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# Growth and Characterization of CuO-doped $SnO_2$ Thin Films Prepared by Sequential Electron Beam Evaporation Method for Application as Hydrogen Sulfide Gas Sensor.

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## ABSTRACT

This paper deals with the preparation and characterization of CuO-$SnO_2$ thin films prepared by sequential electron beam evaporation technique. The results obtained were outstanding in terms of sensitivity of these films towards detection of hydrogen sulfide gas, proving that CuO is a good promoter of hydrogen gas sensitivity of $SnO_2$ . The resistance of the thin films showed a decreasing trend indicating rupture of pn junctions while the I-V characteristics of these films were linear in nature showing that the contacts are ohmic. The best sensitivity values were obtained for film temperature of 160°C. These films hold promise for use in industrial sector where the hydrogen sulfide gas is widely used.

**Key Words:** $H_2S$, CuO, Sensitivity

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## INTRODUCTION

A variety of toxic gases are emitted by the Industries, vehicles, natural calamities and different types of combustion processes into the atmosphere. Out of these gases, hydrogen sulfide is one such toxic and inflammable gas which occurs naturally on earth in oilfields and saltmines and marshes [1]. It is used in large amounts by various chemical industries and heavy water plants for growing technologically important crystals of ZnS by chemical vapor deposition (CVD) technique and as a process gas for the production of heavy water by dual temperature exchange reaction [2]. The human nose is extraordinarily sensitive to $H_2S$ gas and can detect $H_2S$ concentrations as low as 0.02 ppm in air. The occupational exposure limit to $H_2S$ gas is 10 ppm for 8 hours. Therefore, a hydrogen gas sensor capable of detecting $H_2S$ gas when present at few ppm and preferably sub ppm levels in air is urgently needed.

It has been reported in literature that CuO is found to have an outstanding promoter action for SnO2 to detect hydrogen sulfide gas [3].

Thick films of $SnO_2$ doped with about 5 % CuO were found to have very high sensor signal of ~ 35000 for 50 ppm of $H_2S$ in air at sensor operating temperature of 200 °C. The sensor signal, G, is defined as

$$G = R_a / R_g = I_g / I_a \qquad \ldots(1)$$

Where $R_a$ and $R_g$ are the sensor resistances in air and $H_2S$ – air mixture while $I_a$ and $I_g$ are the corresponding sensor currents in air and $H_2S$- air mixture.
The sensitivity, S, is defined as " the derivative of the sensor signal, G, w.r.t C at constant temperature, T.

$$S = (\partial G / \partial C)_T \qquad \ldots(2)$$

These thick films showed switching like recovery in 60 seconds while the sensor response was nearly 15 minutes. Moreover, the sensor response slowed down when $H_2S$ was more dilute than 20 ppm. $SnO_2$ films doped with CuO and prepared by spin coating $SnO_2$ sol solution showed small improvement in the $H_2S$ sensing properties [4,5].

Subsequently, various authors reported the fabrication of the CuO-doped $SnO_2$ thin films by a number of different techniques such as Microwave Plasma Chemical Vapor Deposition (MPCVD), Spray Pyrolysis, Low Vacuum Evaporation, RF sputtering, Laser ablation and High Vacuum Thermal Evaporation [6-9].

In the present study, we report the deposition and characterization of CuO-doped $SnO_2$ thin films prepared by simple technique such as sequential electron beam evaporation and their oxidation in the oxygen gas atmosphere. These films were tested for hydrogen sulfide gas sensitivity at different gas concentrations and sensor operating temperatures.

## EXPERIMENTAL DETAILS

### Sequential Electron Beam Evaporation Technique

The deposition of Sn and Cu metals was done sequentially in a chamber by e- beam evaporation technique. The deposition was carried out on high alumina disks in a vacuum pressure of ~ $10^{-6}$ Torr. Deposition was carried out simultaneously on a number of alumina disks kept on a substrate holder, which was kept about 60 cm from the source. A large source to substrate distance ensured good uniformity of film thickness on all the substrates. The film thickness could be continuously monitored by a quartz crystal oscillator. No substrate heating was done during the entire deposition process. On all the substrates, we first deposited a 2200 Å thick Sn film followed by 80 Å or 103 Å thick Cu layer on top of it. This ratio of the Sn and Cu thicknesses resulted in Cu content of either 3.5 or 5 % by weight in the final thin film element. A 1200 Å tin layer was coated on top with 44 Å thick Cu layer so as to result in the final film of thickness of 1244 Å. The metallic bilayers obtained by sequential e-beam evaporation of Sn and Cu metals was then annealed in the temperature range of 600-800 °C in a tube furnace under oxygen flowing conditions for 8 hours.

### Characterization of CuO-$SnO_2$ Thin Films

### Measurement of Gas Sensing Properties

For studying the electrical conductivity of thin films two contacts were made on top of the films with a gap of about 4 mm between them using high conductivity gold paste. Two aluminum wires were bonded onto these contacts with gold paste. The sensor element was placed in a special assembly made out of aluminum, which could also heat the $Al_2O_3$ disks from the lower side upto a maximum temperature of 250 °C. This entire assembly had a volume of about 35 $cm^3$ and was grounded to provide electromagnetic shielding, necessary to measure small currents in the thin film sensor elements that were placed inside. The sensor assembly was placed in a polycarbonate desiccator, which served as a test-chamber. The total volume of the chamber was 11 liter. The test chamber could be opened into two equal halves by lifting its upper part. The upper half of the chamber had a provision for introducing hydrogen sulfide and other gases using gas tight micro liter syringes. The lower half could be connected to a rotary pump and evacuated. The electrical resistance of thin films was measured using a two probe set up by applying 20 V across the film electrodes and measuring the current directly with an auto ranging digital pico ammeter connected in series with the thin film sensor element. To measure the sensitivity of the thin film elements, known volumes of $H_2S$ were introduced into the upper half of the test chamber with gas tight microliter syringes and changes in the current flowing through the thin film element were continuously monitored with an autoranging digital picoammeter. Time taken for the current to increase to its saturation value in the presence of $H_2S$ gas was taken as the 100 % response time. To measure the recovery time of the sensor element we removed the upper half of the chamber, allowing the surrounding air to rush into the lower, remaining half of the test chamber, containing the sensor assembly. The lower half of the chamber was also evacuated with a rotary pump to quickly remove remaining quantities of $H_2S$ gas. On the removal of $H_2S$ gas, the current flowing through the thin films decreased and time taken for it to restore to its value in air, was taken as the 100 % recovery time. For some of the films which showed a very long 100 % recovery , we defined another recovery time $T_{100}$ , which was defined as the time in which the current reduced to 1/100th to its starting value.

## RESULTS AND DISCUSSION

Fig. 1 shows the variation of the sensor resistance with the temperature of the sample prepared by reactive thermal evaporation technique having thickness of 3200 Å and CuO content of 3.5 % by weight and annealing temperature of 800 °C respectively. This thin film sample was semi-insulating in nature and had a very high resistance in the range of $10^{10}$–$10^{12}$ Ω in the temperature range of 120–200 °C.

Fig. 2 shows the variation of $H_2S$ sensor signal for this sample at four operating temperatures of 140, 160, 180 and 200 °C as a function of gas concentration. From the Figure it is clear that the $H_2S$ signal shows large values of ~ $10^6$ for a few ppm levels of $H_2S$ gas. Also the sensor signal saturates at high $H_2S$ gas concentrations and falls with increasing temperature. The sensitivity falls with increasing temperature and was as high as $4 \times 10^6$ at 140 °C for 50 ppm of gas. The 80 % response time at this operating temperature was about 1 minute and on removal of gas, time, $T_{100}$ , taken for the sensitivity to fall to 1/100 th of its starting value was ~ 4 minutes.

Fig. 3 shows the typical response and recovery plots for 10 ppm $H_2S$ gas at different operating temperatures. It is clear that this CuO–$SnO_2$ sensor element shows switching–like response to $H_2S$ at all four temperatures in about 2 minutes. Recovery on removal of $H_2S$ is slower but improves with increasing temperature. At 200 °C, sensor resistance recovers completely to its initial value in air in about 30 minutes.

Fig. 4 shows the I-V characteristics of a thin film sample prepared by sequential electron beam evaporation technique. This thin film sample had a thickness of 2280 Å, Cu content of 3.5 % and annealing temperature of 800 °C respectively. The linear variation of the sensor current with voltage shows that the gold paste makes ohmic contacts with CuO-$SnO_2$ surface. ppm.

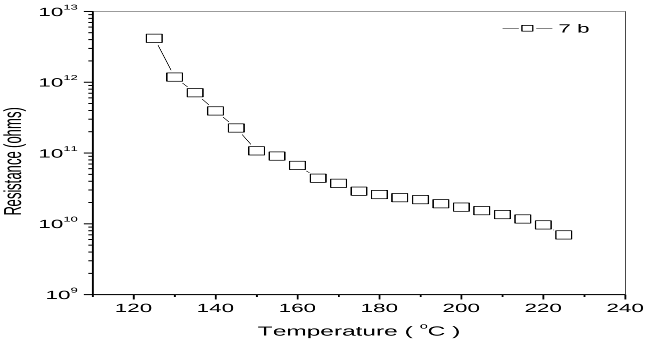

Figure 1: Variation of resistance of CuO-SnO$_2$ thin films with temperature in air

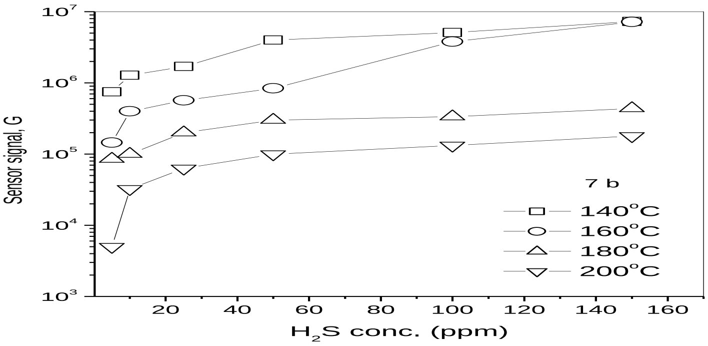

Figure 2: Sensitivity of CuO-SnO$_2$ thin films as a function of H$_2$S concentration and operating temperature

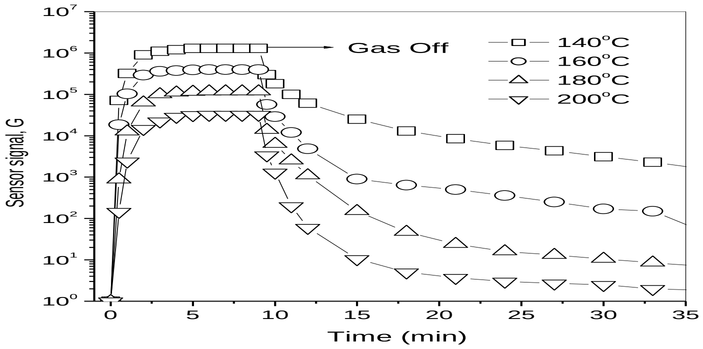

Figure 3: Typical response and recovery plots of sensor in 10 ppm of H$_2$S at different operating temperatures

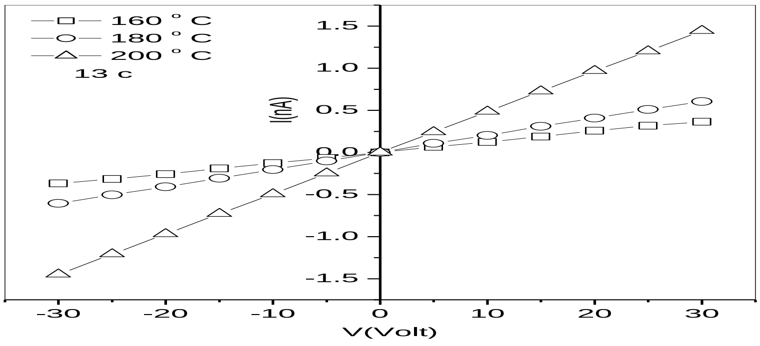

Figure 4: I-V curves for CuO-SnO$_2$ thin film element with gold paste electrodes at three operating temperatures of 160 °C, 180 °C and 200 °C

From the above discussion, it is concluded that a highly sensitive sensor capable of detecting hydrogen sulfide gas at ppm level can be prepared by simple and cost-effective technique such as sequential electron beam evaporation

## REFERENCES

[1] Elvers B, Hawkins S and Schulz G. Eds. Ullmann Encyclopedia of Industrial Chemistry (VCH, Weinheim, 1989;13:467.

[2] Elvers B, Hawkins S and Schulz G. Eds. Ullmann Encyclopedia of Industrial Chemistry (VCH, Weinheim, 1990:15; 55.

[3] Maekawa T, Tamaki J, Miura N and Yamazoe N. Chem Lett 1991;4:575

[4] Maekawa T, Tamaki J, Miura N and Yamazoe N. Sen Actuat 1992;B9:197

[5] Yoo DJ, Tamaki J, Park SJ, Miura N and Yamazoe N. Jpn J Appl Phys Part 2 1995;34:455.

[6] Manorama S, Devi GS and Rao VJ. Appl Phys Lett 1994;64:3163.

[7] Yuanda W, Maosong T, Xiuli H, Yushu Z and Guorui D. Sensors Actuators 2001;B.79: 187

[8] Tamaki J, et al. Yamazoe. Sen Actuat 1998;B.49:121.

[9] Gadkari SC, et al. Sahini Bhabha Atomic Research Center (BARC) Newsletter 2000;193:1.