NANOSTRUCTURED CR_2O_3 BASED THICK FILMS AS ETHANOL GAS SENSOR

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Abstract

Nanocrystalline powder of Chromium oxide (Cr_2O_3) was synthesized by chemical co-precipitation method. The standard crystallite dimension of Cr_2O_3 was observed to be 18 nm. Thick Films of uncontaminated Cr_2O_3 were fabricated by screen-printing technique and Al_2O_3 modified Cr_2O_3 thick films were prepared by dipping method for 4 min. Numerous characterization techniques viz. XRD, SEM, EDX, etc studied the material. The static gas sensing system was used to examine the gas sensing performance of synthesized thick films. 4 min dipped Al_2O_3 modified Cr_2O_3 thick films showed highest response to ethanol (100 ppm) gas at 50^0C as compare to other gases. The immediate response and the speedy recovery are the major characteristics of the sensor.

The effects of surface modification on the gas response, selectivity, response time and recovery time of Cr_2O_3 based thick film gas sensor in the presence of NH_3, Cl_2, LPG, CO_2, H_2S and C_2H_5OH gases were investigated.

Keywords: *Cr_2O_3; XRD; Ethanol gas; Response time.*

Introduction

Nanotechnology has the most valuable application in the region of gas sensors. In the field of gas sensing, nanomaterials have a huge potential in comparison to bulk materials. It has been also reported that bulk and nanostructure of the same material show different physical and chemical properties.

The semiconductor metal oxides based gas sensors have vital role in the recognition of venomous pollutants and have power over the industrialized processes. Generally, two techniques are utilized for the production of semiconductor metal oxide gas sensors, namely "thin film" [1] and "thick film sensors" [2]. It has been observed that, "thick film gas sensors" fabricated by screen-printing technique have some advantages like simple fabrication, the low price and good sensing properties as compared to other gas sensors [3–5]. "It has been also observed that an adsorption of gas molecules on a surface of thick film can make a noteworthy change in the electrical conductivity or resistivity of the material" [6]. Moreover, the morphology, structure and chemical composition of semiconductors metal oxide plays an important role in determining their gas sensing properties. It has been found that, Solid state gas sensors based on transition metal oxides (TiO_2, SnO_2, WO_3, ZnO, Cr_2O_3 and In_2O_3) show fast sensing response, simple execution and low costs [7, 8].

"In recent years, it has been observed that, nanostructure chromium oxide (Cr_2O_3) with large ratio of surface area to volume has attracted more attention [9–13]". "It has been studied that Cr_2O_3 [14-27] was considerably used as gas sensing element". "P-type semiconductor shows high electrical conductivity with reasonable levels of electron transfer [28]". A semiconductor metal oxide Cr_2O_3 is extensively used in many fields' namely "catalytic reactions [29]", "optical coating [30]", "infrared sensors [31]", and "gas sensors [32]", "doping in varistors compound [33]". The sensing mechanism for p-type semiconductor metal oxide is similar to n-type. But in this regard the less number of investigations is carried out [34]. "There are some reports based on Cr_2O_3 thick films for vapor sensing (e.g. ethanol), for gas sensing applications" [35-39].

It well knows that; ethanol (C_2H_5OH) is an inflammable volatile organic compound. It is toxic in nature and also most considerably used alcohols. It is widely used in food industries; bio-medicine and chemical industries [40].It has been observed that exposure to ethanol vapour causes health related problems, such as breathing problems, a continuous pain in the head, sleepiness, eyes irritation, and liver damage [41]. Workers working in the ethanol industries have more chances of being sufferer of digestive and respiratory track cancer. Ethanol sensor plays a vital role in medical, chemical and food industries and also in environmental protection [42, 43].In the recent years; many attempts have been made to enhance the ethanol response of metal oxide sensors with the high response and selectivity [44]. But, still there is a need to fabricate ethanol sensor and monitor ethanol vapors.

The endeavour of this work is to fabricate the thick film sensor element by modifying pure Cr_2O_3 thick films, to detect ethanol. The present paper reports the structure, morphology and gas sensing characteristics of unmodified and 4 min dipped modified Cr_2O_3 based thick films.

Experimental Details

2.1. Synthesis of Nanocrystalline Cr_2O_3 Powders

All chemicals utilized in the synthesis process were of standard analytical grade. Nanocrystalline Cr_2O_3 powders were synthesized by the chemical precipitation method. The details regarding preparation of nanocrystalline Cr_2O_3 was already published in our earlier publication [45]. The synthesized nanocrystalline Cr_2O_3 powders were used for further study.

2.2. Thick film fabrication

Thick films of nanocrystalline Cr_2O_3 Powders were fabricated by using the screen printing technique. The details regarding preparation of pure Cr_2O_3 thick films were already published in our earlier publication [45].

2.3. Al_2O_3 modified Cr_2O_3 thick films

Surface of pure Cr_2O_3 thick films were activated by dipping them into 0.01M aqueous solution of $AlCl_3$ (99%ARgrade, Merck) for 4 min. Dipped thick films were dried under the IR lamp for 1 h. Dried thick films were fired at 500^0C for half hour. The $AlCl_3$ spread on the surface of film was oxidised to Al_2O_3 in the process of firing and sensor element with different quantity of Al_2O_3 on the surface of Cr_2O_3 thick film was obtained. This surface modified thick film is called as 4 min dipped Al_2O_3 modified Cr_2O_3 thick film.

3.1 Thickness measurement

'Marutek film Thickness Measurement System' technique was used for measurement of thickness of unmodified Cr_2O_3 and Al_2O_3 activated Cr_2O_3 thick films. The thickness of all films was measured and is found in between 32 to 36 µm. Thick films of nearly same thickness were used for further study and gas sensing purpose.

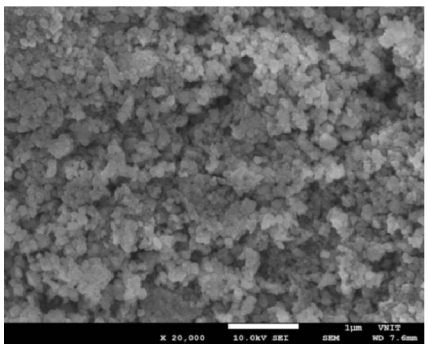
3.2. X-ray diffraction studies

The crystallographic configuration of the prepared Cr_2O_3 nanostructure was characterized by X-ray diffraction method. The details regarding X-ray diffraction of Cr_2O_3 powders was already published in our earlier publication [45].

3.3 Scanning electron microscopy

Fig. 2 (a-b) depicts FE-SEM images of the pure and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films fabricated by screen printing technique. Fig. 2(a) shows the FE-SEM image of the pure Cr_2O_3 film. The pure Cr_2O_3 film consists of randomly distributed grains with smaller size and shape distribution. The average size of Cr_2O_3 grains are approximately 29 nm to 44 nm. Fig. 2 (b) shows the image of

Al_2O_3 modified Cr_2O_3 thick film for 4 min dipping. It is observed from the microstructure that the dipping in Al_2O_3, changed the microstructure of Cr_2O_3. It has huge number of nearly similar sized grains of Al_2O_3 fitted with the comparable sized grains of Cr_2O_3.The grains, surface to volume ratio of Al_2O_3 modified Cr_2O_3 thick films may be increased.



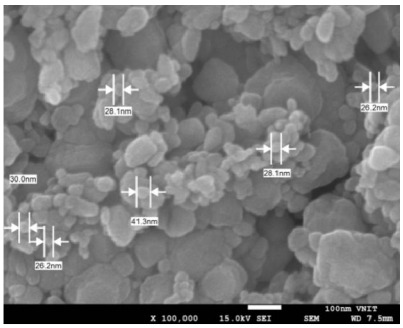
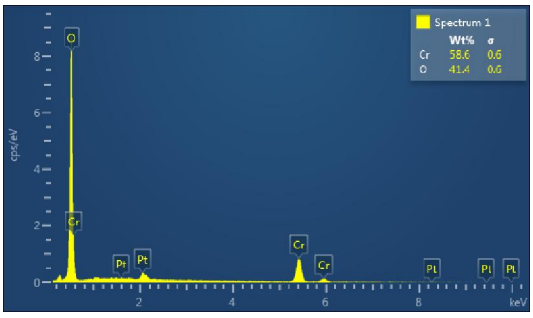


Fig. 2: Micrograph of (a)unmodified (pure) Cr_2O_3 thick film (b) Al_2O_3 modified Cr_2O_3 thick film (4 min. dipping)

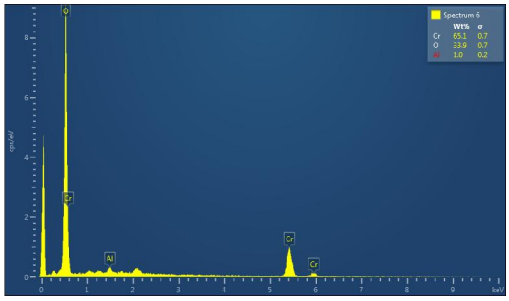
3.4 Energy Dispersive X-ray Spectroscopy (EDX)

The quantitative elemental composition of the unmodified and Al_2O_3 activated Cr_2O_3 thick films were analyzed by means of an Energy Dispersive Spectrometer (EDS). Fig.3 (a-b) represents the EDS patterns of pure and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films. The EDS analysis proved the presence of Cr, Al and O in the Al_2O_3 modified Cr_2O_3 thick films and no other impurity elements were present in the Al_2O_3 modified Cr_2O_3 thick films. The synthesized powder of pure Cr_2O_3 is excess in oxygen. Surfeit or insufficiency of the ingredient element proved the semiconducting behaviour of the sample. Hence pure Cr_2O_3 is semiconducting in nature. Also, the mass % of Cr and O in the modified thick film is not according to stoichiometric percentage and the sample is found deficient in oxygen or excess in chromium. Thus, maximum numbers of electrons are free for current and they behave as the majority charge carriers. The table 3.1shows quantitative elemental analysis of pure Cr_2O_3 and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films.

Also the results of EDS analysis confirmed that only Cr, O and Al are present in the surface modified thick film sample and no impurity elements were present in pure and modified samples



(a)



(b)

Fig.3: EDS patterns of a) unmodified Cr_2O_3 thick film b) Al_2O_3 modified Cr_2O_3 thick film (4 min. dipping)

Table 3.1: Mass % of Cr, O and Al elements in pure and modified thick films

Element	Pure Cr_2O_3	4 min dipped Al_2O_3 modified Cr_2O_3 thick films
O	41.4	33.9
Cr	58.6	65.1
Al	___	1.0

3.5 Fourier Transform infrared (FT-IR)

FT-IR spectroscopy was used to obtain the structural information of the materials. Fig.4 depicts the FT-IR spectrum of Cr_2O_3. In IR analysis, the vibrations of ions in the crystal lattice are generally observed in the range of 4000 – 450 cm^{-1}. All the observed peaks are in well agreement with the standard reported results. The high concentration of the peaks of Cr_2O_3 bands proved the excellent crystalline behaviour of the samples [46].

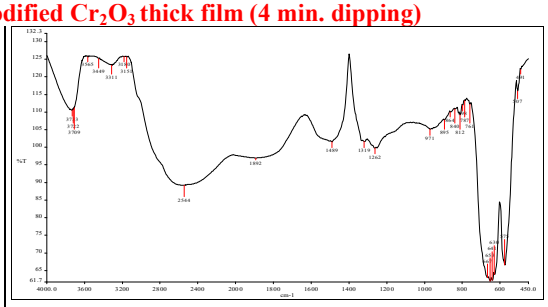


Fig.4: the FT-IR spectrum of Cr_2O_3

3.6. I-V characteristics of pure and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films

Fig.5 depicts the I-V characteristics of pure and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films. The bias voltage was increased in the step of 5V from 0 to 30 V and the corresponding current was recorded. The measurement was repeated with negative voltage. The behaviour of the I-V characteristics curves of given thick films showed the ohmic nature of the contacts.

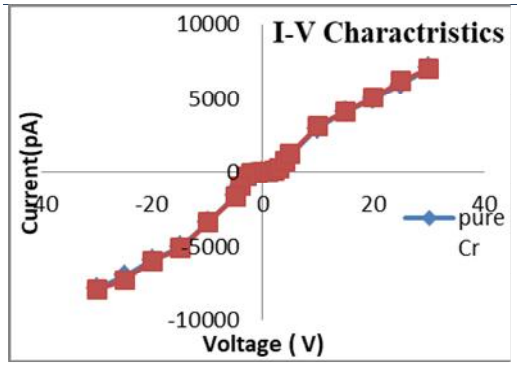


Fig.6: I-V Characteristics of unmodified and 4min dipped Al_2O_3 activated Cr_2O_3 thick films at room temperature.

3.7 Gas sensing performance of sensor

3.7.1 Gas Sensing Performance of *unmodified and* Al_2O_3 *activated* Cr_2O_3 *thick films*

Figure 6 depicts the response of unmodified and Al_2O_3 activated Cr_2O_3 thick films versus operating temperature. At operating temperatures changing from room temperature to 400^0C, the gas response to 100 ppm ethanol by unmodified and Al_2O_3 activated Cr_2O_3 thick films were investigated and studied.

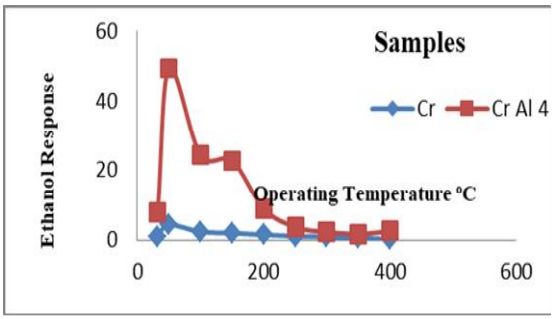


Figure 6: Variation of ethanol response with operating temperature of pure and Al_2O_3 activated Cr_2O_3 thick films

Figure 6 also shows the variation of gas response to 100 ppm ethanol gas by a pure Cr_2O_3 thick film with changing operating temperature from room temperature to 400^0C. It is cleared from figure that upto 50^0C, as operating temperature increase, the response to ethanol gas also go on increasing and then decreases with the further increase of operating temperature. As we know that, the response to an ethanol gas is normally depends on the amount of oxygen ions adsorbed on the film surface with a target gas. Due to less oxygen adsorption, the unmodified Cr_2O_3 thick film showed poor response to ethanol gas. So, to enhance a gas response of unmodified Cr_2O_3, it is necessary to actify unmodified Cr_2O_3.

It is also observed from the figure that 4 min dipped Al_2O_3 activated Cr_2O_3 thick film gives the crucial response to ethanol (100 ppm) at 50^0C. Al_2O_3 activated Cr_2O_3 thick film exhibited the maximum response (49.32) to 100 ppm ethanol vapors at 50^0C. The highest response may be attributed due to the optimal number of Al_2O_3 grains spread over the surface. Upon exposure, ethanol gas gets oxidized due to bulk oxygen at 50^0C.When bulk oxygen gets evolved, it liberates the captured electrons in conduction band of the thick film, increasing the conductivity and hence, the response crucially.

3.7.2 Selectivity

Fig. 7 depicts the selectivity of all, pure and 4 min dipped Al_2O_3 activated Cr_2O_3 thick films for 100 ppm concentration of LPG, C_2H_5OH, CO_2, NH_3, H_2S and H_2 at 50^0C. 4 min dipped Al_2O_3 modified Cr_2O_3 thick film is highly selective to C_2H_5OH (100 ppm) gas against all other gases.

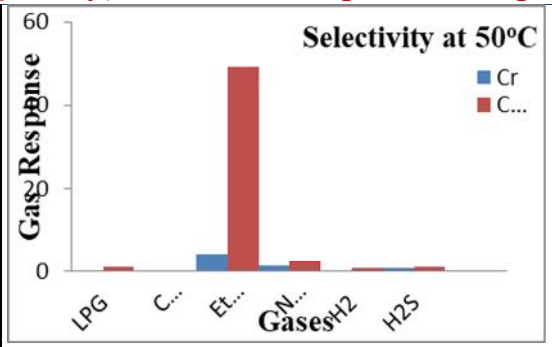


Fig. 7: Selectivity of pure and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films

3.7.3 Active Nature

Fig. 8 exhibits the relation between the ethanol gas response of pure and 4 min dipped Al_2O_3 modified Cr_2O_3 thick films with the different concentration of C_2H_5OH gas at 50^0C. It is observed from the figure that the gas response of 4 min dipped Al_2O_3 modified Cr_2O_3 thick film increases linearly with ethanol up to 100 ppm and saturated beyond 100 ppm. Thus, the dynamic nature for this sensor is up to 100 ppm.

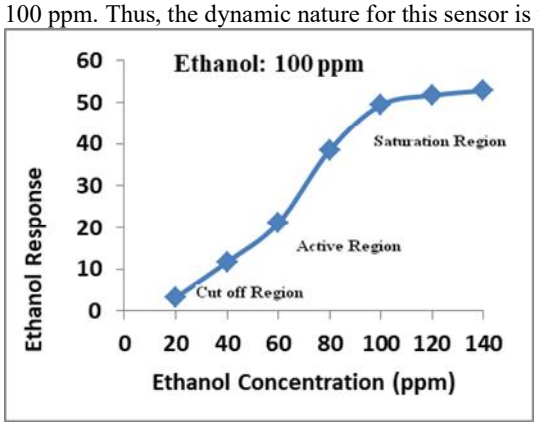


Figure 8: Change of ethanol response versus ethanol concentration (ppm)

3.7.4 Response and Recovery time

The response and recovery time of the 4 min dipped Al_2O_3 modified Cr_2O_3 thick film to 100 ppm of ethanol are 12 s and 20 s respectively. Thus the sensor exhibited very instant response and quick recovery time to ethanol gas. For superior presentation of the sensor the recovery must be very quick. This is the main and important feature of this sensor.

3.7.5 Stability

The ethanol gas response of 4 min dipped Al_2O_3 modified Cr_2O_3 thick film sensor for 100 ppm at 50^0C was constantly measured for 80 days in the interval of 10 days. It has been observed that a sensor showed a very stable response over 80 days, confirming the stability and reproducibility of the sensor.

3.7.6 The ethanol gas sensing mechanism

The semiconductor metal oxide thick film gas sensor is based on the working principle of change in electronic conductivity or resistivity of thick film on exposure to ethanol gas. When ethanol gas molecules respond with the surface of the metal oxide gas sensor, the transfer of electrons between them takes place.

As we know that, oxygen is largely available element in the atmosphere and hence oxygen plays a prime role in the process of adsorption due to its strong electronegativity and lone pairs of electrons. When semiconducting sensor is open to air, oxygen molecules easily get adsorbed on the film surface. During the adsorption process, the oxygen molecules gains an electron from the thick film surface and changed into ionic form (O_2^{-}) which captured electrons from the conduction band. The reaction takes place as follows [47]:

"O_2 (gas) ↔ O_2 (ads)

O_2 (ads) + $e^- \leftrightarrow O_2^-$ (ads)"

This results in increasing electronic resistivity of the film. During the gas sensing mechanism, the molecule of ethanol gas get oxidised with ionic form of oxygen to form CO_2 and H_2O with the release of energy. This released energy is utilized by trapped electrons to return back into the conduction band of activated Cr_2O_3. Thus there is a decrease in resistance of the sensor and hence, the increase in conductivity of the sensor.

Conclusions:

The obtained results can be summarised as below.

Pure Cr_2O_3 thick films are less conductive as compared to 4 min dipped Al_2O_3 activated Cr_2O_3 thick film.

A pure Cr_2O_3 thick film showed poor gas response to all tested reducing gas.

Al_2O_3 activated Cr_2O_3 thick film (4 min. dipping) showed higher gas response to 100 ppm of ethanol gas as compared to pure Cr_2O_3 thick film.

The Al_2O_3 activated Cr_2O_3 thick film exhibited good selectivity to ethanol gas as compared to H_2, LPG, CO_2, H_2S and NH_3 gases at 50^0C.

Al_2O_3 modified Cr_2O_3 thick film (4 min dip) shows fast response (12 s) and rapid recovery (20 s).

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