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Synthesis of Ferric Oxide Nanoparticles for Gas Sensors Using Screen Printed Thick Films

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Abstract

Nano-powders Ferric oxides (Fe2O3) were synthesized by precipitation method. Powders were then used to make thick films on glass substrate by using standard screen printing technique. These films dried and fired at 400 ^{0}C temperature for two hours in air atmosphere. The gas sensing performance was studied using static gas sensing system. The films were tested for various gases such as NH3, Ethyl Alcohol, LPG, H2S and Cl2. The nano Fe2O3 film showed maximum sensitivity to chlorine gas at room temperature at1000 ppm concentration at small response time and large recovery time. Morphological and structural properties of the films were studied using the scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDAX) and X-ray diffraction (XRD) techniques.

Keywords: Ferric oxides; thick films; SEM; XRD; gas sensitivity

Introduction

In recent years considerable attention has been focused on use of metal oxide semiconductors for the purpose of gas sensing application. Iron oxide, metal oxide semiconducting material, can exist in various forms such as α-Fe2O3, γ-Fe2O3 and Fe3O4. The gas sensing properties of α & γ forms are still not established and contrasts are available in Iron oxide literature [1, 2]. Some papers attribute to gas–sensing properties of γ-Fe2O3 and Fe3O4 rather than to α-Fe2O3. The α-Fe2O3 form has been recognized as having minimal gas-sensing response [1]. It has been reported that the thermal stability of the γ-Fe2O3 limits its use as gas sensor [2] Iron titanium oxide solid solutions have shown response to ethanol [3]. Some report says α-Fe2O3, the most stable iron oxide with n–type semiconducting properties under ambient conditions, is extensively used as gas sensor, catalysts [4, 5-9]. In metal oxide semiconductor thick film gas sensor, surface structure of the film and surface to volume ratio play very important role in sensing performance. In present work nano Fe2O3, being smaller in size, was especially studied to observe the effect of change in surface to volume ratio on the gas sensing performance of the material. As it is known a specific area is sharply increased with decrease of grain size. A high specific surface area and comparability of grain size (D) with the thickness surface charge layer can take great advantage for the development of high–sensitive gas sensors [10]. It is known that the surface of nano structure with high surface to volume ratio is very unstable and it easily adsorbs foreign molecules for stabilization [9, 10]. Structural factor for nanoscaled material is complicated conception and apart from

size, crystallite shape, nanoscopic structure, crystallographic orientation of nanocrystallites planes forming gas sensing surface affect sensing performance of the sensing material [11].

Experimental

Synthesis of Fe2O3 nano powder

200 ml (0.1M) of Fe(NO3)3, 9H2O (precursor solution) was gelated by using 800 ml of mono hydrated citric acid solution, 0.05 to 0.2M (ligand molecules) and distilled water (solvent). The iron solution was added to the citric acid solution drop wise with vigorous stirring followed by heating to 70°C, while maintaining vigorous stirring until the gel was formed and the contained water was evaporated. The dried gel was annealed at temperatures ranging from 180- 400°C, typically yielding 1.6g of Fe2O3 ranging in size from 22-56 nm.

Thick Film Preparation

The obtained nano Fe2O3 powder was taken and the thixotropic paste was formulated for printing the films. Thixotropic paste was formulated by mixing nano Fe2O3 powder with the organic binder. Thick films of the material were prepared by screen printing technique. The prepared thick films were fired at 400^0C for 2 hours in air atmosphere.

Structural, Morphological and Gas sensing Studies

The structural properties of Fe2O3 films were investigated using X-ray diffraction. The scanning electron microscopy was employed to characterize the surface morphology. The Composition of Fe2O3 thick film samples were analyzed by Energy Dispersive spectrometer. The thickness of the Fe2O3 thick films was measured by using Taylor-Hobson system. The thickness of the films was observed uniform in the range of 20µm to 25µm. The D.C. Resistance of the films was measured by using half bridge method in atmosphere at different temperatures. The gas sensing studies were carried out on a static gas sensing system under normal laboratory conditions. The gas response of thick films was studied in test assembly. The electrical resistances of thick film in air (*R*a) and in the presence of gas (*Rg*) were measured to evaluate the gas response (*S*) given by the relation,

$$S = \frac{Ra - Rg}{Ra} \qquad \text{---------- (1)}$$

Where Ra is the resistances of the thick film sample in air and Rg is the resistances of the thick film sample in gas atmosphere.

The Fe2O3 thick films were characterized by X-ray diffraction technique.The average crystallite size was determined using Scherrer formula [30],

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad \text{…….. (1)}$$

Where

D = average crystalline grain size, β = Full angular width of diffraction peak at the half maximum peak intensity (FWHM)

λ = wavelength of X-ray diffraction (1.542 Å)

θ = angle of diffraction

The surface morphology and chemical composition of the films were analyzed using a scanning electron microscope [SEM model JEOL 6300 (LA) Germany] coupled with an energy dispersive spectrometer (EDS JEOL, JED-2300, Germany).

Results And Discussion

Composition of Fe2O3 thick film

Table-1 shows the composition of the films fired at 400^{o}C. The EDAX spectrum showed the presence of only Fe and Oxygen. From the analysis it was found that the Fe2O3 films are nonstoichiometric. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity. Tin oxide looses oxygen on heating so that tin is then in excess. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess tin ion in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to nonstoichiometry in the solid. This leads to the formation of the n-type semiconductor [12].

Table-1: Composition of the Fe2O3 films at 400^{0}C firing temperature

Element	Mass %	At.%
O	14.89	40.91
Fe	85.11	59.09
Total	100	100

X-ray diffraction analysis

Fig. 1 shows X-ray diffraction patterns of nano- powder Fe2O3 screen printed thick film deposited on glass substrate. XRD pattern show the different peaks of Fe2O3 phases. It has been observed that the peaks with the plane (2 0 0), (3 1 1), (5 1 1), (4 0 0) and all other found to be exactly matched with the standard peaks with corresponding planes values. The XRD found well matched with the file no.39-1346 of JCPDS data and all peaks matched well with the JCPDS data [13, 14]. This clearly indicates that the structure of Fe2O3 film is polycrystalline in nature. Besides except Fe2O3 peaks, no other impurity peak is seen, suggesting formation of the single phasic Fe2O3.

Scanning Electron Microscopy

The scanning electron microscopy is useful technique to observe surface morphology of deposited films. SEM images shows that the structure like porous and wafer type. This is because of porosity of the film as deposited at room temperature. Fig.2 shows SEM images of nanostructure Fe2O3 thick film fired at

400°Cin the air. Microstructural characterization was carried out by using scanning electron microscopy. The film shows small circular shaped grains of the Fe2O3 along with the porous nature of the film. This porosity, which causes increase in surface to volume ratio eventually increase in interaction with gas molecule, is beneficial for gas sensing properties of the film. The film fired at 400°C has good adhesion. Therefore it is used for gas sensing.

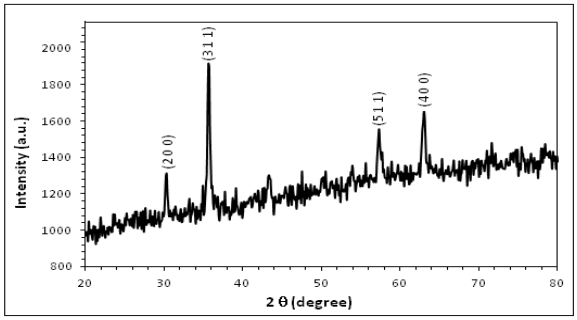

Fig.1. X-ray Diffraction Pattern of Fe2O3 Thick Film

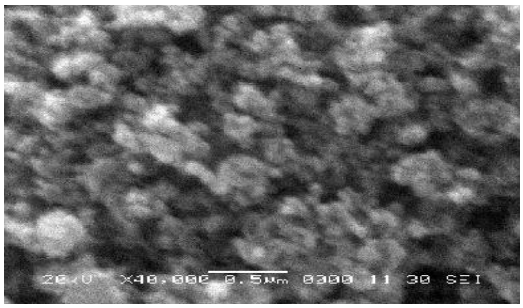

Fig.2. SEM micrograph of nano Fe2O3 Thick Film

Gas Sensing Response

Chlorine Gas Sensing

Fig.3 shows the variation of response of nano Fe2O3 fired at 400°C to 1000 ppm Chlorine gas with operating temperature. The gas response is maximum at room temperature for 1000 ppm. The response of nano Fe2O3 to Chlorine gas is 98 % at room temperature. In present work, every time prior to exposing the Fe2O3 film to Chlorine, it was allowed to stabilize at an operating temperature for 15 min and the stabilized resistance was taken as Ra. After exposing the film to the Chlorine gas, the changed resistance was taken as Rg. Chlorine is reducing gas. It reacts with surface oxygen ions of the film. Reduction of film increases the number of free carriers. Therefore resistance of the film decreases with reducing gases [15, 16, 17].

Gas Response and Fe2O3 Concentration

The variation of gas response of the Fe2O3 film sample with Chlorine gas concentration at room temperature is represented in Fig.4. This film was exposed to different gas concentrations of Chlorine.

The sensitivity values were observed to increase continuously with increasing the gas concentration up to 1000 ppm.

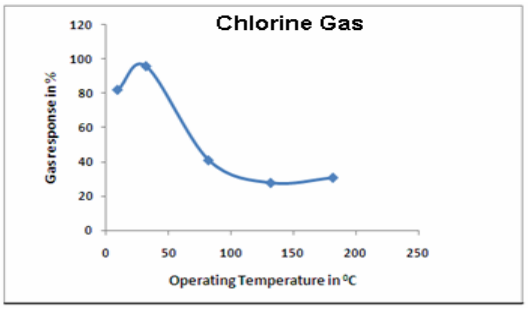

Fig.3. Variation of response with operating temperature for Fe2O3 gas at 1000 ppm.

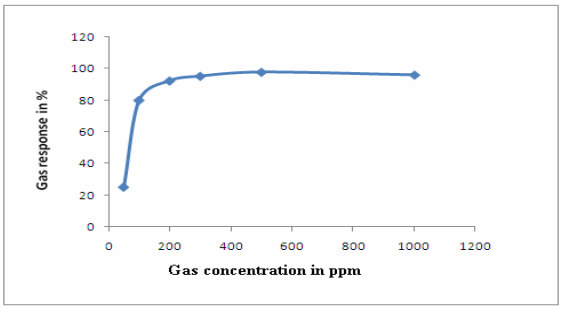

Fig.4. Variation of gas response with gas concentration

Selectivity for Fe2O3 against Other Gases

It is observed from Fig.5 that the Fe2O3 sample shows maximum response to Chlorine gas (1000 ppm) at room temperature. Sample showed highest selectivity for Chlorine gas against all other tested gases viz: NH3, Ethyl Alcohole, LPG and H2S.

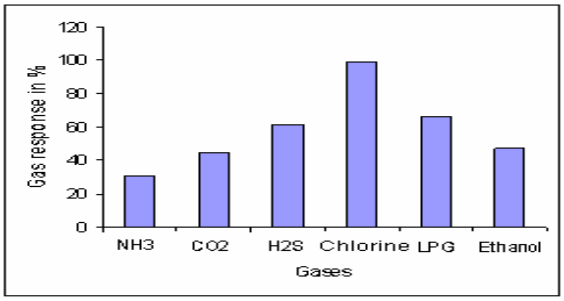

Fig. 5. Selectivity of Fe2O3 sample for various gases

Response and Recovery Time

The response and recovery times of Fe2O3 film sample are represented in Fig.6. The response was quick (~ 30 s) to 1000 ppm of Chlprine while the recovery was fast (~ 40 s). The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response and fast recovery to its initial chemical status.

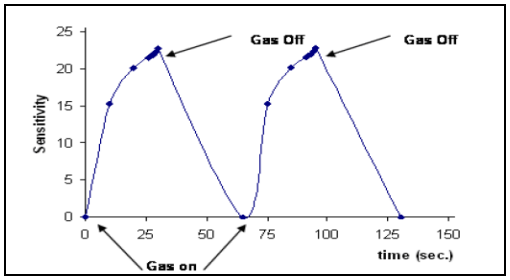

Fig. 6. Response and recovery of Fe2O3 sample

Conclusions

Nano powders Fe2O3 screen printed thick film shows good adhesive to glass substrate employing a simple, inexpensive method and capability of the Fe2O3 films for Chlorine gas sensing. The film fired at 400ºC exhibited good sensing performance to Chlorine gas at room temperature.

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References:

[1] G.Telipan, *Proc. Int. Sym. Digital Earth, Sci Press*, 1-4 (1999).

[2] M.Ivanvokaya, D. Kosikau, G. Fagila, P. Nelli, Irkaev, *Sens.Actuators B: Chem.,* Vol.93, 422-430 (2003).

[3] O. K.Tan, W. Cao, W. Zhu, J. W. Chai, J. S. Pan, Sens. Actuators B: Chem., Vol. 93, 396- 401 (2003).

[4] X.L. Gou, G.X. Wang, X.Y. Kong, D. Wexler, J. Horvat, J. Yang, J. Park, Chem. Eur. J., Vol. 14, , 5996–6002(2008).

[5] H. Liu, G.X. Wang, J. Park, J.Z. Wang, C. Zhang, Electrochim. Acta, Vol. 54,1733–1736 (2009).

[6] L. Chun, X.Z. Wu, X.M. Lou, Y.X. Zhang, Electrochim. Acta, Vol. 55, No. 9, 3089–3092 (2010),

[7] J.G. Yu, X.X. Yu, B.B. Huang, X.Y. Zhang, Y. Dai, Cryst. Growth Des, Vol. 9, 1474–1480 (2009).

[8] J.M. Gu, S.H. Li, E.B. Wang, Q.Y. Li, G.Y. Sun, R. Xu, H. Zhang, J. Solid State Chem., Vol. 182, No. 5, 1265–1272 (2009).

[9] M.V. Reddy, T. Yu, C.H. Sow, Z.X. Shen, C.T. Lim, G.V.S. Rao, B.V.R. Chowdari, Adv. Funct. Mater., Vol. 17, 2792–2799 (2007).

[10] G. Korotcenkov, Material Science and Engineering B, Vol. 139, 1-23(2007).

[11] G. Kortcenkov, , Sensors and Actuators B, Vol. 107, No. 1, 209-232 (2005).

[12] D. R. Patil, L. A. Patil, IEEE Sensors Journal, 7[3], 434-439 (2007).

[13] B.D. Cullity, in “Elements of X-ray diffraction 2nd Edition” (Addison Wesley), (1978).

[14] JCPDS Card Number 21-1486 ZnO (1992).

[15] H. Tang, K. Prased, R. Sanjine’s F. Levy, Sens. & Actu. B, 26- 27, 71-75 (1995).

[16] S. C. Gadkari, Solid State Physics Symposium, 41, 1998, Kurukshetra Uni. Kurukshetra. Jia Grace Lu, SPIE