

Synthesis, Characterization and Gas Sensing Performance of Pure and Modified Cr₂O₃ Thick Films

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ABSTRACT: Thick films of pure chromium oxide (Cr₂O₃) were prepared by screen-printing technique. Pure (Cr₂O₃) thick films were almost insensitive to reducing gases. The surfaces of thick films of pure Cr₂O₃ were modified by dipping them into 0.01 M aqueous solution of ferric chloride (FeCl₃) for different intervals of time followed by firing at 500^oC for 30 min. Firing results into the oxidation of FeCl₃ additive into Fe₂O₃. The characterizations and the gas sensing properties of pure and surface activated Cr₂O₃ thick films were investigated. The surface activated Cr₂O₃ (30 min) thick films were observed to be sensitive to 1000 ppm of LPG at 400^oC. The grains of Fe₂O₃ dispersed around the grains of Cr₂O₃ would act as the barriers. Upon exposure of Liquefied Petroleum Gas (LPG), the barrier heights would decrease greatly leading to drastic increase in conductance. The quick response and fast recovery are the main features of this sensor. The effects of microstructure and additive concentrations on the gas response, selectivity, response time and recovery time were studied and discussed.

KEYWORDS: Fe₂O₃-activated Cr₂O₃, screen printing, thick film, LPG sensor, gas response.

I. INTRODUCTION

Environmental pollution is the burning global issue [1-4]. Atmospheric Pollution in urban areas has become a critical problem in recent years. All the components of the environment are so badly affected that, no one can be excluded from its fatal hazards. Hazardous and toxic gases from auto and industrial exhausts are polluting the environment in all sense. Therefore, all industries should have an alarm system detecting and warning for dangerous exhaust gas concentration levels. Thus, there is a need to monitor and control these gases. This leads to research and development of a wide variety of sensors using different materials and technologies. The Cr₂O₃ is an important refractory material because of its high melting temperature (~ 2300^oC) and crystallizes in Hexagonal-Rhombic corundum structure showing p-type semiconductivity. It is well known that, semiconducting oxides such as ZnO, Cr₂O₃, SnO₂, BaTiO₃ and Fe₂O₃ [5-16] are sensitive to various polluting gases. It has been studied that Cr₂O₃ [17-20] has been used as a gas-sensing element.

Now days, there is increase in usage of Liquefied Petroleum Gas (LPG) and Liquefied Natural Gas (LNG) as fuels. The frequency of accident explosions due to leakage of LPG and LNG have increased. LPG is highly inflammable gas. It is explosively utilized in industrial and domestic fields as a fuel. It is referred to as town or cooking gas. The constituent components of LPG are: CH₄ (6%), C₄H₆ (8%),

C₃H₈ (11.5%), C₄H₈ (15%), C₄H₁₀ (55%) and C₅H₁₂ (4.5%). Cooking gas consists chiefly of butane (55-vol %) [6, 21], a colourless and odorless gas. It is usually mixed with compound of sulphur (methyl mercaptan and ethyl mercaptan) having foul smell, so that the leakage can be noticed easily. This gas is potentially hazardous because explosion accidents might be caused when it leak out by mistake or by any means. It has been reported that, at the concentration up to noticeable leakage, it is much more than the lower explosive limit (LEL) of the gas in air. So, there is a great demand and emerged challenges [22] for monitoring it for the purpose of control and safety application in domestics and industrial fields.

The aim of the present work is to develop the LPG sensor by modifying pure Cr₂O₃ based thick films which could be able to detect the LPG at trace level. Among the various metal oxide additives tested, Fe₂O₃ in Cr₂O₃ is outstanding in promoting the sensing properties of LPG.

II. EXPERIMENTAL

A. PREPARATION OF THICK FILMS

Pure AR grade (99.9 %) Cr₂O₃ powder was ball milled to ensure sufficiently fine particle size. The fine powder was calcined at 1000^oC for 8 h in air and re-ground. Thick films of so obtained powder were prepared by adopting the procedure explained elsewhere [11-14]. These films were surface modified by dipping them into a 0.01 M aqueous solution of FeCl₃ for different intervals of time followed by firing at 500^oC for 30 min. The FeCl₃ dispersed on the film surface was oxidized to Fe₂O₃ in firing process. Thus, the sensor elements with different mass % of Fe₂O₃ were obtained. Silver contacts were made by vacuum evaporation for electrical measurements.

B. CHARACTERIZATIONS

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.

C. DETAILS OF GAS SENSING SYSTEM

The sensing performance of the sensors was examined using 'static gas sensing system'. The static system is built in our laboratory, which consists sensor element, heating element, gas inject unit, temperature-measuring unit, Pico-ammeter, glass dome and steel base plate are major components of static gas system. The components of old vacuums system are utilized for assembling the static gas system. There are electrical feeds through on the base plate. Heating unit is fixed on base plate It provides the desired temperature to sensor for its proper functioning. Sample under test can be mounted on the heater. Cr-Al thermocouple is mounted to measure the temperature. The output of thermocouple is connected to temperature indicator. Gas inlet valve fitted at one of the part base plate. Gas concentration inside the static system is achieved by injecting a known volume of test gas-by-gas injecting syringe. 20-v dc voltage is applied to the sensor element constantly and current meter can measure current. Single gas hit were delivered to the sensor.

III. MATERIALS CHARACTERIZATIONS

A. THICKNESS MEASUREMENT

Thicknesses of thick films were measured by using the Taylor-Hobson (Talystep, UK) system. The thicknesses of the films were observed in the range from 15 to 25 μm. The reproducibility of the film thickness was achieved by maintaining proper rheology and thixotropy of the paste.

B. STRUCTURAL PROPERTIES (X-RAY DIFFRACTION STUDIES)

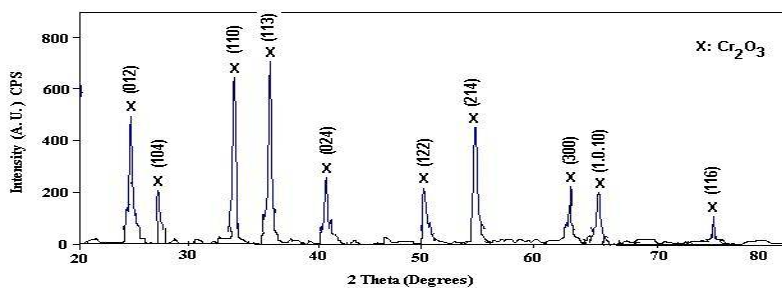


Fig. 1 XRD of Fe₂O₃-activated Cr₂O₃ (30 min).

The crystalline structures of the films were analysed with X-ray diffractogram (RIGAKU DMAX 2500) using CuKα radiation with 1.5418 Å. Fig. 1 depicts the XRD patterns of Fe₂O₃-activated Cr₂O₃

(30 min) sample. The observed peaks are matching well with ASTM reported data of pure Cr₂O₃. The Cr₂O₃ material was observed to be microcrystalline in nature. There are no prominent peaks of Fe₂O₃ associated with XRD pattern which may be due to smaller wt % of Fe₂O₃ associated with Cr₂O₃.

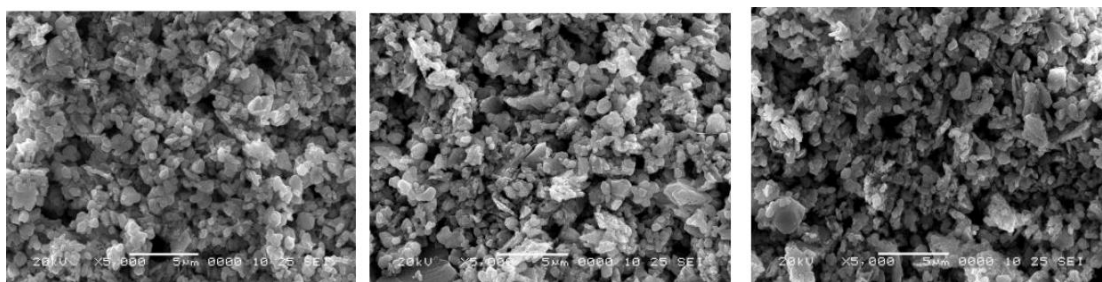
C. ELEMENTAL ANALYSIS

Table 1: Elemental analysis of unmodified (pure) and Fe₂O₃-modified films

Mass %	Dipping time (min)					
	0	5	10	20	30	60
Fe	0.00	0.41	0.44	0.55	0.63	0.68
O	29.87	32.41	30.36	28.92	27.11	28.46
Cr	70.13	67.18	69.20	70.53	72.26	70.87
Fe ₂ O ₃	0.00	0.59	0.63	0.79	0.90	0.97
Cr ₂ O ₃	100	99.41	99.37	99.21	99.10	99.03
Fe ₂ O ₃ -Cr ₂ O ₃	100	100	100	100	100	100

Quantitative elemental composition of pure and Fe-modified Cr₂O₃ 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. It is clear from Table 1 that, the mass % of Fe and Fe₂O₃ goes on increasing with the dipping time.

D. MICROSTRUCTURE-SEM



(a) (b) (c)

Fig. 2 Micrographs of (a) Unmodified Cr₂O₃, (b) Fe₂O₃-activated Cr₂O₃ (30 min) and (c) Fe₂O₃-activated Cr₂O₃ (60 min) thick films

Unmodified Cr₂O₃ thick films in Fig. 2 (a) consist of randomly distributed grains with larger size and shape distribution. Fig. 2 (b) depicts the microstructure of Fe₂O₃-modified film (30 min). This film consists of some smaller grains distributed on the larger grains. Smaller grains may be of Fe₂O₃ and larger ones may be of Cr₂O₃. Fig. 2 (c) depicts the microstructure of a Cr₂O₃-modified film for largest time interval (60 min) consists of particles with smaller size and shape associated with the Cr₂O₃ grains. The porosity of the film in figure 2(b) seems to be largest as compared to films shown in figure 2(a) and 2(c). Thus the effective surface area was expected to increase largely, which enhances the adsorption of oxygen at higher temperatures.

IV. ELECTRICAL PROPERTIES OF THE SENSOR

A. I-V CHARACTERISTICS

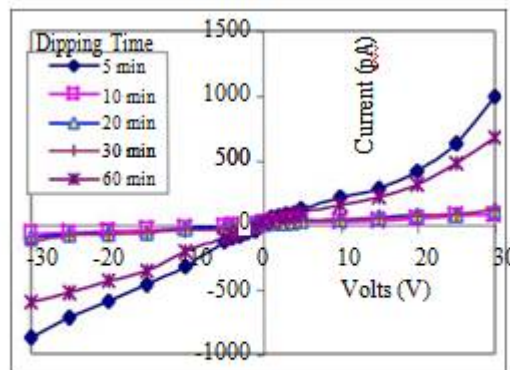


Fig. 3 I-V characteristics of Fe₂O₃-modified Cr₂O₃ films.

Fig. 3 depicts the I-V characteristics of the Fe₂O₃-modified Cr₂O₃ films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film are ohmic in nature. The conductivity of film dipped for 5 minute and

60 minute are more as compared to film dipped for 10,20 and 30 minutes. The conductivity of film dipped for 10 minute is least among all.

B. ELECTRICAL CONDUCTIVITY

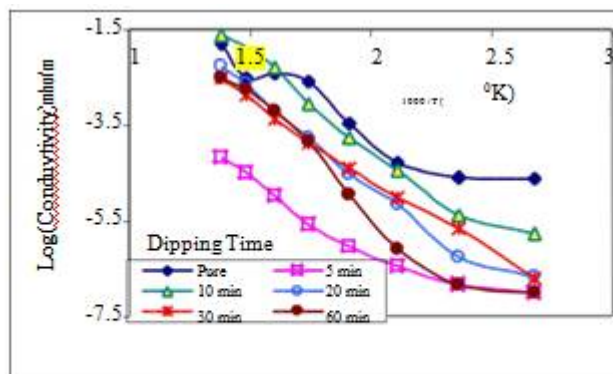


Fig. 4 Conductivity – temperature profile of Fe₂O₃-modified Cr₂O₃ films.

The semiconducting nature of Fe₂O₃-modified Cr₂O₃ was observed from the measurements of conductivity with reciprocal temperature. The semiconductivity in Cr₂O₃ may be attributed to oxygen deficiency in it. It is clear from fig.4 that, the conductivity of pure Cr₂O₃ and Fe₂O₃-modified Cr₂O₃ films increases with increases in operating temperature. This behavior confirmed the semiconducting nature of modified Cr₂O₃. The increase in the conductivity 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 Cr₂O₃ would contribute to increase in conductivity. It is observed from fig.4 that the electrical conductivity of the pure and Fe₂O₃ modified Cr₂O₃ films are nearly linear from 150^oC to 300^oC in air ambient. We observed from Fig.4 that the electrical conductance of the pure Cr₂O₃ was larger than modified Cr₂O₃ films in air ambient. It may be due to the intergranular potential barrier. Pure Cr₂O₃ has only one kind of grain arranged uniformly, whereas in the case of modified films, the grains are of different natures, such as Fe₂O₃ and Cr₂O₃.

V. SENSING PERFORMANCE OF THE SENSOR

5.1 Gas response, Selectivity, Response and Recovery time

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

$$S = (Gg - Ga) / Ga$$

where, Ga and Gg 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 mixture of gases.

The time taken for the sensor to attain 90 % of the maximum increase in conductance on exposure of 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.

5.2 Sensing performance of pure Cr₂O₃ thick films

Fig. 5 shows the variation of gas (1000 ppm) responses of pure Cr₂O₃ thick film. The pure Cr₂O₃ thick film showed highest response to H₂S at 300°C. The response of pure Cr₂O₃ thick film to H₂S gas at such higher temperature may be attributed to the oxidation of the H₂S at 300°C.

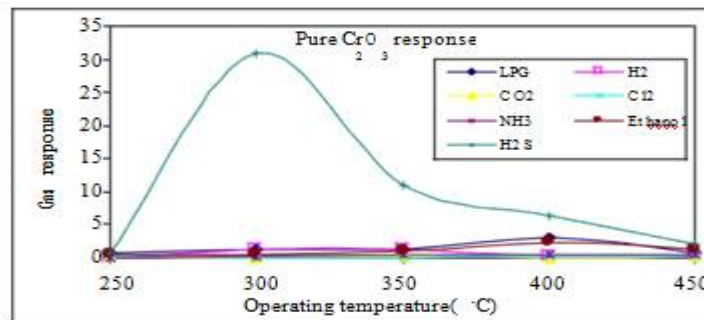


Fig. 5 Variation of gas responses of pure Cr₂O₃ thick films

5.3 Sensing performance of Fe₂O₃-modified Cr₂O₃ thick films 5.3.1 Selectivity

Sensing performances of the films modified for 5 to 60 minute were tested against H₂, CO₂, Cl₂, H₂S and NH₃ gases. The sensitivity values of each film to each gas are represented in figure 6.

It is observed from figure 6 that the Fe₂O₃-modified Cr₂O₃ (30 min) sensor gives highest response to LPG (1000 ppm) at 400°C. The sensor showed highest selectivity to LPG against H₂, CO₂, H₂S, Cl₂ and NH₃ gases.

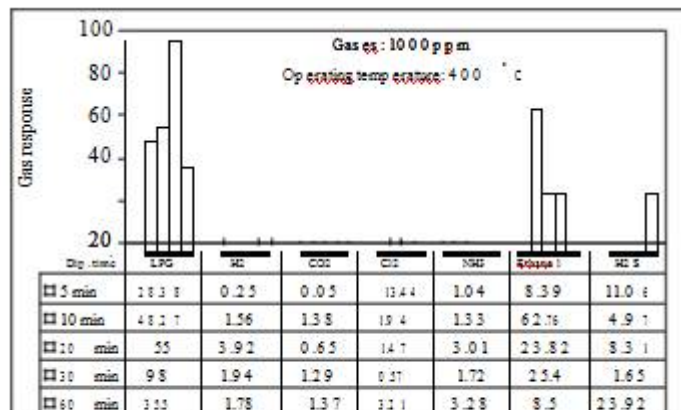


Fig. 6 Selectivity factor of the sensor for various gases

5.3.2 Effect of operating temperature

The variation of gas responses of Fe₂O₃-modified Cr₂O₃ (30 min) sample with operating temperature is represented in figure 7. It is clear from figure that the Fe₂O₃-modified Cr₂O₃ (30 min) sample shows the largest response (98) to LPG at 400°C. The LPG gas response goes on increasing, reaches to maximum at 400°C and then decreases further with increase in operating temperature. Gas response at lower operating temperature is limited due to poor gas reactivity and at higher temperature it is limited due to poor gas diffusion towards surface. Smaller gas responses at lower and higher operating temperatures may be respect such due to weaker gas reactivity and weaker gas diffusion.

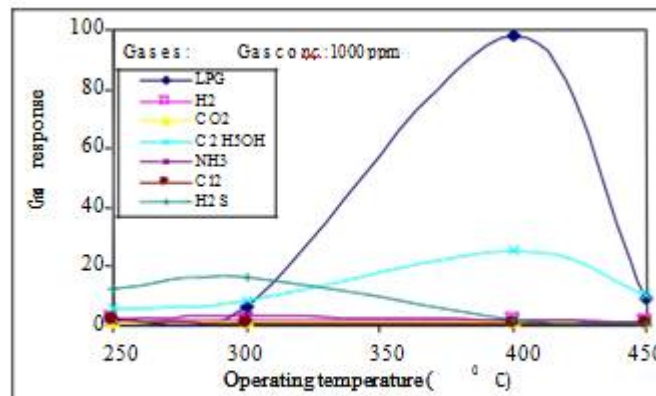


Fig.7 Variation of gas responses with operating temperature

5.3.3 Active region of the sensor

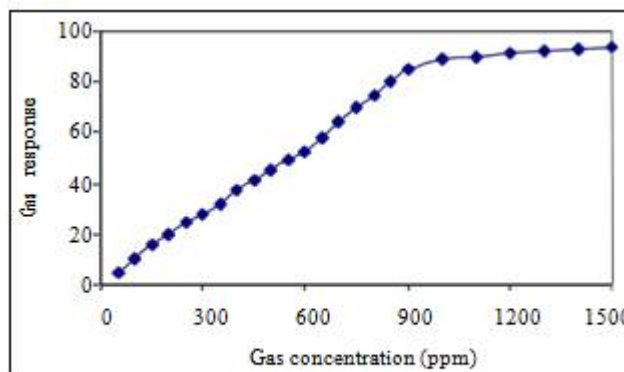


Fig. 8 Variation of gas response with gas concentrations (ppm)

Fig. 8 depicts the variation of LPG gas response of Fe₂O₃-modified Cr₂O₃ (30 min) sample with concentrations in ppm. It is clear from figure that the gas response goes on increasing linearly with gas concentration up to 1000 ppm. The rate of increase of gas response was relatively larger up to 1000 ppm. The monolayer of gas molecules formed on surface could cover the whole surface of the film. The excess gas molecules would remain idle and would not reach surface active sites of the sensor. So, the gas response at higher concentration of the gas would not increase further in same extent, but it saturates above 1000 ppm. Thus the active region of the sensor would be up to 1000 ppm.

5.3.4 Response and recovery time:

The response and recovery profiles of Fe₂O₃-modified Cr₂O₃ (30 min) sensor are represented in figure 9. The response of the sensor was quick (16 s) and the recovery was also fast (38 s). The quick response may be due to faster oxidation of gas. The negligible quantity of the surface reaction product and its high volatility explains its quick response and fast recovery to its initial chemical status.

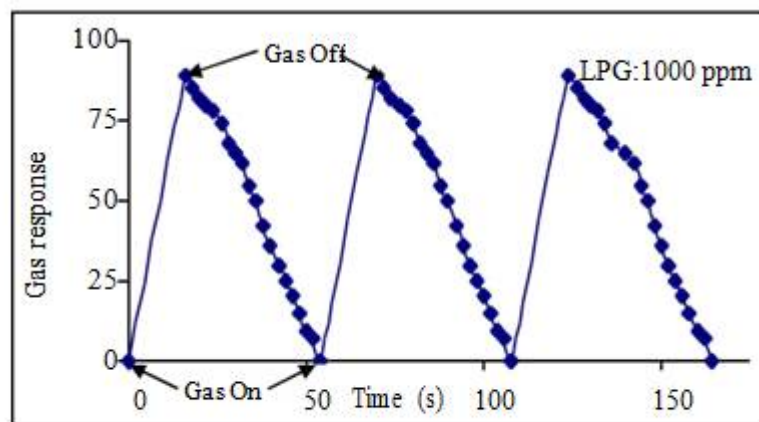


Fig. 9 Response and recovery of Fe₂O₃ -modified Cr₂O₃ sample

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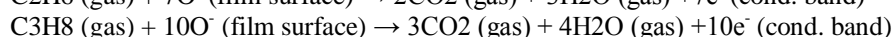
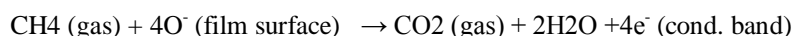
VI. DISCUSSION

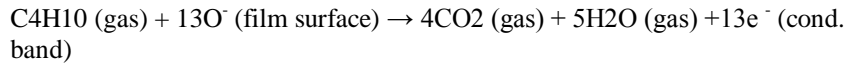
Fe₂O₃ and Cr₂O₃ are transition metal oxide. Properties of transition-metal oxides stem from the different bonding properties associated with d orbital. These include the existence of variable oxidation states. Trends in the stability of different oxidation states are very important in surface chemistry, as the control both the types of defect that may be formed easily, and the type of chemisorptions that may take place. The range of band gap energy of transition metal oxides (Cr₂O₃, WO₃, NiO, Fe₂O₃) is 2-3 eV. It is relatively lower as compared to SnO₂ and ZnO like materials. Therefore, these types of oxides could be more preferable for the use of gas sensors. Cr₂O₃ has an electron configuration of d³. It is the most catalytically active. Cr₂O₃ and Fe₂O₃ are P-type and N-type semiconductor respectively and provide an opportunity of oxygen chemisorption.

LPG is the composition of carbon and hydrogen. Carbon-Carbon and Carbon- hydrogen bonds are quite strong due to strong Van der Waal's forces. They may break out only at high temperature. The higher temperature dissociates the carbon-carbon and carbon-hydrogen bonds. This dissociation forms the carbon dioxide and H₂O vapours which are volatile and may escape easily from the surface of the sensor. The reaction mechanism is shown in figure.10.



The dissociability of LPG on activated surface explains quick response, liberating the electrons captured by oxygen ions such as:





The oxygen reacts with LPG releasing electrons into the conduction band. So, after exposure of LPG, the conductivity of the film increases.

The high volatility of the by-products explains the fast recovery of the sensor. The sensor showed better recovery to LPG than other gases.

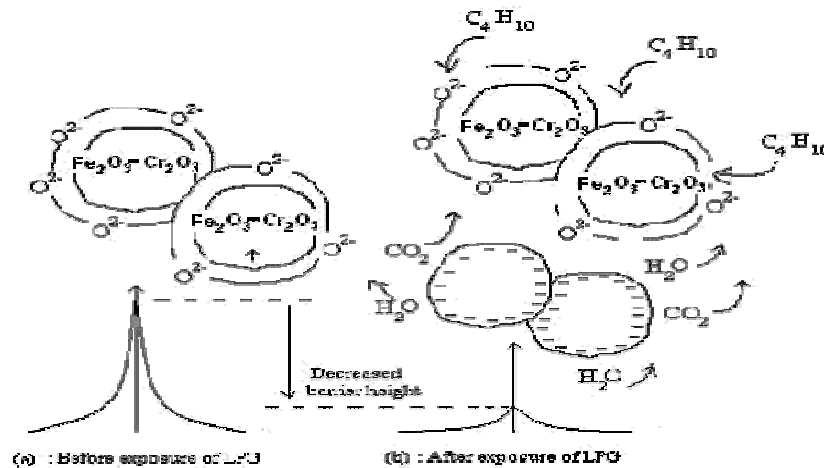


Fig. 10 LPG sensing mechanism of the sensor

VII. CONCLUSIONS

1. Pure Cr₂O₃ shows highest response to H₂S at 300^oC and not to LPG.
2. Fe₂O₃ modified Cr₂O₃ (30 min) sample showed highest sensitivity to LPG at 400^oC and not to H₂S gas.
3. Surface modification found beneficial for enhancing the sensing performance of the sensor.
4. Transition metal oxides are observed to be more sensitive to change in environment.
5. The sensor showed very rapid response and recovery to LPG.

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