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## RESEARCH ARTICLE

### SrO<sub>2</sub> MODIFIED NANOSTRUCTURED SnO<sub>2</sub> THICK FILMS AS H<sub>2</sub>S GASENSORSOPERABLE AT ROOM TEMPERATURE

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#### ABSTRACT

Thick films of bulk tin oxide powder were observed to be less sensitive to polluting, hazardous and inflammable gases. So, nanostructured SnO<sub>2</sub> powder was synthesized by disc type ultrasonicated microwave assisted centrifuge technique. Thick films of nanostructured pure SnO<sub>2</sub> powder were fabricated by screen printing technique. These films were surface functionalized by SrCl<sub>2</sub>·6H<sub>2</sub>O for different intervals of time followed by firing at 450°C for 30 min. The surface morphology, chemical composition, crystal structure, electrical and gas sensing performance of the unmodified and surface functionalized nanostructured SnO<sub>2</sub> powder by SrO<sub>2</sub> have been investigated by FESEM, E-DAX, XRD, etc.

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## INTRODUCTION

SnO<sub>2</sub> has been found to be the most promising material to detect the toxic and hazardous gases (Patil, 2006). It has been studied that modified SrO<sub>2</sub> was used as a gas-sensing element. SrO<sub>2</sub> activated SnO<sub>2</sub> was reported to be a gas sensor. The biogenic decomposition of sulfur containing organic matter occurs both on the land and in the sea. The major sulfur compounds generated in biogenic decomposition is hydrogen sulfide (H<sub>2</sub>S). H<sub>2</sub>S is one of the major pollutants, hazardous and toxic in nature, which is also released from industries and laboratories. The primary standard of sulfur oxides promulgated to protect human health is few ppm. However, sulfur oxides alone produce no acute response in human up to 1.0 ppm. But if sulfur oxides condense on smoke or particulate matter, it can be inhaled quite deeply into the respiratory track causing infection to respiratory track. This makes breathing difficult and strains the victim's heart.

Higher concentrations of gases containing sulfur leads to bronchitis and lung cancer. These gases containing sulfur destroy plant cells and interfere with chlorophyll synthesis. Leaf blotching and reduction in crop yield occur even at the concentration less than 1 ppm. The exposure of gases containing sulfur can also affect the nonliving things viz. stone leprosy, increase the rate of corrosion of metals and retardation of drying of paints, etc. (Patil, 2011). The purpose of the present work is to develop the H<sub>2</sub>S sensor by modifying SnO<sub>2</sub> thick films, which could be able to detect the trace amount of H<sub>2</sub>S. It was studied that the gas sensing performance of the materials can be improved by incorporating few additives into the base material and/or surface activation of the thick films (Patil, 2007; Patil, 2006; Patil, 2007).

## MATERIALS AND METHODS

### Synthesis of nanostructured SnO<sub>2</sub> powder

Nanostructured SnO<sub>2</sub> powder was synthesized by disc type ultrasonicated microwave assisted centrifuge technique, by hydrolysis of AR grade tin chloride in aqueous-alcohol solution.

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An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol in the ratio of 1:1. This solution was then mixed with aqueous solution of tin chloride with the alcohol to water ratio as 1:1. The special arrangement was made to add drop wise aqueous ammonia (0.1ml / min.) with constant stirring until the optimal pH of solution becomes 7.9. After complete precipitation, the hydroxide was washed with distilled water until chloride ions were not detected by AgNO<sub>3</sub> solution. Then the hydroxide in a glass beaker was placed in a microwave oven for 10 minutes with on-off cycles, periodically. The dried precipitate was ground by agate pestle-mortar and annealed in a muffle furnace at 450°C for 3h. The phase purity and degree of crystallinity of SnO<sub>2</sub> powder were monitored by XRD analysis.

### Thick Film Fabrication

The synthesized ultrafine powder of pure SnO<sub>2</sub> was calcined at 450°C for 3 h in air and reground to ensure sufficiently fine particle size. The thixotropic paste (Shriver and Atkins, 2003), (Pokhrel *et al.*, 2003; Patil, 2006), was formulated by mixing the synthesized nanostructured powder of pure SnO<sub>2</sub> with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpeneol. The ratio of inorganic to organic part was kept as 80:20 in formulating the paste. The thixotropic paste was screen printed on the glass substrates in the desired patterns. The size of the film prepared is 4 mm x 9 mm. Films prepared were dried at 80°C under an IR lamp, followed by firing at 500°C for 30 min in air ambient.

### Surface Functionalization of Thick Films

Surface functionalization (Patil, 2006), (Chung *et al.*, 1994; Chaudhary *et al.*, 1999), of thick films of pure SnO<sub>2</sub> powder was achieved by dipping them in to a 0.01 M aqueous solution of strontium chloride for different intervals of time such as 5 min, 15 min, 30 min and 45 min and dried at 80°C under an IR lamp, followed by firing at 500°C for 30 min in ambient air. The particles of strontium chloride dispersed on the film surface would be transformed to strontium oxide (SrO<sub>2</sub>) during firing process. Thus, the sensor elements with different mass percentage of SrO<sub>2</sub> incorporated in to thick films of pure SnO<sub>2</sub> were prepared. Silver contacts were made by vacuum evaporation for electrical measurements and monitoring the gas sensing performance of thick films.

## RESULTS AND DISCUSSION

### Materials characterizations

#### Structural properties (X-ray diffraction studies)

Fig. 1 shows the X-ray diffract gram of the SrO<sub>2</sub> activated (for 45 min) SnO<sub>2</sub>, which was observed to be the most sensitive film to H<sub>2</sub>S at room temperature (30°C). The observed peaks are matching well with JCPDS reported data of SnO<sub>2</sub>. The sharp peaks of the XRD pattern correspond to SnO<sub>2</sub> material and are observed to be polycrystalline in nature. No peaks corresponding to SrO<sub>2</sub> may be due to its very small mass% dispersed on the surface of SnO<sub>2</sub>.

The crystals show anisotropy because different directions within the repeating pattern interact differently with incident radiations. The average crystallite size was determined from Scherer's formula and was found to be in the range of 18-32 nm.

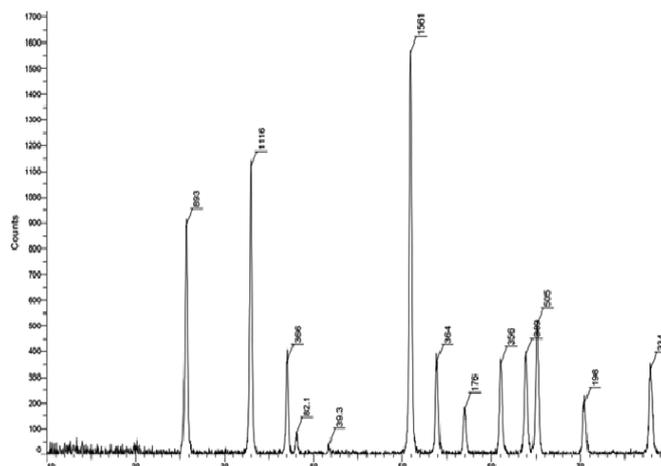


Fig. 1. XRD of SrO<sub>2</sub>-modified (45 min) SnO<sub>2</sub> fired at 550°C for 24 h

### Micro structural analysis (SEM)

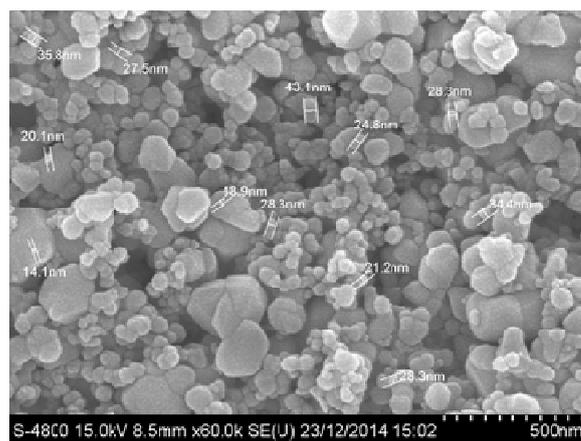


Fig. 2 (a). SEM Micrograph of unmodified SnO<sub>2</sub> thick film

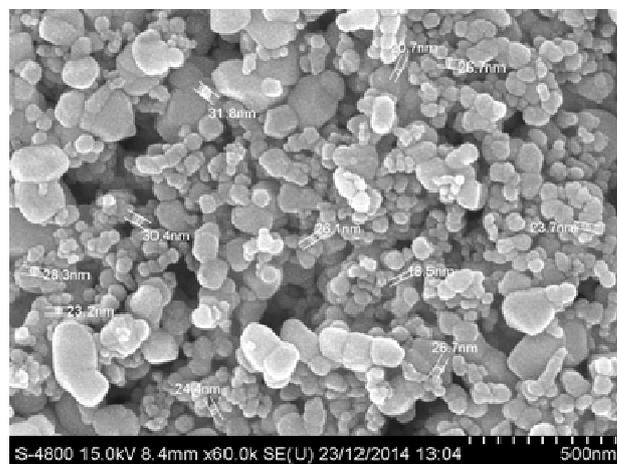


Fig. 2 (b). SEM Micrograph of SrO<sub>2</sub>modified (45') SnO<sub>2</sub> thick film

Fig. 2 (a) depicts the scanning electron micrograph of pure SnO<sub>2</sub> powder having randomly distributed grains with larger size and shape distribution. Fig. 2 (b) depicts the scanning electron micrograph of SrO<sub>2</sub> activated SnO<sub>2</sub> film (45 min), showing SrO<sub>2</sub> grains are associated with the SnO<sub>2</sub> grains. SrO<sub>2</sub> grains may reside in the intergranular regions of SnO<sub>2</sub>. The effective surface area was thus, expected to increase largely. This may be the reason of giving maximum gas response of this film. The entire SnO<sub>2</sub> films dipped for larger times were observed to be masked as SrO<sub>2</sub> grains fully cover the film. Thus reducing the effective surface area. The gas molecules would not reach the interstitial sites of SrO<sub>2</sub>-SnO<sub>2</sub> grains. The surface only possesses the molecules of SrO<sub>2</sub>.

### Quantitative elemental analysis-EDAX

Table 1. Elemental analysis

| Mass %                              | Dipping time |       |        |        |        |
|-------------------------------------|--------------|-------|--------|--------|--------|
|                                     | Pure         | 5 min | 15 min | 30 min | 45 min |
| O                                   | 63.78        | 60.74 | 62.99  | 67.85  | 52.03  |
| Sn                                  | 36.22        | 39.12 | 36.33  | 31.22  | 46.92  |
| Sr                                  | 00           | 0.13  | 0.18   | 0.93   | 1.05   |
| SrO <sub>2</sub> + SnO <sub>2</sub> | 100          | 100   | 100    | 100    | 100    |

Stoichiometrically expected mass % of Sn and O in SnO<sub>2</sub> are 78.77 and 21.23, respectively. It is clear from EDAX that the mass % of Sn and O in each samples are not as per the stoichiometric proportion and all samples are observed to be the oxygen deficient, leading to the semiconducting nature to SnO<sub>2</sub>. It is also clear from the above study that the mass percentages of SrO<sub>2</sub> go on increasing with the dipping time, reach to their respective maxima and then decrease with further increase in dipping time.

### Thermal and Electrical properties of the sensor

#### Conductivity profile

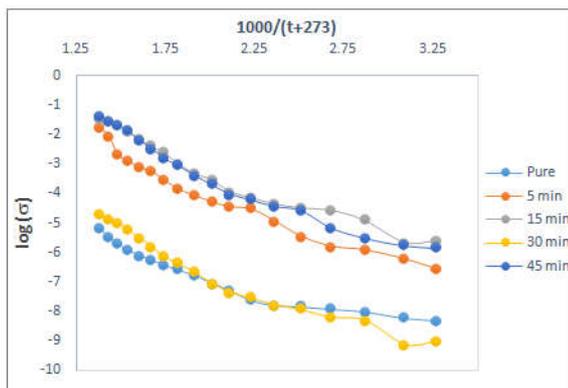


Fig. 3. Conductivity profile for pure and SrO<sub>2</sub> modified SnO<sub>2</sub>

Fig. 3 shows the d.c. electrical conductivity profile of the plots of  $\log(\rho)$  vs  $1000/T^{\circ}\text{K}$  up to 450°C without any break or inflexion. Silver contacts are used at both the ends of the films for proper contact and connections. The results of electrical measurements show an increase in conductivity (i.e. decrease in resistivity) with increasing temperature proving the “negative temperature coefficient (NTC) of resistance” for the samples to be studied.

Increase in temperature of the sample will help the trapped charges to be liberated and participate in the conduction process, with the result of decrease in the resistivity.

### I-V characteristics

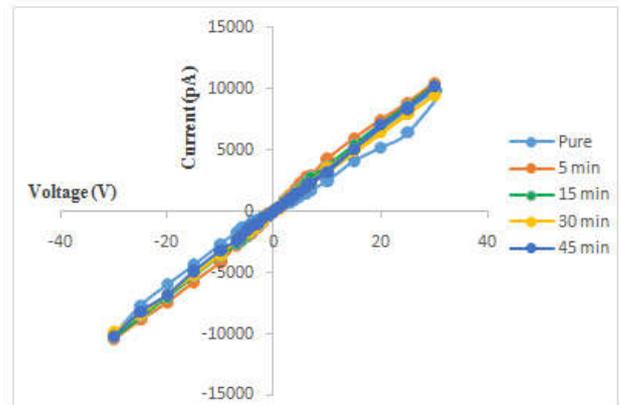


Fig. 4. I-V characteristics for pure and SrO<sub>2</sub> modified SnO<sub>2</sub>

Fig. 4 depicts the I-V characteristic which was found to be symmetrical in nature indicating the ohmic type of contacts.

### Gas sensing performance of the sensor

#### Details of static gas sensing system

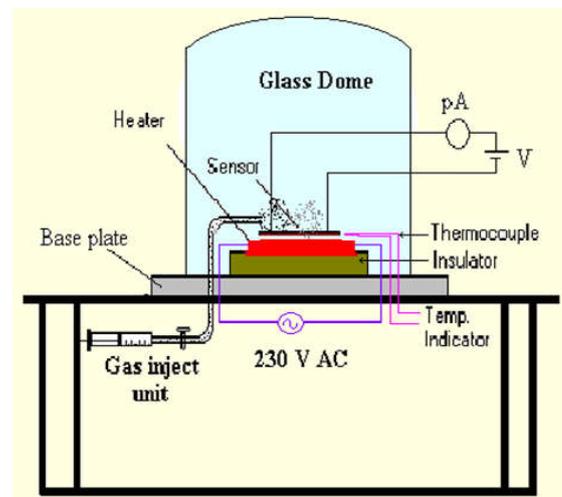


Fig. 5. Block diagram of static gas sensing system

Fig. 5 represents “static gas sensing system” to examine the sensing performance of the thick films. There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperature. The current passing through the heating element was monitored using a relay with adjustable ON and OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system

was achieved by injecting a known volume of test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and current was measured by a digital pico-ammeter. Air was allowed to pass into the glass dome after every H<sub>2</sub>S gas exposure cycle.

### Measurement of the gas response

Fig. 6 depicts the variation of gas response with operating temperature of pure SnO<sub>2</sub> thick film for 1000 ppm H<sub>2</sub>S gas. It is clear from figure that SrO<sub>2</sub> modified SnO<sub>2</sub> at 45 min dipping time gives better response to 100 ppm H<sub>2</sub>S gas at room temperature (30°C). In case of pure SnO<sub>2</sub>, oxygen adsorption on the surface of the film seems to be poor which may be the result of poor response to reducing gases. To improve the sensing performance of pure SnO<sub>2</sub> thick film, it is essential to modify its surface.

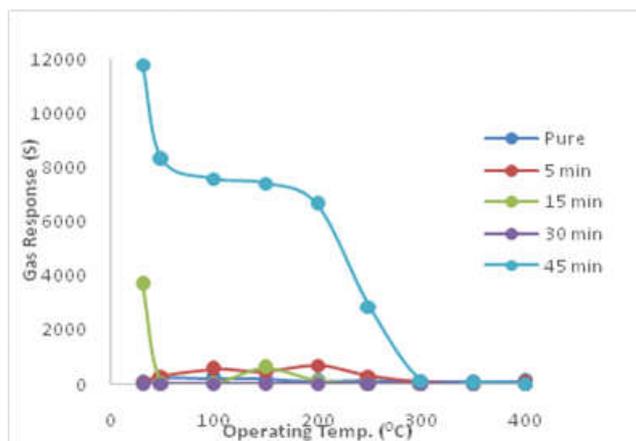


Fig. 6. Variation of gas response with operating temp (°C)

Response of the sensor for the particular gas can be defined as the ratio of the change of conductance of the sample upon exposure to the gas to the conductance in air ambient. The gas response (S) can be written as:

$$\text{Gas Response} = \frac{G_g}{G_a} = \frac{\Delta G}{G_a}$$

where G<sub>a</sub> = conductance in air and G<sub>g</sub> = conductance in a target gas.

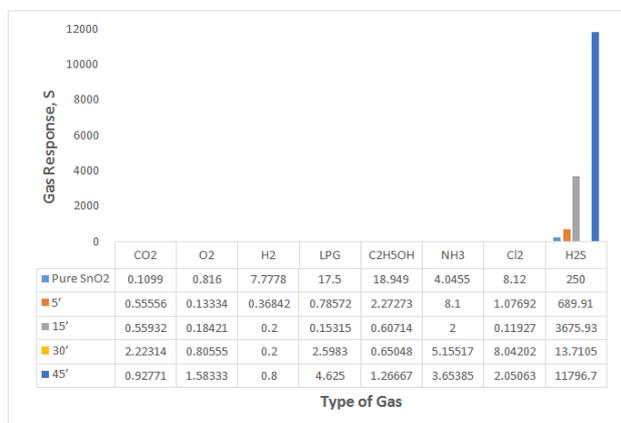


Fig. 7. Selectivity of the sensor to H<sub>2</sub>S gas

### Selectivity

Selectivity or specificity is defined as, 'the ability of a sensor to respond to a certain gas in the presence of other gases.' It is observed from the fig. 7 that SrO<sub>2</sub> modified SnO<sub>2</sub> gives better selectivity to H<sub>2</sub>S gas. But pure SnO<sub>2</sub> has least selectivity against different gases. This is the main drawback of pure SnO<sub>2</sub> thick film sensor.

### Response and Recovery time

Response time (RST) is defined as the time required for a sensor to attain the 90% of the maximum increase in conductance after exposure of the test gas. Recovery time (RCT) is the time taken to get back 90% of the maximum conductance in air. The SrO<sub>2</sub> modified nanostructured SnO<sub>2</sub> thick films were found to have very good response time as well as good recovery time to the H<sub>2</sub>S gas.

### Conclusion

- Pure tin oxide was almost less sensitive to H<sub>2</sub>S.
- Among various additives tested, SrO<sub>2</sub> in SnO<sub>2</sub> is outstanding in promoting the H<sub>2</sub>S sensing.
- Surface modification by dipping is one of the most suitable methods of modifying the surface.
- The sensor has good selectivity to H<sub>2</sub>S gas against LPG, NH<sub>3</sub>, O<sub>2</sub>, CO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH.
- The sensor has quick response time and also quick recovery time to the H<sub>2</sub>S gas.

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