



## EFFECT OF Cr<sub>2</sub>O<sub>3</sub> BY DOPING AND DIPPING ON GAS SENSING CHARACTERISTICS OF ZnO THICK FILMS

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### ABSTRACT

Thick films of pure ZnO and various concentrations (1 wt. %, 3 wt. %, 5 wt. %, 7 wt. % and 10 wt. %) of Cr<sub>2</sub>O<sub>3</sub>-doped ZnO were prepared on alumina substrates using a standard screen printing technique. Surface modified ZnO thick films by Cr<sub>2</sub>O<sub>3</sub> were obtained by dipping pure ZnO thick films into 0.1M aqueous solution of chromium trioxide (CrO<sub>3</sub>) for different time intervals. The dipped and doped films were fired at a temperature of 700°C for two hours in an air atmosphere. The surface resistance of thick film decreases when the films were exposed to LPG gas. At 300°C, the 5 wt. % Cr<sub>2</sub>O<sub>3</sub> doped films have shown significant sensitivity (57.48%) to LPG gas whereas 15 min dipped films have shown highest sensitivity (80.12%) to LPG gas at 300°C.

**Keywords:** ZnO; Cr<sub>2</sub>O<sub>3</sub>; XRD; SEM; LPG

### I. INTRODUCTION

The sensors are required basically for measurement of physical quantities and use of controlling some systems. Presently, the atmospheric pollution has become a global issue. Gases from auto and industrial exhausts are polluting the environment. In order to detect/measure and control these gases, one should know the amount and type of gases present in the ambient. Thus the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies. The ZnO is a multifunctional material. Because of its high chemical stability, low dielectric constant, large electromechanical coupling coefficient and luminous transmittance, ZnO based materials have been used as dielectric ceramic, pigment, catalyst and sensing material [1]. As gas sensing material, is one of the earliest discovered and most widely applied oxide gas sensing material [2-5]. It is sensitive to many sorts of gases and has satisfactory stability. The sensitivity of ZnO thick films is due to the adsorption-desorption phenomena [6, 7] that happen on its surface leading to an increase or decrease in resistivity of the films. To increase the gas sensitivity, the films must have a high electrical resistivity associated with a small crystallite size [7]. However, these sensors are not

selective for a particular gas and various attempts are being made to improve their sensitivity and selectivity. One approach is to use dopants and additives which can modulate the gas sensing characteristics. A suitable catalyst or promoter is often added in small percentage to enhance the sensitivity and selectivity [8-13]. Low cost metals and metal oxides have been doped to achieve higher sensitivity and selectivity [14].

A growing number of different ceramic materials are used today for gas/humidity sensing. The primary mechanism associated with their potential use involves several microstructure parameters that influence sensing behavior [15]. Among them, small grain size plays an important role since it was shown that decrease of the grain size to the nanometer level leads to many interesting and new properties [16, 17]. Additionally, when oxides with a spinel structure are considered, the determination of the cation distribution and site occupancy, defect concentration and non-stoichiometry are of considerable relevance for understanding how a ceramic material interacts with its environment [18, 19, 20]. It is already established that some spinels have advanced gas sensing and catalytic properties. The spinels such as ZnCr<sub>2</sub>O<sub>4</sub> are very suitable for aggressive

environments [15, 21, 22]. Catalyst prepared by various methods, and concluded that any ZnO–Cr<sub>2</sub>O<sub>3</sub> mixed catalyst is composed of two phases, i.e. ZnO and ZnCr<sub>2</sub>O<sub>4</sub>, and presents higher resistance to the aging of catalyst than non-promoted ZnO catalyst, and that promoting action is mainly due to the hindering action of the promoter, Cr<sub>2</sub>O<sub>3</sub> upon the recrystallization of ZnO [23]. ZnO promoted with Cr<sub>2</sub>O<sub>3</sub> possesses improved catalytic activity for the synthesis reaction and also has a better sulphur tolerance [24]. A small additive of Cr<sub>2</sub>O<sub>3</sub> increases the electric breakdown by decreasing the grain size [25]. It has been studied that Cr<sub>2</sub>O<sub>3</sub> [26] was used as a sensing element.

Liquefied Petroleum Gas (LPG) is highly inflammable gas. It is explosively utilized in industrial and domestic fields as fuel. It is referred as town or cooking gas. Cooking gas consists chiefly of butane (55-vol %) [27], a colorless and odorless gas. It is usually mixed with compounds of sulfur (methyl mercaptan and ethyl mercaptan) having foul smell, so that its leakage can be noticed easily. This gas is potentially hazardous because explosion accidents might be caused when it leak out by mistake. It has been reported that, at the concentration up to noticeable leakage, it is very much more than the lower explosive limit (LEL) of the gas in air. So there is a great demand and emerged challenges [28] for monitoring it for the purpose of control and safety applications in domestic and industrial fields. The main aim of the present study is to focus the LPG sensing by modifying the ZnO based thick films.

## II. EXPERIMENTAL

### II.1 Films prepared by doping

The ZnO: Cr<sub>2</sub>O<sub>3</sub> pastes used in screen printing were prepared by maintaining the inorganic to organic materials ratio at 70:30. Inorganic part consists of a functional material (Analar grade ZnO powder calcined at 400 °C for 2 h in a muffle furnace), dopant (Cr<sub>2</sub>O<sub>3</sub>) and glass frit (70 wt. % PbO, 18 wt. % Al<sub>2</sub>O<sub>3</sub>, 9 wt. % SiO<sub>2</sub> and 3wt. % B<sub>2</sub>O<sub>3</sub>). Organic parts consist of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA). The Analar (AR) grade ZnO with x wt. % Cr<sub>2</sub>O<sub>3</sub> (x = 1, 3, 5, 7 and 10%) and 5 wt. % of glass frit were mixed thoroughly in an acetone medium with mortar and pestle. A solution of EC and BCA prepared at the ratio 8:92 was added drop by drop until proper thixotropic properties of the paste were achieved. ZnO: Cr<sub>2</sub>O<sub>3</sub> thick films were prepared on alumina substrates using a standard screen-printing technique. A nylon screen (40s, mesh no.355) was used for screen-printing. The required mask (2 x 1.25 cm) was developed on the screen using a standard

photolithography process. The paste was printed on clean alumina substrates (5 x 2 cm) with the help of a mask. The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under infrared radiation for 45 minutes to remove the organic vehicle and then fired at a temperature of 700°C for 2 h ( which includes the time required to achieve the peak firing temperature , constant firing for 30 minutes at the peak temperature and then to attain the room temperature) in a muffle furnace. During the firing process glass frit melted and the functional material and dopant were sintered. The function of glass frit is to bind the grains of functional and dopant materials together and also to adhere the film firmly to the substrate surface.

### II.2 Films prepared by dipping

Analar grade ZnO powder was calcined at 400 °C for 2 h in a muffle furnace. Then this powder was crushed and thoroughly mixed with a glass frit as a permanent binder. Organic vehicles such as butyl carbitol acetate (BCA) and ethyl cellulose (EC) were added to this mixture to achieve proper thixotropic properties of the paste. The ratio of inorganic to organic parts was maintained at 70:30 (the ratio of active powder to permanent binder was kept at 95:5 in 70 % and the ratio of EC to BCA was 8:92 in 30 %). Undoped ZnO thick films were prepared on alumina substrates using a standard screen-printing technique as discussed above. These films were surface modified by dipping them into a 0.1M aqueous solution of CrO<sub>3</sub> for different intervals of time followed by firing (700°C). The CrO<sub>3</sub> dispersed on the film surface was reduced to Cr<sub>2</sub>O<sub>3</sub> in firing process. Thus the sensor elements with different mass% of Cr<sub>2</sub>O<sub>3</sub> were obtained.

### II.3 Characterization

The structural properties of ZnO: Cr<sub>2</sub>O<sub>3</sub> films were investigated using X-ray diffraction analysis from 20-80° [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) with CuK $\alpha$ ,  $\lambda=0.1542$  nm radiation] with a 0.1°/step (2 $\theta$ ) at the rate of 2 s/step. A scanning electron microscopy (SEM- JOEL JED-2300) was employed to characterize the surface morphology. The composition of ZnO thick film samples were analyzed by an energy dispersive X- ray spectrometer (JOEL-JED 6360 LA). The thickness of the films was measured using a Taylor-Hobson (Taly-step UK) system and was observed to be uniform in the range of 20 $\mu$ m to 25 $\mu$ m.

The D.C. resistance of the films was measured by using half bridge method in an air atmosphere at different temperatures. The gas sensing studies were carried out on a static gas sensing system under

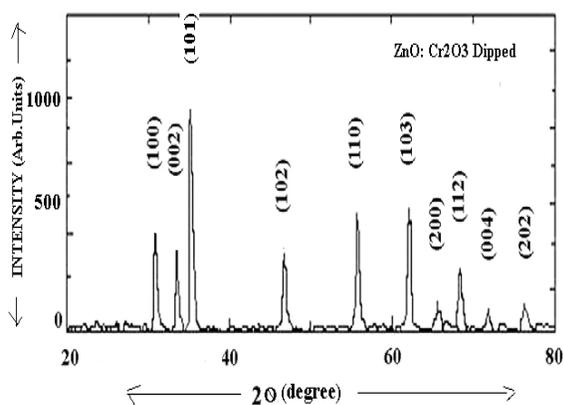
normal laboratory conditions. The electrical resistance of thick films in air ( $R_a$ ) and in the presence of LPG ( $R_g$ ) was measured to evaluate the gas response ( $S$ ) given by the relation,

$$S = \frac{R_a - R_g}{R_a} \quad (1)$$

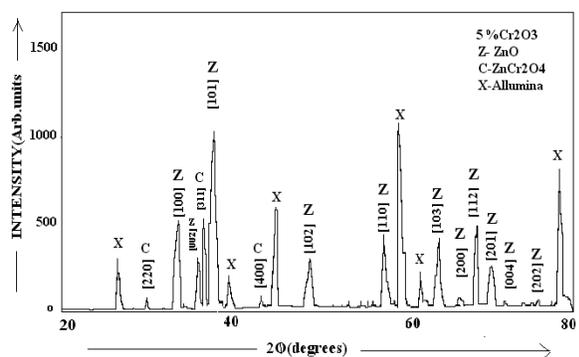
where  $R_a$  is the resistance of the ZnO: Cr<sub>2</sub>O<sub>3</sub> thick films in an air and  $R_g$  is the resistance of the ZnO: Cr<sub>2</sub>O<sub>3</sub> thick films in the presence of LPG.

### III. RESULT AND DISCUSSION

#### III.1 X-Ray diffraction



**Fig.1(a):** XRD of 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films



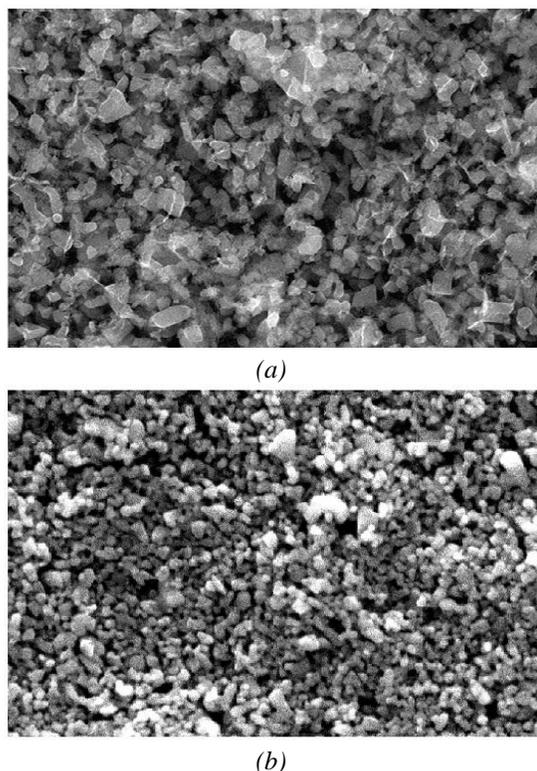
**Fig.1(b):** XRD of 5wt.% Cr<sub>2</sub>O<sub>3</sub> doped ZnO films

Fig. 1(a) shows XRD pattern of 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO film and fig.1 (b) shows 5 wt. % Cr<sub>2</sub>O<sub>3</sub> doped ZnO thick film. From Fig.1 (a), the observed peaks are matching well with JCPDS data of ZnO. The sharp peaks of the XRD patterns correspond to ZnO material and are observed to be polycrystalline in nature. No peaks corresponding to Cr<sub>2</sub>O<sub>3</sub> were

observed. It may be due to very small mass% of Cr<sub>2</sub>O<sub>3</sub> dispersed on the surface of ZnO. From Fig. 1(b), the observed diffraction peaks correspond to the hexagonal wurtzite structure of ZnO (JCPDS 36-14510) and cubic spinel phase of ZnCr<sub>2</sub>O<sub>4</sub> (JCPDS 22-1107). There could be solid state reaction between ZnO and Cr<sub>2</sub>O<sub>3</sub>. This could be a result of nucleation process and the initial stage of reaction product formation, the spinel phase of ZnCr<sub>2</sub>O<sub>4</sub>. This indicates that Cr<sup>3+</sup> and Zn<sup>2+</sup> distribute in molecular level, and lead to the formation of ZnCr<sub>2</sub>O<sub>4</sub> phase, which distributes at the grain boundaries [29]

#### III.2 Microstructural analysis (SEM)

Fig. 2(a) shows SEM of 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO thick film and fig. 2(b) shows SEM of 5 wt. % Cr<sub>2</sub>O<sub>3</sub> doped ZnO thick films. Fig. 2(a) shows Cr<sub>2</sub>O<sub>3</sub> grains associated with the ZnO grains. Fig. 2(b) shows that, for 5 wt. % doping, Cr<sub>2</sub>O<sub>3</sub> grains may reside in the intergranular regions of ZnO. ZnCr<sub>2</sub>O<sub>4</sub> exist between ZnO and Cr<sub>2</sub>O<sub>3</sub> phase can stabilize surface zinc active sites and promote the increase in the effective surface area [30, 31].



**Fig.2:** SEM images of (a) 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films (b) 5 wt. % Cr<sub>2</sub>O<sub>3</sub> doped ZnO films

### III.3 Quantitative elemental analysis-EDAX

Table 1 and table 2 shows EDAX analysis of Cr<sub>2</sub>O<sub>3</sub> dipped and doped ZnO films respectively. The EDAX analysis showed the presence of only Zn, Cr and O as expected. No other impurity elements were present. As shown in table 1, the films dipped in Cr<sub>2</sub>O<sub>3</sub> were observed to be most oxygen deficient than the pure ZnO film. The film dipped for 15min was observed to be rich in oxygen than other dipped films. Excess or deficiency of the constituent material particles leads the semiconducting nature of the material.

Table 1. Composition of the Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films at time intervals

Element (Mass %)	Dipping Time(min.)				
	0	3	5	15	25
O	5.63	5.14	5.21	5.39	5.02
Zn	94.37	94.82	94.58	94.25	94.47
Cr	0	0.04	0.21	0.36	0.51

As shown in table 2, the entire samples were observed to be oxygen deficient. The film doped with 5 % Cr<sub>2</sub>O<sub>3</sub> was observed to be most oxygen deficient. Deficiency or excess of the constituent material results in a distorted band structure with a corresponding increase in conductivity. Zinc oxide loses oxygen on heating so that the zinc is in excess. The oxygen of course evolves as electrically neutral substance so that it is associated with each excess zinc ions in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to non-stoichiometricity in the solid. This leads to the formation of the semiconducting nature of the material [32].

Table 2: Composition of the Cr<sub>2</sub>O<sub>3</sub> doped ZnO films at different doping conc.

Element (mass %)	Cr <sub>2</sub> O <sub>3</sub> (Wt. %)				
	1	3	5	7	10
O	15.52	16.96	15.32	15.60	15.93
Zn	83.61	80.57	80.48	78.63	75.42
Cr	0.87	2.47	4.20	5.77	8.65

### III.4 Gas sensing characteristics

#### III.4.1 Films prepared by dipping

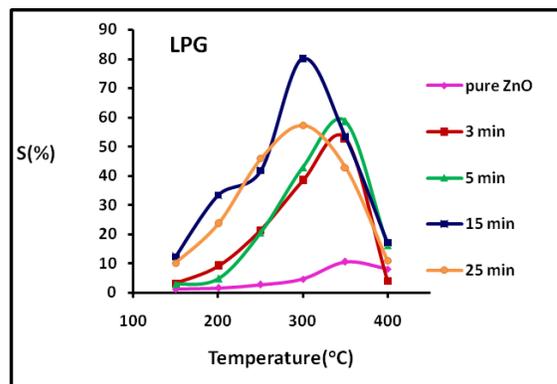


Fig.3 (a): Gas sensing characteristics of Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films

Fig. 3 shows the gas sensing characteristics of 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films fired at 700<sup>0</sup>C and exposed to 1000 ppm of LPG. As shown in Fig.3 (a), pure ZnO is notably less sensitive than dipped films. The 15 min. Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films were found to be more sensitive (80.12%) to LPG than other timed dipped films at 300<sup>0</sup>C. Fig. 3(b) indicates the selectivity of 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films for different gases at 300<sup>0</sup>C. Fig.3 (c) shows the variation of sensitivity of 15 min dipped ZnO films with LPG concentration (ppm) at 300<sup>0</sup>C. Fig.3 (d), represents the response and recovery time of 15 min dipped films at 300<sup>0</sup>C. The response was quick (~ 11 sec) and recovery was fast (~13 sec). From fig.3 (a) it has been observed that, for 15 min dipped films, the sensitivity increases up to 300<sup>0</sup>C. After that sensitivity decreases.

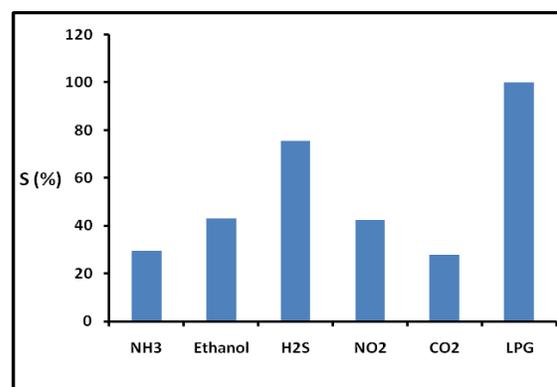
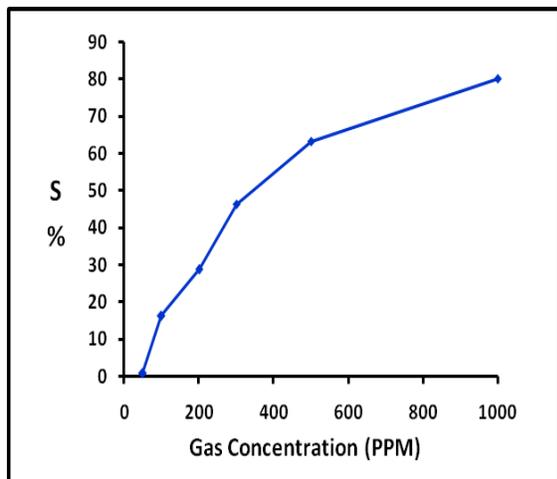
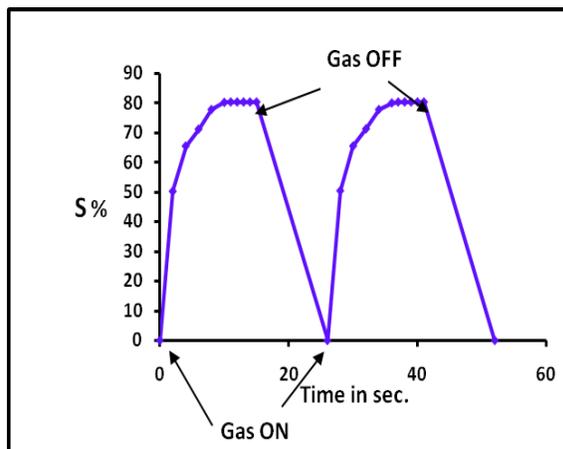


Fig.3 (b): Selectivity of 15 min Cr<sub>2</sub>O<sub>3</sub> dipped ZnO films for different gases at 300<sup>0</sup>C



**Fig.3 (c):** variation of sensitivity of 15 min dipped ZnO films with LPG concentration (ppm) at 300°C



**Fig.3 (d):** response and recovery time of 15 min dipped films at 300°C

Operating temperature plays a vital role in determining the response of the film. In fact, there exists an optimum operating temperature of a sensor to achieve the maximum response to a gas of interest. The temperature being dependent upon the kind of gases, i.e. the mechanism of dissociation and further chemisorptions of a gas on the particular sensor surface [33]. Also, the adsorption of atmospheric oxygen on the film surface depends upon the operating temperature.

The temperature (thermal energy) at which the gas response is maximum is the actual thermal energy required to activate the material for progress in reaction. However the response decreases at higher operating temperature, as the oxygen adsorbates are

desorbed from the surface of the sensor [34]. Also at higher temperature, the carrier concentration increases due to intrinsic thermal excitation and Debye length decreases. This may be one of the reasons for decreased gas response at higher temperature [35].

At a low operating temperature, the response of the films to LPG is restricted by the speed of the chemical reaction because the gas molecules do not have enough thermal energy to react with the surface adsorbed oxygen species. In fact, during adsorption of atmospheric oxygen on the film surface, a potential barrier to charge transport is developed.

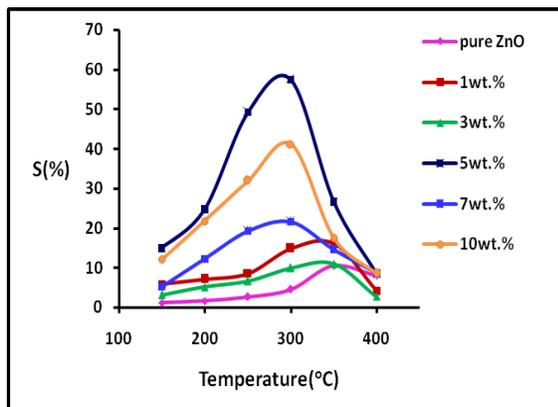
At 15 min dipping time, the optimum mass% of  $\text{Cr}_2\text{O}_3$  would be dispersed on the surface of the film, and mass% of oxygen was also higher than other dipped films (Table 1a). The optimum mass% of  $\text{Cr}_2\text{O}_3$  on the surface of ZnO would form misfit regions non-uniformly on the film surface. The surface misfit regions enhance the oxygen adsorption on the surface. Thus the number of oxygen species adsorbed on the activated surface would be larger. The larger the number of oxygen species adsorbed, the faster would be the oxidization of LPG. This would increase the conductance of the film crucially, enhancing gas response. At lower dopant concentrations, the numbers of Cr-misfits on the film surface are less, which would adsorb less oxygen species on the film surface. However, at higher dopant concentrations, the Cr-dopant would mask the entire base material-ZnO and would resist the gas to reach up to the surface active sites, so gas response would decrease further. Fig.3 (b) shows that these films are more selective to LPG than other gases.

From fig. 3(c), the sensitivity values were observed to be increased by increasing the gas concentration up to 1000 ppm. The response was highest for 1000 ppm of LPG. From the above graph, it has been observed that the sensitivity of thick films for LPG at 300°C increases linearly with increase in gas concentration up to 300 ppm. Above 300 ppm the increase in sensitivity is slow and almost saturates at 1000 ppm. Thus the active region of the sensor would be up to 300 ppm. At lower gas concentrations, the unimolecular layer of gas molecules would be formed on the surface of the sensor which could interact more actively giving larger response. At the higher gas concentrations, the multilayer of gas molecules may be formed that would result into saturation in response beyond 300 ppm. 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 [36].

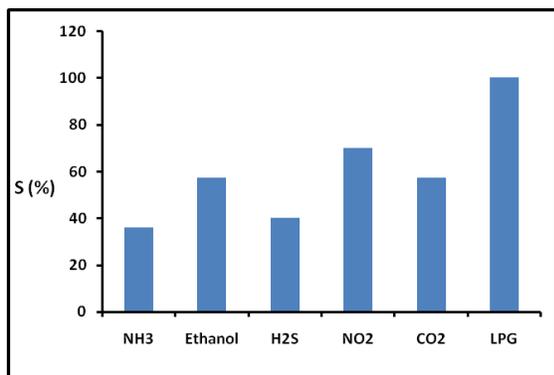
The quick response may be due to faster oxidation of a gas. The Cr species catalyses the reaction, promoting the rapid electron transfers between the adsorbate and substrate.

### III.4.2 Films prepared by doping

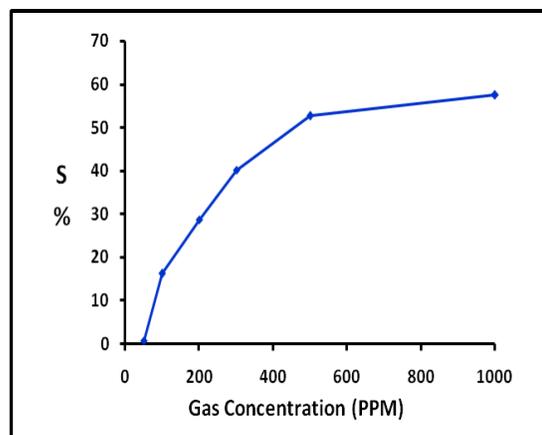
Fig.4 shows the gas sensing characteristics of 5 wt. %  $\text{Cr}_2\text{O}_3$  doped ZnO films fired at  $700^\circ\text{C}$  and exposed to 1000 ppm of LPG. As shown in Fig. 4(a), pure ZnO is notably less sensitive than doped films. 5 wt. %  $\text{Cr}_2\text{O}_3$  doped ZnO films were found to be more sensitive (57.48%) to LPG than other doped films at  $300^\circ\text{C}$ . Fig.4 (b) indicates the selectivity of 5 wt. %  $\text{Cr}_2\text{O}_3$  doped ZnO films for different gases at  $300^\circ\text{C}$ . Fig.4 (c) shows the variation of sensitivity of 5 wt.% doped ZnO films with LPG concentration (ppm) at  $300^\circ\text{C}$ . Fig.4 (d), represents the response and recovery time of 5wt.% doped films at  $300^\circ\text{C}$ . The response was quick ( $\sim 18$  sec) and recovery was fast ( $\sim 25$  sec).



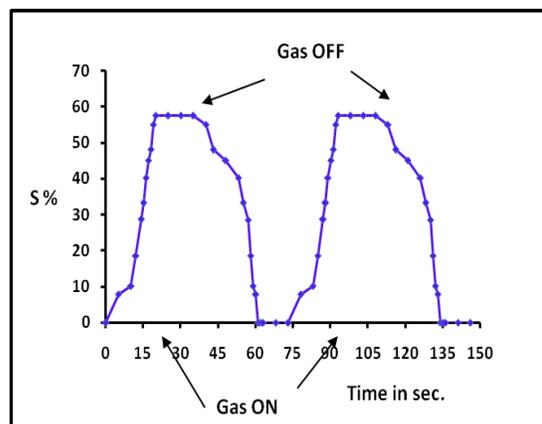
**Fig 4 (a):** Gas sensing characteristics of  $\text{Cr}_2\text{O}_3$  doped ZnO films



**Fig.4 (b):** Selectivity of 5wt. %  $\text{Cr}_2\text{O}_3$  doped ZnO films for different gases at  $300^\circ\text{C}$



**Fig.4 (c):** variation of sensitivity of 5wt. % doped ZnO films with LPG concentration (ppm) at  $300^\circ\text{C}$



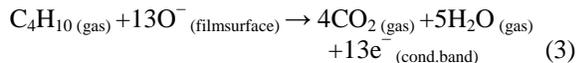
**Fig.4 (d):** response and recovery time of 5 wt.% doped films at  $300^\circ\text{C}$

Basic mechanism of doped films is same as that of dipped films. As compared to dipped films, doped films were observed to be less sensitive to LPG. It may be attributed that due to dipping, more misfits would be created on the surface of the films. So dipped films were observed more a more sensitive to LPG than doped films.

Gas sensing mechanism is generally explained in terms of conductance either by adsorption of atmospheric oxygen on the surface and/or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. In case of former, the atmospheric oxygen adsorbs on the surface by extracting an electron from conduction band, in the form of superoxides or peroxides, which are mainly responsible for the detection of the test gases. At higher temperature, the adsorbed oxygen captures the electrons from conduction band as:



It would result in decreasing conductivity of the film. When LPG reacts with the adsorbed oxygen on the surface of the film, it gets oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by following series of intermediate stages. This liberates free electrons in the conduction band. The final reaction takes place as:



This shows n-type conduction mechanism. Thus generated electrons contribute to a sudden increase in conductance of the thick film. The  $\text{Cr}_2\text{O}_3$  misfit regions dispersed on the surface would enhance the ability of base material to adsorb more oxygen species giving high resistance in air ambient. Therefore, the higher response was obtained to 1000 ppm LPG. The mass% of Zn and O in each samples were not as per the stoichiometric proportion and all samples were observed to be the oxygen deficient. This deficiency gets reduced (though in less extent) due to adsorption of atmospheric/molecular oxygen. This helps in decreasing electronic conductivity of the film. Upon exposure, LPG molecules got oxidized with the adsorbed oxygen ions by following the series of intermediate stages, producing  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This results in evolving oxygen as an electrically neutral atom trapping behind the negative charges (electrons). Upon exposure, the energy released in decomposition of LPG molecules, would be sufficient for trapped electrons to jump into the conduction band of activated ZnO, resulting in increase in the conductivity of the film. The drastic increase in conductivity of the sensor could be attributed to the adsorption-desorption mechanism resulted from the electronic defects.

#### IV. CONCLUSION

1. Pure zinc oxide was almost less sensitive to LPG.
2.  $\text{Cr}_2\text{O}_3$  in ZnO is outstanding in promoting the LPG sensing.
3. Surface modification by dipping process is one of the most suitable methods of modifying the surface of thick films.
4. 15 min  $\text{Cr}_2\text{O}_3$  dipped incorporated in pure ZnO thick film is the most sensitive element to the LPG.
5. The sensor has good selectivity to LPG against  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , Ethanol and  $\text{NO}_2$ .

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