Solid State Science and Technology, Vol. 17, No 2 (2009) 197-207
ISSN 0128-7389

AMMONIA GAS SENSING PERFORMANCE OF Cr_2O_3-LOADED TiO_2 THICK FILM RESISTORS

C.G. Dighavkar[1], A.V. Patil[1], S. J. Patil[2] and R.Y. Borse[2]

[1]*Department of Electronic Science, L.V.H.College, Panchawati, Nasik, Maharashtra., India,*

[2] *Thick film laboratory, Department of Electronic Science, M.S.G. College, Malegaon Camp, Dist- Nasik , Maharashtra, India.*

ABSTRACT

This work investigated the use of Cr_2O_3 loaded TiO_2 thick films gas sensor. The titania thick films were prepared by a standard screen printing technique. Pure TiO_2 was observed to be insensitive to NH_3 gas. In order to check the NH_3 gas sensitivity various concentrations (1 wt. %, 3 wt. %, 5 wt. %, 7 wt. % and 10 wt. %) of Cr_2O_3 was added in TiO_2. The maximum sensitivity (88.23 %) was obtained for NH_3 at of 5 wt. % Cr_2O_3 loaded TiO_2 thick films at 250 ^{0}C. The sample was observed to be oxygen deficient. Upon exposure to NH_3 gas, the barrier height of TiO_2-Cr_2O_3 intergranular regions decreases markedly due to the chemical transformation of Cr_2O_3 into well conducting chromic ammonium hydroxide leading to a drastic decrease in resistance. The crucial gas response was found to NH_3 gas at 250 ^{0}C and no cross response was observed to other hazardous and polluting gases. Phase evaluation of screen printed thick films of TiO_2-Cr_2O_3 composite was examined by XRD technique. XRD showed polycrystalline nature with anatase and rutile structure. SEM investigation revealed that the size of particles ranged from 180 to 200 nm. The effect of loading of Cr_2O_3 concentration in TiO_2 thick films on the gas sensitivity, selectivity, response and recovery times of the sensor in the presence of NH3 gas were studied and discussed.

INTRODUCTION

Titanium dioxide (TiO_2) has been extensively studied owing to its wide range of applications which include photocatalysis, heterogeneous catalysis, energy storage, solar cell components, corrosion-protective coatings and optical coatings [1–5]. Titanium dioxide can be synthesized in three crystalline phase: rutile, brookite and anatase [6]. Rutile is more thermodynamically stable than other phase. Anatase phase is stable for TiO_2 at comparatively low temperatures. Titanium dioxide in the anatase crystalline phase is one of the most studied materials for photocatalysis. It has been shown that sensitivity of TiO_2 sensors can be improved by addition of dopants such as Cr, Nb, Sn, Al, Pt, La and Y. Most important effects of dopant addition in TiO_2 are increasing the conductivity, slowing down anatase to rutile transformation and reducing grain growth. [7,8]. Among the various metal oxides that can be used in gas sensors, only those materials based on stannic oxide and titanium oxide have been widely manufactured and utilized [9]. The aforementioned background justifies the need to

Corresponding Author: cgdighavkar@gmail.com

improve the properties and features of these oxides in order to obtain a more efficient material for gas sensing purposes. The advantage of TiO_2 is that it is highly stable material at high temperature and harsh environment and has thermal expansion coefficient matching with alumina making it suitable for the fabrication as thin or thick film based sensors [10]. TiO_2 doped Cr_2O_3 films were reported to have sensitive to NO_2, O_2 and humidity [11-13]. Recently sensors based on Cr_2-xTiO_3[x = 0.05-0.4] has been commercialized by capteur sensors [12].

Several deposition methods have been used to grow undoped and doped TiO_2 films such as Spray pyrolysis, Vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique and screen printing technique [14, 15]. Screen printing technique was introduced in the later part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Screen printing is viable and economical method to produce thick films of various materials [16, 17].

The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Therefore all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentration. It is therefore, necessary to monitor ammonia gas and to develop the ammonia gas sensor. Efforts are made to develop the TiO_2 loaded with Cr_2O_3 thick film based NH_3 gas sensors. There are many techniques for measuring NH_3 described in the literature. [18, 19] The ammonia gas sensors that have been manufactured in the largest quantities are mostly based on SnO_2 material. Ternary oxide compound $Cr_{2-x}TixO_{3+\delta}$ has been reported for NH_3 monitoring at 300 ^{0}C for 500ppm [20].

The aim of present paper is to prepare Cr_2O_3 loaded TiO_2 thick films by a screen printing technique on alumina substrate to investigate the sensing properties for NH_3 gas.

EXPERIMENTAL

Analar Reagent (AR) grade TiO_2 powder (99.9%pure) and Cr_2O_3 were mixed mechanochemically to obtain Cr_2O_3 doped TiO_2 powders in various weight percentages such as 1, 3, 5, 7, and 9 wt. %. This prepared powder was then calcined at 400^{0}C for 2 hours in muffle furnace. The ratio of inorganic to organic part was kept as 70:30. The inorganic part consists of a functional material (TiO_2), loading material (Cr_2O_3) and glass frit (70 wt.% PbO,18 wt.% Al_2O_3,9wt.% SiO_2 and 3wt.% B_2O_3) as permanent binder. The organic part consists of 8 % ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA). TiO_2 powder with Cr_2O_3 and 5 wt. % of glass frit were mixed thoroughly in an acetone medium with mortar and pestle to ensure sufficiently fine particle size. A solution of EC and BCA in the ratio of 8:92 was added drop wise until proper thixotropic properties of the paste were achieved. TiO_2 loaded with Cr_2O_3 thick films were prepared on alumina substrate by using a standard screen-printing technique. The printed pattern was allowed to settle for 15 to 20 minutes in air. The films were

Corresponding Author: cgdighavkar@gmail.com

dried under IR radiation for 45 minutes to remove the organic vehicle and then fired at temperature of 800^{o}C for 1.5 to 2 hrs in muffle furnace. The glass frit was used to bond the film to surface of the substrate.

The phase evaluation of the thick film materials was examined by a high resolution X-ray diffractometer (Miniflex Model, Rigaku, Japan)) using CuKα radiation in 20-80^{o} with 0.1^{o}/step (2θ) at the rate of 2 sec/step. The surface morphology and composition of the films were evaluated from the scanning electron microscopy (SEM- JOEL JED-2300 micrographs) and energy dispersive X-ray spectrometry (EDS-JOEL-JED 6360 LA) respectively. Thickness of the films was measured by using Taylor-Hobson (Taly-step UK) system and was observed uniform in the range of 20μm to 25μm.

The specific surface area was calculated for spherical particles using the following equation [21].

$$Sw = 6 / \rho d \qquad (1)$$

Where d is the diameter of the particles, ρ is the density of the particles.
The D.C. Resistance of the films was measured by using half bridge method in ambient at different temperatures. The NH_3 gas sensing was carried out in a static gas sensing system under normal laboratory conditions. The electrical resistances of thick film in an air (*R*a) and in the presence of NH_3 gas (*Rg*) were measured to evaluate the gas response (*S*) given by the relation,

$$S = \frac{R_a - R_g}{R_a} \qquad (2)$$

Where R_a and R_g are the resistance of thick film samples in air and NH_3 gas atmosphere respectively.

RESULT AND DISCUSSION

Elemental Analysis

Table 1**:** Composition of Cr_2O_3 loaded TiO_2 obtained from EDS

Element (Wt. %)	TiO_2	Cr_2O_3				
		1wt. %	3wt. %	5wt. %	7wt. %	10wt. %
O	42.37	34.28	37.83.	34.27	34.29	37.49
Ti	57.63	65.02	60.55	62.02	61.29	56.12
Cr	--	0.70	1.62	3.71	4.42	6.39

The quantitative elemental compositions of the Cr_2O_3 loaded TiO_2 films were analyzed using an energy dispersive spectrometer as shown in table 1. The wt. % of Ti and O in

Corresponding Author: cgdighavkar@gmail.com

each sample was not as per stoichiometric proportion. The Wt. % of Cr increases as Cr_2O_3 concentration increases. TiO_2 samples loaded with Cr_2O_3 were observed to be oxygen deficient. The sample loaded with 5 wt. % Cr_2O_3 was observed to be most oxygen deficient. The deficiency or excess of the constituent material particles leads to the semiconducting behaviour of the material [22].

Structural analysis

Figure 1 shows XRD pattern (20 - 80^0) of the TiO_2 thick films loaded with x wt.% of Cr_2O_3 (x = 0,1,3,5,7 and 10 wt.%) prepared by a screen printing method and fired at 800^0C. The XRD patterns shows the film samples are polycrystalline in nature. It was observed that the both anatase and rutile phase coexisted in the TiO_2-Cr_2O_3 composite film samples fired at 800^oC [23]. In the 2θ range, the 101 anatase peak, located at 25.8^O, is present. This is the most pronounced peak of an anatase structure for film sample fired at 800 ^{0}C. All values of (hkl) plane are matched with JCPDS data 21-1272 and 21-1276 for anatase and rutile structure respectively. XRD pattern shows that all samples were dominated by anatase phase. The electrical mobility of anatase films is much larger due to the smaller electron effective mass and also the Fermi level is higher by about 0.1 eV compared to the rutile structure. These properties are useful for gas sensing and optoelectronic. [24-28]. The segregation of Cr was evident from the appearance of diffraction peaks ascribable to Cr_2O_3 based on JCPDS pattern 38-1479. XRD pattern-shows effect of Cr_2O_3 addition slowing down anatase to rutile transformation. Subsequently the rutile phase decreases as Cr_2O_3 dopant concentration increases.

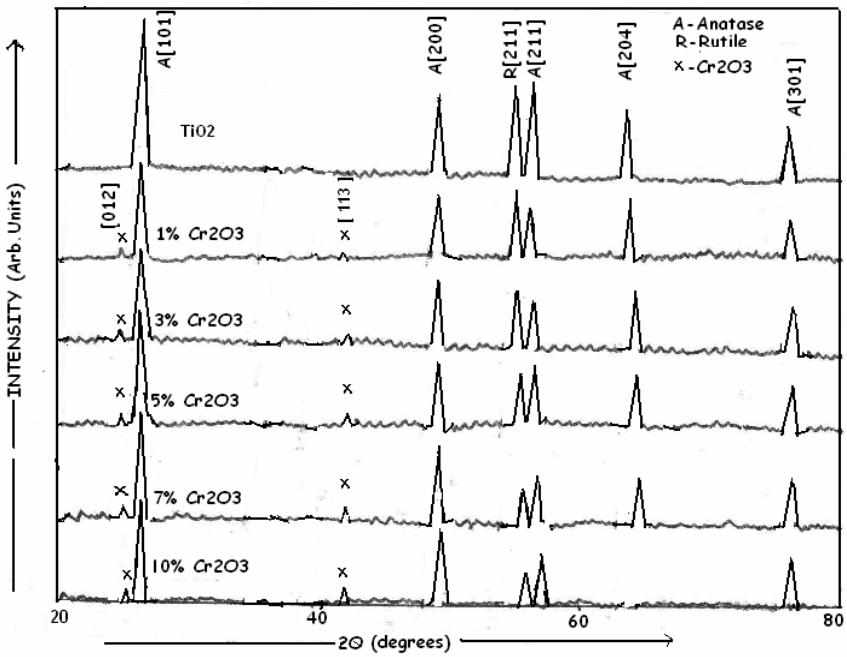

Figure 1**:** XRD pattern of TiO_2 and TiO_2 films loaded with 1wt. %, 3wt. %, 5wt. %, 7 wt. % and 10 wt. % of Cr_2O_3

Corresponding Author: cgdighavkar@gmail.com

SEM analysis

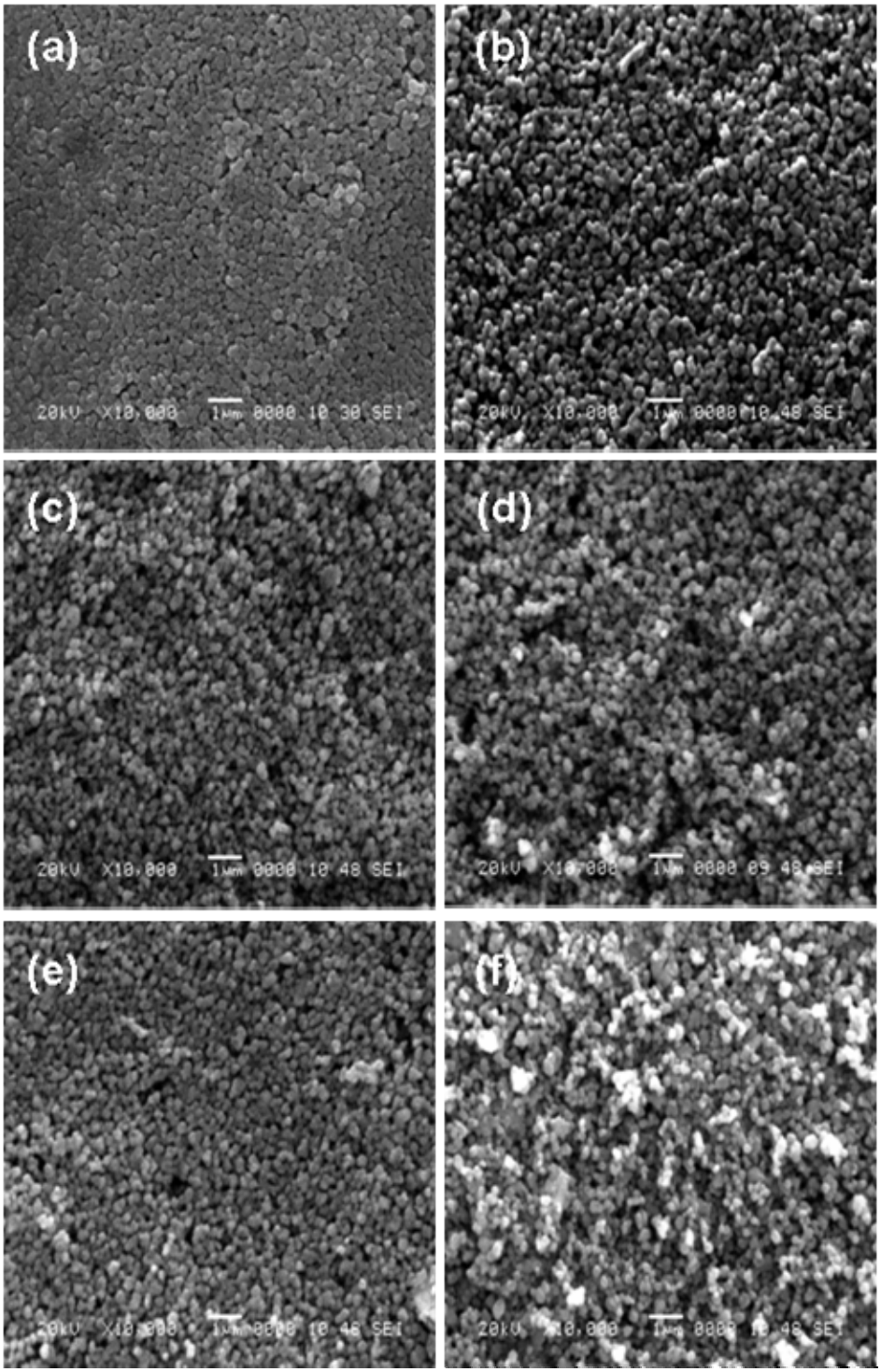

Figure 2:SEM images of (a)TiO_2, (b)1Wt.%, (c)3Wt.%, (d)5Wt.%, (e)7Wt.% and (f)10Wt.%

Corresponding Author: cgdighavkar@gmail.com

It is well known that gas sensing properties of a metal oxide thick film strongly depends on its morphological features. A high surface area facilitates the chemisorption process by increasing the adsorption and desorption rates [29]. Scanning electron microscopy (Figure 2) shows the surface morphology of the sensing layers of TiO_2 and TiO_2 loaded with x wt. % of Cr_2O_3 (x = 1, 3, 5, 7 and 10 wt. %) thick films. Figure 2(a) shows the surface morphology of pure TiO_2 thick film. It consists of randomly distributed grains with smaller size and shape distribution. Figure 2- b, c, d, e and f show the surface morphology of 1, 3, 5, 7 and 10 wt % Cr_2O_3 loaded TiO_2 thick films.

The titania thick film loaded with 5 Wt. % Cr_2O_3 which was observed most sensitive. The film consists of a large number of grains leading to high porosity and large effective surface area available for the adsorption of oxygen species. The titania films loaded with 7 and 10 Wt. % Cr_2O_3 are comparatively less porous and grains are agglomerated. Effective surface to volume ratio would be decreased and less number of oxygen ions would be adsorbed as compared to the film in figure 2(d) [30].

The specific surface area was calculated by using equation (1). The specific surface area increases as the size of the grains decreases [30]. Table 2 presents the particle size and surface area of TiO_2 thick films loaded with different wt. % of Cr_2O_3. The titania film loaded with 5 Wt. % Cr_2O_3 available large surface areas for oxygen adsorption compare to other films.

Table 2: Particle size and surface area of TiO_2-Cr_2O_3 composite thick films

Wt. % of Cr_2O_3	Particle size in nm	Specific Surface Area in m^2/g
Pure TiO_2	200	7.71
1	195	7.88
3	190	8.05
5	185	8.21
7	190	7.93
10	190	7.85

Gas sensing properties

Electrical characterization of TiO_2-Cr_2O_3 composite thick films fabricated by screen printing method and fired at 800^oC has been carried out in a gas test chamber. The resistance of the films was measured by using equation (2). The resistance of the films decreased upon exposure to NH_3 (1000ppm) diluted in air. Figure 3 shows gas sensing response to 1000 ppm of diluted NH_3, at different operating temperatures (100–500^oC) for thick films of pure TiO_2 and TiO_2 loaded with x wt.% of Cr_2O_3 (x=1, 3, 5, 7, and 10wt.%). In this figure it is observed that the 5 wt. % Cr_2O_3 loaded TiO_2 thick film had the largest sensing response (88.23 %) in the range of the operating temperature studied, exhibiting a slightly marked maximum at 250^oC. The response could be attributed to the adsorption-desorption type of sensing mechanism. The maximum sensitivity for 5 wt. %

Corresponding Author: cgdighavkar@gmail.com

Cr_2O_3 loaded TiO_2 film sample as compared to other may be due to the optimum porosity and largest effective surface area available to react the gas. Cr_2O_3-loaded TiO_2 thick films were characterized by means of X-ray diffraction techniques in order to study the influence of this additive on the grain growth inhibition and phase transformation of TiO_2 thick films to evaluate the gas sensing properties. Cr_2O_3 hindered the grain growth of TiO_2.

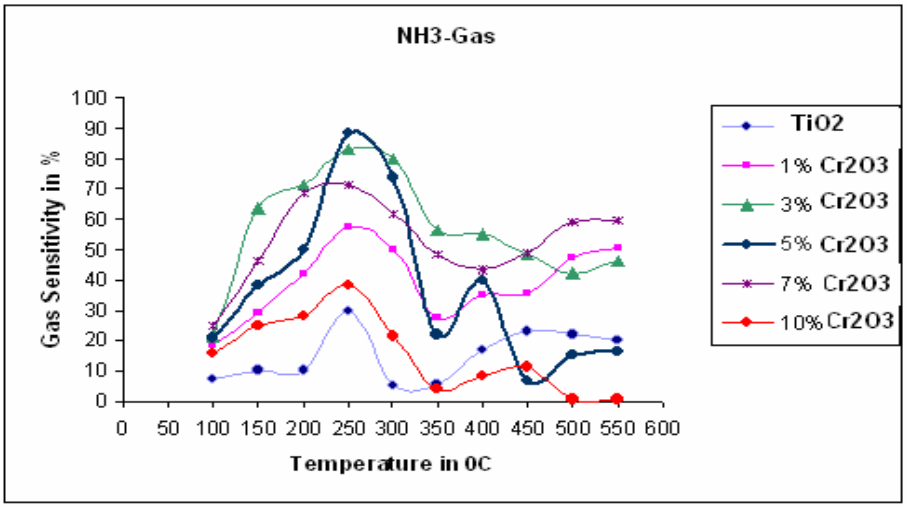

Figure 3: Variation of NH_3 Gas sensitivity with operating temperature for 1000 ppm.

Figure 4 shows the plot of variation of sensitivity for different gases for 5 wt. % Cr_2O_3 loaded TiO_2 thick films. The plot showed highest sensitivity for NH_3 at 250 ^{0}C against all other tested gases viz: H_2S, LPG, CO_2, NO_2 and Ethanol.

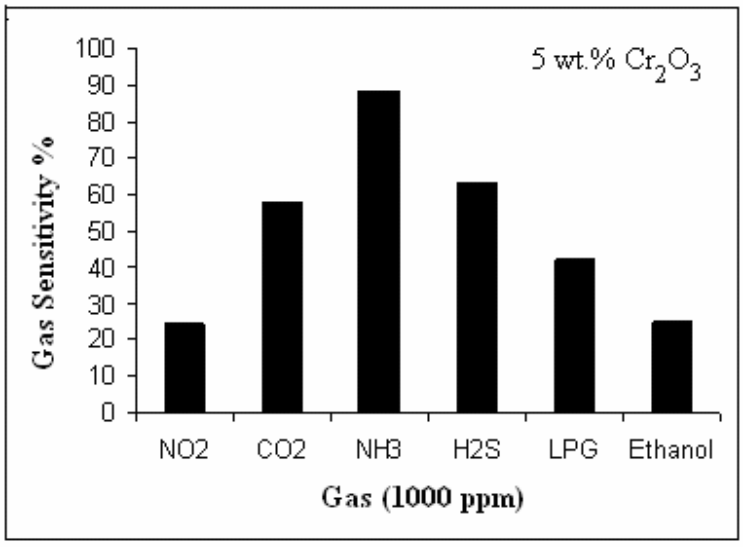

Figure 4: Selectivity of 5 wt. % Cr_2O_3 loaded TiO_2 films for different gases

Corresponding Author: cgdighavkar@gmail.com

Solid State Science and Technology, Vol. 17, No 2 (2009) 197-207
ISSN 0128-7389

Figure 5 is plotted for the calibration curves of the sensing response/sensitivity to NH_3 gas recorded at 250°C of the TiO_2-Cr_2O_3 composite thick film fired at 800°C. The film sample was exposed to different gas concentrations of NH_3. TiO_2 films loaded with 5wt. % of Cr_2O_3 originated an enhancement of the sensitivity to NH_3. For other wt. % of Cr_2O_3, resulted in a decrease of the sensing response. Moreover, the sensing capability of the films to different concentrations of NH_3 has been also monitored and it was noticed that the films were sensitive to NH_3 up to 1000 ppm. Thus, the active region of the TiO_2 film sensor would be up to 1000 ppm.

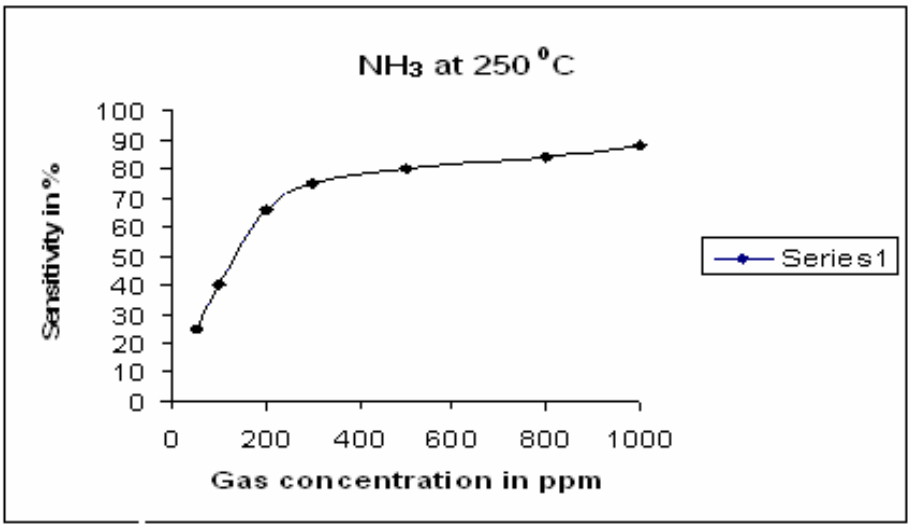

Figure 5: Variation of gas sensitivity with gas concentration.

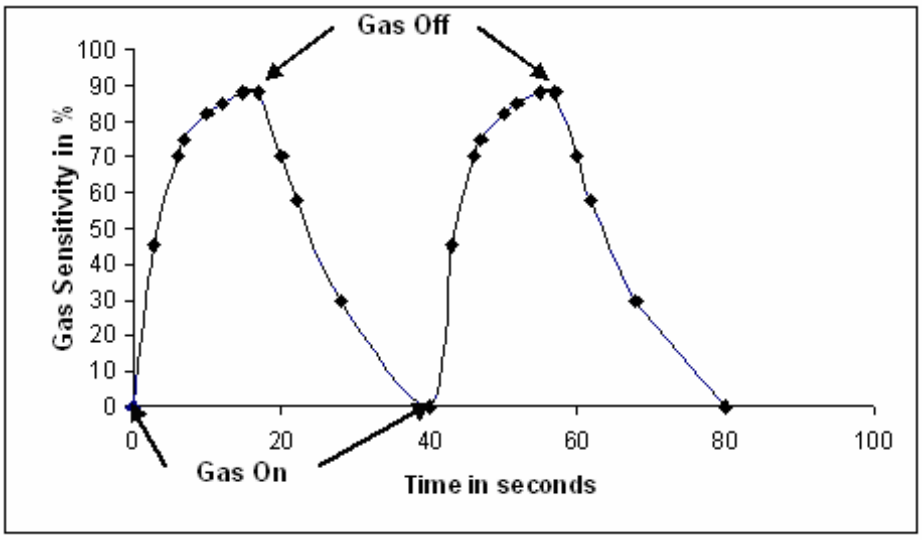

Figure 6: Response and recovery time of 5 wt. % Cr_2O_3 loaded TiO_2 film

Corresponding Author: cgdighavkar@gmail.com

Solid State Science and Technology, Vol. 17, No 2 (2009) 197-207
ISSN 0128-7389

The response and recovery times of 5 wt. % Cr_2O_3 loaded TiO_2 films are represented in Figure 6. The response was quick (~ 18 s) to 1000 ppm of NH_3 while the recovery was fast (~20 s). The quick response may be due to faster oxidation of NH_3 gas. The negligible quantity of the surface reaction product and its high volatility explain its quick response and fast recovery to its initial chemical status.

Sensor Mechanism

The sensitivity of 5 Wt. % of Cr_2O_3 titania to NH_3 could be attributed to the high oxygen deficiency and defect density leads to increased oxygen adsorption. Larger the amount of oxygen adsorbed on the surface, larger would be the oxidizing capability and faster would be the oxidation of NH3 gas. The reactivity of NH_3 would have been very large as compared to other gases with the surface under same condition [31]. When NH_3 reacts with the adsorbed oxygen on the surface of the film, it gets oxidized to nitrogen oxide gas and chromic ammonium hydroxide, liberating free electrons in the conduction band by following reaction as:

$$Cr_2O_3 + 5NH_{3\,(gas)} + 4O_{2-\,(film\ surface)} \rightarrow Cr_2(NH_4OH)_{3\,(film\ surface)} + 2NO_{2\,(gas)} + 8\ e_{-\,(cond.\ band)}$$

This shows n-type conduction mechanism. Thus generated electrons contribute to sudden increase in conductance of the thick film. The Cr_2O_3 misfit regions dispersed on the surface would enhance the ability of material to adsorb more oxygen species giving high resistance in air ambient. On exposure to the NH_3 containing atmosphere, Cr_2O_3 would be converted into chromic ammonium hydroxide and the resistance was observed to decrease in large extent. Therefore, the high response was obtained to 1000 ppm NH_3 gas. The monolayer of gas molecules formed on the surface could covered the whole surface of the film and the excess gas molecules could remain idle and would not reach the surface active sites of the film. So the response at higher concentration of the gas is not expected to increase in a large extent. The titania film with 5 wt. % loading of Cr_2O_3 film was shown more oxygen deficiency owing to reduces the resistivity of the sample. The gas response is largest at 5 Wt. % of the Cr-dopant on the surface of the film and falls down for higher and lower dopant concentrations. At lower dopant concentrations, the numbers of Cr-misfts on the film surface are less, which would adsorb less oxygen species on the film surface. However, at higher dopant concentrations, the Cr-dopant would mask the entire base material-TiO_2 and would resist the gas to reach up to the surface active sites, so gas response would decrease further. The response could be attributed to the adsorption-desorption type sensing mechanism. The amount of oxygen adsorbed on the surface would depend on the number of Cr_2O_3 misfits on the TiO_2 surface and operating temperature. The high response, high selectivity, fast response, recovery and easy operation of the sensor are the main features achieved in the present investigation [32].

CONCLUSION

From the results obtained, Cr_2O_3 loaded titania thick films were found to be selective for ammonia gas. 5 wt. % Cr_2O_3 loaded TiO_2 thick film has been observed that most

Corresponding Author: cgdighavkar@gmail.com

oxygen deficient, porous and largest specific surface area which showed maximum sensitivity to NH_3 gas at 250^0C. Sensitivity to NH_3 gas increases with increase in operating temperature attains 88.23% at 250 ^{0}C and then decreases further with an increase the temperature. The sensitivity increases with the test gas concentration up to 1000 ppm. The 5 wt. % Cr_2O_3 loaded TiO_2 thick films sensor has good selectivity to NH_3 gas against LPG, H_2S, Ethanol vapours, CO_2 and NO_2 at 250 ^{0}C. Also this sensor showed very rapid response and recovery to NH_3 gas. Over long exposure it was observed that sensor exhibited a good stability and repeatability as gas sensor with consistent pattern and response magnitude. These studies show that screen printed thick film of TiO_2 (5 wt. % Cr_2O_3 loaded) on alumina substrate can be used as ammonia sensor.

ACKNOWLEDGMENT

The authors are thankful to management authorities of M.G. Vidyamandir Malegaon camp Dist:-Nasik, The Principal, M.S.G. College, Malegaon and The Principal, L.V.H. College, Nashik for providing all the required infrastructural facilities for doing this work.

REFERENCES

[1]. Colón, G., Maicu, M., Hidalgo, M.C., and Navio, J.A. (2006); Appl. Catal. B: Environ. **67**, 41.
[2]. Amezcua, J.C., Lizama, L., C., Salcedo, Puente, I., Dominguez, J.M., and Klimova, T. (2005**);** Catal.Today. **107–108**, 578.
[3]. Wawyzyniak, B., Waldemar, A., and B.Tryba. B. (2006**);** J. Photoenergy, **1.**
[4]. Barborini, E, Bongiorno, G., Forleo, Francioso, A.L., Milani, P., Kholmanov, I.N., Piseri, P., Siciliano, P., A.M.Taurino, and Vinaty, S. (2005**);** Sensors and Actuators B, **22**, pp111–112
[5]. Prabir, K.D., and de Lucia, M.F. (2006**);** Sensors Actuators B **115,** 1.
[6]. Tompsett, G.A., Bowmaker, G.A., Cooney, R.P., Metson, J.B., Rodgers, K.A., and Seakins, J.M. (1985**);** J. Raman Spectroscopy **26,** 57.
[7]. Choi, Y.J., Seeley, Z., Bandyopadhy, A., Bose, S., Sheikh, A.A., (2001); Sensors and Actuators B: Chemical.**124**, 111-117.
[8]. Radecka, M., Zakrezwskka, K., Rekas, M. (1998); Sensors and Actuators B: Chemical, **47**,194-204.
[9]. K. Ihokura, and Watson, J. (1994**),** The Stannic Oxide Gas Sensor: Principles and Applications (Boca Raton, FL: CRC Press).
[10]. Sharma, R.K., Bhatnagar, M.C., Sharma, G.L. (1997); Sensors and Actuators B: Chemical, **45** 209-215.
[11]. Li, Y., Wlodarski, W., Golatsis, K., Moslih, S.H., Cole, J., Russo, S., Rockelmann, N. (2000); Sensors and Actuators B**,** pp160-163.
[12]. Neri, G., Bonavita, A., Rizzo, G., Galvangno, S. (2004); J. Euro. Ceramic Society, **24**, 1435-1438.
[13]. Du, J., Wu, Y., Choy, K.L. (2006); Thin Solid Films, **497**, 42-47.

Corresponding Author: cgdighavkar@gmail.com

[14]. Joseph, B., Gopalchandran, K.G., Manoj, P.K., Koshy, P., Vaidyan, V.K. (1999); Bull.Mater.Sci.**22**, 921.
[15]. JaydevDayan, N., Sainkar, S.R., Karekar, R.N., Aiyer, R.C. (1998); Thin Solid Films **325,** 254
[16]. Krishnan, B., Nampoori, V.N. (2005); Bull. Mater.Sci. **28**,239.
[17]. Guidi, V., Butturi, M.A., Carotta, M.C., Cavicchi, B., Ferroni, M., Malagu, C., Martinelli, G.,Vincenzi, D., Sacerdoti, M., Zen, M. (2002); Sensors and Actuators B **84**, 72–77.
[18]. Timers, B., Olthus, W., Berg, A.V. (2005); Sensors and Actuators B, **107,** p 666.
[19]. Yamazoe, N. (2005); Sensors and Actuators, **108,** p 2.
[20]. Jayaraman, V., Gnanansekara, K., Prabha, E., Ganansekaran, T., Periaswami, G. (1999); Sensors and Actuators B**55,** pp 175-179.
[21]. Gao, L., Li, Q., Song, Z., Wang, J. (2000); Sensors and Actuators B **71**,179-183.
[22]. Jain, G.H., Patil, L.A., Patil, P.P., Mulik, U.P., Patil, K.R. (2007); Bull.Mater.Sci*,* Vol.**30**-1**,** pp 9-17.
[23]. Ruiza, A.M., Sakaib, G., Corneta, A., Shimanoeb, K., Morantea, J.R., Yamazoeb, N. (2003); Sensors and Actuators B **93**, 509–518.
[24]. Akbar, S.A., Younkanan, I.B. (1997); J. Electrochem.Soc. **144**, 1750-1753.
[25]. Sawage, N., Akabar, S.A., Datta, P.K., Ginwalla, A., Patton, B.R. (2001); Sensors and Actuators B: Chemical **79**, 17-27.
[26]. Sawage, N., Akabar, S.A., Datta, P.K. (2001); Sensors and Actuators B: Chemical **72**,239-248.
[27]. Maruska, H.P., A.K.Ghosh, A.K. (1978); Solar Energy, **20**, 443-458.
[28]. Tank, H., Prasad, K., Sanjines, R., Levy, F.(1995); Sensors and Actuators B: Chemical**, 26-27,** 71-75.
[29]. Kupriyanov, L.Y., (1996); Semiconductor Sensors in Physico-Chemical Studies, Elsevier, Amsterdam.
[30]. Li, W., and Ni, C. (2004); Journal of Applied Physics, Vol.**96**-11, 6663-6669.
[31]. Arbiol, J. (2001); "Metal Additive Distribution in TiO2 and SnO2 Semiconductor Gas Sensor Nano-Structured Materials", Doctoral thesis, Universitat de Barcelona, Department d'Electrónica**.**
[32]. Patil, D.R., Patil, L.A., Amalnerkar, P.P. (2007); Bulletin of material science, Vol-**30**, No.553-559.

Corresponding Author: cgdighavkar@gmail.com