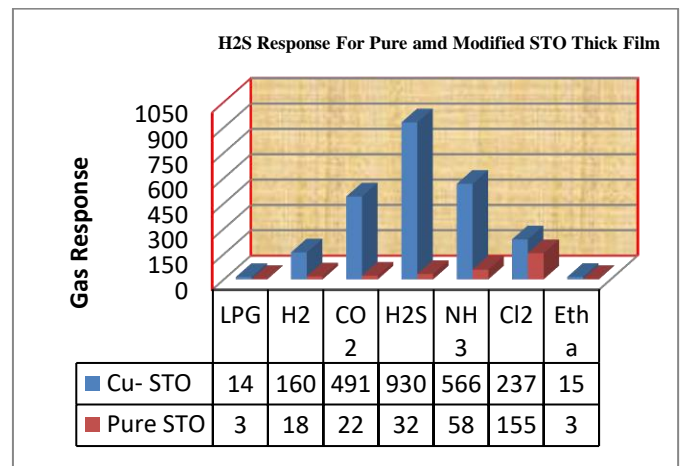


Fig.5 Histogram of selectivity of unmodified STO.

Fig.5 depicts the selectivity profile of pure STO film at operating temperature 400°C. It is noted that the sensor showed

poor selectivity of H<sub>2</sub>S than for Cl<sub>2</sub> and LPG. The selectivity of H<sub>2</sub>S is good than other gases. Thus, sensor is highly selective to H<sub>2</sub>S gas.

#### IV. CU-STO THIN FILM FOR H<sub>2</sub>S GAS SENSING

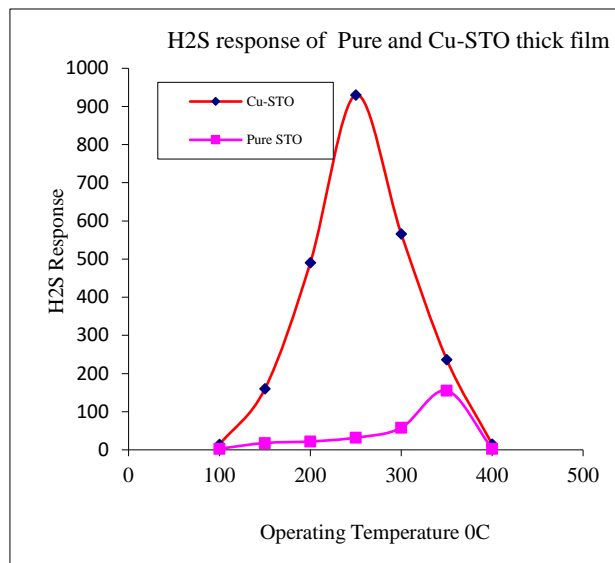


Fig.6 shows comparison of gas response to pure and Cu-STO.

It shows that the variation in sensitivity to H<sub>2</sub>S with operating temperature. It is noted from graph that the response to H<sub>2</sub>S goes on increasing with increasing the operating temperature, reaches to the maximum (930) at 250°C and decreases with further increase in operating temperature. Response to a gas generally related to the number of oxygen ions adsorbed on surface of the film. If surface chemistry of the film was favorable for adsorption, response and selectivity would enhance. In case of pure STO, oxygen-adsorption seems to be poor which may the result in poor response. To improve the sensing performance of STO, it was modified by adding CuO on its surface by dipping technique.

It is observed from Fig.6 that the CuO-modified STO thick film (dipping time 10 min) gives highest response (930) at operating temperature 300°C to H<sub>2</sub>S gas for Cu doped STO and the (155) for Pure STO. Hence the synthesized sensor could be treated as H<sub>2</sub>S gas.

Hence surface modification enhances the gas response with reducing the operating temperature. Therefore, the surface cuprication of STO is more effective to H<sub>2</sub>S gas sensing than unmodified STO.

#### V. DISCUSSION

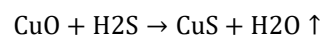
##### A. CuO-modified STO as H<sub>2</sub>S gas sensor

In presence of reducing agent, solids are known as to give up lattice oxygen (be reduced-ion exchange) and in presence of oxygen they become oxidized. This semiconductor could be used as gas sensor on redox principle. The ion exchange between a gas

and a semiconductor could have a strong influence on the conductivity of the semiconductor. WO<sub>3</sub> has been reported to be completely converted to WS<sub>2</sub> by a few torr of H<sub>2</sub>S resulting in increase in conductivity (Roy Morrison, 1982).

Ion exchange mechanism between CuO and H<sub>2</sub>S gas would be the reason behind the change in conductance. When H<sub>2</sub>S gas is exposed on CuO modified STO film surface, the strong affinity of sulfur (electronegativity = 2.44) to the Cu atoms weakens the sulphur-hydrogen bond and facilitates dissociation to an S<sup>2-</sup> or an SH<sup>-</sup> ion and two or one H<sup>+</sup> ions, CuO would be converted into well conducting CuS.

It is well known that additive lowers the activation energy of the reaction. The lowering of the activation energy can be described by simple illustrations:



Ion exchange in above equation requires little energy. H<sub>2</sub>S could easily be dissociated in presence of CuO. To dissociated H<sub>2</sub>S in absence of CuO would require large energy input. Larger the dissociation energy required to dissociate H<sub>2</sub>S would be great extent removed (lowered) by using CuO misfits as activator.

##### B. Effect of dipping time on CuO dispersion and sensitivity

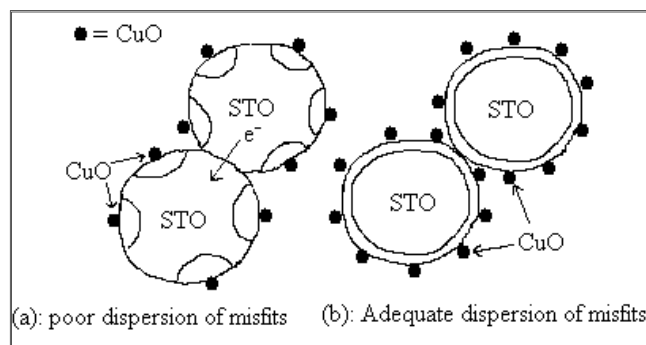


Fig. 7. Dispersion of additive

Figure 16 illustrates the effect of dispersion of surface additive on the film conductivity. Uniform and optimum dispersion of an additive dominates the depletion of electrons from semiconductor. Oxygen adsorbing on additive (misfit) removes electrons from additive and additive in turn removes electrons from the nearby surface region of the semiconductor and could control the conductivity.

For optimum dipping time (10 min), the number of CuO misfits would be optimum and would disperse uniformly covering the complete film surface (Figure 7). Adequate dispersion of CuO misfits (60 min) on film surface would produce depletion region on the grain surfaces and conductivity could be monitored systematically. The film conductivity would be very low in air and very high on exposure of H<sub>2</sub>S gas (due to conversion of CuO into

CuS) and therefore, the sensitivity would be enhanced.

For dipping time smaller than the optimum, the number of CuO misfits would be smaller, their dispersion would be poor and the depletion regions would be discontinuous and there would be the paths to pass electrons from one grain to another (Fig. 7). Due to this, the initial conductance (air) would be relatively larger and in turn, sensitivity would be smaller.

#### CONCLUSION

The conclusions are summarized as follows:

1. Surface modification by dipping process was employed to modify the surface of the film and not the bulk portion of the base material STO.
2. The precursor was not completely transformed into single phase STO at 800°C.
3. The CuO-modified STO was observed to be semiconducting in nature and showed a negative temperature coefficient of resistance.
4. The sensing mechanism of the CuO-modified STO is surface-controlled mechanism (adsorption/desorption of oxygen). The oxidation of sulphides (CuS) and the reduction of CuO have also boosted the gas response.
5. Copper oxide formed misfits on the surface region. The larger the misfits on the surface, the larger would be the number of oxygen ions adsorbed on the surface, leading to high resistance.
6. The surface cuprication facilitated adsorption of a large number of oxygen ions on the surface, which could immediately oxidize the exposed H<sub>2</sub>S gas, leading to enhance the sensitivity.
7. Surface modified STO was observed to be more sensitive to H<sub>2</sub>S gas than unmodified STO.
8. The modified STO was observed to be highly selective to H<sub>2</sub>S gas.
9. The repeatability and reproducibility of the sensor was observed to be improved through the cuprication process.

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