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Electrical, Structural and Gas Sensing Properties of CuO loaded ZnO Nanocomposites Thin Films Prepared by Thermal Evaporation Technique

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Abstract:

In this work, Pure and CuO loaded ZnO nanocomposites thin films have been prepared on alumina substrate by thermal evaporation technique. Electrical, structural and gas sensing properties of pure ZnO and Cu loaded ZnO films were investigated in details. Electrical properties were calculated in the form of electrical resistivity, activation energy and temperature coefficient resistance. Structural properties were studied using standard tools FESEM, EDAX and XRD. Cu loaded ZnO film shows maximum sensitivity 89.23% to dichlorodifluoromethane **(**R12) gas at 50°C temperature and 100 ppm. Films also show fast response time (~ 8 sec) and recovery time (~ 14 sec).

Keywords- *Thin films, FESEM, TCR, R12, Sensitivity.*

1. Introduction:

Over the years, Scientists and researchers have been focusing their efforts to develop real-time novels gas sensors. Gas sensors are important for human health problems and environmental protection. Thus it is necessary to control and monitor such pollutants to avoid health hazards. Now a day's air pollution increases tremendously because of sophisticated life of humans. Dichlorodifluoromethane **(**R12) is a colorless gas. It belongs to family of green house gases and these gases are main source which increases the ozone depletion. Climate change is a major problem facing mankind due to increasing temperature on earth. Thus it is necessary to control and monitor such pollutants to avoid health and natural hazards. R12 mostly produced from refrigeration and air conditioning appliances. Such types of appliances are used at home, office, malls, hospitals, and also in vehicles [1, 2].

To detect such types of pollutant recently thick and thin film methods were implemented, The thick and thin film define of the basis of thickness of film. The film below 1 μm or in nanometer range is considered as thin film, and film above it is considered as thick film. There are many techniques recently utilized for preparation of thin films like spin coating, spray pyrolysis, SILAR, chemical vapour deposition and physical vapour deposition. Physical vapour deposition method broadly divided into two ways one is sputtering and second is evaporation. Evaporation method again divided into three types such as 1) ion sputtering 2) thermal evaporation and 3) arc discharge, among them thermal evaporation is best method for preparation of thin film [3,4].

The metal oxide semiconductor (MOS) gas sensor works on the principle of chemiresistance. When the gas molecule interacts with surface of MOS, it acts as either an acceptor or donor. This changes film electrical resistivity or conductivity [5]. Adding two different nanomaterials is a great advantage in the field of nanotechnology.

ZnO is an n-type semiconductor material. The direct band gap of zinc oxide is ~3.3 eV at room temperature. Zinc oxide based sensors are attracted much attention because of their chemical, electrical, optical and physical properties. ZnO has been widely applied for detecting hazard gases, such as NO_2, ethanol, methanol, CO, NH_3 and H_2S [6]. Copper (II) oxide is the inorganic compound. The chemical formula of copper oxide is CuO. Cuprous oxide (CuO) is direct band gap p type semiconductor material with direct band gap 2.2eV [7]. Production of nanocomposites thin films with controllable shapes, sizes, and surface properties is important for different practical applications. Nanocomposites were made by doping with various nanomaterials like noble metals, metal oxide, and some complex oxides. Among all Cu-doped zinc oxide nanocomposites attained more attention because of its higher efficiency as a catalyst, gas sensor, solar cell, and optoelectronic device [5].

2. Experimental work

Preparation of pure ZnO and CuO loaded ZnO thin films [8, 9,12]

In this research work, commercial available ZnO and CuO nano powder was used. ZnO is functional materials and CuO as a dopant for preparing the thin films. Thin films were prepared by using thermal evaporation method. This method includes a conventional vacuum system, which was evacuated to 10^{-6} mbar by rotary and diffusion pump arrangement. The chamber was filled with vacuum and for deposition purpose alumina substrates were used. Before placing into the deposition chamber, the alumina substrates were cleaned using acetone and IR lamp. The substrates were placed 30 minutes under IR lamp for cleaning purpose. After that, ZnO powder place in Molybdenum boat by some appropriate arrangement, which was used as the target for evaporation. After deposition nanopowder of pure ZnO and CuO (3%) loaded ZnO on a substrate. Then, prepared thin films were followed by thermal oxidation in air using furnace at temperature 650 ^oC for 2 hours, after oxidation the samples were cooled at room temperature and used further study.

The structural properties of prepared thin films were investigated using X-ray diffraction analysis from 20-800 [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having CuKα, λ=0.1542 *nm* radiation]. Surface morphology and average particle size have been investigated by using field emission scanning electron microscopy (FESEM- JOEL JED-2300). The composition of pure ZnO and CuO loaded ZnO thin films were analyzed by Energy Dispersive spectrometer (JOEL-JED 6360 LA). The thickness of the thin films was measured by using Taylor-Hobson (Taly-step UK) system. The thickness of the films was found in the nm range. Resistance of the thin films was measured by using half bridge method in surrounding at different temperature ranges. The gas sensing studies of thin films were carried out by using less expensive home made static gas sensing system [8, 10].

3. Result and Discussion

3.1. Electrical characterization [10, 16].

$$\rho = \left(\frac{R \times b \times t}{l} \right) ohm - m \qquad \text{..... (1)}$$

Where, t = thickness of the film sample, b = breadth of the thick film resistor in cm

$$TCR = \frac{1}{R_o} \left(\frac{\Delta R}{\Delta T} \right) \ /^{O} C \qquad \text{..... (2)}$$

Where, ΔR = change in resistance between temperature T_1 and T_2, ΔT = temperature difference between T_1 and T_2 and R_o = Initial resistance of the film sample

$$R = R_o e^{-\Delta E/KT} \qquad \text{..... (3)}$$

Where, R_o = the constant, ΔE = the activation energy of the electron transport in the conduction band (eV), K = Boltzman constant and T = Absolute temperature.

The resistivity, temperature coefficient of resistance (TCR) and activation energy was calculated using equations 1, 2 and 3 respectively.

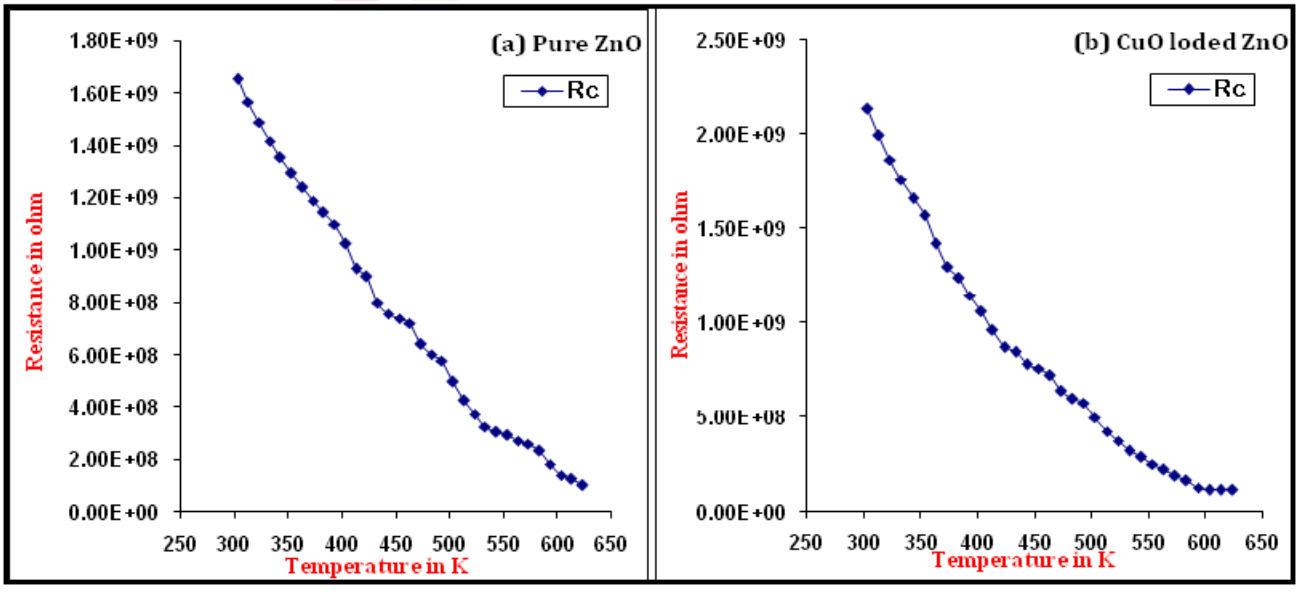

Figure 1 (a) Resistance verses temperature of pure ZnO thin films with and (b) Resistance verses temperature of CuO loaded ZnO thin films.

Figure 1 (a) and (b) shows resistance decreases with increase in temperature it confirmed that the semiconductor behavior of thin films. Resistance of films was calculated by using half bridge method. The resistivity of pure ZnO and CuO loaded ZnO thin films were calculated 76.50 Ω-m and 97.65 Ω-m respectively. The resistivity was found highest to CuO loaded ZnO thin films.

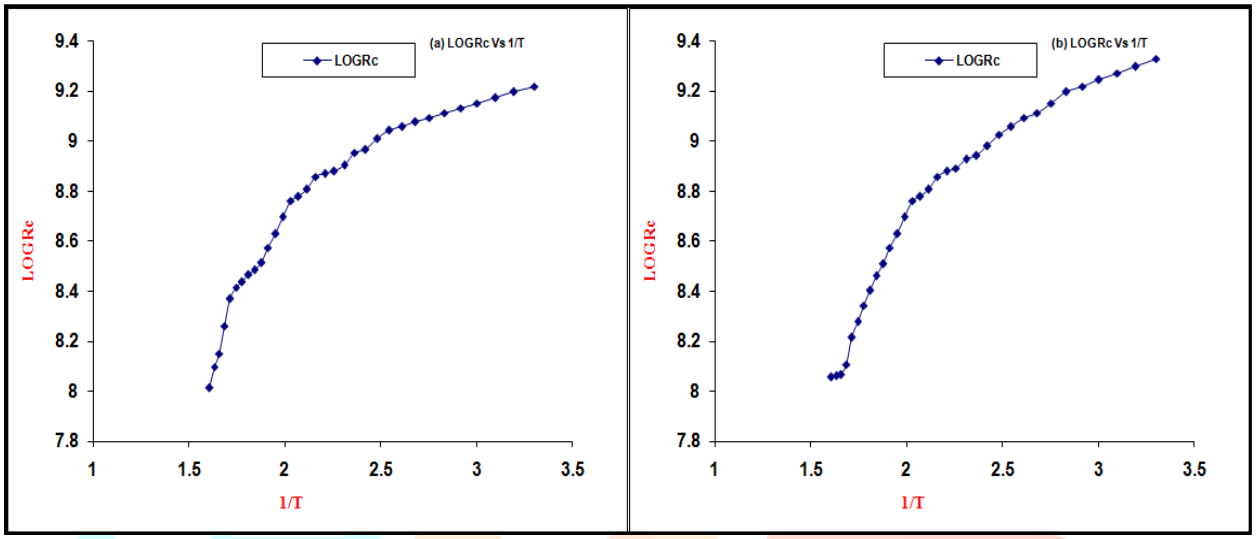

Figure 2 (a) Resistance variation plot of *log R* versus reciprocal of temperature of pure ZnO thin films and (b) plot of *log R* versus reciprocal of temperature of CuO loaded ZnO thin films.

Figure 2 (a) and (b) shows the plot is reversible in both heating and cooling cycles obeying the Arrhenius equation. The Activation energy at high temperature and at low temperature was found 0.74361 eV and 0.12018eV respectively to pure ZnO thin films and the activation energy at high temperature and at low temperature was found 0.57445 eV and 0.32201eV respectively to CuO loaded ZnO thin films.

The temperature coefficient of resistance has found -0.00001841/^{0} C and -0.00036197/^{0} C to pure ZnO thin films and CuO loaded ZnO thin films respectively. TCR of both thin films observed negative. Negative sign also indicate semiconductor behavior of films.

Table 1: Summary of electrical characterization

Thin film	Resistivity **(Ω m)**	TCR **/ ^{0} C**	Activation Energy **(eV)**	
			Low temperature	High temperature
Pure ZnO	76.50	-0.00001841	0.74361	0.12018
CuO loaded ZnO	97.65	-0.00036197	0.57445	0.32201

3.2 Structural characterizations

3. 2.1 Field Emission Scanning Electron Microscope (FESEM):

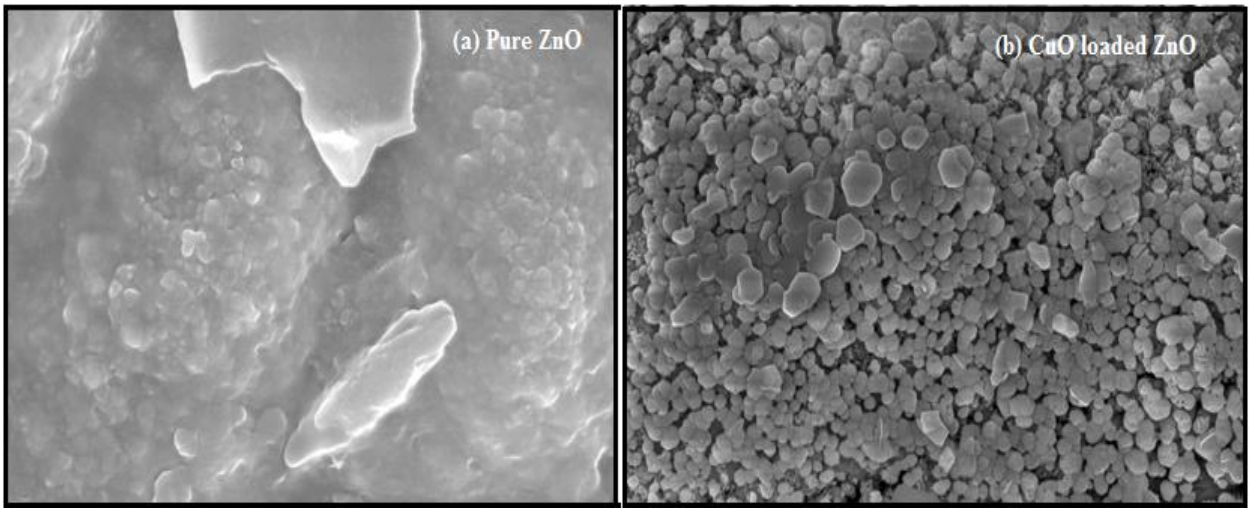

Figure 3 (a) FESEM of pure ZnO thin films with and (b) FESEM of CuO loaded ZnO thin films.

Figure 3 (a) and (b) shows prepared thin films are non porous. The average particle size of film was calculated by using image J software for spherical particles. CuO loaded ZnO thin films shows more spherical nanoparticles with agglomeration. The average particle size of pure ZnO and CuO loaded ZnO thin films were found 103 and 124 nm respectively [10, 13, 15].

3.2.2 Energy-dispersive X-ray spectroscopy (EDAX):

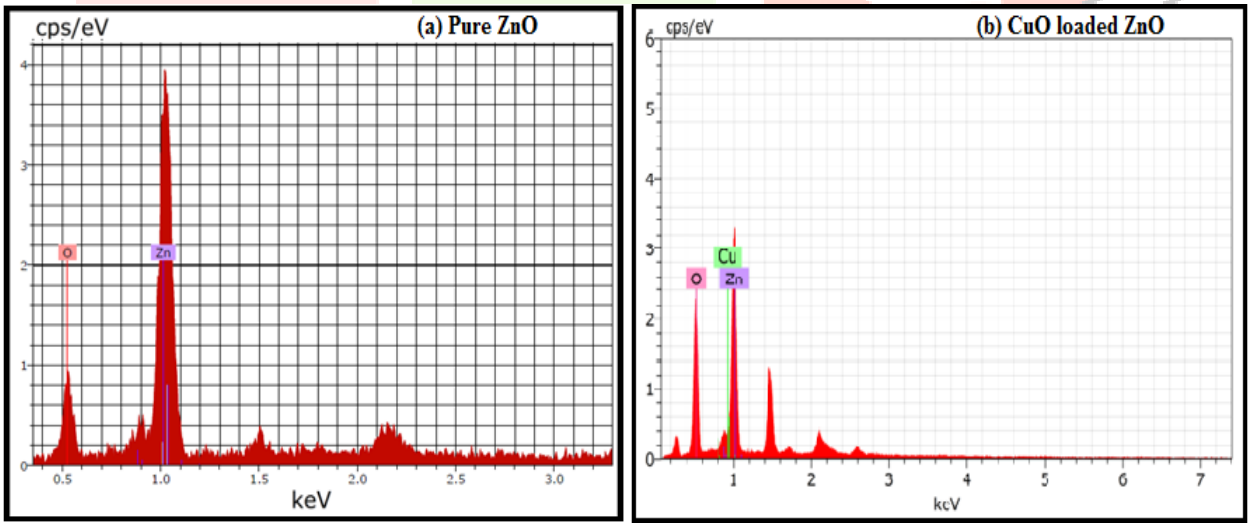

Figure 4 (a) EDAX of pure ZnO thin films with and (b) EDAX of CuO loaded ZnO thin films.

Figure 4 (a) and (b) shows the EDAX result of prepared thin films, it shows the composition of pure and doped materials with variation of oxygen. From the EDAX graph, it is found that mass% and at. wt. % of Zn, dopant Cu and O is nearly matched. It was found that prepared thin films are non-stoichiometric.

3.2.3 X-ray powder diffraction (XRD):[10, 14]

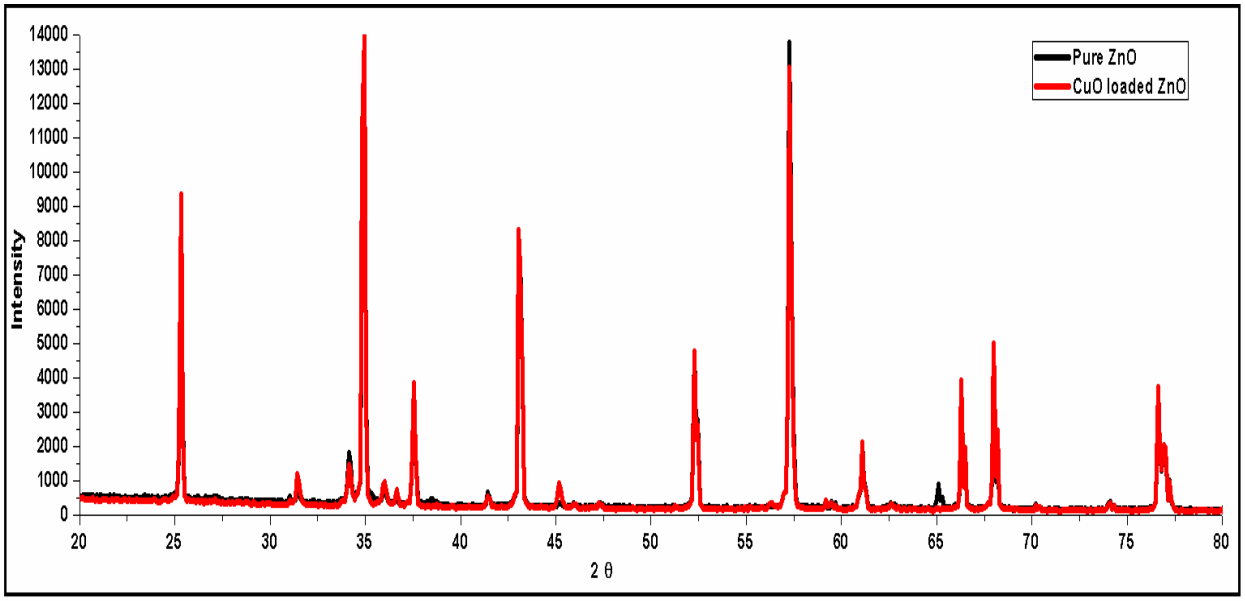

Figure 5 XRD pattern of pure ZnO and CuO loaded ZnO thin films.

From XRD pattern observed that diffraction peaks corresponds to the hexagonal structure of ZnO (JCPDS card No. 75-1533) and monoclinic structure of CuO (JCPDS Card No. 80-1916). It has been observed that the prominent peak at 34.89 and 57.29 for pure ZnO and CuO loaded ZnO respectively. The maximum peak intensities of CuO loaded ZnO thin films XRD pattern shows better crystallinity and large crystallite size can be attributed to the particles agglomeration. As per structural analysis the grain size were calculated by using Scherrer formula. The grain size of pure ZnO and CuO loaded ZnO were found 45 nm and 60 nm respectively.

Table 2 Summary of Structural and morphological characterization

Thin films	Average particle size, d nm **(SEM)**	Atomic % **(EDAX)**			Crystallite (grain) size, D nm **(XRD)**
		Zn	Cu	O	
Pure ZnO	103	54.94	00	45.06	45
CuO loaded ZnO	124	27.88	3.91	68.21	60

3.3 Gas sensing study ZnO thin films

3.3.1 Sensitivity [10, 15]

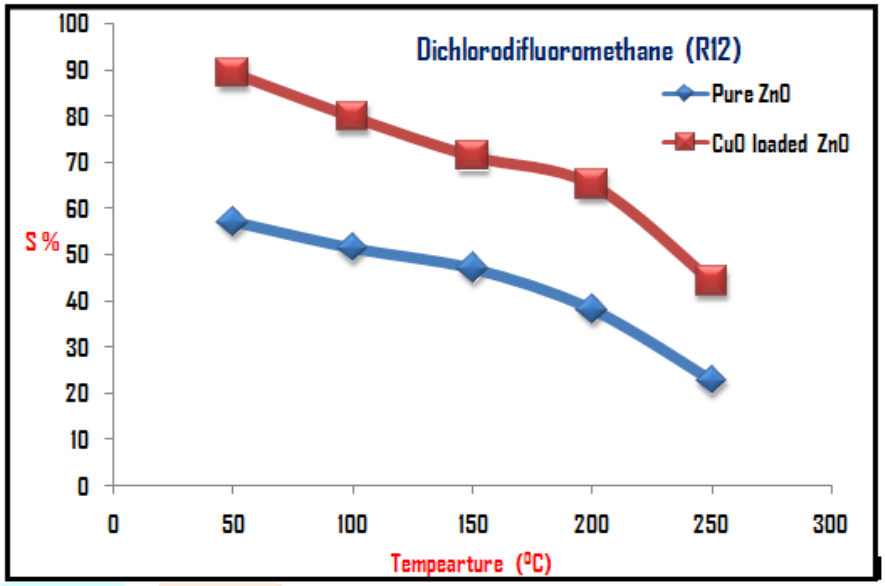

Figure 6 Sensitivity of pure ZnO and CuO loaded ZnO thin films.

Figure 6 shows the sensitivity of ZnO and CuO loaded ZnO thin films. The resistance measurement has been carried out at different operating temperature and various parts per million (PPM) of R12 gas.The CuO loaded ZnO thin films showed maximum sensitivity 89.23% for dichlorodifluoromethane gas at operating temperature 50^0C and gas concentration was at 100 ppm.

3.3.2 Response and recovery time [10]

The time required for the sensor to attain 90% of the maximum increase in conductance on exposure of the target gas is known as response time. The time required by the sensor to get back 10% of the maximum conductance when the flow of gas is switched off is known as recovery time. Figure 7 shows response and recovery time of CuO loaded ZnO thin film.

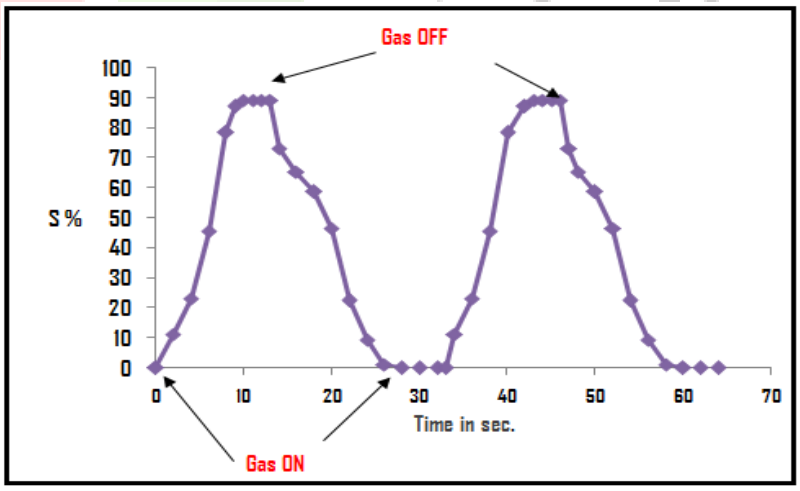

Figure 7 Response and recovery of CuO loaded ZnO thin film for dichlorodifluoromethane gas

From Figure 8 the response was very quick (~ 8 sec) while the recovery was fast (~ 14 sec) to dichlorodifluoromethane gas at 100 ppm concentration. Fast response may be due the reducing nature of R12 gas.

3.3.3 Dichlorodifluoromethane gas sensing mechanism for CuO loaded ZnO thin film

The nature of dichlorodifluoromethane gas is reducing. When the molecules of R 12 gas are interact with the surface of the CuO loaded ZnO thin film, the film resistance is change, the change in resistance measured in the form of gas response of the film. In the presence of R12 gas, the resistance of thin film decreases. The gas detection precept of metal oxide is based totally on the versions of the depletion layer at the grain boundaries inside the presence of gas, which lead to modulations inside the top of the energy barriers for free charge carriers to move, consequently main to a exchange inside the resistivity of the film [11, 13, 15].

4. Conclusion

From the obtained results, following conclusions can be made for the sensing performance of CuO loaded ZnO nanocomposites thin films:

(1) It has become possible to make CuO loaded ZnO nanocomposites thin film gas sensors using thermal evaporation method.

(2) Pure ZnO thin films showed low response to R12 gas.

(3) 3 % CuO loaded ZnO nanocomposites thin films showed maximum sensitivity to R 12 gas at 50^0C, also observed that as operating temperature increases sensitivity of films decreases.

(6) The sensor depicted very fast response and recovery to R 12 gas.

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