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# Surface Activated $Cr_2O_3$ Based Thick Film for Ammonia Gas Sensing

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**Abstract:**

*Pure chromium oxide ($Cr_2O_3$) nanoparticles powder was prepared by chemical co-precipitation method. The structural behaviour of $Cr_2O_3$ nanoparticles was examined by X-ray diffraction. Thick films of pure chromium oxide were prepared by the screen printing technique. The $Fe_2O_3$-modified films obtained by dipping pure $Cr_2O_3$ thick films into an aqueous solution of ferric chloride ($FeCl_3$) for 3min. and fired at 500$^0$C for 30 min. Pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films were examined by FE-SEM and EDX. Thick film of pure chromium oxide was almost insensitive to ammonia gas. Thick film of $Fe_2O_3$-modified $Cr_2O_3$ (3 min dipped) was observed to be highly sensitive to ammonia at100$^0$C. The instant response and fast recovery are the main features of this 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 ware studied and discussed.*

**Keywords**: Chromium oxide, X-ray diffraction, Ammonia gas, Gas response.

## Introduction

The metal oxides based semiconductor gas sensors are playing an important role in the detection of toxic pollutants in air and to control the industrial processes. It is observed that when the sensors are exposed to the atmosphere, the chemical species to be detected in the atmosphere can enter in to the interface of the p-n junction. So there are changes in electrical properties at the junction [1-3]. Therefore, the gas sensors were synthesised by using, ZnO, $SnO_2$, $TiO_2$, $WO_3$, $Cr_2O_3$, etc. materials in pure and modified forms to detect toxic, harmful, flammable and explosive gases [4,5] in the environment. $Cr_2O_3$ has a Hexagonal-Rhombic corundum crystal structure showing p-type semi- conductivity and has a high melting temperature (~ 2300$^0$C). In the recent years, p-type $Cr_2O_3$ is useful for sensor applications as it has an energy band gap of ~3.4 eV and widely been used in variety of applications, such as, catalytic reactions, optical coating and infrared sensors [6–9]. It has been studied that $Cr_2O_3$ [10-13] is used as a gas-sensing materials. $Cr_2O_3$ is the transition-metal oxide and the transition-metal oxides are more sensitive to the change of outside ambient and these types of oxides could be more preferable for the use in gas sensors [14]. It has been found that a pure $Cr_2O_3$ thick film has poor gas sensitivity to reducing gases but $Fe_2O_3$ modified $Cr_2O_3$ thick film is the most sensitive to LPG, $C_2H_5OH$, $NH_3$ and $Cl_2$ gases [12].

The particle size plays an important role in gas sensing. The reduction in grain-size is one of the prominent factors for enhancing the gas sensing properties of semiconducting oxides. Many preparation techniques for synthesis of $Cr_2O_3$ nanoparticles are described, such as hydrothermal reduction [15], solid thermal decomposition [16], urea method [17], and mechanochemical reaction [18], etc. In present work, co-precipitation methods (chemical route methods) were adopted, as they are easy, suitable and economically low coast to synthesize $Cr_2O_3$ nanostructures.

The aim of the present work is to fabricate the ammonia sensor by modifying pure $Cr_2O_3$ thick films, which is able to detect ammonia at trace levels. Among the various metal oxide additives tested, $Fe_2O_3$ is outstanding in promoting the sensing properties of the $Cr_2O_3$ sensor for ammonia. The present paper reports the structural, morphological and gas sensing properties of pure and $Fe_2O_3$ modified $Cr_2O_3$ based thick films.

## Experimental Details

### Preparation of Nanocrystalline $Cr_2O_3$ Powders

All chemicals were of analytical grade and used directly without further purification. Nanocrystalline $Cr_2O_3$ powders were synthesized by chemical precipitation method. The details regarding preparation of nanocrystalline $Cr_2O_3$ was already published in our earlier publication [19]. The synthesized $Cr_2O_3$ nanostructure product was used for further study.

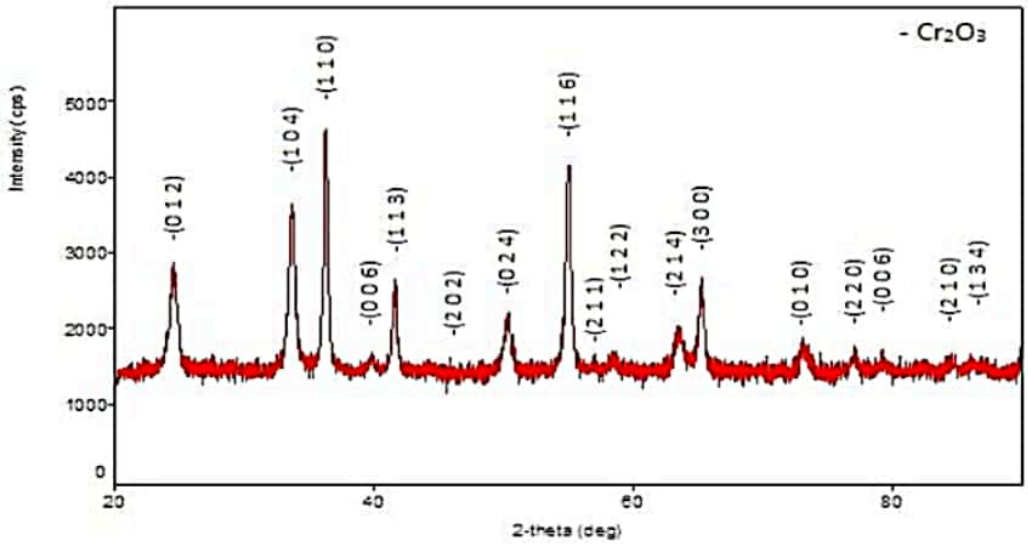
### Fabrication of thick films and $Fe_2O_3$ modified $Cr_2O_3$ thick films

Thick films of pure chromium oxide were prepared by the screen printing technique. In this process thixotropic paste was formulated by proper method and then the thixotropic pastes were screen printed on a glass substrate in desired patterns. The films prepared were fired at $500^0$C for 12 h. Prepared thick films termed as pure $Cr_2O_3$ thick films. The surfaces of pure $Cr_2O_3$ thick films were modified by dipping them into 0.01M aqueous solution of $FeCl_3$ for 3 min. The $FeCl_3$ dispersed on the film surface was oxidised to $Fe_2O_3$ in firing process and sensor elements with $Fe_2O_3$ on the surface of $Cr_2O_3$ thick films were obtained. These surface modified thick films are termed as $Fe_2O_3$ modified $Cr_2O_3$ thick films.

## Results and discussion

### X-ray diffraction

Fig. 1 shows X-ray diffraction (XRD) pattern of synthesized pure $Cr_2O_3$ powder sample. The observed peaks are matching well with JCPDS reported data of pure $Cr_2O_3$ with hexagonal in structure (JCPDS card no.70-3766). The characteristic peaks observed in the spectrum are higher in intensity which indicates that the as-synthesized samples are of good crystalline in nature. The domain size of the crystal can be estimated from the full width at half maximum (FWHM) of the peaks by means of the Scherrer formula [20]. The average crystallite size (D) was estimated from the Debye–Scherrer's equation: $D = 0.9\ \lambda / \beta \cos\theta$; where $\lambda$ is the wavelength of X-rays (1.54056 Å), $\beta$ is the FWHM of the peak in radians, $\theta$ is the diffraction angle at which the full width at half maximum (FWHM) measured and k =0.9, is Scherrer constant. The average crystallite size of the synthesized $Cr_2O_3$ nanoparticles calculated from (110) peak was approximately 26 nm.

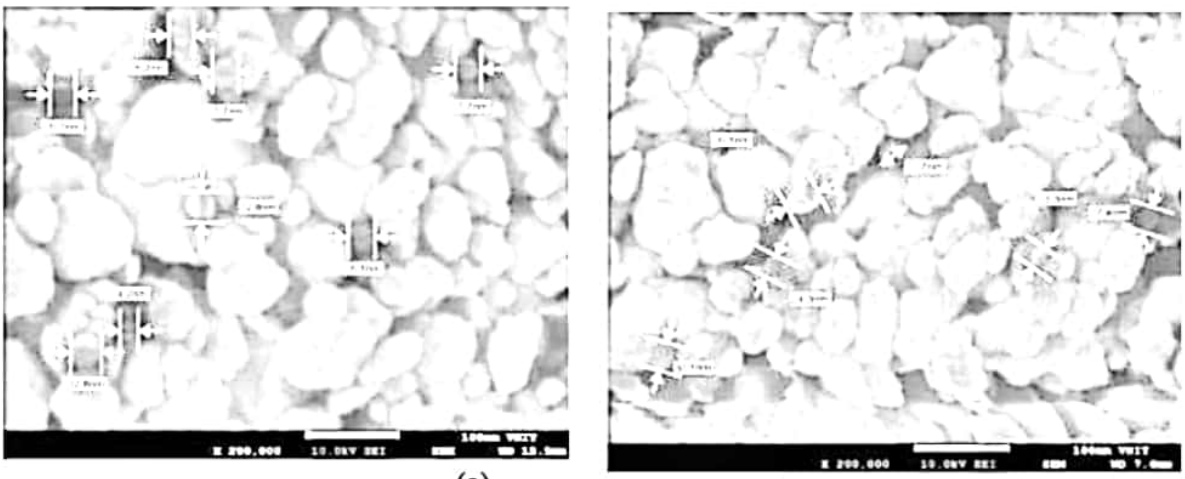



**Fig**

**Scanning electron microscopy**

Fig. 2 (a-b) depicts the FE-SEM images of the pure $Cr_2O_3$ film and $Fe_2O_3$ modified $Cr_2O_3$ thick film (3 min dipped). Fig. 2 (a) shows the FE-SEM image of the pure $Cr_2O_3$ film, which consists of randomly distributed grains with larger size and shape distribution. The average size of $Cr_2O_3$ grains are approximately 37 nm. The appearance of the film looks porous, which supports the adsorption and desorption type of gas sensing mechanism. The nano scaled grains exhibit high surface to volume ratio.

Fig. 2 (b) depicts the microstructure of $Fe_2O_3$ modified $Cr_2O_3$ thick film for 3 min dipped consists of large number of almost similar sized grains of $Fe_2O_3$ associated with the comparable sized grains of $Cr_2O_3$.The film consists of grains with sizes ranging from 19 nm to 33 nm distributed non-uniformly. The appearance of the film looks porous in nature (not looks masked). Thus increase in surface to volume ratio, which enhances the large number of gas adsorption upon exposure giving larger gas response. This film is observed to be the most sensitive to 100 ppm $NH_3$ gas at 100 $^0$C due to its porous nature.



(a)

(b)

**Fig. 2: FE-SEM microstructures for (a) Pure $Cr_2O_3$ thick film (b) $Fe_2O_3$ modified $Cr_2O_3$ thick film (3 min dipped)**

**Quantitative Elemental Analysis (EDX)**

The quantitative elemental composition of the pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films were analyzed using an Energy Dispersive Spectrometer (EDS). Fig.3 (a-b) represents the EDS patterns of pure and $Fe_2O_3$ modified $Cr_2O_3$thick films (3min dipped). In chromium oxide, stoichiometric mass percentage of chromium and oxygen are 68.420 and 31.580 respectively.

The prepared powder of pure $Cr_2O_3$ is excess in oxygen, which increases its p-typeness characteristic. It leads to semiconducting nature of the synthesized pure $Cr_2O_3$. Excess or deficiency of the constituent element leads to the semiconducting nature of the material. Also, the mass % of Cr and O in each activated samples are not as per the stoichiometric proportion and all samples are observed to be oxygen deficient or excess in chromium. Thus, the maximum numbers of electrons are free to conduct the current and electrons behave as the majority current carriers. This enhances n-typeness of activated $Cr_2O_3$. Thus, dipping process is the simple and low cost technique to activate the surface of the film. This forms heterojunctions on the surface of the film which increases the resistivity.

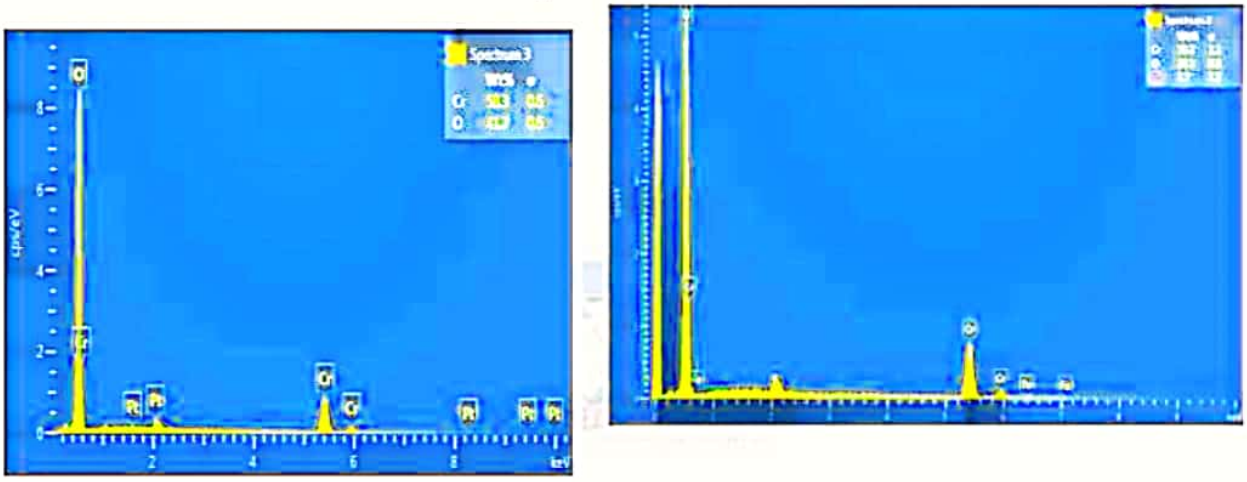


**Fig.3:** EDS patterns for a) pure $Cr_2O_3$ thick film b) $Fe_2O_3$ modified $Cr_2O_3$ thick film (3 min dipped)

**I-V characteristics pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films**

Fig.4 depicts the I-V characteristics of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film were ohmic in nature. Fig. 4 also shows that the conductivity of pure $Cr_2O_3$ film is larger than $Fe_2O_3$ modified $Cr_2O_3$ thick films.

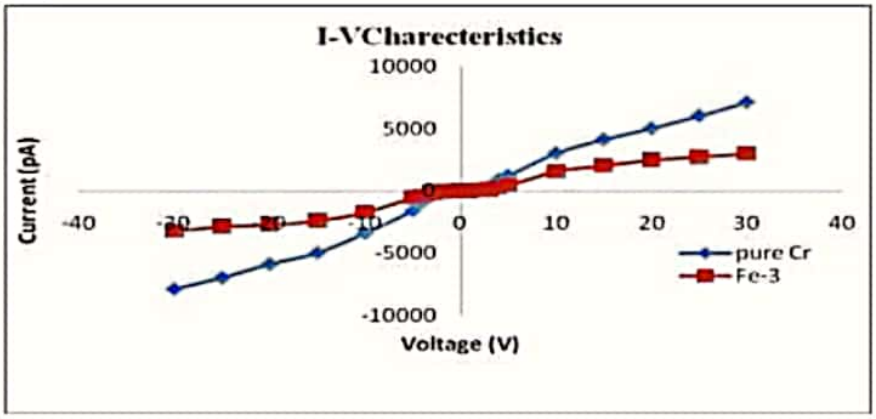


**Fig.4:** I-V characteristics of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films at room temperature.

**Gas Sensing Performance of Pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films**

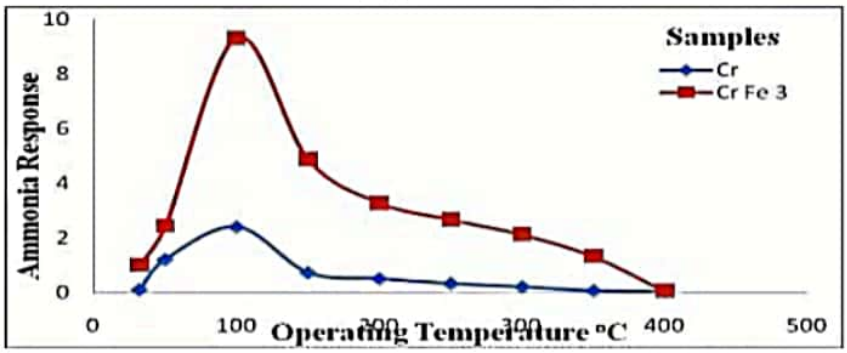



**Fig 5:** Variation of gas response of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films with operating temperature

Fig. 5 depicts the gas response of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films versus operating temperature. The gas response of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films to 100 ppm $NH_3$ were investigated at various operating temperatures ranging from room temperature to $400^0$C. Fig. 5 also shows that the gas response to $NH_3$ gas goes on increasing with operating temperature, reaches to a maximum at $100^0$C and then decreases with the further increase of operating temperature. As we know that, response to a $NH_3$ gas is generally depends on the number of oxygen ions adsorbed on the surface of the film with a target gas. If the film surface chemistry was favourable for adsorption, response and selectivity would be enhanced. In the case of pure $Cr_2O_3$ thick film, oxygen adsorption seems to be poor and hence it shows poor response to $NH_3$. So, to improve and enhance the sensing performance of pure $Cr_2O_3$, it is essential to modify pure $Cr_2O_3$. It is also clear from figure that $Fe_2O_3$ modified $Cr_2O_3$ thick film at 3 min dipping time gives highest response to 100 ppm $NH_3$ at $100^0$C. When the optimum amount of $Fe_2O_3$ (3 min dipping) is dispersed on the surface of $Cr_2O_3$ thick film, the $Fe_2O_3$ grains would be distributed uniformly throughout the surface film. These $Fe_2O_3$ grains form potential barrier (p-n heterojunctions) with $Cr_2O_3$. Due this potential barrier, sensor element offers high resistance. So such amount of high resistance would be sufficient to promote the catalytic reaction effectively. These overall changes lead to high gas response when this type of sensor element expose to $NH_3$ gas.

Fig. 6 depicts the selectivity of all, pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films towards LPG, $C_2H_5OH$, $CO_2$, $NH_3$, $H_2S$ and $Cl_2$ for 100 ppm concentration at$100^0$C. It is observed from figure that the 3 min. dipped $Fe_2O_3$ modified $Cr_2O_3$ thick film is most sensitive to $NH_3$ gas at$100^0$C among all other tested gas.

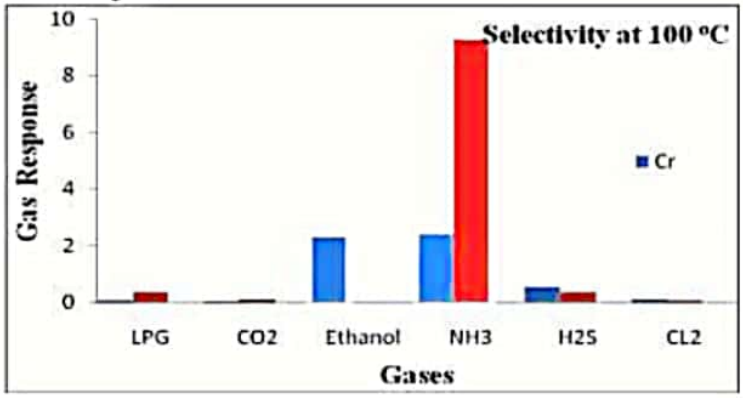


**Fig. 6:** Selectivity of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films.

Fig. 7 exhibits the relation between gas response of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films and concentration of $NH_3$ gas at $100^0$C. It is clear from the figure that the gas response of $Fe_2O_3$ modified $Cr_2O_3$ thick film (3 min dipping) increases linearly with gas concentration up to 100 ppm. The rate of increase in response was relatively larger up to 100 ppm and saturated beyond 100 ppm. The active region for the ammonia sensor is up to 100 ppm. At low gas concentration, the monolayer of $NH_3$ gas molecules formed on the surface of film. So, the $NH_3$ response increases in proportion up to active region. At high gas concentration, the multilayer of $NH_3$ gas molecules on the sensor surface would result into saturation in response beyond 100 ppm gas. So, for proper functioning, the sensor should work in the active region only.

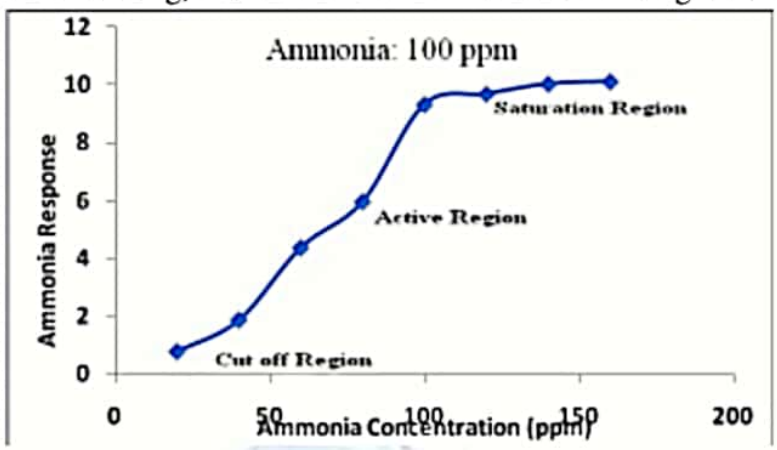



**Fig 7: Variation of $NH_3$ response with $NH_3$ concentration (ppm)**

The response and recovery of the $Fe_2O_3$ modified $Cr_2O_3$ thick film (3 min. dipped) to 100 ppm of $NH_3$ are 7 s and 10 s respectively. Thus the sensor showed very rapid response and recovery time to $NH_3$ gas. For better performance of the sensor the recovery should be very fast. When the gas exposure was switched off, the sensor returned back to its original chemical status, within very short time (10 s). This is the main feature of this sensor.

The response of this sensor towards 100 ppm of $NH_3$ gas at $100^0$C was measured for two month in the interval of 10 days and found almost constant. The good stability could be attributed to calcinations at high temperature and aging of sample for a few days. Thus the sensor showed a very stable response confirming the stability and hence reproducibility of the material.

**Gas sensing mechanism**

In sensor, the surface is the region where periodicity of the crystal can be interrupted. Due to this, localized energy levels are formed in the forbidden gap, which can either capture electrons or give up electrons. In case of pure or $Fe_2O_3$ modified $Cr_2O_3$, the surface oxygen ions donate electrons. The response could be attributed to the adsorption-desorption type sensing mechanism. Gas Oxidation depends upon the amount of oxygen species ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$) adsorbed on the surface. Gas sensing mechanism is mostly explained in terms of conductance, by adsorption of atmospheric oxygen on the surface or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. The working principle of thick film semiconducting gas sensors is based on the change of the electronic conductivity of the semiconducting material on exposure of target gas. In such mechanism, the atmospheric oxygen molecules $O_2$ (air) are adsorbed on the surface of the thick film. They capture the electrons from the conduction band of the thick film material as:

$$O_{2\,(air)} + 4\,e^-_{(cond.band)} \rightarrow 2\,O^{2-}_{(film\ surface)}$$

It would result in decreasing conductivity of the film. As we know that, the lone pair of electrons of $NH_3$ provides strong electron acceptor behaviour. But it acts as an electron donor to the metal oxide, when reacted with the adsorbed oxygen ions on the surface by returning the trapped electrons to conduction band. The reactions that generates free electrons when the number of oxygen ions reacted with $NH_3$ molecules, given in the following equations [21].

$$4NH_3 + 3O_{2\,(adsorbed)} \rightarrow 6H_2O + 2N_2 + 6e-$$

Or

$$2NH_3 + 3O^-_{(adsorbed)} \rightarrow 3H_2O + N_2 + 3e-$$

Upon exposure, ammonia molecules react with adsorbed oxygen on the surface of the film got oxidized to nitrogen oxide gas and water vapors as the products liberating free electrons in the conduction band. The following possible reaction would take place.

$$2\,NH_3 + 7\,O^{2-}_{(film\ surface)} \longrightarrow 2\,NO_2\uparrow + 3\,H_2O\uparrow + 14\,e^-$$

**Conclusions**

The results of pure and $Fe_2O_3$ modified $Cr_2O_3$ thick films can be summarized as follows

1. The pure $Cr_2O_3$ film was more conductive than $Fe_2O_3$ modified $Cr_2O_3$ thick film (3min dipped).
2. $Fe_2O_3$ was found to be outstanding in enhancing the gas sensing performance of $Cr_2O_3$ based gas sensors.
3. Surface modification by dipping process was one of the most useful methods of modifying the thick film surface for the gas sensing performance of metal oxide based gas sensors.
4. A pure $Cr_2O_3$ thick film was almost insensitive to all tested reducing gases.
5. $Fe_2O_3$ modified $Cr_2O_3$ thick film (3 min dip) showed higher gas response to 100 ppm at $100^0$C.
6. The sensor showed good selectivity to $NH_3$ gas against $Cl_2$, LPG, $CO_2$, $H_2S$ and $C_2H_5OH$ gases at $100^0$C.
7. The sensor showed very rapid response and recovery time to $NH_3$ gas.

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