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Environmental gas pollutant detection by using Metal Oxides doping of Titanate thick films

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ENVIRONMENTAL GAS POLLUTANT DETECTION BY USING METAL OXIDES DOPING OF TITANATE THICK FILMS

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Abstract – *Thick films of pure TiO2 and various concentrations (1 wt. %, 3 wt. %, 5 wt. %, 7 wt. % and 10 wt. %) of Cr2O3 and Nb2O5 doped TiO2 were prepared on alumina substrates using a screen printing technique. The doped films were fired at a temperature of 800ºC for two hours in an air atmosphere. Morphological, compositional and structural properties of the samples were obtained using the scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDAX) and X-ray diffraction (XRD) techniques respectively. Various oxidizing and reducing gases were tested for these metal oxides doped films. Among these NH3 and H2S gas sensing properties for these thick films were investigated for Cr2O3 and Nb2O5 doped TiO2 respectively at different operating temperatures. Pure TiO2 was observed to be insensitive to these gases. At 250oC, the 5 wt. % Cr2O3 doped films have shown significant sensitivity (88.23 %) to NH3 gas whereas 1 wt. % Nb2O5 doped films have shown highest sensitivity (98.78 %) to H2S gas at 200oC than any other doped films with fast response and recovery time.*

Keywords: *TiO2; Cr2O3; Nb2O5; thick films; NH3; H2S.*

I. Introduction

Titanium dioxide (TiO2) 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 phases: rutile, brookite and anatase [6]. Rutile is more thermodynamically stable than other phases. Anatase phase is stable for TiO2 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 TiO2 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 TiO2 are increasing the conducting, 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]. alumina substrate and to investigate their sensing properties for various gases.

II. Experimental

The TiO2 loaded with Cr2O3 and loaded with Nb2O5 pastes used in screen printing were prepared by maintaining the inorganic to organic materials ratio at 70:30.The inorganic part consists of a functional material (TiO2), loaded material and glass frit (70 wt.% PbO,18 wt.% Al2O3,9wt.% SiO2 and 3wt.% B2O3).The organic part consisted of 8% ethyl cellulose(EC) and 92% butyl carbitol acetate(BCA).The AR grade TiO2 with x wt.% loaded material (x = 1,3,5,7 and10%) and 5 wt.% of glass frit were mixed thoroughly in an acetone medium with mortar and pestle. A solution of EC and BCA in the ratio 8:92 was made, which was added drop wise until proper thixotropic properties of the paste were achieved. TiO2 thick films were prepared on alumina substrate by using standard screen-printing technique. The screen of nylon (40s, mesh no.355) was selected for screen-printing. The required mask (2 x 1.25 cm) was developed on the screen

The aforementioned background justifies the need to improve the properties and features of these oxides in order to obtain a more efficient material for gas sensing purposes. The advantages of TiO2 are that it is highly stable material at high temperatures and harsh environments and has thermal expansion coefficient matching with alumina making it suitable for the fabrication as thin or thick film based sensors [10]. Several deposition methods have been used to grow undoped and doped TiO2 films such as Spray pyrolysis, Vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique and screen printing technique [11].Screen printing technique was introduced in the later part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film technique has attracted by the sensor field [12]. Screen printing is viable and economical method to produce thick films of various materials [13, 14].
The aim of present study is to prepare Cr2O3 and Nb2O5 loaded TiO2 thick films by screen printing technique on

by using standard photolithography process. . The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under IR radiation for 45 minutes to remove the organic vehicle and then fired at temperatures 800oC for1.5 to 2 hrs (includes time required to achieve the peak firing temperature and then constant firing for 30 minutes at peak temperature) in muffle furnace. During the firing process glass frit melts and the functional and loaded materials are sintered. The function of glass frit is to bind grains together and also to hold the film firmly to the substrate. The structural properties of TiO2 films were investigated using X-ray diffraction analysis from 20-800 [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having CuKα, λ=0.1542 nm radiation] with 0.1o/step (2θ) at the rate of 2 sec/step. The scanning electron microscopy (SEM- JOEL JED-2300) was employed to characterize the surface morphology. The Composition of TiO2 thick film samples were analyzed by Energy Dispersive spectrometer (JOEL-JED 6360 LA). The thickness of the TiO2 thick films was measured by using Taylor-Hobson (Taly-step UK) 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 (Ra) and in the presence of gases (Rg) were measured to evaluate the gas response (S) given by the relation,

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

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.

III. Result and Discussion

A) Elemental Analysis

The quantitative elemental compositions of the loaded TiO2 films were analyzed using an energy dispersive spectrometer as shown in table 1. The mass % of Ti and O in each sample was not as per stoichiometric proportion. Mass % of Cr and Nb increases as loading concentration increases. The entire samples loaded with Cr2O3 and Nb2O5 were observed to be oxygen deficient. The sample loaded with 5 wt. % Cr2O3 and 1 wt. % of Nb2O5 were observed to be most oxygen deficient. The deficiency or excess of the constituent material particles leads to the semiconducting nature of the material [15].

Element (mass %)	Cr2O3				
	1wt. %	3wt. %	5wt. %	7wt. %	10wt. %
O	36.28	37.83.	34.27	34.29	37.49
Ti	63.02	60.55	62.02	61.29	56.12
Cr	0.70	1.62	3.71	4.42	6.39

Element (mass %)			Nb2O5		
	1wt. %	3wt. %	5wt. %	7wt. %	10wt. %
O	36.64	36.71	37.46	39.55	40.87
Ti	63.00	61.60	59.31	55.90	52.49
Nb	0.36	1.69	3.23	4.55	6.64

Table 1. Composition of Cr2O3 and Nb2O5 loaded TiO2 obtained from EDS

B) Structural analysis

The crystalline structure of the films was analyzed with X-ray diffract gram in the 20-80 0 range using Cukα radiation. Figure 1 a) and b) depicts the XRD pattern of TiO2 and 1,3,5,7 and10 wt. % Cr2O3 and Nb2O5 loaded thick films respectively. The peaks in XRD patterns observed for TiO2 and loaded Cr2O3 and Nb2O5 are polycrystalline in nature. The plots show polycrystalline nature with a pronounced (1 0 1) anatase peak of TiO2 at 2θ = 25.80 .This is the most pronounced peak of an anatase structure. All values of (hkl) plane are matched with JCPDS data 21-1272 and 21-1276 for anatase and rutile respectively. Anatase phase is an n-type semiconductor and its resistance has been found to decrease on reduction with gases. On the other hand rutile phase exhibits p-type conductivity.

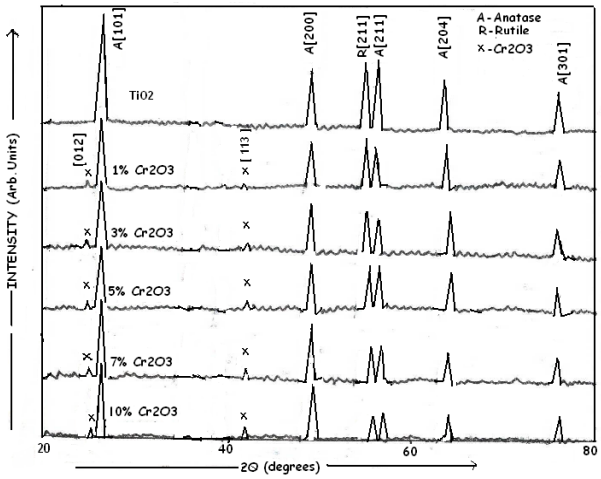

Figure.1. a) XRD pattern of pure and Cr2O3 loaded TiO2 films.

Their composite mixtures show percolating conductivity which exhibit n-type behavior when sample contains less than 75 % rutile component. XRD-shows 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 other applications. [16-21].

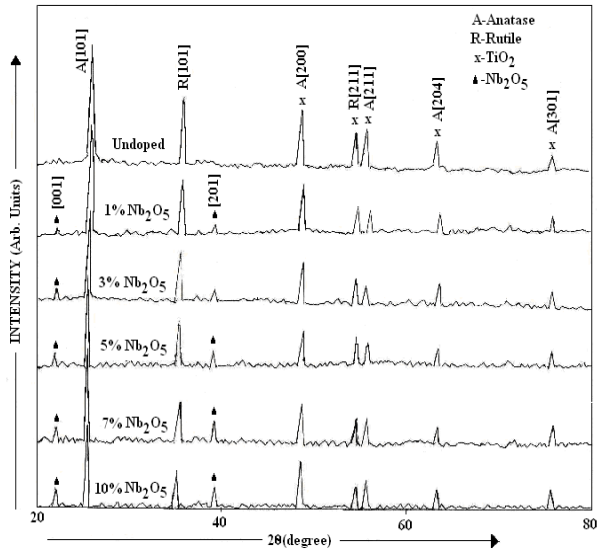

Figure.1. b) XRD pattern of pure and Nb2O5 loaded TiO2 films.

C) Surface morphology analysis

Figure.2 depicts the SEM images of TiO2, 5 wt. % Cr2O3 and 1 wt. % Nb2O5 loaded TiO2 thick films. Figure (a) depicts the microstructure of pure TiO2 thick film. It consists of randomly distributed grains with larger size and shape distribution. Fig. (b) depicts the microstructure of 5wt % Cr2O3 loaded TiO2 thick film which has observed smaller in particle size. It consists of smaller particles of Cr-species distributed on the TiO2 grains [22]. This film shows more porosity, giving largest effective surface area. Fig. (c) shows maximum porosity and small in particles as compared to unloaded TiO2. This enables larger surface for the gas to react giving more response. The film seems to be highly porous for oxygen adsorption.

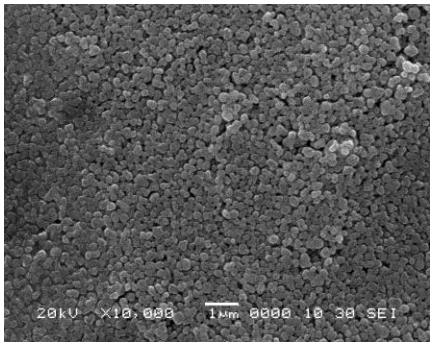

Figure.2. (a) Unloaded TiO2 thick films

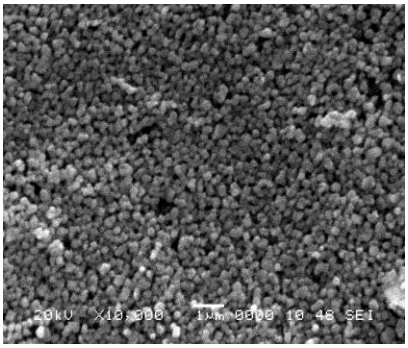

Figure 2 (b): 5 wt. % of Cr2O3 doped thick films

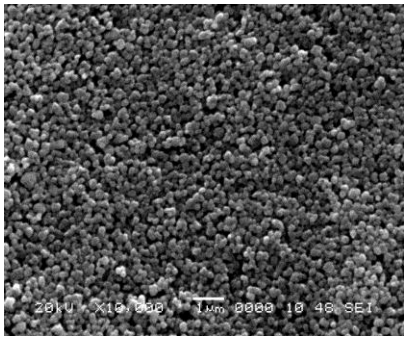

Figure 2 (c): 1wt. % of Nb2O5 loaded TiO2 thick films

D) Gas sensing properties

Figure 3 shows variation of NH3 gas sensitivity with operating temperature for various amounts of Cr2O3 loaded in TiO2 exposed to 1000 ppm in air.

The significant enhancement in sensitivity (88.23 %) of NH3 was observed at of 5 wt. % Cr2O3 loaded TiO2 at 250 0C than pure TiO2 and other loading concentrations.

The response could be attributed to the adsorption-desorption type of sensing mechanism.

The higher sensitivity of this sample as compared to TiO2 and other Cr2O3 loaded samples may be due to the optimum porosity and largest effective *area* available to react to gas.

Figure.4. shows gas sensing response to 1000 ppm of diluted H2S, at different operating temperatures (100–550oC) for thick films of pure TiO2 and TiO2 doped with x wt.% of Nb2O5 (x=1, 3, 5, 7, and 10 wt.%). The resistance of the films decreased upon exposure to H2S (1000ppm) diluted in air. Also, it is observed that the 1 wt. % Nb2O5 loaded TiO2 thick film has the largest sensing response (98.78 %) in the range of the operating temperature studied, exhibiting a slightly marked maximum at 200oC. The response could be attributed to the adsorption-desorption type of sensing mechanism. The maximum sensitivity for 1 wt. % Nb2O5 loaded TiO2 film sample as compared to other may be due to the optimum porosity and largest effective surface area available to react the gas.

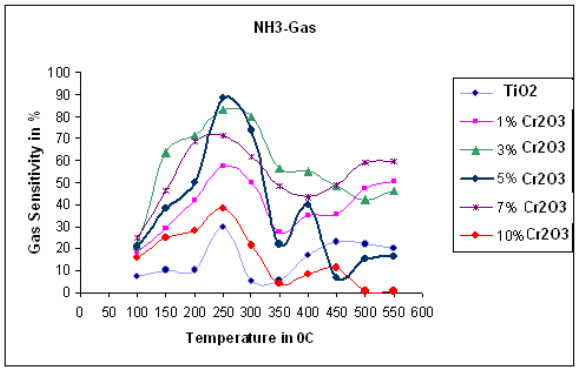

Figure. 3. Variation of NH3 Gas sensitivity for 1000 ppm

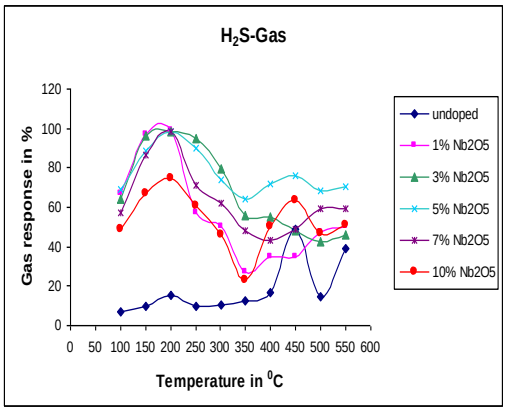

Fig. 4. Variation of H2S Gas sensitivity for 1000 ppm

Figure.5 (a) shows the selectivity of 5 wt. % Cr2O3 loaded TiO2 films for different gases. Sample showed highest selectivity for NH3 at 250 0C against all other tested gases viz: H2S, LPG, CO2, NO2 and Ethanol.

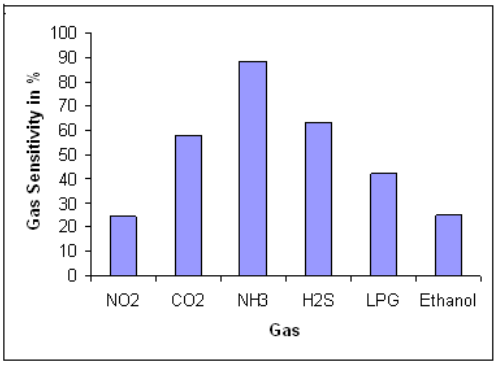

Figure.5. (a) Selectivity of the sensor
5 wt. % Cr2O3 for various gases

Figure.5. (b) shows the selectivity of 1wt. % Nb2O5 loaded TiO2 films for different gases. Sample showed highest selectivity for H2S at 200 0C against all other tested gases viz: NH3, LPG, CO2, NO2 and Ethanol.

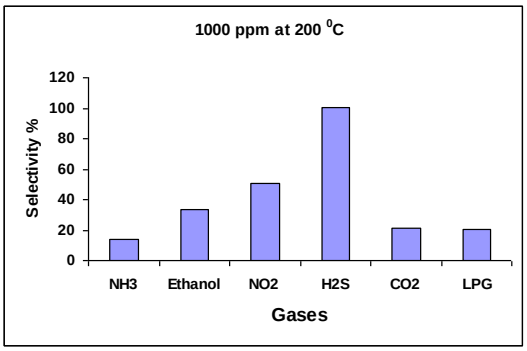

Figure.5. (b) Selectivity of the sensor
1 wt. % Nb2O5 for various gases

The response and recovery times of 5 wt. % Cr2O3 loaded TiO2 films are represented in Figure.6.(a). The response was quick (~ 18 s) to 1000 ppm of NH3 while the recovery was fast (~20 s). The quick response may be due to faster oxidation of NH3 gas.

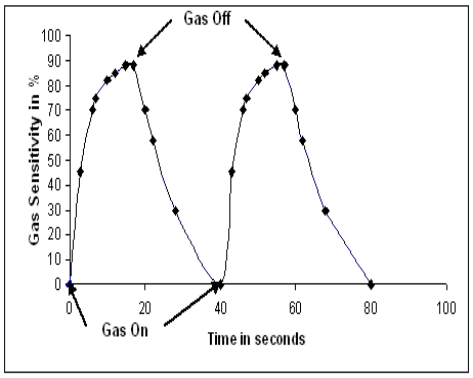

Figure.6. (a) Response and recovery time of
5 wt. % Cr2O3 loaded TiO2 film

The response and recovery times of 1 % Nb2O5 loaded TiO2 films are represented in Figure.6. (b).

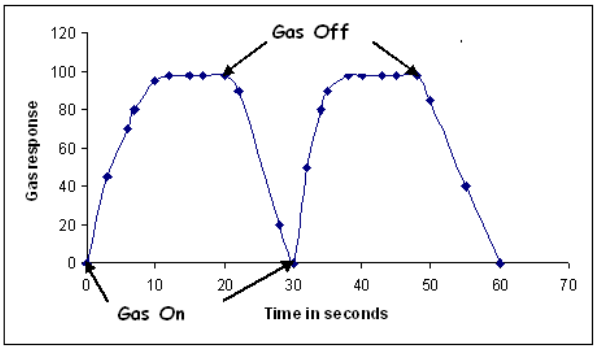

Figure.6. (b): Response and recovery time of
1% Nb2O5 doped TiO2 film

The response was quick (~ 10 s) to 1000 ppm of H2S while the recovery was fast (~ 12 s). So these Nb2O5 doped films have faster response than Cr2O3 loaded films. 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.

IV. Sensor Mechanism

When NH3 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:

Cr2O3 + 5NH3 (gas) + 4 O2- (film surface) →Cr2 (NH4OH) 3 (film surface) + 2 NO2 (gas) + 8 e- (cond. band)

The amount of oxygen adsorbed on the surface would depend on the number of Cr2O3 misfits on the TiO2 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 [23, 24].

In case of Nb2O5 loaded film sample response switch over to H2S which reacts with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band of TiO2. The energy released during decomposition of adsorbed H2S molecules would be sufficient for electrons to jump up into conduction of TiO2, causing on increase in the conductivity of the sensor. The possible reaction is:

$$2H2S + 3O\text{-}2 \rightarrow 2H2O + 2SO2 + 6e\text{-}$$

When the optimum amount of Nb2O5 (1 Wt. %) is incorporated on the surface of TiO2 film, the Nb species would be distributed uniformly throughout the surface of the film. Conductivity of Nb2O5-doped TiO2 is higher than pure TiO2. Since ionic radii for Nb and Ti are close to each other (0.68A0 for Ti4+ and 0.70A0 for Nb5+) [25]. Nb can occupy a regular cation position forming a substitutional solid solution. To maintain electrical neutrality such substitutions will create oxygen vacancies and donate electrons and the overall change in the resistance on exposure of H2S gas leading to high sensitivity. At the higher concentration, Nb atoms would be distributed more densely. As a result, overall change in the resistance on the exposure of gas would be smaller leading to lower response to the target gas [26-27]. H2S is reducing gas decrease the resistance of n-type semiconductors (eg.TiO2), while oxidizing gases increase it [28]. The reducing gas (H2S) donates electrons to TiO2. Therefore its resistance decreases, or the conductance increases. This is the reason why the gas response increases with operating temperature. The point at which the gas response reaches maximum is the actual thermal energy needed for the reaction to proceed. However, the response decreases at higher operating temperatures, as the oxygen adsorbates are desorbed from the surface of the sensor [29]. Also, at high temperatures the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for the decreased gas response at high temperatures [30]. As the species are desorbed from the surface, oxygen is adsorbed again.

Conclusion

From the results obtained, Cr2O3 loaded titania thick films were found to be selective for ammonia gas. 5 wt. % Cr2O3 loaded TiO2 thick film has been observed that most oxygen deficient, porous and largest specific surface area which showed maximum sensitivity to NH3 gas at 2500C. Sensitivity to NH3 gas increases with increase in operating temperature attains 88.23% at 250 0C and then decreases further with an increase the temperature. The sensitivity increases with the test gas concentration up to 1000 ppm. The 5 wt. % Cr2O3 sensor has good selectivity to NH3 gas against LPG, H2S, Ethanol vapours, CO2 and NO2 at 250 0C. Whereas gas response switch over from Cr2O3 to Nb2O5 loaded from NH3 to H2S. Pure and heavily doped TiO2 thick films showed low response to H2S gas1wt. % or lower concentration of Nb2O5 doped TiO2 thick films showed highest response to H2S gas at 2000C.

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