

SYNTHESIS AND CHARACTERIZATION OF PURE AND MODIFIED Cr_2O_3 THICK FILMS AS A LPG SENSOR

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ABSTRACT

Thick films of pure chromium oxide (Cr_2O_3) were prepared by screen-printing technique. Pure (Cr_2O_3) thick films were almost insensitive to reducing gases. The surfaces of thick films of pure Cr_2O_3 were modified by dipping them into 0.01 M aqueous solution of copper chloride (CuCl_2) for different intervals of time followed by firing at 500°C for 30 min. Firing results into the oxidation of CuCl_2 additive into CuO . The characterizations and the gas sensing properties of pure and surface activated Cr_2O_3 thick films were investigated. The surface activated Cr_2O_3 (60 min) thick films were observed to be sensitive to

1000 ppm of LPG at 300°C . The grains of CuO dispersed around the grains of Cr_2O_3 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: CuO -activated Cr_2O_3 , screen printing, thick film, LPG sensor, gas response.

INTRODUCTION

Gas sensor researches are focused on new studies to developed smaller and most efficient device, which are very important in the electronic industry and are pursued with increasing demand. Some ceramic sensors semiconductor such as Cr_2O_3 , SnO_2 , ZnO with controlled

porous bodies show the change in an electrical conductivity as function of trace amount of inflammable gases. Gas sensing in semiconductors like Cr_2O_3 is achieved by the change in conductivity as a function of operating temperature, gas concentration, doping methods, doping concentration, sintering parameters like temperature, period etc. The reasons for change in conductivity is explained by desorption of oxygen absorbed on the surface and grain boundaries of metal oxide at high temperature in air.^[1] Recently, it has been of great interest in searching the sensors with novel properties, for various toxic and polluting gases, as the environment has been lost its balance, by pollution in much extent.

Cr_2O_3 crystallizes in Hexagonal-Rhombic corundum structure showing p-type semiconductivity.^[2] It has been utilized in wide range of application.^[3-10] Now days, there is increase in usage of LPG and LNG gases, the frequency of accident explosions due to leakage has increased. Liquefied Petroleum Gas (LPG) is highly inflammable gas. It is explosively utilized in industrial and domestic fields as a fuel. It is referred as town or cooking gas. Cooking gas consists chiefly of butane (55-vol %),^[11] a colorless and odorless gas. 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^[12] for monitoring it for the purpose of control and safety application in domestics and industrial fields.

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 was calcined at 1000°C for 4 h. in air, so as to remove the volatile impurities. The calcined powder was again ball milled to ensure sufficiently fine particle size.

Preparation of thick films

Thick films of pure Cr_2O_3 were prepared using following procedure. Thixotropic pastes^[13] were formulated by mixing the resulting fine powder with a solution of ethyl cellulous (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitols acetate and turpineol. The ratio of inorganic part was kept as 80:20 in formulating paste. The

thixotropic paste was screen printed on a glass substrate in desired patterns. The films prepared were fired at 500⁰C for 30 min. Thus thick films of pure Cr₂O₃ were prepared.

Modification of thick films

Pure Cr₂O₃ films prepared as above. Now, dipping them into a 0.01 M aqueous solution of CuCl₂ for different intervals (viz. 5, 10, 20, 30 and 60 min) and followed by firing at 500⁰C for 30 min. The CuCl₂ dispersed on the film surface was oxidized to CuO in firing process. Thus the sensor elements with different mass % of CuO were obtained. Silver contacts were made by vacuum evaporation for electrical measurements.

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.

Thermo electrical power measurement

The p-type or n-type semiconductivity of thick film Cr₂O₃ was confirmed by measuring thermoelectromotive force of thick film sample. The Cr₂O₃ was observed to be p-type material.

Structural Properties (X- ray diffraction studies)

The microcrystalline structures of the films were analyzed with x- ray diffractogram (RIGAKU DMAX 2500) using CuKα radiation with a wavelength 1.5418 Å⁰.

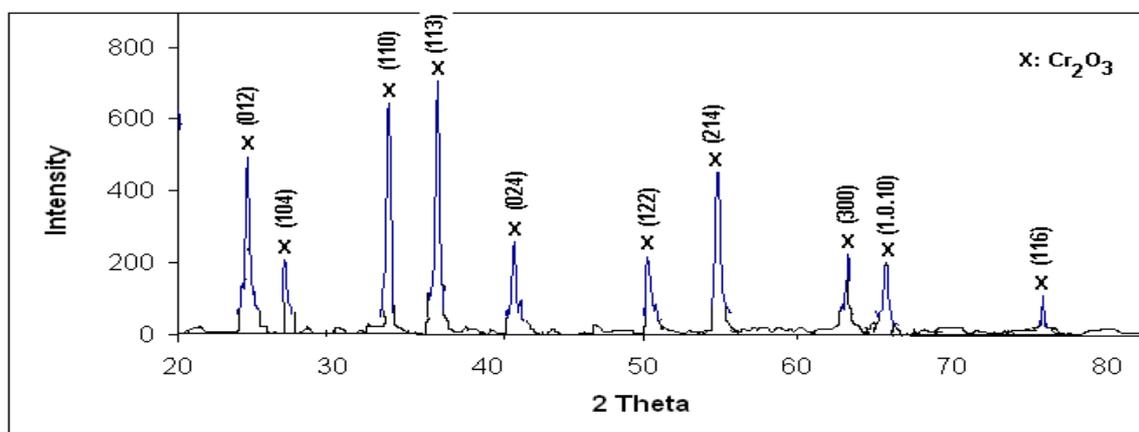


Fig. 1: XRD of unmodified and modified Cr₂O₃.

Fig.1 depicts the XRD of unmodified film CuO- modified film for (60 min). The observed peaks 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 CuO associated in XRD pattern, due to smaller wt % of CuO in comparison with Cr_2O_3 .

Quantitative elemental Analyses

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

Mass %	Dipping time (min)					
	0	5	10	20	30	60
Cu	0.00	0.03	0.21	0.03	0.70	0.12
O	29.87	30.84	29.95	31.15	29.20	28.85
Cr	70.13	69.13	69.84	68.82	70.10	71.03
CuO	0.00	0.04	0.3	0.04	0.89	0.17
Cr_2O_3	100	99.96	99.70	99.96	99.11	99.83
CuO -C r_2O_3	100	100	100	100	100	100

The quantitative elemental composition of Cu-modified films was analyzed using an energy dispersive spectrometer and mass % of Cu, O, Cr, CuO, and Cr_2O_3 are represented in Table 1.

Pure dark green Cr_2O_3 is expected to be stoichiometric and showing insulating properties.^[14] The pure green Cr_2O_3 powder turns faint green on calcination at higher temperature (1000°C for 4 h). It may be due to the deficiency of oxygen. Stoichiometric mass % of Cr and O in Cr_2O_3 are 68.43 and 31.57 respectively. The mass % of Cr and O in each samples were not as per the stoichiometric proportion, leading to semiconducting nature (Table 1). It is clear from Table 1 that, all activated films are observed to be oxygen deficient.

Microstructure Analysis

Unmodified Cr_2O_3

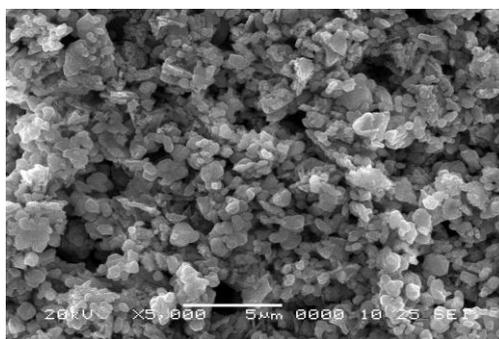


Fig 2: Micrograph of unmodified Cr_2O_3 film

Fig.2 depicts the SEM image of an unmodified (pure) Cr_2O_3 thick film fired at 500°C for 30 min. Unmodified Cr_2O_3 film consists of randomly distributed grains with larger size and shape distribution. The film consists of voids and a wide range of grains with grain size 510 nm.

CuO-activated Cr_2O_3

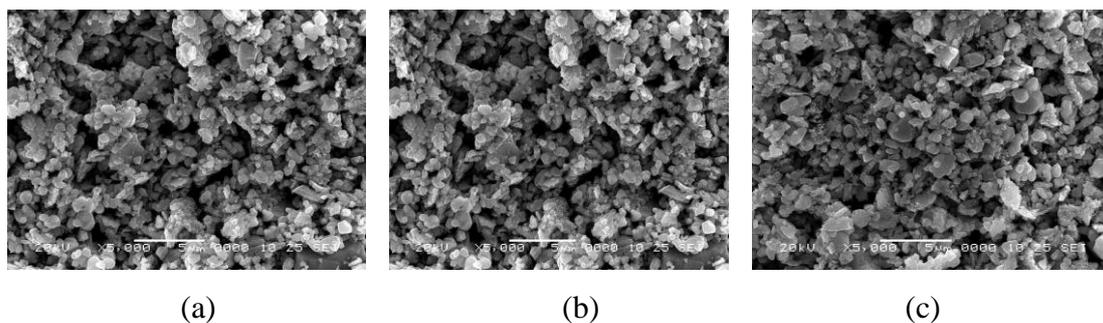


Fig. 3: Micrograph of CuO-activated Cr_2O_3 samples (a) 5min, (b) 20 min, (c) 60min.

Fig. 3 (a) depicts the microstructure of CuO-modified film (5 min). This film consists of smaller grain distributed on large grains. Smaller grains may be of CuO and larger grains may be of Cr_2O_3 . Fig. 3 (b) (20 min) the smaller number of small grains of CuO distributed on Cr_2O_3 . Fig 3 (c) depicts the microstructure of a CuO–modified film for a largest time interval (60 min) consists of particles with smaller size and shape associated with the Cr_2O_3 grains. Therefore 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 522 to 532 nm, calculated by Scherer’s formula.

Electrical properties

I-V Characteristics

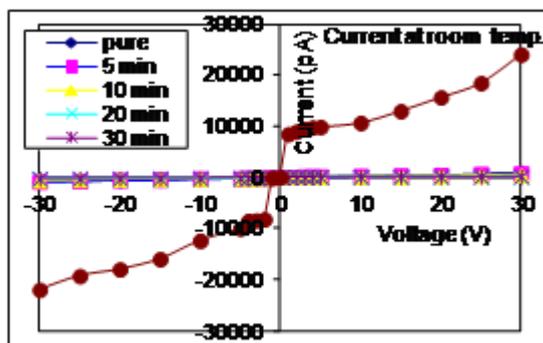


Fig. 4: I-V Characteristics of CuO modified Cr_2O_3 films.

Fig. 4 depicts the I-V Characteristics of CuO-modified Cr₂O₃ films. It is clear from the symmetrical I-V characteristics that the silver contacts on the films were ohmic in nature.

Electrical Conductivity

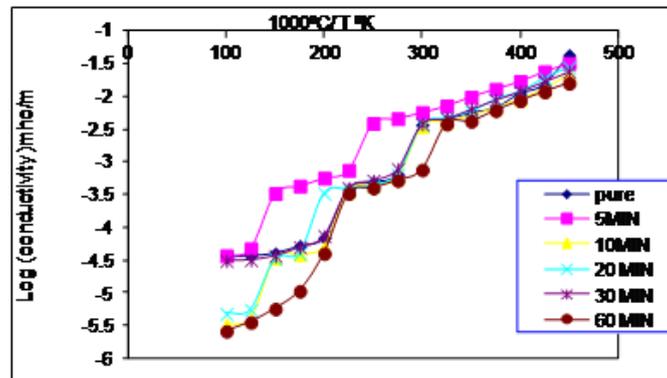


Fig. 5: Variation of log (conductivity) with operating temperature ($^{\circ}\text{K}^{-1}$).

Fig. 5 shows the variation of log (conductivity) with temperature. The conductivity values of all samples increase with operating temperature. The increase in conductivity with increasing temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of the CuO-modified Cr₂O₃.

Gas sensing properties

Unmodified Cr₂O₃

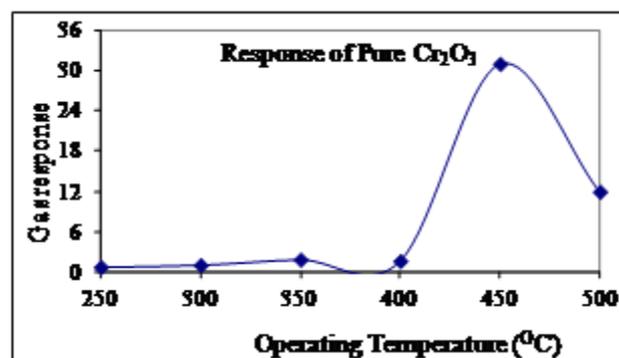


Fig. 6: Variation of gas response of pure Cr₂O₃ with operating temperature.

Fig. 6 depicts the variation of gas response with operating temperature of pure Cr₂O₃ thick film for 1000-ppm H₂S gas. The response to H₂S gas goes on increasing with operating temperature, reaches to maximum at 450°C and decreases with the further increase of operating temperature.

CuO-modified Cr₂O₃

Effect of operating temperature

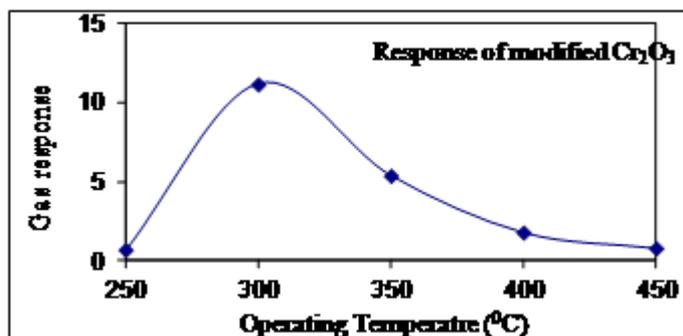


Fig. 7: variation of gas response of CuO-modified Cr₂O₃ with operating temperature.

Fig.7 depicts the variation of gas response of CuO-modified Cr₂O₃ thick films to LPG gas (1000 ppm) with operating temperature. The largest response of CuO-modified Cr₂O₃ (5 min) was observed to be 11.2 at 300⁰C. It is observed from figure that the gas response increases with operating temperature, reaches to its respective maximum at 300⁰C and decreases with increase in operating temperature. The response could be attributed to the adsorption-desorption type mechanism.

Selectivity

It is observed from the Fig. 8 that the modified Cr₂O₃ is sensitive to LPG gas. But it has least selectivity against different gases.

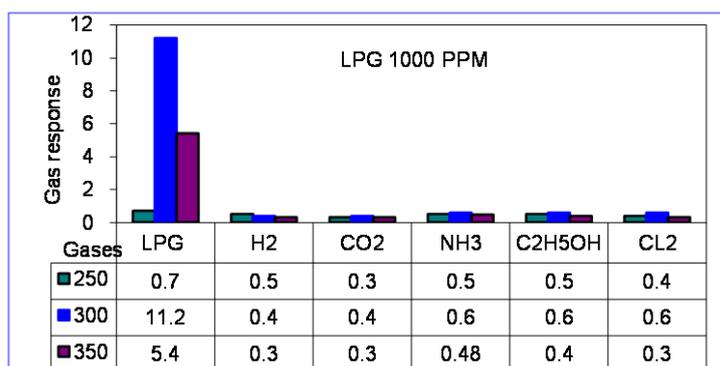


Fig. 8: Selectivity of modified Cr₂O₃ to different gases.

Response and recovery time

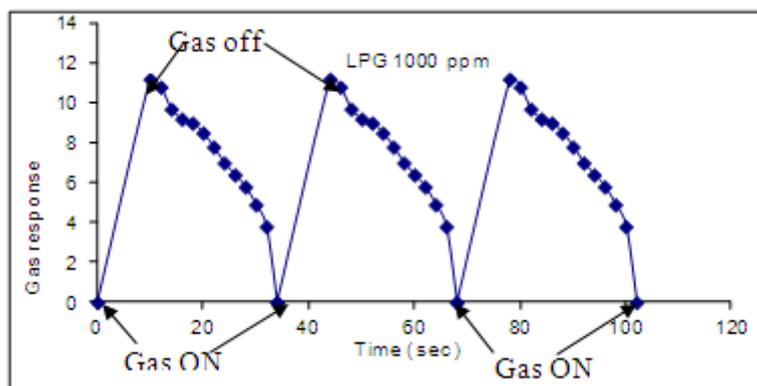


Fig. 9: Transient response of CuO modified Cr₂O₃ to LPG gas.

Fig. 9 depicts the variation in gas responses of CuO- modified Cr₂O₃ thick films to 1000 ppm LPG gas, with time in seconds, operated from room temperature through 450⁰C. The 90 % response and recovery levels are attained within 10 second and 24 second respectively.

DISCUSSION

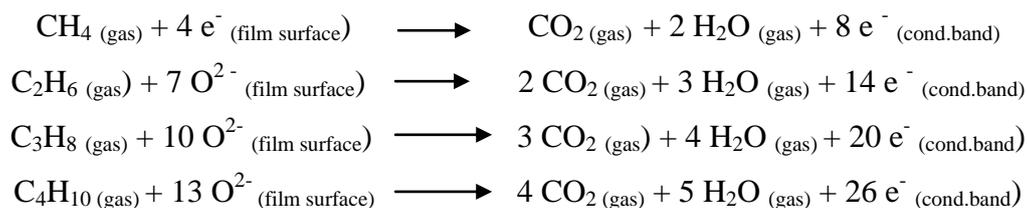
Table 2:

Composition (Vol. %)	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
	6	8	11.5	15	55	4.5

As the butane is the major constituent of LPG (Table 2), it requires high temperature to dissociate into lower alkanes. Carbon-carbon and carbon-hydrogen bond are quite strong due to strong Vander Walls forces. They break only at higher temperature resulting in carbon and hydrogen separation. The atmospheric oxygen O₂ adsorb on the surface of the thick film. It captures the electrons from conduction band as:



It would result in decreasing conductivity of the film. When alkanes react with oxygen, a complex series of reaction^[15] take place, ultimately converting the alkanes to carbon dioxide and water as:



This shows n- type conduction mechanism. At higher temperature molecular oxygen O_2^- and alkanes decompose producing hydrogen ions H^+ in the reaction. The anion super- oxide O_2^- reacts with H^+ giving water molecule and molecular oxygen O_2 :

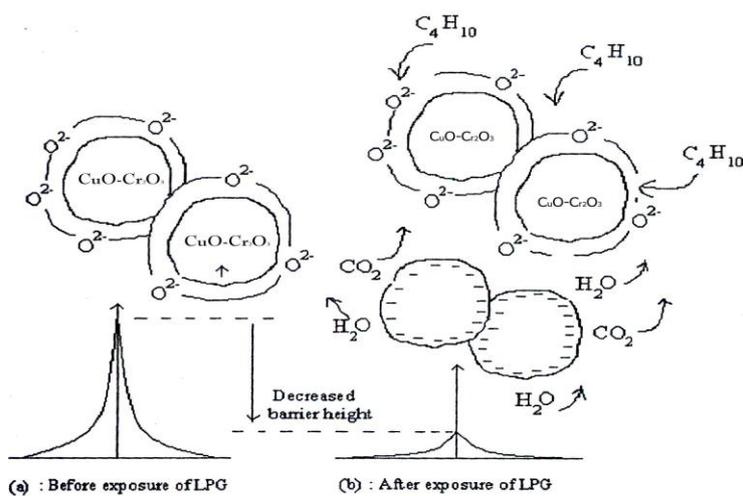
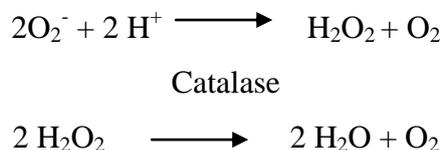


Fig. 10: LPG gas sensing mechanism of CuO- Cr₂O₃ films at 350⁰C.

LPG gas on exposure decomposes into carbon and hydrogen species, which reacts with adsorbed oxygen, liberating the captured electrons into conduction band resulting in enhancing the catalytic activity of the film surface (Fig.10). The rate of adsorption and reaction between the adsorbed species depends, of course, on temperature. Gas response versus operating temperature curves of semiconductor gas sensors shows a maximum at certain temperature, which is used as working temperature of the sensor. In addition to the effect of temperature on the kinetics of the reaction between the adsorbed species, finding on Cr₂O₃ sensors reveal another effect of temperature on sensing. It was observed that, as the temperature was changed, the form of adsorbed oxygen was also changed. Therefore, the generally observed shape of the gas response curve is also affected by the changes in the nature and coverage of adsorbed oxygen as a function of temperature. This temperature, which shows maximum response, can be used as a means of selectivity between reducing gases having maximum at different temperature. If surface additive that specifically adsorbs or reacts with the gas of interest is used, then this can increase selectivity.

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