Sensing Behavior Of CuO-Doped SnO_2 Thick Film Sensor For H_2S Detection

J.K. Srivastava, Amit Gupta, Anand A. Bhaskar

Abstract: The effect of CuO doping on the electrical resistance and the sensitivity of thick film gas sensors based on CuO-doped (1%, 2% and 5% by wt.) SnO_2has been investigated by us. A suitable gas sensor structure wasfabricated on 1˝x1˝ alumina substrate using thick film technology**.** The fabricated sensor's reaction with H2S gas (250 ppm-1000 ppm)was tested in the temperature range of 150- 350˚C. At 250˚C the sensor with 5% CuO doping was found to be most sensitive for H_2S gas .The electrical resistance and the sensitivity were increased by increasing the concentration of CuO. The substitution of Sn^{+4} by Cu^{+2} leads to the creation of oxygen vacancies. The increased oxygen deficiency is believed to be responsible for enhancing the resistance.

Key words: gas sensor, thick film, screen printing, sol-gel, sensitivity, tin oxide.

1. Introduction

An increased concern over safety in civilian homes and industrial settings has generated great interest in semiconductor gas sensor for reliable gas detection in the past several decades. As environmental regulations become more stringent, the need to develop highly sensitive gas sensors grows. To meet the demand of low level gas detection, gas sensors should be upgraded in sensitivity, selectivity, stability and speed of response [1]. At the same time they should be cost effective and reliable over long term [2]. H_2S is a bad smelling and toxic gas andthe detection of H_2S gas finds many applications in fields such as oil exploration, auto ventilation units, and medical field of dentistry [3, 4]. Among a variety of oxide semiconductors, tin oxide (SnO_2) has proved itself to be one of the most attractive materials for gas sensor applications from a view point of gas sensitivity as well as chemical stability. The change of the electrical conductivity of SnO_2upon exposure to reducing gases (CO, H_2 etc.) has been used for gas detection. SnO_2 in its pure form is an n-type semiconductor with a band gap of 3.5eV [5]. Its electrical conductance results from point defects, such as oxygen vacancies and interstitial tin atoms (i.e. non stoichiometric composition), that acts as donor [6]. When exposed to air, freshly prepared tin-oxide particles adsorb oxygen atoms on the surface [7]. These oxygen atoms pick up the e^{-s} from the conduction band of tin oxide and are adsorbed on the particle surface as O^- ions. Each tin oxide particle is covered with negatively charged O^- ions on the surface. On the other hand, due to depletion of e^{-s}, there exists a layer of positively charged donor atoms just below the particle surface.

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When the sensor is exposed to reducing gases at elevated temperature, the O^-adsorbents react with the gases and release the e^{-s} to the conduction band. Consequently, the depth of the space-charge layer decreases, which result's in a decrease in the height of the potential barrier for the electronic conduction at the grain boundaries. The overall resistance of sensor drops and its electrical conductivity increases. The gas sensing properties of SnO_2 sensors seems to be influenced by many intrinsic as well as extrinsic factors. Modification of surface and bulk properties of tin oxide through doping of impurities is an effectiveway to improve sensitivity and selectivity [8,9].It has been observed that the sensitivity of a SnO_2 gas sensor can be increased with basic oxides while sensitivity decreases with acidic oxides [10]. The copper oxide (CuO) is a p-type semiconductor with a narrow bandgap (1.2 eV) which shows the interesting catalytic properties [11, 12].CuO doped SnO_2 is known to show very high sensitivity and selectivity in its response to H_2S gas [13-16]. It is reported that CuO does not react with SnO_2 [14,16] and high sensitivity has been attributed to p-n junction's formed between n type SnO_2 and p type CuO , that are destroyed by the formation of CuSon exposure to H_2S gas [17,18]. In the present study CuO doped SnO_2 powder was used to fabricate a thick film gas sensor by utilizing the screen printing technique. The effect of CuO doping, on the sensing behavior of SnO_2 thick film gas sensor for H_2S gas has been discussed.

2. Experimental

Tin oxide sensors were fabricated by thick film screen printing technique shown in fig-1. It consists of gas sensing layer (doped SnO_2), a pair of electrodes underneath the gas sensing layer serving as a contact pad for sensors, and a heater element on back side of the substrate. A temperature sensor adjacent to the gas sensor is also incorporated to measure the sensor temperature. Alumina (96%) has been used as a substrate for sensor fabrication [9].Tin oxide was available in the form of indium doped tin oxide paste, supplied by Electro Science Laboratories (ESL3050, USA). This indium doped tin oxide paste (SnO_2) has been taken as the base sensing material and further doped with copper oxide (CuO) to modify its sensitivity for different gases. For the preparation of CuO-doped paste,

dopants were added to base SnO_2paste in calculated amount (1%, 2% and 5% by weight) with cellulose based thinner.CuOis weighed and mixed with tin oxide paste in a ball mill. The composition is thoroughly mixed by ball milling process for 8 to 10h. The thermistor pattern is screen printed first (paste NTC 2413 ESL), dried at a temperature of 100^0C and fired at 950^0C. In the second step, finger electrode pattern is screen printed using gold conductor paste (No. 5754 B Haraeus, Gmbh) and dried at a temperature of 100^0C. Subsequently, a heater element is screen printed on the back side of the substrate using silver palladium conductor paste (No. C1214, Heraeus,Gmbh) and is dried at the same temperature. The dried films are fired at 850^0C. In the third step, CuOdoped and undoped tin oxide pastes were screen printed over the electrode pattern and the print is allowed to dry at a temperature 100^0C for 20min. The dried film is then fired in a thick film furnace (DEK model 840) in a set temperature profile with peak temperature zone of 550^0C. The sensor is allowed to remain in this peak temperature zone for at least 20 minutes. Four sets of sensors were prepared i.e. undoped, 1%, 2% and 5% (by weight)CuO-doped and they were exposed to varying concentration of H_2S in a locally developed test chamber having volume 2047 cm^3 kept at metal base. The change in resistance of sensors is measured using KEITHELY 195A multimeter. The complete description about the used measurement set-up has been given in fig.2.

3. Results and Discussions

3.1 Effect of CuO doping on the resistance (in air)

Temperature dependence of electrical resistance of undoped and CuO (1%, 2% and 5%) doped sensors are shown in the fig.3. From fig 3 it is revealed that the resistance of SnO_2 film increases as the concentration of dopant metal oxide (CuO) is increased. The increase in the resistance can be explained by considering the position occupied by the Cu^{+2} in tin oxide lattice. Copper ions can be introduced either at substitutional or interstitial positions in the tin oxide lattice. Since the radii of Cu^{+2}(0.72 Å) is nearly same as that of Sn^{+4} (0.71Å), it is more probable that Cu^{+2} will occupy the substitutional position in the lattice. The substitutional reaction occurs as follows [19]

$$CuO + \frac{1}{2}O_2 \xrightarrow{SnO_2} Cu''_{Sn} + 2O_0 + 2h^{\bullet} \qquad (1)$$

The reaction implies that substitution by Cu^{+2} causes increase in concentration of oxygen vacancy (or the hole concentration) and consequently, decrease in the free electron concentration. The decrease in free electron concentration also results in an increase in depletion layer width, thus increasing the energy barrier between adjacent grains, which ultimately causes the increase in the resistance of SnO_2 film. On increasing the CuOconcentration the resistance should increase as also evident from the fig.3.

3.2 Sensitivity of undoped and CuO doped sensors

The variation of sensitivity (% change in resistance i.e. $S = \frac{R_{a-}R_g}{R_a} \times 100$, where $R_a$and $R_g$are the resistances of sensor in clean air and in presence of the gas, respectively) with different concentration of H_2S was studied for all the fabricated (undoped, 1% CuO, 2 % and 5% CuO doped)SnO_2 sensor, at different fixed temperatures (150^0C-350^0C). The observed results are shown in fig.4-7. The sensors exhibit an increase in sensitivity as concentration of $H_2S$is increased from 250 ppm to 1500 ppm in air and then get saturated. It is also evident from the figs. that the maximum sensitivity of undoped SnO_2 sensor is at 350˚C while 1%, 2% and 5% CuO doped sensors show maimum sensitivity at 150˚C, 200˚C and 250˚C respectively. Fig.8 is the plot of the sensitivity as a function of operating temperature for all the fabricated (undoped and CuOdoped) sensors at fixed H_2S concentration (1500 ppm). From the figure.8 it is clear that the addition of CuO markedly change the sensitivity of SnO_2 thick film sensor. The sensitivity of undoped SnO_2 sensor isleast andincreases with increasing the concentration of CuO i.e. 5% CuO doped SnO_2 sensor exhibits maximum sensitivity for H_2S gas.

3.3 Sensing mechanism of sensors

The increase in the sensitivity of SnO_2 thick film sensor on doping of CuO can be explained by considering the formation of p-n junction at the interface between CuO and SnO_2[20]. CuO is known to possess p-type conductivity [21] where as SnO_2 shows n-type conductivity. Gas sensors are composed of a mixture of CuO and SnO_2 which are calcined at an appropriate temperature, thus CuO can disperse spontaneously onto the surface of SnO_2 [22]. Consequently, a depletion layer is formed near the grain surface of SnO_2 as a p-n junction. This depleted region leads to reduction in the flow of electrons through n-type SnO_2 hence the SnO_2sensor with CuO doping shows higher resistance than undopedSnO_2 sensor. Nakhara et al [23] have proposed that SnO_2 sensors with basic additives like CuO should be more sensitive towards H_2S gas due to acidic character of the gas. When undoped SnO_2 sensor is exposed to H_2S gas, the molecules of gas react with adsorbed oxygen on the surface of SnO_2 and remove them. This removal leads to release of electrons to the conduction band and consequently the overall resistance of the sensor drops. On exposing the CuO- doped SnO_2 sensor to H_2S gas it chemically reacts with CuO and converts CuO into copper sulphide (CuS) which has metallic character [21].

$$CuO + H_2S \rightarrow CuS + H_2S \qquad (2)$$

Incorporation of metallic conductor is equivalent to incorporation of free electrons into the p-type material, which makes it less p-type. This facilitates the easy flow of electrons from CuS to $SnO_2$and vice versa and results in further decrease in electrical resistance of the sensor. Once H_2S atmosphere cease to exist, the resistance attains its original values as CuS converts back to CuO when heated in air at high temperature.

$$CuS + \frac{3}{2}O_2 \longrightarrow CuO + SO_2$$

4. Conclusion

CuO has strong effect on the sensitivity of SnO_2 thick film for sensing H_2S. The sensor with 5% CuO doping exhibits the maximum sensitivity at 250˚C while for sensor with 1% CuO doping maximum sensitivity is found at 150˚C. Thus doping of SnO_2 with CuO not only enhances the sensitivity but also reduces the operating temperature.The substitution of Sn^{+4}ions by Cu^{+2} ions created more oxygen vacancies, leading to decrease in free e^- concentration and increase in sensitivity. The increase in sensitivity is primarily due to modulation of electronic barriers due to interaction of H_2S with CuO via grain boundary.

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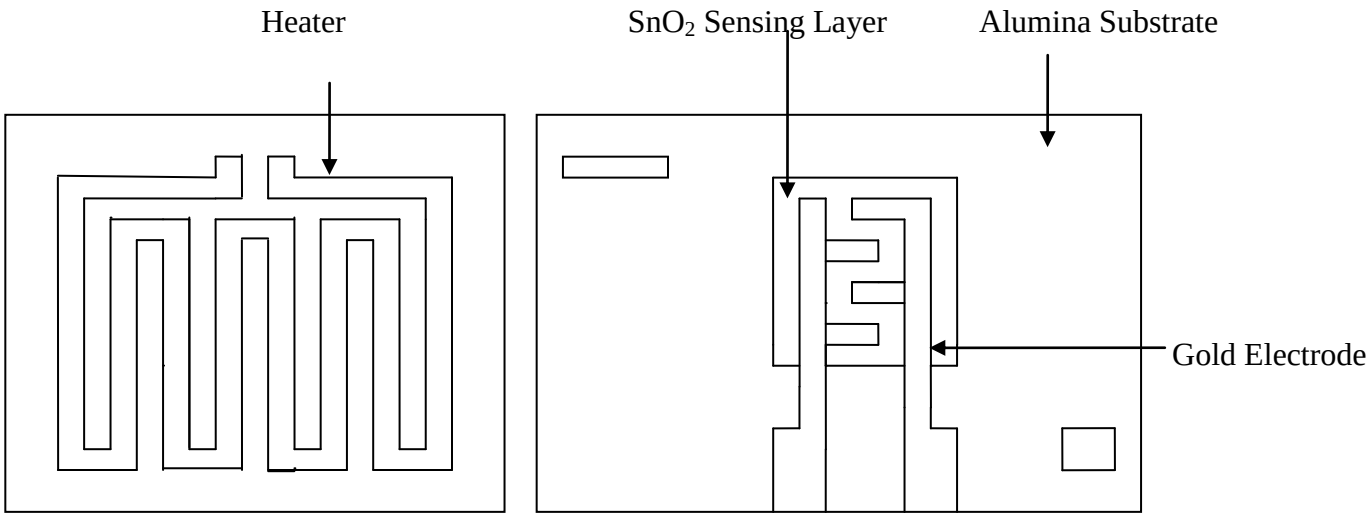

Fig. 1 Schematic of fabricated sensors

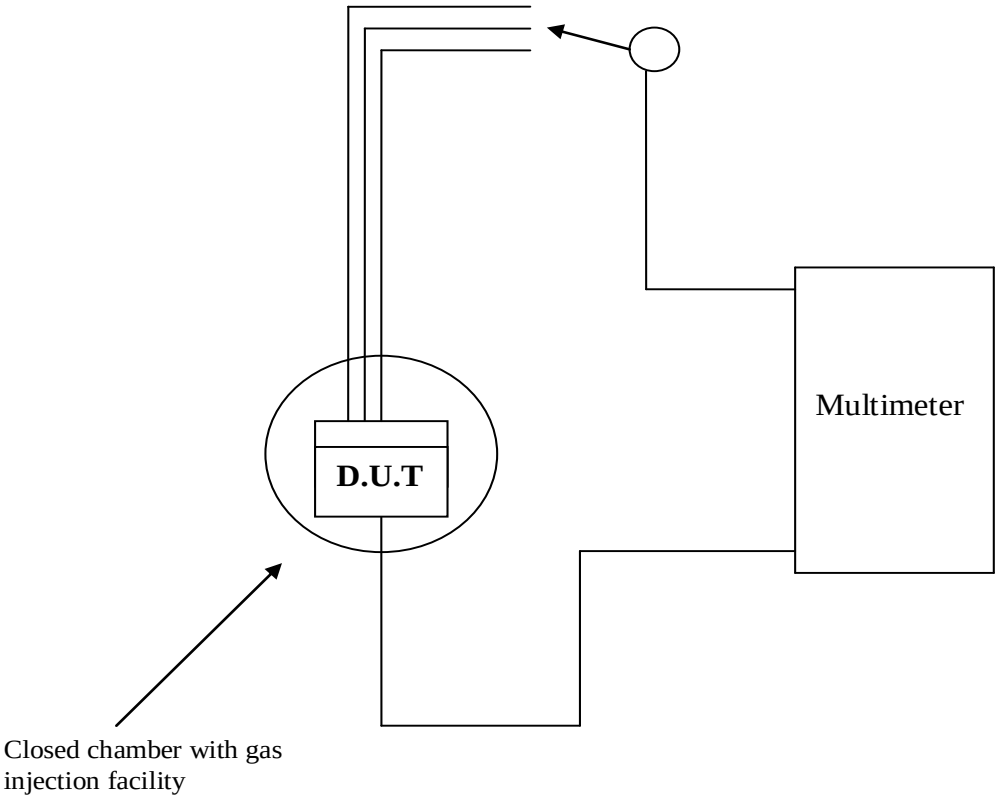

Fig. 2 Schematic diagram of measurement setup

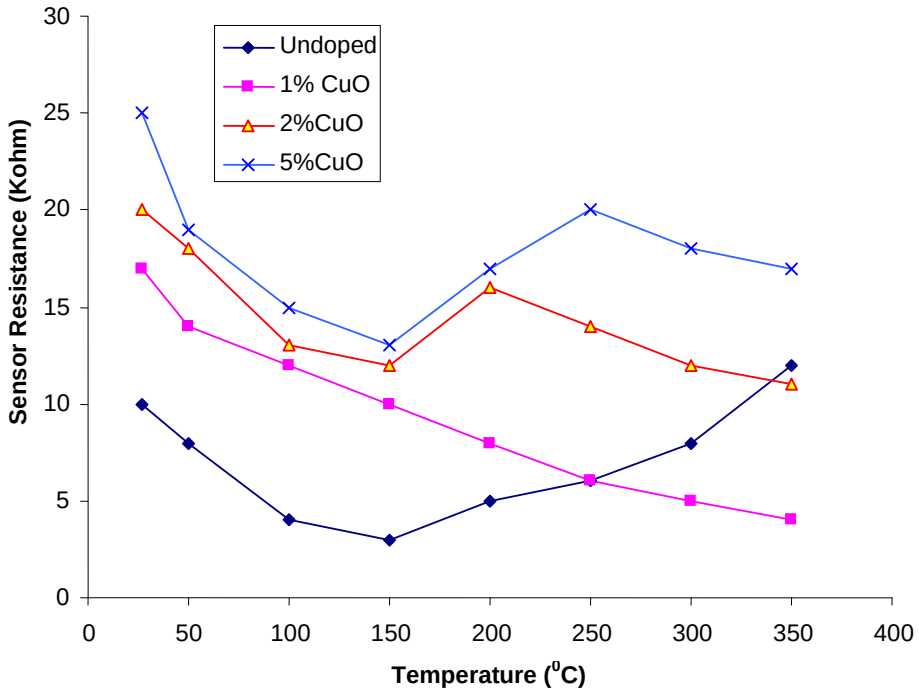

Fig. 3 Resistance variation of the sensors with temperature

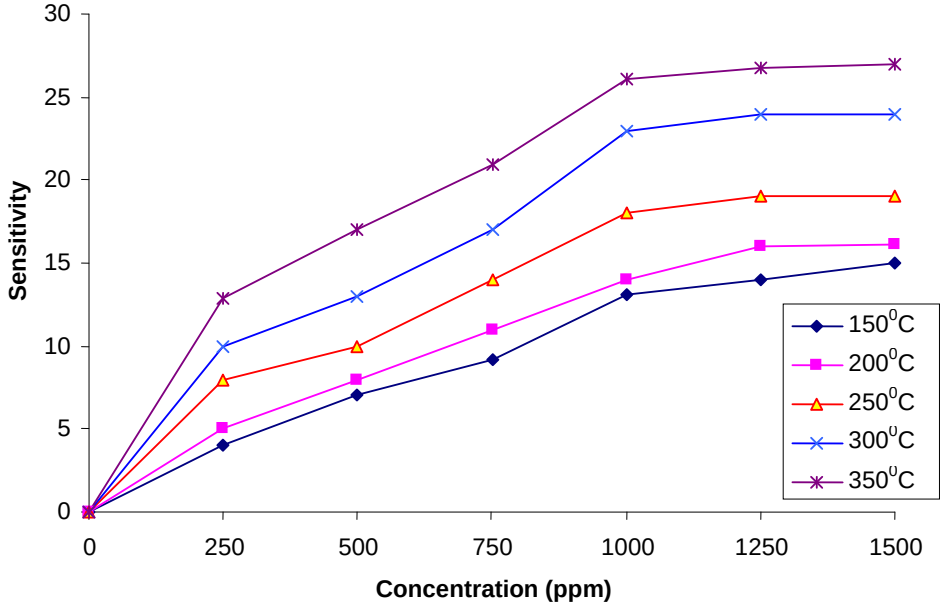

Fig 4 The variation in sensitivity of undoped SnO_2 sensor with H_2Sconcentration

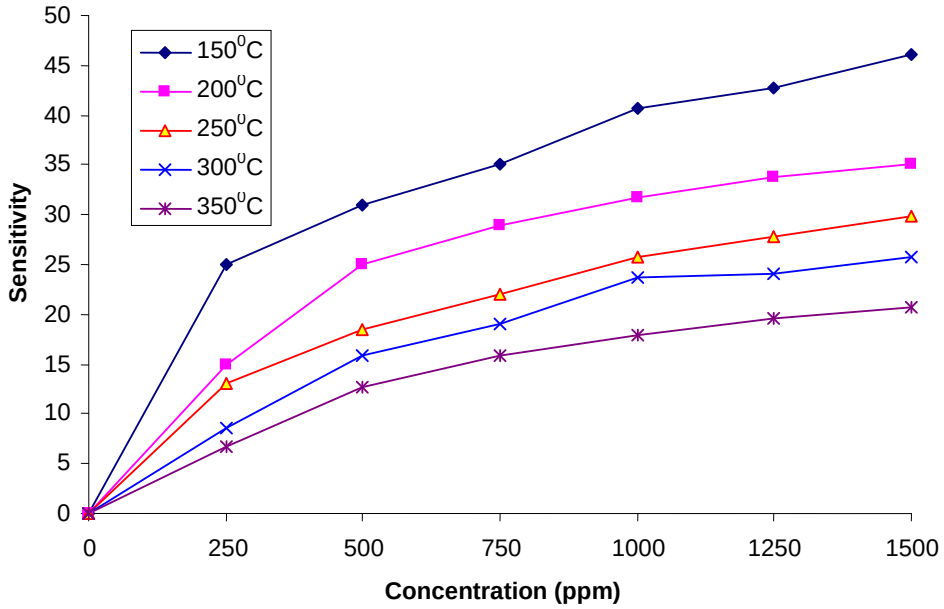

Fig.5 The variation in sensitivity of 1% SnO_2 sensor with H_2Sconcentration

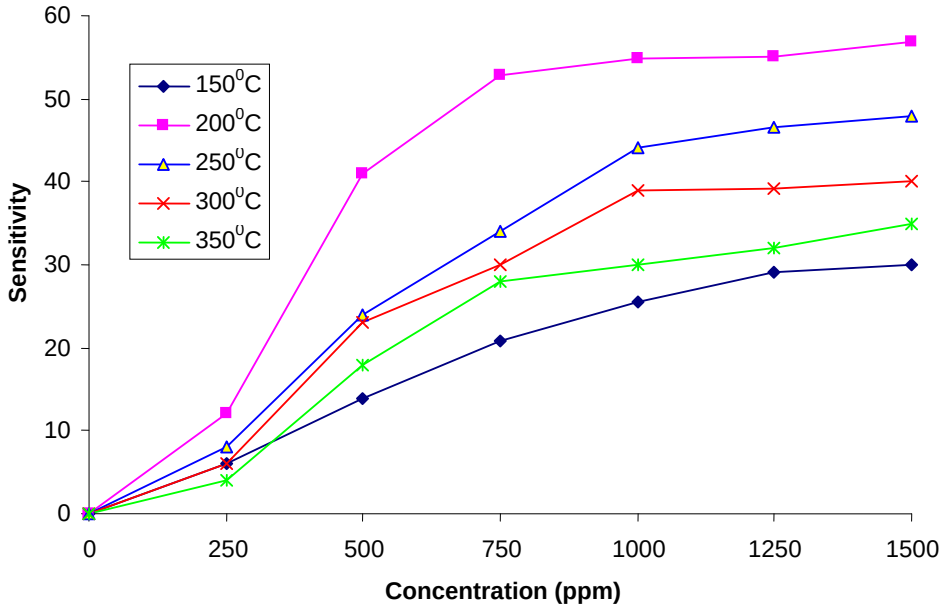

Fig.6 The variation in sensitivity of 2% CuO-doped SnO_2 sensor with H_2Sconcentration

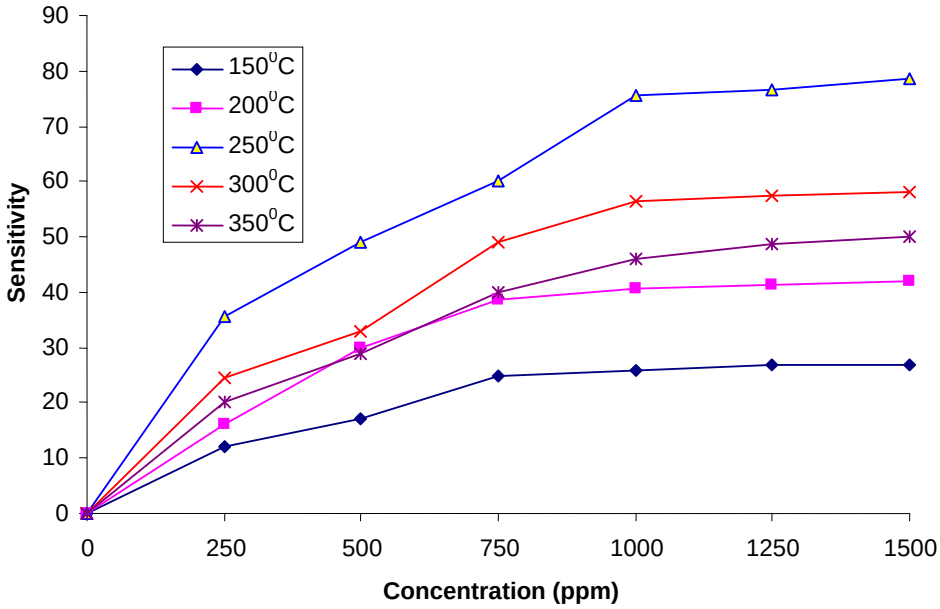

Fig.7 The variation in sensitivity of 5% CuO-doped SnO_2 sensor with H_2Sconcentration

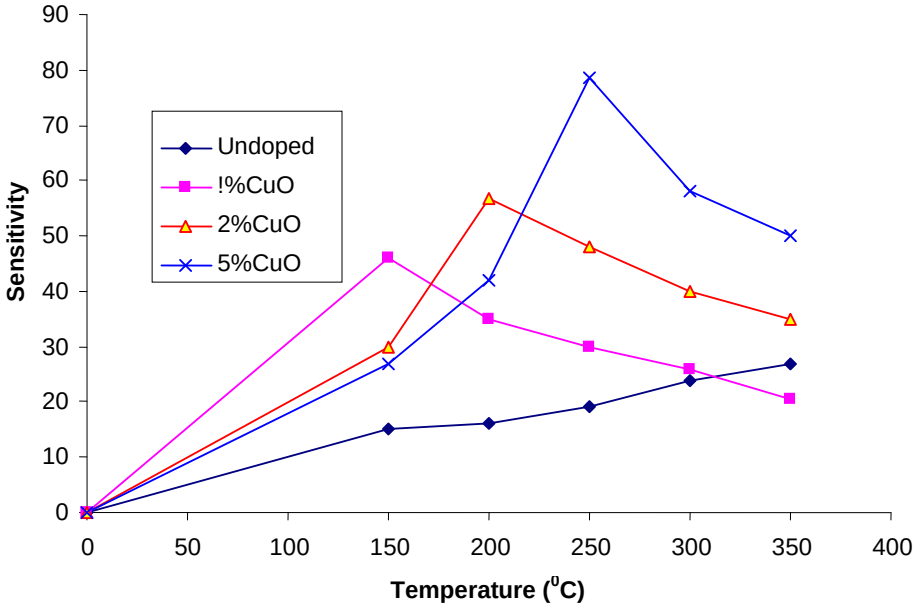

Fig.8 Effect of temperature on the sensitivity of undoped and CuO-doped (1%, 2% and 5%) SnO_2 sensor at fixed concentration (1500 ppm) of H_2S.