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Fe_2O_3- Modified Cr_2O_3 thick Films: Ethanol Sensor

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ABSTRACT

Thick films of pure Cr_2O_3 were prepared by screen-printing technique. The surfaces of these films were modified by dipping them into 0.01 M aqueous solution of ferric chloride ($FeCl_3$) for different intervals of time, followed by firing at 550^0C for 30 min. firing results the oxidation of $FeCl_3$ additive in to Fe_2O_3. The characterizations and the gas sensing properties of pure and surface activated Cr_2O_3 thick films have been investigated. The sensor gives response to Ethanol gas at 350^OC. The quick response and fast recovery are the main features of this sensor. The effects of microstructure and activators concentration on the gas response, selectivity, response time and recovery reducing gases were studied and discussed.

Keywords: Fe_2O_3-activated Cr_2O_3, thick film, Ethanol sensor, gas response.

INTRODUCTION

Hazardous and toxic gases from auto and industrial exhausts are polluting the environment. Environmental pollution [1-4] is a burning global issue; pollution has raised its ugly head high in the global environment. Therefore, all industries should have an alarm system detecting and warning for dangerous exhaust gas concentration levels. Thus, the need to monitor and control these gases has led to research and development of a wide variety of sensors using different materials and technologies. The Cr_2O_3 is an important refractory material because of its high melting temperature (2300^0C) and crystallizes in Hexagonal-Rhombic corundum structure showing p-type semi conductivity. It is well known that, semiconducting oxides such as ZnO, Cr_2O_3, SnO_2, $BaTiO_3$ and Fe_2O_3 [5-16] are sensitive to various polluting gases. It has been studied that Cr_2O_3 [17-20] was used as a gas-sensing element. In fact, pure Cr_2O_3 was reported to have poor gas sensitivity.

Pure ethanol is called as an absolute alcohol. Ethanol is used for beverages, scientific and industrial purposes. Ethanol is hypnotic (sleep producer) (Solomans and Fryhle 2004) gas having toxic nature. Heavy exposure and consumption of alcoholic beverages, particularly by smokes, increase the risk of cancer (Sodi 2002) of the upper respiratory and digestive tracks. Alcoholic cirrhosis leads to leaver cancer. Amongst the women, of breast cancer increase with alcoholic consumption or exposure. Those working on ethanol synthesis have great chances of being victims of respiratory and digestive track cancer. So there is great demand and emerging challenges for monitoring ethanol gas at trace level.

The gas sensing performance of the material can be improved by incorporating few additives into the base material and/or surface activation (Matsushima et al 1989; Xiangfeng et al 2000) of thick films. Although few researchers have conducted studies on ethanol (Takao et al 1989; Miremadi et al 1994) gas sensors, it has not been possible to produce ethanol sensors in sufficient quantities to meet the demand.

The aim of the present work is to be developing the sensor by modifying pure Cr_2O_3 base material, which could be able to detect the C_2H_5OH vapors. Among the various metal oxide additives tested. Fe_2O_3 in Cr_2O_3 is outstanding in promoting the sensing properties of C_2H_5OH in air.

EXPERIMENTAL

Preparation of material powder

AR grade (99.9 % pure) Cr_2O_3 powder was ball milled to ensure sufficiently fine particle size. The fine powder

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was calcined at 1000^0C for 4 h, in air and re-ground. Thick films of so obtained powder were prepared by adopting the procedure explained elsewhere [10]. These films were surface modified by dipping them into a 0.01 M aqueous solution of $FeCl_3$ for different intervals of time followed by firing at 500^0C for 30 min. The $FeCl_3$ dispersed on the film surface was oxidized to Fe_2O_3 in firing process. Thus the sensor elements with different mass % of Fe_2O_3 were obtained. Silver contacts were made by vacuum evaporation for electrical measurements.

Preparation of thick films

The thixotropic paste was formulated by mixing the sintered fine powder of pure Cr_2O_3, with solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyal carbitol acetate and terpinol. The ratio Inorganic to organic part was kept as 80:20 in formulating the paste. The paste was then used to prepare thick films of pure Cr_2O_3.

Characterization

The microstructure and chemical composition of the films were analysed using scanning electron microscope (SEM,JEOL JED 2300) coupled with energy dispersive spectrometer (EDS JEOL 6360 LA). Thickness measurements were carried out using a Taylor-Hobson (Talystep, UK) system. Electrical and gas sensing characteristics were measured using a static gas sensing system.

Details of gas sensing system

The sensing performance of the sensors was examined using 'static gas sensing system' reported elsewhere (Patil et al 2006b).

MATERIALS CHARACTERIZATIONS

Thickness measurement

Thickness of thick film was measured by using the Taylor-Hobson (Talystep, UK) system. The thickness of the film was observed in the range from 30 to 40 μm. The reproducibility of the film thickness was archived by maintaining the proper rheology and thixotropy of the paste.

Structural properties (X-ray diffraction studies)

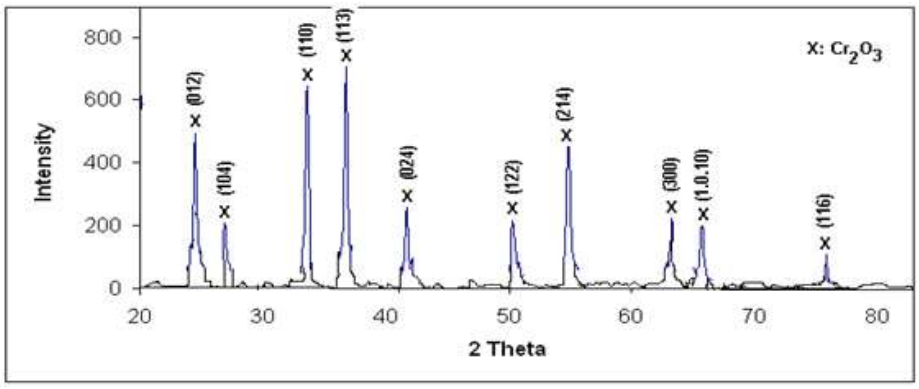

Figure 1. XRD of (**a**) unmodified Cr_2O_3 and (**b**) Fe_2O_3-activated Cr_2O_3 powder (5 min).

The crystalline structures of the films were analysed with X-ray diffractogram (RIGAKU DMAX 2500) using CuK_α radiation with 1.5418 A^0.

Figure 1(a) depicts the XRD patterns of unmodified (pure) and Fe_2O_3-activated Cr_2O_3 (5 min). The observed peaks 1(a) are matching well with ASTM reported data of pure Cr_2O_3. The material was observed to be microcrystalline in nature. There are no prominent peaks of Fe_2O_3 associated in XRD pattern, due to smaller wt % of Fe_2O_3 in comparison with Cr_2O_3.

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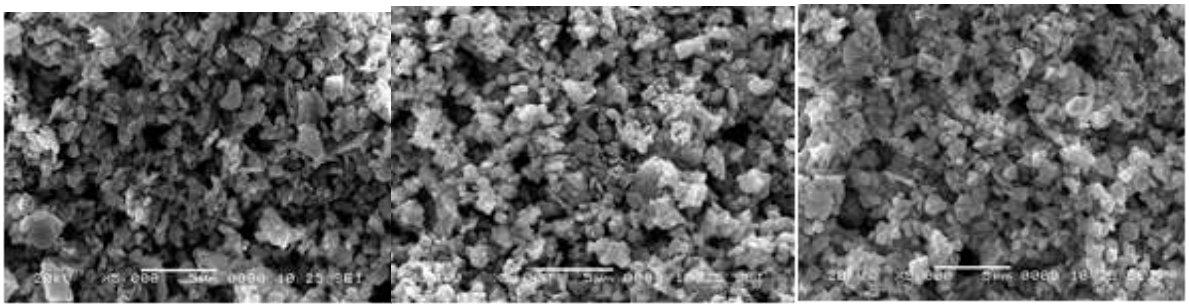
Elemental analysis

The quantitative elemental composition of pure and Fe-modified films were analysed using an energy dispersive spectrometer. The mass % of Cr and O in each samples were not as per stoichiometric proportion and all samples were observed to be oxygen deficient. Excess or deficiency of the constituent material particles leads to semiconducting nature of the material.

Microstructure-SEM



(a) (b) (c)

Figure 2. Micrographs of (a) Unmodified Cr_2O_3, (b) Fe_2O_3-activated Cr_2O_3 (5 min) and (c) Fe_2O_3-activated Cr_2O_3 (60 min) thick films

Unmodified Cr_2O_3 film in Fig. 2 (a) consists of randomly distributed grains with larger size and shape distribution. Fig. 2 (b) depicts the microstructure of Fe_2O_3-modified film (5 min). This film consists of smaller grains distributed on the larger grains. Smaller grains may be of Fe_2O_3 and larger ones may be of Cr_2O_3. Fig. 2 (c) depicts the microstructure of a Cr_2O_3-modified film for largest time interval (60 min) consists of particles with smaller size and shape associated with the Cr_2O_3 grains. It is observed from Fig. 2 (b) that the grains of Fe_2O_3-Cr_2O_3 are arranged in manner that, the porosity of the film is larger among all. Thus the effective surface area was expected to increase explosively, which enhances the optimum adsorption of oxygen at higher temperatures. The average grain size of highly sensitive film is observed to be 621 nm, calculated by Scherrer's formula.

ELECTRICAL PROPERTIES OF SENSOR

I-V Characteristics

Fig. 3 depicts the I-V characteristics of the Fe_2O_3-modified Cr_2O_3 films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film are ohmic in nature.

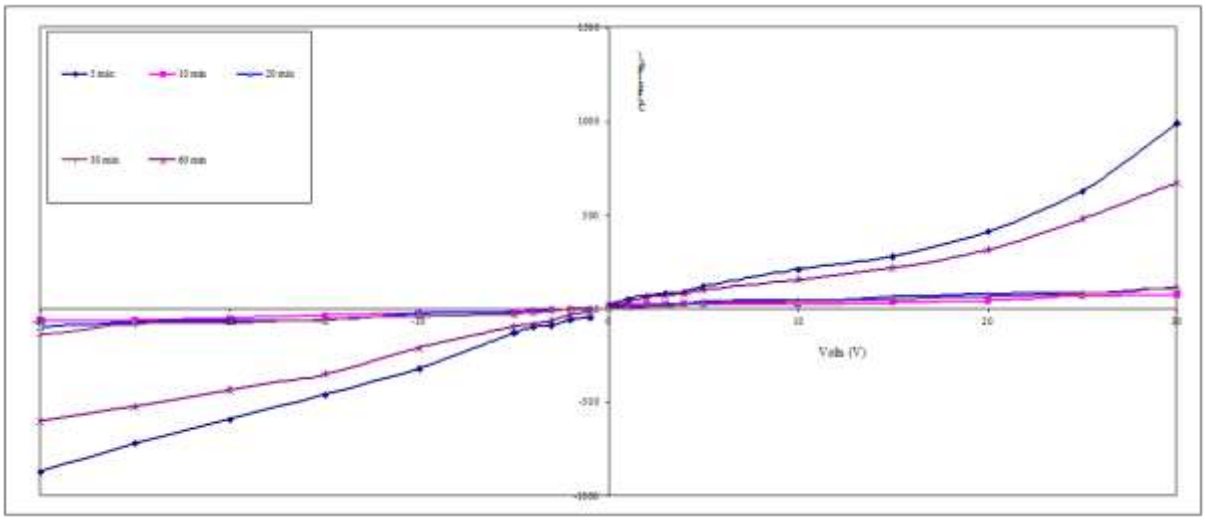


Figure 3. I-V characteristics of Fe_2O_3-modified Cr_2O_3 films.

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Electrical conductivity

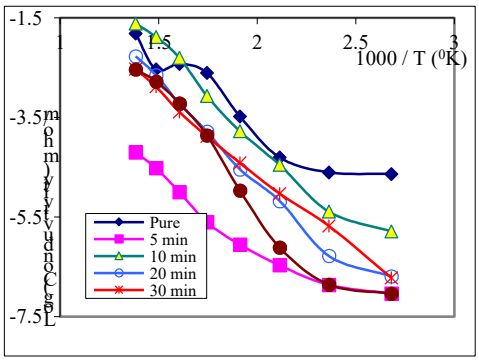

Figure 4. Conductivity – temperature profile of Fe_2O_3-modified Cr_2O_3 films.

The semiconducting nature of Fe_2O_3-modified Cr_2O_3 is observed from the measurements of conductivity with temperature. The semiconductivity in Cr_2O_3 may be attributed to oxygen deficiency in it. The material would then adsorb the oxygen species at higher temperatures ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$). The adsorption chemistry of Fe-modified Cr_2O_3 surface would be different from the pure Cr_2O_3 thick film surface. The Fe_2O_3 misfits on the surface enhance the oxygen adsorption capability of the surface. The Fe_2O_3 misfits distributed evenly on the surface would have made it possible to adsorb the oxygen ions even at low temperatures. From figure 4 it is clear that, the conductivities of Fe-modified films increase with increase in operating temperature. This behavior confirmed the semiconducting nature of modified Cr_2O_3. The increase in the conductivity of Fe_2O_3-modified Cr_2O_3 could be attributed to the charge-carrier generation mechanism resulted from the electronic defects. These generated electrons and the donor level in the energy band gap of Cr_2O_3 will contribute to increase conductivity.

SENSING PERFORMANCE OF THE SENSOR

Gas response, Selectivity, Response and Recovery time

Gas response (S) is defined as the ratio of the change in conductance of the sensor on exposure to the target gas to the original conductance in air. The relation for S is as:

$$S = (G_g - G_a) / G$$

where, G_a and G_g are the conductance of sensor in air and in a target gas medium, respectively.

Selectivity or specificity is defined as the ability of a sensor to respond to certain gas in the presence of other gases.

The time taken for the sensor to attain 90 % of the maximum increase in conductance on exposure to the target gas is the response time. The time taken by the sensor to get back 90 % of the original conductance is the recovery time.

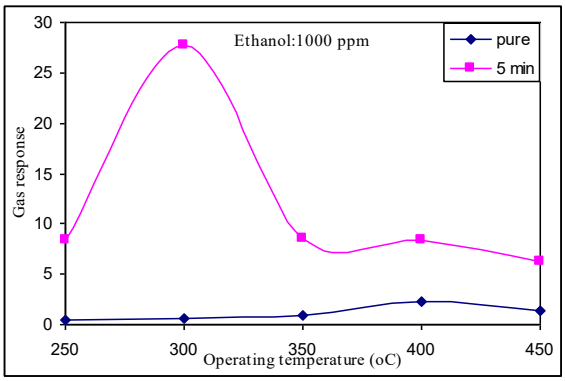

Figure 5. Variation of gas response of pure and modified (5 min) Cr_2O_3 thin films.

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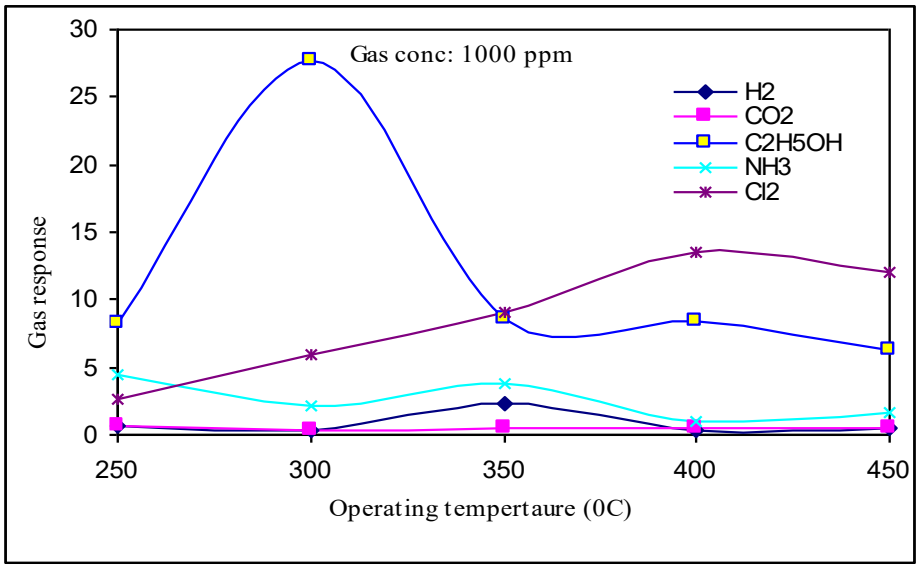
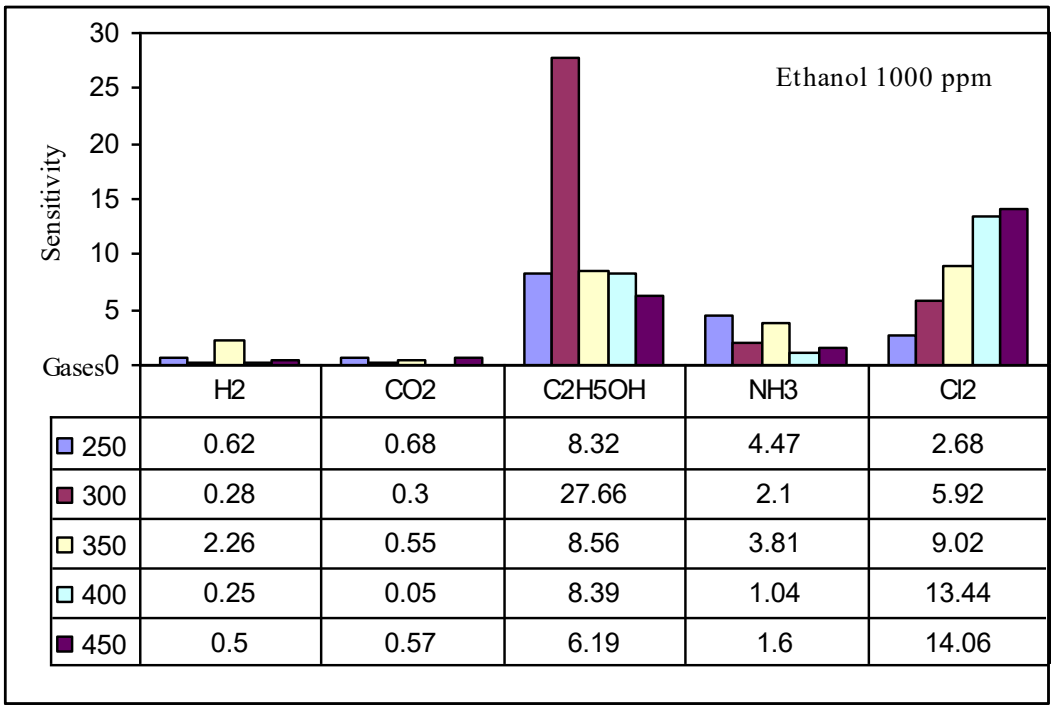


Figure 6. Variation of different gas responses with operating temperature.



Gases	H2	CO2	C2H5OH	NH3	Cl2
250	0.62	0.68	8.32	4.47	2.68
300	0.28	0.3	27.66	2.1	5.92
350	2.26	0.55	8.56	3.81	9.02
400	0.25	0.05	8.39	1.04	13.44
450	0.5	0.57	6.19	1.6	14.06

Figure 7 Variation of gas response with dipping (5 min) of Fe_2O_3 in Cr_2O_3 samples.

Sensing performance of pure Cr_2O_3 thick films

Figure 5 shows the variation of ethanol (1000 ppm) responses of pure and modified Cr_2O_3 thick film. It is observed that pure and modified Cr_2O_3 film having maximum response to be 2.30 and 27.66 at 400^0C and 300^0C, respectively.

Sensing performance of Fe_2O_3-modified Cr_2O_3 thick films

a. Response of sensor to various gases:

The variation of different gas responses of Fe_2O_3-modified Cr_2O_3 (5 min) sample with operating temperature is represented in figure 6.It is clear from the figure that the gas responses go on increasing, reach to their respective maxima and decreased further with increase in operating temperature. It is clear from figure that the Fe_2O_3-modified Cr_2O_3 (5 min) sample shows the largest response to ethanol vapours at 300^0C.

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b. Active region of the sensor:

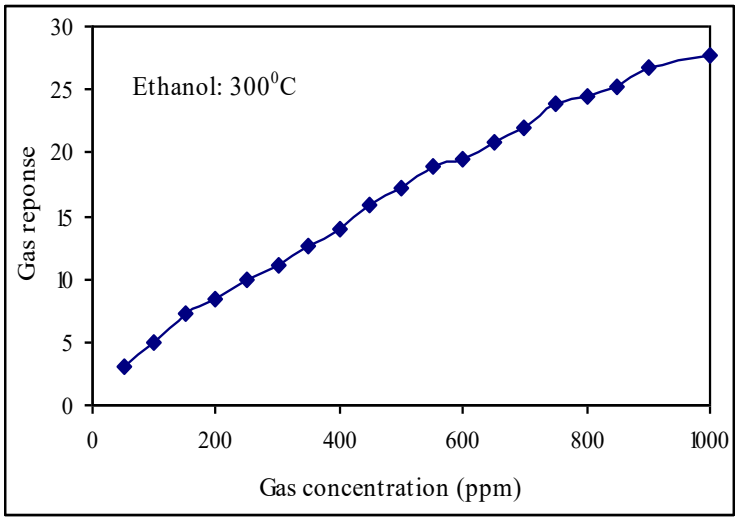

Figure 8. Variation of gas response with gas concentration.

Figure 8 depicts the variation of gas response of Fe_2O_3-modified Cr_2O_3 (5 min) sample with ethanol vapour concentrations. It is clear from the figure that gas response goes on increasing linearly with gas concentration up to 1000ppm. The rate of increase in gas response was relatively larger up to 1000 ppm. The monolayer of gas molecules formed on surface could cover the whole surfaces of the film. The excess gas molecules would remain ideal and would not reach surface active sides of the sensor. So, the gas response at higher concentration of the gas is not expected to increase further in large extent. Thus active region of the sensor would be up to 1000 ppm.

c. Effect of operating temperature:

Figure 6 depicts the variation of gas response to ethanol vapours (1000 ppm) with operating temperature. The largest response Fe_2O_3-modified Cr_2O_3 (5 min) to ethanol was observed to be 27.66 at 300^{0}C.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 Fe2O3 misfits on the Cr2O3 surface and operating temperature.

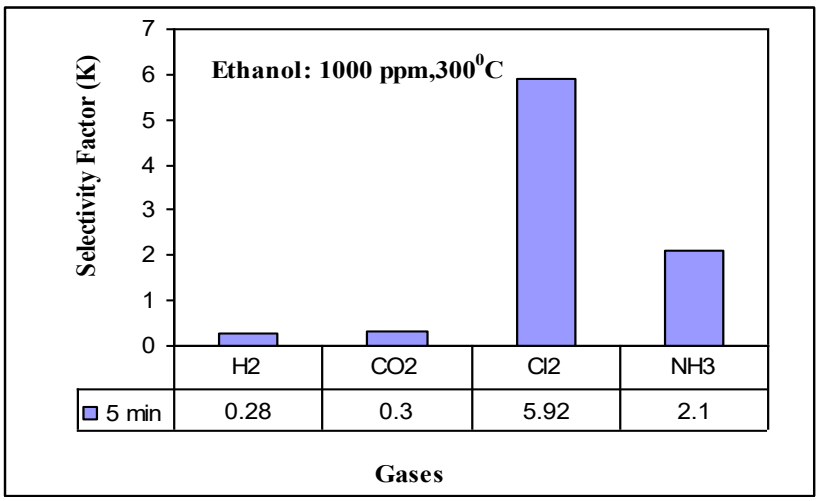

Figure 9. Selectivity factor of the sensor for various gases.

d. Selectivity factor of Fe_2O_3-modified Cr_2O_3 (5 min) for various gases*:*

It is observed from figure 9 that the Fe_2O_3-modified Cr_2O_3 sensor gives maximum response to ethanol vapours (1000 ppm) at 300^{0}C.The sensor showed highest selectivity for ethanol against all other tested gases: H_2, CO_2, Cl_2 and NH_3.

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e. Response and recovery time:

The response and recovery of Fe_2O_3-modified Cr_2O_3 (5 min) of sensor are represented in figure 10. The response was quick (≈ 16 sec) to 1000 ppm of ethanol, while the recovery was fast (≈ 38 sec). The quick response may be due to faster oxidation of gas. The negglible quantity of the surface reaction product and its high volatility explains its quick response and fast recovery to its initial chemical status.

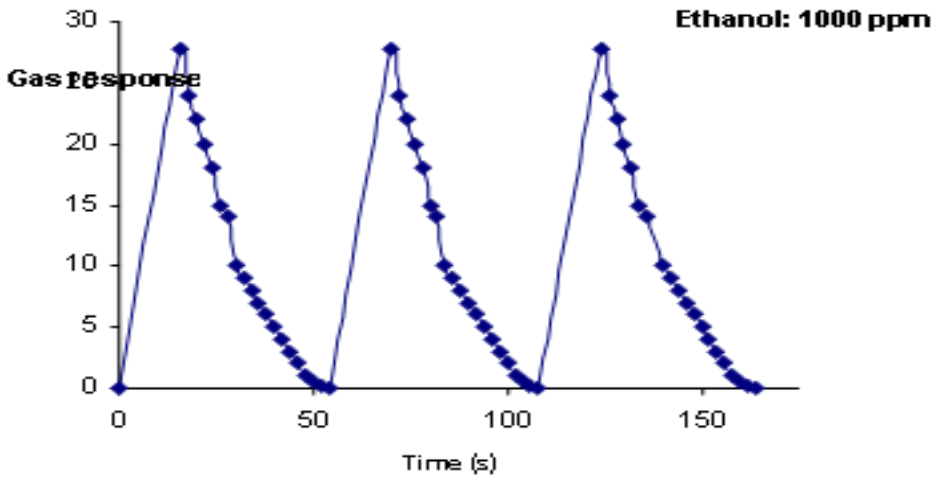

Figure 10. Response and recovery of Fe2O3 -modified Cr2O3 sample.

CONCLUSIONS

From the result obtained, following conclusions can be made for sensing performance of the sensors.

1. Pure Cr_2O_3 showed low response to ethanol vapours.
2. Among all other additives tested, Fe_2O_3 in Cr_2O_3 is outstanding in promoting the ethanol gas sensing mechanism.
3. The sensitivity of TiO2 based sensors was found to be changing with operating temperature.
4. The doping was observed to be an appropriate method to enhance sensitivity and selectivity to LPG and Cl2 gas.
5. By controlling the distribution and amount of activator in the semiconductor oxide, it could be possible to fabricate the sensor with good sensing properties.

REFERENCES

1. W. B. Durham, Industrial Pollution, Sax, N.I. (Ed.), Van Nostrand Reinhold Co, New York, (1974) pp. 10-35.
2. R. F. Dasmann, Environmental conservation, (4th Ed.) John Wiley and sons, Inc., New York, (1976) pp. 310-338.
3. L. A. Patil, D. R. Patil, Heterocontact type CuO-modified SnO2 sensor for the detection of a ppm level H2S gas at room temperature, Sens. Actuators B 120 (2006) 316-323.
4. D. R. Patil, L. A. Patil, P. P. Patil, Cr2O3-activated ZnO thick film resistors for ammonia gas sensing operable at room temperature, Sens. Actuators B 126 (2007) 368-374.
5. Z. Chen, K. Colbow, MgO doped Cr2O3 solubility limit and the effect of doping on the resistivity and ethanol sensitivity, Sens. Actuators B 9 (1992) 49- 53.
6. D. R. Patil, L. A. Patil, G. H. Jain, M. S. Wagh, S. A. Patil, Surface activated ZnO thick film resistors for LPG gas sensing, Sensors and Transducers 74 (2006) 874-883.

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XII Issue VII July 2025

7. D. R. Patil, L. A. Patil, Preparation and study of NH3 gas sensing behaviour of Fe2O3 doped ZnO thick film resistors, Sensors and Transducers 70 (2006) 661-670.
8. D. F. Shriver, P. W. Atkins, Inorg. Chem. (3rd ed.), Oxford University press, 2004, pp. 184-190.
9. G. S. Sodhi, Fundamental concepts of Environmental Chemistry, (1st edition) Narosa Publishing House New Delhi, 2002, pp. 215-302, 405-427.
10. A. M. Ruiz, G. Sakai, A. Cornet, K. Shimanoe, J. R. Morante, N. Yamazoe, Cr-doped TiO2 gas sensor for exhaust NO2 monitoring, Sens. Actuators B 93 (2003) 509-518.
11. D. R. Patil, L. A. Patil, Ammonia sensing resistors based on Fe2O3-modified ZnO thick films, Sensors IEEE 7 (2007) 434-439.
12. D. R. Patil, L. A. Patil, Room temperature chlorine gas sensing using surface modified ZnO thick film resistors, Sens. Actuators B 123 (2007) 546-553.
13. D. R. Patil, L. A. Patil, Al2O3-modified ZnO based thick film resistors for H2-gas sensing, Sensors and Transducers 81 (2007) 1354-1363.
14. G. H. Jain, L. A. Patil, M. S. Wagh, D. R. Patil, S. A. Patil, D. P. Amalnerkar, Surface modified BaTiO3 thick film resistors as H2S gas sensors, Sens. Actuators B 117 (2006) 159-165.
15. M. S. Wagh, G. H. Jain, D. R. Patil, S. A. Patil, L. A. Patil, Modified zinc oxide thick film resistors as NH3 gas sensor, Sens. Actuators B 115 (2006) 128-133.
16. M. S. Wagh, G. H. Jain, D. R. Patil, S. A. Patil, L. A. Patil, Surface customisation of SnO2 thick films using RuO2 as a surfactant for the LPG response, Sens. Actuators B 122 (2007) 357-364.
17. T. Jantson, T. Avarmaa, H. Mandar, T. Uustave, R. Jaaniso, Nanocrystalline Cr2O3-TiO2 thin films by pulsed laser deposition, Sens. Actuators B 109 (2005) 24-31.
18. L. P. Martin, A. Q. Pham, R. S. Glass, Effect of Cr2O3 electrode morphology on the nitric oxide response of a stabilized zirconia sensor, Sens. Actuators B 96 (2003) 53-60.
19. D. N. Suryawanshi, D. R. Patil, L. A. Patil, Fe2O3-activiated Cr2O3 thick films as temperature dependent gas sensors, Sens. Actuators B 134 (2008) 579-584.
20. D. F. Shriver, P. W. Atkins, Inorg. Chem.), Oxford University press, 2004, pp. 652-627.