Role of CuO-ZnO Heterojunctions in Gas Sensing Response of CuO-ZnO Thick Films

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Abstract: The CuO-doped ZnO thick films were prepared by the screen printing technique. The CuO doped ZnO composite materials were obtained by mixing AR grade (99.9% pure) Zinc Oxide powder mechanochemically in acetone medium with various weight percentages of Copper Chloride ($CulCl_2.2H_2O$) powder (1, 3, 5, 7 and 9wt.%). The prepared materials were sintered at 1,000 ^oC for 12 h in air ambience and ball milled to ensure sufficiently fine particle size. The films were characterized by different techniques with respect to their surface morphology and compositional property by means of SEM (scanning electron microscope) and EDXA (energy dispersive x-ray analysis). The surface morphology of the films was studied by SEM and it shows the films are porous in nature and petal-shaped grains of sizes varies from 220 nm to 250 nm were observed. The final composition of each film was determined by the EDXA analysis. The gas response of undoped ZnO and CuO doped ZnO films was studied for different gases such as CO, Cl_2, NH_3, Ethanol, H_2S and LPG at operating temperature ranging from 50 ^oC to 400 ^oC. The 7wt.% CuO-doped ZnO film shows good response to H_2S gas (100 ppm) at 250 ^oC.

Nomenclature

O: Oxygen
Z: Zinc Cu- copper
At.%: Atom percent
Wt.%: Weight percent
G_{air}= Conductance of thick film in air
G_{gas} = Conductance of thick film in gas
S: Gas response

Greek letters

S_{area} Specific surface area
ρ- Density of functional material

1. Introduction

With the recent awareness of environmental pollution, there is a growing need for a reliable and inexpensive gas sensor. Thus, the use of sensors has been increasing at an astounding rate during the last few decades for a variety of purposes such as detection and monitoring of hazardous gases, highly inflammable gases, humidity, etc. A wide range of gas sensors are developed using MOS (metal oxide semiconductors) because of their advantageous features like sensitivity to the air ambient conditions, low material cost, easy processing and simplicity in fabrication. The most commonly used MOS ZnO [1, 2], SnO_2 [3], Fe_2O_3 [4], In_2O_3 [5], CeO_2 [6] in gas sensors are based on their change in electrical conductivity when they are exposed to test gases. At elevated temperatures (100-600 ^oC), these materials show large variations of electrical conductivity in response to the presence of traces of reactive gases in air. Gas sensors based on MOS in a thick-film form, have been developed for detection and control of gases like CO, O_2, NH_3, NO_2, Ethanol, H_2S, LPG, etc.

The gas sensing characteristics of the materials can be improved by incorporating some additives [7] into oxide films. Catalysts like Pt, Pd, Ag, Ru and Au

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[8-11] are often added to the base material to improve gas sensitivity and selectivity which are expensive. However, low cost metals or metal oxides have also been doped to achieve higher sensitivity and selectivity [12].

The most general adsorption-desorption gas sensing mechanism [13, 14]of semiconductor gas sensors is a simple resistivity change, due to desorption of surface oxygen adsorbates via reactions with reducing gases such as H_2S, CO and H_2. The p-n hetero-contact concept is used in the present investigation, instead of adsorption-desorption mechanism, which was introduced in 1979 and has been applied as humidity sensors, liquid sensors and gas sensors. The hetero-contact concept was found very effective for the H_2S gas sensing at room temperature. The hetero-contact type works on the principle of a barrier mechanism, which needs no adsorption and desorption of oxygen for the detection of hazardous and highly inflammable gases. Some well-known materials for H_2S gas sensing are SnO_2-CuO [15], CuO-ZnO [16], SnO_2-ZnO [17], CuO-$BaTiO_3$ [18], SnO_2-WO_3 [19].

In 1996, Sang-Jin-Jung et al. reported CuO/ZnO hetero-contact type gas sensor is more sensitive to CO gas, In 2006, Mridha, S. et al. reported p-CuO/n-ZnO thin film heterojunction type gas sensor is more sensitive to H_2 gas at 3,000 ppm level and in 2014, Ghosh, Amrita et al. development of a p-CuO/n-ZnO heterojunction and its application as a selective gas sensor including CH_4, H_2S and CO in the presence of 10,000 ppm level. In the present work CuO has been doped in ZnO to enhance gas response and selectivity of ZnO sensor. CuO doping into ZnO shows reduction of the electrical conductivity of ZnO and the reduced conductivity of ZnO is proposed to be responsible for the increase of the gas sensitivity of CuO-ZnO composite by increasing the current through p-n junction.

2. Experimental Setup

2.1 Preparation of Functional Materials

The CuO doped ZnO composite materials were obtained by mixing AR grade (99.9% pure) Zinc Oxide powder mechanochemically in acetone medium with various weight percentages of Copper Chloride ($CulCl_2.2H_2O$) powder (1, 3, 5, 7 and 9wt.%). The prepared powders were sintered at 1,000 ^{o}C for 12 h in air ambience and ball milled to ensure a sufficiently fine particle size.

2.2 Preparation of Thick Films

The thixotropic paste was formulated by mixing the fine powder of functional material with ethyl cellulose (a temporary binder) with organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol, etc. This paste was screen-printed [20, 21], on a glass substrate in a desired pattern (1.5 cm × 0.5 cm). The films were dried under infrared radiation for 45 minutes to remove the organic vehicle and then fired at the peak temperature of 550 ^{o}C constantly for 30 min and is brought to room temperature in a muffle furnace.

2.3 Thickness Measurements

The thickness of the films was observed in the range from 65 to 75 μm. The reproducibility of thickness in the films was possible by maintaining proper rheology and thixotropy of the paste.

3. Physical Characterization

3.1 Microstructural Analysis of the Films

It is well known that gas sensing properties of metal oxide thick films are strongly dependent on its morphological features. A high surface area facilitates the chemisorption process by increasing the adsorption and desorption rates [20]. The surface morphology and chemical composition of the films were analyzed using a SEM [scanning electron microscope model JEOL 6300 (LA) Germany] coupled with an EDXA (energy dispersive x-ray analysis, JEOL, JED-2300, Germany). It shows the films are porous in nature and petal-shaped grains of sizes varies from 220 nm to 250 nm were observed.

Fig. 1a shows the micrograph of undoped ZnO thick film. It consists of randomly distributed grains with smaller size and shape and with limited porosity. Figs. 1b and 1c show that, at lower concentration of dopant, the numbers of CuO additives distributed on ZnO grains are very less as they are not sufficient to accelerate the sensing reaction with the target gas, hence it shows the poor sensitivity.

Figs. 1b-1d show that, at lower concentration of dopant, the numbers of CuO additives distributed on ZnO grains are very less. They are not sufficient to accelerate the sensing reaction with the target gas, hence it shows the poor sensitivity. Fig. 1e shows the micrograph of 7 wt.% CuO doped ZnO thick film which was most sensitive. It showed that the grain size decreases giving large effective surface area. The larger surface area gives more response to react with the target gas. The film seems to be highly porous for oxygen adsorption. Also CuO segregates at the grain boundaries. The segregation of CuO around the boundary of ZnO forms a heterojunction between ZnO(n) and CuO(p), facilitating the efficient charge transfer, which enhances sensitivity and selectivity under certain conditions. Fig. 1f shows, large number of CuO additives are distributed uniformly over ZnO. They are agglomerated around ZnO grains and the surface of the film becomes less porous. It resists reaching the target gas to the inter-grain boundary of CuO-ZnO. Also the agglomeration increases the particle size, hence effective surface to the volume ratio would decrease and less number of oxygen ions would be adsorbed on the film surface, hence it shows poor gas response.
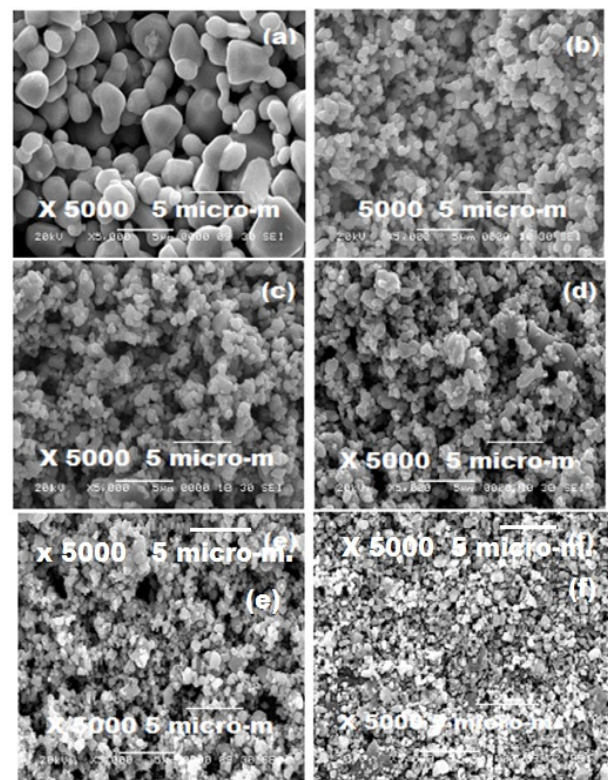
3.2 Elemental Analysis of the Films

The elemental composition of undoped and CuO doped ZnO thick films with different concentrations were analyzed by energy dispersive spectrometer.

Table 1, shows the composition of the film doped at different level. At.% of Zn, Cu and O in each sample was observed to be non-stoichiometric. The ZnO film

doped with 7 wt.% CuO was observed to be most oxygen deficient. The deficiency or excess of the constituent material results in distorted band structure with corresponding increase in conductivity. The deficiency of the constituent material particles or an excess of it leads to the semi conducting behavior of the material [22].

The grain size of undoped and CuO doped ZnO thick films was determined from the SEM micrographs and the specific surface area was calculated by using Eq. (1)

Fig. 1   SEM images of (a) undoped ZnO, (b) 1wt.% (c) 3wt. % (d) 5wt. % (e) 7wt.% and (f) 9wt. % of CuO doped ZnO films.

Table 1   Quantative elemental analysis of undoped and CuO doped ZnO films.

Doping level	Elements (At.%)			
	O	Zn	Cu	Total
Undoped ZnO	21.18	78.82	-	100
1wt.% CuO-ZnO	41.46	58.27	0.27	100
3wt.% CuO-ZnO	41.87	57.81	0.33	100
5wt.% CuO-ZnO	39.91	59.92	0.17	100
7wt.% CuO-ZnO	18.38	80.85	0.77	100
9wt.% CuO-ZnO	43.90	55.72	0.38	100

$$S_{area} = \frac{6}{\rho \times D} \qquad (1)$$

where S_{area}-Specific surface area, ρ-Density of functional material, D-Grain size.

Table 2, shows the grain size and specific surface area of undoped and CuO doped ZnO thick films. It is evident that the increase in doping concentration reduces the grain size and increases the specific surface area.

The higher response may be attributed to the optimum porosity and largest effective surface area available to react with the gas. The response could be attributed to the adsorption-desorption type of sensing mechanism. The amount of oxygen adsorbed on the surface would depend on the number of Cu misfits to adsorb the oxygen which in turn would oxidize the exposed gas. When the optimum amount of Cu (0.77 At.%) is incorporated on the surface of the ZnO film, Cu species would be distributed uniformly throughout the surface of the film. As a result the initial resistance of the film is high and this amount would be sufficient to promote the catalytic reaction effectively and the overall change in the resistance on the exposure of H_2S leading to an increase in the gas response. When the amount of Cu on the surface of the film is less than the optimum, the surface dispersion may be poor and the sensitivity of the film was observed to be decreased, since the amount may not be sufficient to promote the reaction more effectively. On the other hand, as the amount of Cu on the surface is more than the optimum, the Cu atoms would be distributed more densely. Therefore the initial resistance of the film would decrease and the overall change in the resistance on the exposure of H_2S would be smaller leading to lower response.

4. Sensing Performance

The gas sensing performance of undoped ZnO and CuO doped ZnO thick films was studied using a "static gas sensing system" [23], shown in Fig. 2.

There were electrical feeds through the base plate.

The heater (2,000 watt) was fixed on the base plate to heat the sample under test up to required operating temperatures (from room temperature to 500 ^{o}C). The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON-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 a test gas using a gas-injecting syringe. The air was allowed to pass into the glass chamber after every gas exposure cycle.

The conductance of thick film was measured by means of conventional circuitry by applying constant voltage and measuring the current by digital Pico ammeter as a function of temperature in air as well as in H_2S, LPG, CO, NH_3, Cl_2, and Ethanol vapour gas

Table 2   Grain size and specific surface area of undoped and CuO doped ZnO films.

Sample type	Cu (At. %)	Grain size d (nm)	Specific surface area (m^2/gm)
Undoped ZnO	-	2207	0.48
1wt.% CuO-ZnO	0.27	1333	8.69
3wt.% CuO-ZnO	0.33	1349	9.90
5wt.% CuO-ZnO	0.17	1278	11.84
7wt.% CuO-ZnO	0.77	1156	14.61
9wt.% CuO-ZnO	0.38	949	19.68
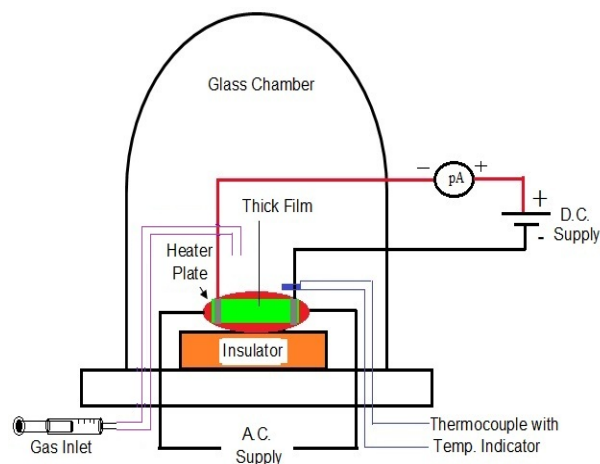
Fig. 2   The Schematic diagram of static gas sensing system.

atmosphere. The operating temperature was varied at the interval of 50 $^{\circ}$C. From the measured conductance in air as well as in gas atmosphere, the gas response(S) was determined at particular operating temperature using the Eq. (2) [21].

$$S = \frac{(G_{gas} - G_{air})}{G_{air}} \qquad (2)$$

where G_{air}= Conductance of thick film in air. G_{gas} = Conductance of thick film in gas.

4.1 Gas Sensing Performance of Undoped and CuO Doped ZnO Films

Figs. 3a and 3b show the variation in the gas response of undoped and 7 wt.% of CuO doped ZnO thick films. The films were tested for various gases viz: CO, Cl$_2$, NH$_3$, H$_2$S, LPG and Ethanol as the function of operating temperatures ranging from 50 $^{\circ}$C to 400 $^{\circ}$C. It has been observed that the 7 wt.% CuO doped ZnO thick film is more sensitive to H$_2$S gas(100 ppm) at temperature 250 $^{\circ}$C while the undoped ZnO film shows very poor response to H$_2$S gas at temperature 300 $^{\circ}$C than other tested gases viz: CO, Cl$_2$, NH$_3$ and LPG. The gas response goes on increasing with increase in operating temperature, attains its maximum (at 250 $^{\circ}$C) and then decreases with a further increase in operating temperature. It is clear from the figure that the optimum operating temperature for H$_2$S gas is 250 $^{\circ}$C. The undoped ZnO is notable less sensitivity than the doped ZnO. Thus the dopants or an additive increases sensitive of gas sensor by enhancing the chemisorptions of the specific gases [24].

Fig. 4 shows the variation in H$_2$S gas response with operating temperature of undoped and CuO doped ZnO films at different doping concentrations (1, 3, 5, 7 and 9 wt.%) as a function of operating temperatures ranging from 50 $^{\circ}$C to 400 $^{\circ}$C. It is evident that the gas response increases with increase in concentration of dopant (CuO) up to optimum level and further decreases with increase in dopant concentration.
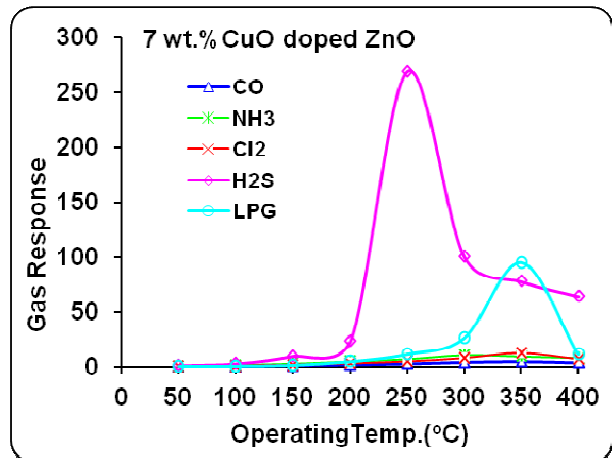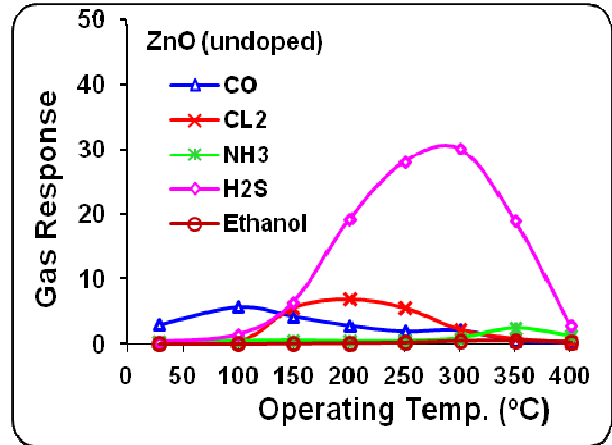

Fig. 3 **Variation in gas response with operating temperature of (a) undoped and (b) 7 wt.% CuO doped ZnO thick films.**
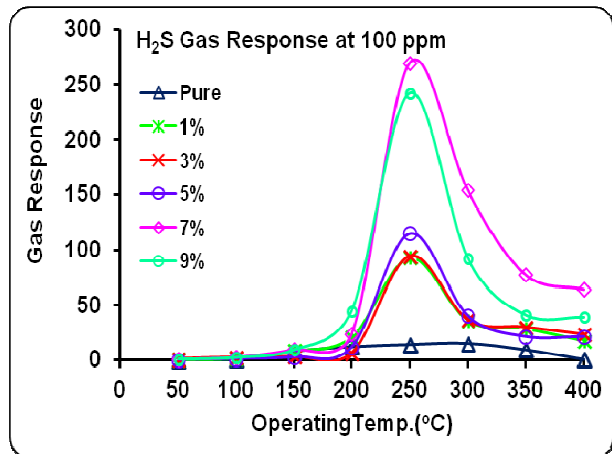

Fig. 4 **Variation in H$_2$S gas response with operating temperature of undoped and CuO doped ZnO film.**

4.2 Effect of Gas Concentrations on CuO Doped ZnO Film

Fig. 5 shows the variation of H$_2$S gas response with

different gas concentrations at optimum temperature 250 °C. Gas response was observed to have increased continuously by increasing the gas concentration from 50 ppm to 1,000 ppm. If the gas concentration increases above 1,000 ppm, the monolayer of the gas molecules formed on the surface could cover the whole surface of the film. The excess gas molecules would remain idle and would not reach the surface active sites of the film. So, the response at higher concentrations of the gas was not expected to increase in large extent. Thus, the active region of the film is up to 1,000 ppm.

4.3 Selectivity of 7 wt.% CuO Doped ZnO Film

The selectivity is the ability of a sensor to respond of certain gas in the presence of other gases. Percentage selectivity of one gas over the other is defined as the ratio of maximum response of other gas to the maximum response of the target gas at the optimum temperature. It was calculated by Eq. (3) [25].

$$\% \text{ Selectivity} = \frac{S_{(\text{other gas})}}{S_{(\text{target gas})}} \quad (3)$$

where $S_{(\text{other gas})}$ = maximum response to other gas,

$S_{(\text{target gas})}$ = maximum response to target gas.

The bar diagram in Fig. 6 indicating percentage selectivity of thick ZnO film doped with 7 wt.% CuO and operated at different operating temperatures for different test gases. It was clear from the bar diagram that the doped thick film is more selective to H_2S gas against the other gases viz CO, Cl_2, and NH_3. Thus, the dopants or additives increases selective of gas sensor by enhancing the chemisorptions of the specific gases.

4.4 Response and Recovery Time of 7 wt.% CuO Doped ZnO Film

The response/recovery time is an important parameter used for characterizing gas sensor sensors. The time taken for the sensor to attain 90% of maximum change in resistance on exposure to gas is

the response time and the time taken by the sensor to get back 90% of the original resistance is the recovery time [26].

Fig.7 shows the variations in H_2S (100 ppm) response of with time at temperature 250 °C for 7
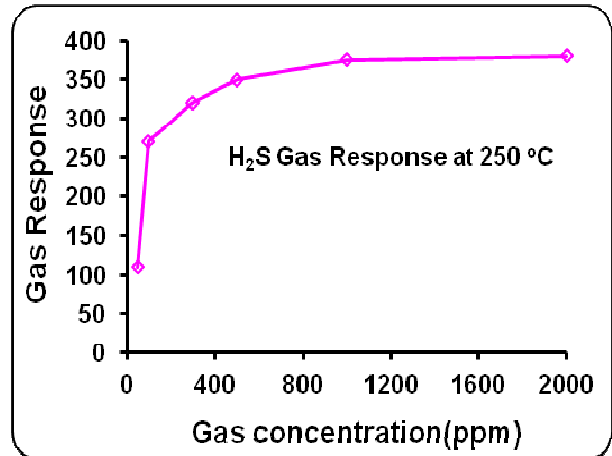

Fig. 5   Variation in H_2S gas response with gas concentration of 7 wt. % CuO doped ZnO film.
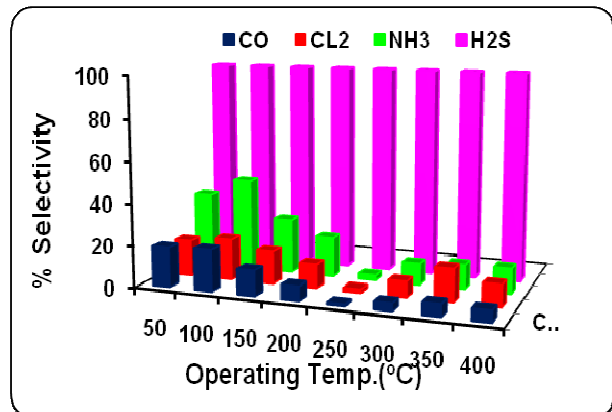

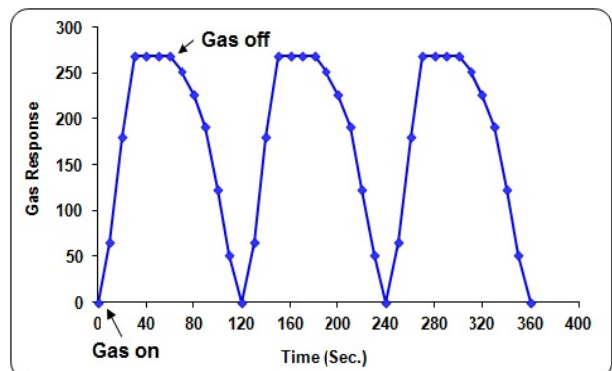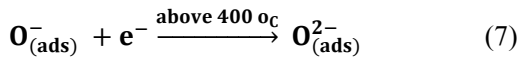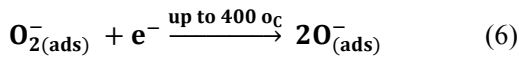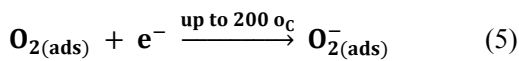**Fig. 6   % Selectivity of 7 wt. % CuO- doped ZnO film to H_2S gas against other gases.**

Fig. 7   Response transients of the 7 wt.% CuO doped ZnO thick film to H_2S (100 ppm).

wt. % CuO doped ZnO film. The response was quick (~ 30 s) while the recovery time was fast (~ 120s). The quick response may be due to faster oxidation of gas. The long recovery time would be due to the conversion of p-CuS/n-ZnO to again its initial chemical status (p-CuO/n-ZnO), it was essential to heat it above 200 °C in air atmosphere after every H$_2$S sensing cycle.

5. Discussion

5.1 H$_2$S-Sensing Mechanism of Surface Cupricated ZnO Thick Film Resistor

The gas sensing mechanism of the metal oxide semiconductor sensors belongs to the surface controlled type, which is based on the change in conductance of the semiconductor. The oxygen adsorbed on the surface directly influence to the conductance of metal oxide based sensors. Oxygen adsorbed on the oxide crystals surface as ions are formed by abstracting free electrons from the metal oxide semiconductors, reducing the electrical conductivity. The amount of oxygen adsorbed on the sensor surface depends on the operating temperature, concentration of additives, particle size, and specific surface area of the sensor. In the aerial atmosphere where the partial pressure of oxygen is taken as constant, oxygen is adsorbed on sensor surfaces in the form of O$^-$, O$_2^-$ and O^{2-}, depending on the temperature. The state of oxygen on the surface of metal oxide sensor undergoing the following reactions [27-30]

$$O_{2(gas)} \rightarrow O_{2(ads)} \tag{4}$$

$$O_{2(ads)} + e^- \xrightarrow{\text{up to 200 o}_C} O_{2(ads)}^- \tag{5}$$

$$O_{2(ads)}^- + e^- \xrightarrow{\text{up to 400 o}_C} 2O_{(ads)}^- \tag{6}$$

$$O_{(ads)}^- + e^- \xrightarrow{\text{above 400 o}_C} O_{(ads)}^{2-} \tag{7}$$

These oxygen adsorbates (O$_2^-$, O$^-$ and O^{2-}) on the surface of metal oxide semiconductor can induce an electron-depleted surface region, resulting in the increase of surface potential barrier and electrical

resistance.

The CuO which is oxygen excess shows the p-type conductivity by holes and oxygen deficient ZnO shows the n-type conductivity by electrons. In an oxidizing atmosphere, a thick charged depletion layer is formed across the grain boundaries of ZnO and CuO which would be formed as p-n heterojunctions shown in Fig. 8a. The electron associated with this charged species was drawn from the conduction band of bulk material, leading to an increasing resistance of the film. As a result, a potential barrier appears at boundary forming a continuous chain of p-n-p-n junctions. The band diagram of hetrojunction between p-type (CuO) and n-type (ZnO) semiconductor at equilibrium is as shown in Fig. 8b. The discontinuity in the conduction band allows the electrons to spill over
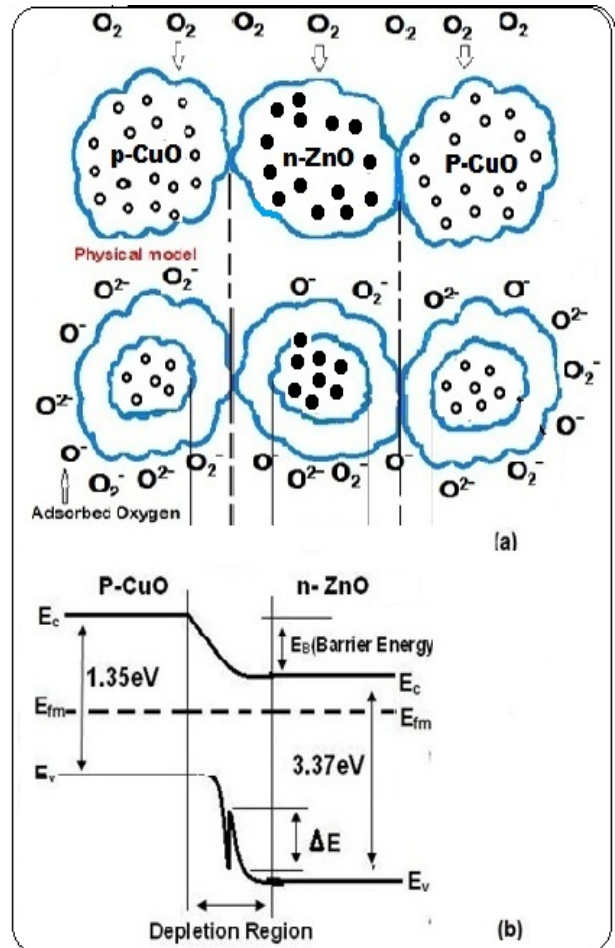

Fig. 8 **Schematic diagram of CuO-ZnO sensing mechanism (a) p-n-p-n-hetro Junction, (b) Energy band diagram of heterojunctions at equilibrium.**

from the donor CuO to ZnO, where they became trapped in the potential well [31].

When film exposed to reducing H_2S gas, the gas molecules get oxidized with the adsorbed oxygen ions (O^-, O_2^- and O^{2-}) and there is desorption of oxygen. The reaction of H_2S gas with the adsorbed oxygen ions at the specific temperature 250 ^{o}C where the film shows the maximum gas response can be represented as:
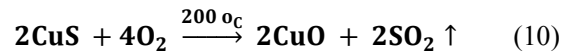
$$H_2S + 3O^- \xrightarrow{250\,^o_C} H_2O + SO_2 \uparrow + 3e^- \quad (8)$$
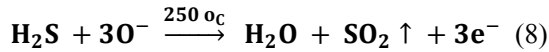
Simultaneously the CuO on the film react with the H2S gas and converted into CuS, the reaction can be represented as:

Fig. 9 Schematic energy band diagram of metal CuS –ZnO(n) at equilibrium.

$$CuO + H_2S \xrightarrow{250\,^o_C} CuS + H_2O \quad (9)$$

The CuS is known as metallic in nature and thus p-n-p-n hetrostructure as well as charge depletion layer would be destroyed and transformed to metal (CuS)-semiconductor (n-type ZnO) configuration. A typical band diagram at equilibrium is as shown in Fig. 9. The work function of CuS is lower than ZnO (n-type), In this situation the Fermi levels are aligned at equilibrium by transferring electron from lower work function CuS to higher work function ZnO, Since there is no barrier between them which results in decrease of electrical resistance and gives the higher response to H_2S gas.

The increase in resistance back to the original value once the H_2S atmosphere ceases to exist. It is because of the CuS convert back to the CuO, when heated in an air at the operating temperature of about 200 ^{o}C and returns to normal its state and the change is given by following reaction [28, 32, 33]:

$$2CuS + 4O_2 \xrightarrow{200\,^o_C} 2CuO + 2SO_2 \uparrow \quad (10)$$

and the potential barrier appears again.

6. Conclusions

(1) The undoped ZnO film shows the poor response to the various test gases viz: CO, Cl_2, NH_3, H_2S and Ethanol;

(2) The undoped ZnO thick films were doped by adding the Copper Chloride ($CulCl_2. 2H_2O$) additives by mechanochemicaly at different wt.%;

(3) The doped ZnO films would form the p (CuO)-n (ZnO) heterojunctions which attributes the high film resistance;

(4) The barrier height of p-CuO/n-ZnO heterojunctions decreased markedly due the chemical transformation of highly resistive p-CuO into well conducting CuS leading to drastic decrease in resistance;

(5) The 7 wt.% CuO doped ZnO film shows the good response to H_2S (100 ppm) at 250 ^{o}C;

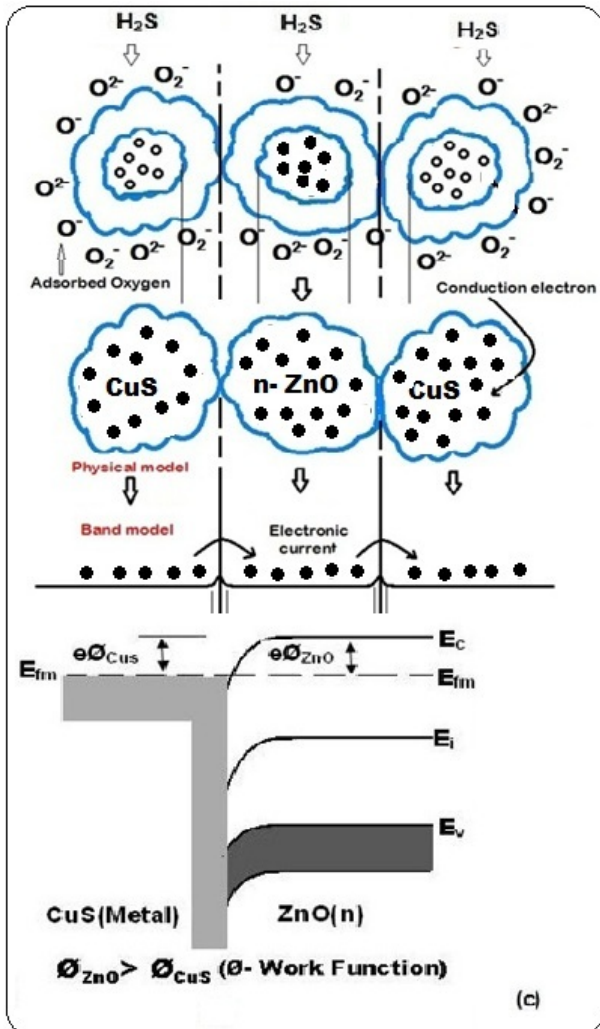(6) The CuO-doped ZnO films showed the rapid response (~ 30 s) and recovery time (~ 120 s) to H_2S;

(7) The film doped with CuO is more selective to H_2S gas against the other test gases.

Acknowledgments

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