

Mechanism in Nb doped titania oxygen gas sensor

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Abstract

Doping in titania (TiO_2) with pentavalent Nb^{5+} metal ion has shown significant enhancement in the sensitivity which is about 65 times higher than the undoped material at lower operating temperatures. The higher sensitivity and the shorter response time has been observed with low concentration of Nb doping i.e. 0.05, 0.2 and 0.4 wt.% Nb at 400°C. The electronic interaction of TiO_2 with Nb metal ion has been investigated using x-ray photoelectron spectroscopy (XPS). The maximum shift in binding energy (B.E.) of Ti 2p peak has been observed with 0.2 wt.% Nb indicating maximum interaction at this Nb concentration. The spin-orbit (s-o) splitting of Ti 2p peak indicates the change in the oxidation state of Ti.

Keywords: Titania; Oxygen sensor; XPS; Sensitivity; Sensitization mechanism

1. Introduction

Due to a recent impetus on environmental consciousness the need for highly efficient combustion engines, controlled industrial processes and controlling and monitoring the hazardous gas level in the environment has led to a quest for an efficient solid state gas sensor. An efficient gas sensor must have high sensitivity, short response time and reasonably good selectivity at low operating temperatures. The sensitivity and selectivity of the gas sensors can be tailored to some extent by adding catalytically active dopant [1–6]. The dopant takes part in sensing of a gas directly or indirectly by modifying interaction at the gas-solid interface of a semiconductor. The work function of a semiconductor is very sensitive to surface states, which are created due to gas adsorption. This property of semiconducting oxides has been exploited for gas sensing applications [7].

The semiconducting oxides such as Ga_2O_3 , CeO_2 , SrTiO_3 , ThO_2 , Cr_2O_3 , TiO_2 etc. are reported in the literature as oxygen sensing materials, among them titania (TiO_2) is preferred as a oxygen sensor material. When this material is doped with pentavalent impurity ions, it shows higher sensitivity towards oxygen gas.

The higher sensitivity and fast response makes it more suitable for automobile applications. The doped material shows low impedance and hence it is easier to design associated electronic circuitry [8]. It is reported that in pure TiO_2 material doubly charged oxygen ion vacancies, Ti^{3+} and Ti^{4+} interstitial are present. The charge neutrality can be achieved by incorporation of Nb metal ions (Nb^{5+}) which improve the sensor characteristics including sensitivity and response time [9]. It has also been reported that TiO_2 – Nb_2O_5 system shows higher sensitivity and shorter response time than pure TiO_2 [9–12]. It has been observed in the present study that higher sensitivity can be achieved at low Nb concentration i.e. 4 mol% at 580°C. The incorporation of Nb metal ion in TiO_2 lattice is a substitutional doping and it does not effect the basic rutile structure [13] of TiO_2 , as the ionic radii of Nb^{5+} (0.70 Å) is comparable to that of Ti^{4+} (0.68 Å). It acts as a donor type impurity and leads to a decrease in the resistivity of the semiconductor [13,14].

In doped semiconducting oxides two types of sensitization mechanisms have been proposed, viz chemical sensitization and electronic sensitization [15]. In chemical sensitization, the sensing gas molecule gets adsorbed at the sensor surface, where it is dissociated or activated with the help of a dopant. This dissociated molecule at the sensor surface interacts with the semiconducting oxide. This will lead to a change in the conductivity at

the sensor surface. On the other hand, electronic sensitization is followed by direct exchange of electrons between added dopant and the semiconductor surface. There is a change in the oxidation state of dopant on contact with sensing gas molecule due to electron exchange from dopant to oxygen, which leads to a change in the conductivity of the sensor surface. The conduction mechanism is classified into two types viz bulk and surface conduction type [16]. Bulk conduction type mechanism dominates at high temperature i.e. 700°C and above, where as surface conduction becomes important at low temperatures in the range 400–600°C. At low operating temperatures, bulk defects are usually very slow, therefore, electronic transportation dominates within bulk while at higher temperatures diffusion of oxygen in to the bulk material takes place. When an oxygen molecule gets adsorbed at the sensor surface, it extracts electrons from the conduction band of the host material. This reduces the concentration of electrons in the conduction band of the host material, leading to a decrease in the conductivity of the host material. As oxygen concentration increases, the number of conduction band electrons decreases further and conduction starts taking place through holes. Therefore, above certain oxygen partial pressure the material becomes *p*-type and conductivity of the material is governed by holes [13,16]. In the reduced or non-stoichiometric TiO₂, electrical conduction is due to electronic charge transfer or hopping conduction from one ion site to another. At higher temperatures, electronic and hopping conduction mechanisms are main contributing factors. Polaron theory has shown that in the case of transition metal oxides like TiO₂, the hopping conduction dominates at temperatures above 300 K [17], but at very high temperature i.e. above 600°C the electronic conduction mechanism is prominent.

In this paper, the sensing characteristics of Nb doped TiO₂ has been reported. The role of the Nb metal ion in TiO₂ and the sensing mechanism of the sensor material has been discussed on the basis of results obtained from X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Experimental

The ceramic material was prepared through a solid state reaction between niobium oxide (Nb₂O₅) and titanium oxide (TiO₂) at 1300°C. These oxides were mixed in the appropriate ratio to get 0.0, 0.05, 0.2, 0.4, 0.8 and 1.5 wt.% of Nb (i.e. wt.% of Nb₂O₅ in the mixture of Nb₂O₅ and TiO₂) and then this mixture was ground for 3–4 h in dry environment. The fine powder was sintered at 1300°C for 4 h in a resistively heated computer controlled furnace to get only the rutile phase of the material. The sintered material was again ground to the

previous constancy. This powder was converted into thick circular pellets of 18 mm diameter using die and hydraulic press at 12 tons of pressure. Platinum wires were embedded into the pellets for electrical contacts and these pellets were again sintered at 1300°C for 2 h.

The sensitivity measurements were carried out in a gas chamber equipped with a temperature controller as shown in Fig. 1. The sensitivity of the sensor (*S*) is defined as the ratio of the resistivity of the material (ρ_g) in presence of oxygen to the resistivity (ρ_0) in the absence of oxygen i.e. ($S = \rho_g/\rho_0$). The partial pressure of oxygen in the range 400–1200 ppm was controlled in the chamber by mixing Ar with oxygen in the appropriate ratio by using mass flow controllers (MFCs). The response time of the sensor was recorded on a X-t recorder.

The XPS was obtained using spectrometer (Physical Electronics, model PHI-1800) which consisted of a double pass cylindrical mirror analyzer (CMA). An X-ray beam of nearly 6 mm² area from Mg K α source of energy 1253.6 eV and full width and half maximum (FWHM) is 0.8 eV, was used to excite the spectra from freshly fractured samples at room temperature and at an analyzer chamber pressure of 2×10^{-9} Torr. The analyzer calibration was carried out using Au 4f_{7/2} (83.9 eV, FWHM = 1.1 eV) and Ag 3d_{5/2} (368.2 eV, FWHM = 1.1 eV) at pass energy of 50 eV. The accuracy of the measurements is within ± 0.1 eV [18].

The structural properties were studied using an X-ray diffractometer (Rigaku, model RB-RU200) and surface topography was investigated using SEM (Philips SEM-525M).

3. Results and discussion

The XRD spectra of undoped and Nb doped samples exhibit only rutile phase of the TiO₂ as shown in Fig. 2. It has been observed that the intensity of all the ob-

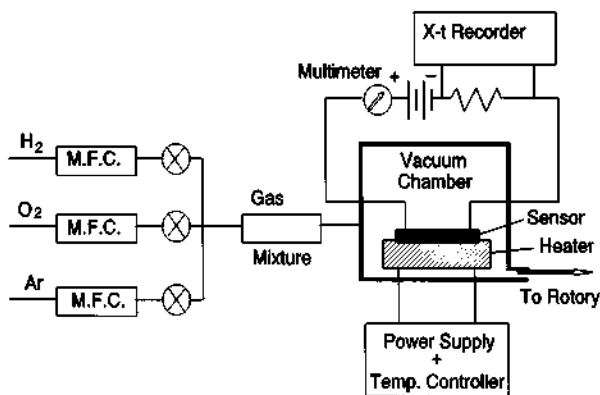


Fig. 1. Experimental setup for sensitivity and response time measurements.

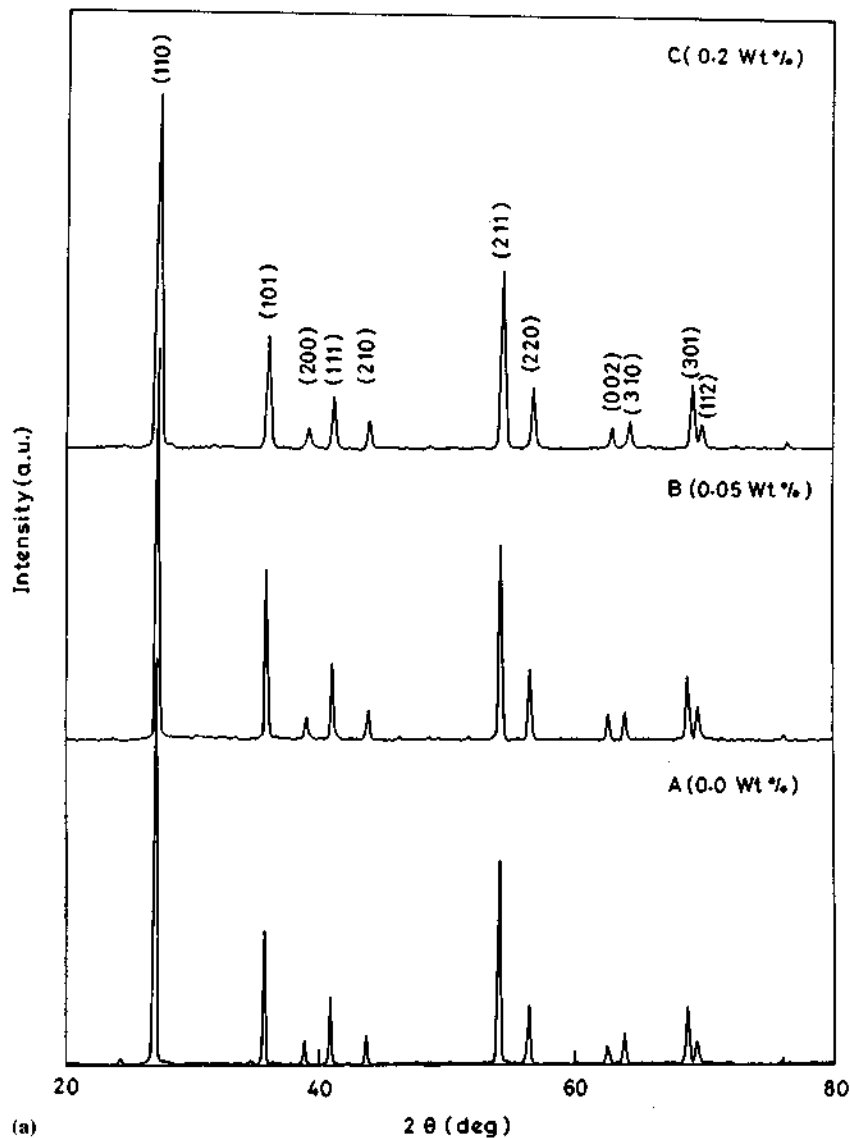


Fig. 2. A typical GAXRD pattern of different Nb doped TiO_2 samples: (a) A = 0.0, B = 0.05, C = 0.2; (b) D = 0.4, E = 0.8 and F = 1.5 wt.% Nb.

served peaks reduces systematically with increasing Nb concentration. The half width of all the peaks increases with increase in Nb concentration in TiO_2 . It indicates that grain growth of TiO_2 crystallites is hindered by the addition of Nb. This observation is also supported by SEM photographs as shown in Fig. 3.

The sensitivities of the sensor doped with 0.0, 0.05, 0.2, 0.4, 0.8 and 1.5 wt.% Nb as a function of operating temperature at fixed oxygen partial pressure of 1200 ppm is shown in Fig. 4. The pure TiO_2 sensor shows higher sensitivity at 800°C whereas Nb doped sensors exhibit maximum sensitivity in the temperature range of 400–550°C. The reduction in operating temperature of the doped samples is very significant. The samples containing Nb concentration in the range of 0.05–0.2 wt.% show maximum sensitivity of 48–65 at 400°C. As Nb concentration increases further up to 1.5 wt.% the

maximum sensitivity of 3 has been achieved at 550°C. Fig. 5b shows that at 0.2 wt.% Nb doping, the sensor exhibits best sensor characteristics i.e. the highest sensitivity and shortest response time. The maximum shift in binding energy (B.E.) has also been observed at this concentration as shown in Fig. 5a. This may be due to optimum electronic interaction taking place at 0.2 wt.% of Nb doping [19]. All the samples show maximum value of sensitivity at a particular operating temperature only above and below this temperature, sensitivity of the sensor decreases. This may be due to maximum adsorption and dissociation of oxygen molecules taking place at the optimum temperature.

The response time of the sensor has been measured at 1200 ppm oxygen concentration at different operating temperatures i.e. 400, 500 and 600°C. The response time has been defined as the time taken to change the

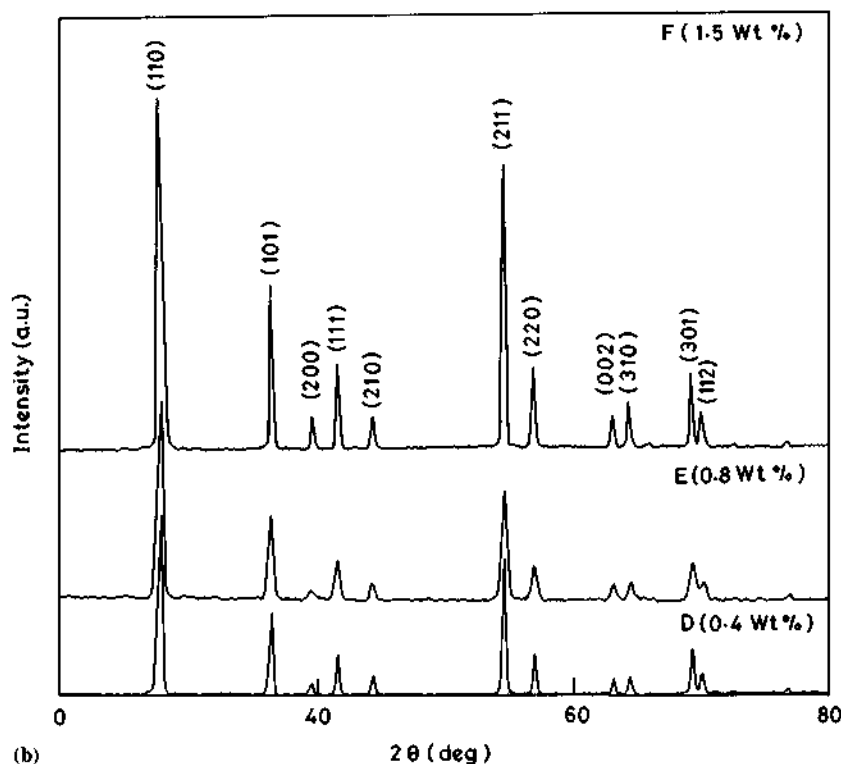


Fig. 2. (Continued)

resistivity from 10–90% change of maximum value when exposed to oxygen gas. Fig. 6 shows the response time for 0.0, 0.2, 0.4 and 0.8 wt.% Nb doped sensor at 500°C. At low dopant concentrations i.e. 0.2 and 0.4 wt.%, response times of 4 and 6 s, respectively, was observed at 500°C. Whereas in the case of pure and 0.8

Table 1
Response behavior of Nb doped TiO₂ oxygen gas sensor at different operating temperatures at 1200 ppm oxygen partial pressure

Temperature in °C ↓ Nb wt.% →	Response time (s)			
	0.0	0.2	0.4	0.8
400	34	3	4	7
500	30	4	6	16
600	28	6	7	36

wt.% Nb doped sensor the response times of 30 and 16 s, respectively, have been recorded. Response time of the sensor is controlled by diffusion of oxygen vacancies and the rate of surface reaction. Response time can be reduced by increasing the diffusivity of oxygen vacancies and surface reactivity. In the bulk material the diffusivity of the oxygen vacancies plays an important role. Doped sensor material has shown increase in porosity, which may have increased the diffusivity of the oxygen vacancies. Porosity is also required for fast equilibration of the TiO₂ material which improves the response behavior [20]. The response time of the sensors at different operating temperatures is given in Table 1.

Fig. 7 shows the response time variation of the sensors as a function of doping concentrations at different operating temperatures i.e. 400, 500 and 600°C. The 0.2 and 0.4 wt.% Nb doped sensor showed the shortest

Table 2
XPS observations of Nb doped TiO₂ oxygen gas sensor I/I₀ for Ti 2p is intensities ratio of 2p_{1/2}/2p_{3/2} and Nb 3d is 3d_{3/2}/3d_{5/2}

Nb concentration wt.%	Peak position (eV)		I/I ₀		ΔE (eV) s-o	
	Ti 2p (FWHM)	Nb 3d (FWHM)	Ti 2p	Nb 3d	Ti	Nb
0.0	458.6 (2.3)	—	0.38	—	5.8	—
0.2	458.3 (2.3)	207.6 (2)	0.39 0.72	5.6	2.4	—
0.4	458.4 (2.6)	207.2 (2)	0.40	0.68	5.6	2.6
0.8	458.5 (2.3)	207.2 (2)	0.54	0.59	5.6	2.7

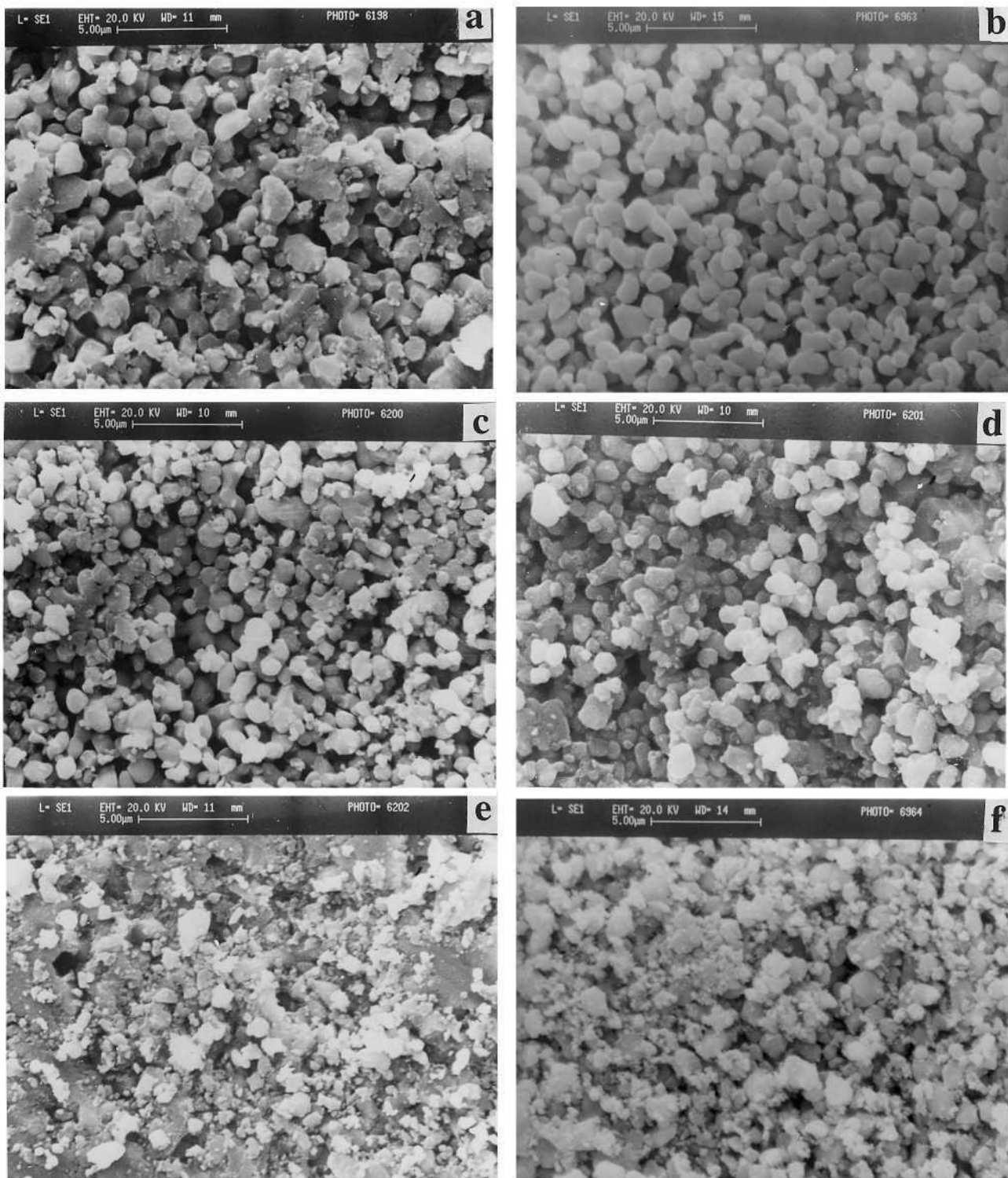


Fig. 3. SEM micrographs of TiO₂ doped with different wt.% Nb concentration: a = 0.0; b = 0.05; c = 0.2; d = 0.4; e = 0.8; and f = 1.5 wt.% Nb.

response time of 3 and 4 s, respectively, at 400°C and on increasing the operating temperature to 600°C the response time has increased. This may be due to more number of oxygen molecules get adsorbed on the surface at 400°C. As operating temperature increases, the desorption rate of oxygen molecules become higher as

compared with adsorption rate. Therefore, less number of oxygen molecules are available on the sensor surface at higher operating temperatures. Since adsorption and desorption of gas molecules is a temperature dependent process, therefore, response and recovery time of the sensor also depends on the operating temperature [7].

Fig. 8 shows the core level XPS spectra for Ti 2p and Nb 3d peaks taken for the material having different Nb concentrations in TiO₂. The parameters such as peak

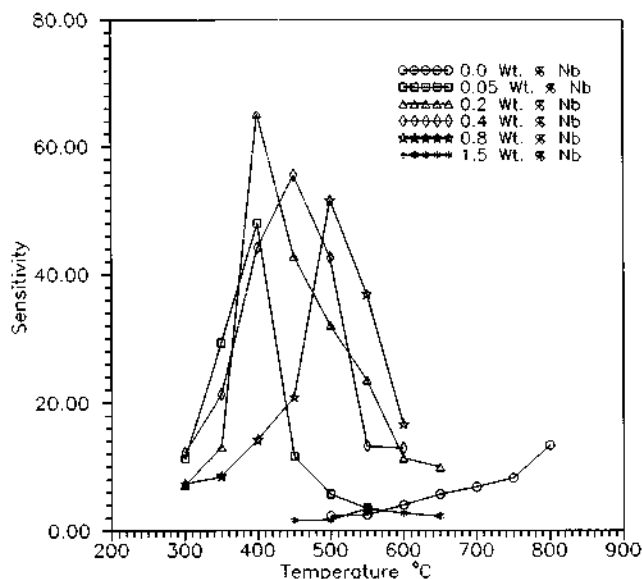


Fig. 4. Sensitivity of the sensor as a function of operating temperature and at different doping concentration.

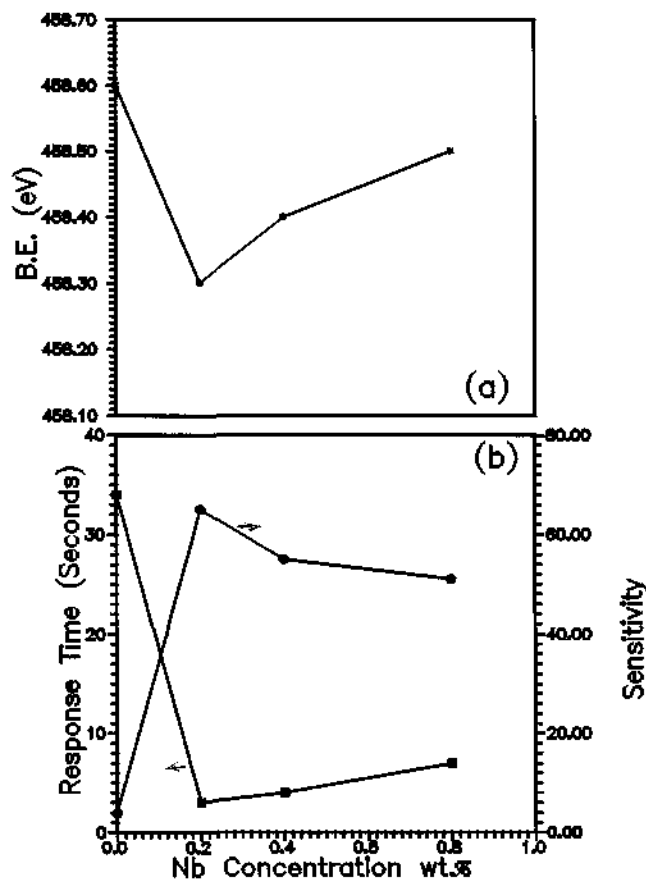


Fig. 5. (a) Change in B.E. of Ti_{2p_{3/2}} as a function of Nb concentration. (b) Variation of sensitivity and response time as a function of Nb concentration.

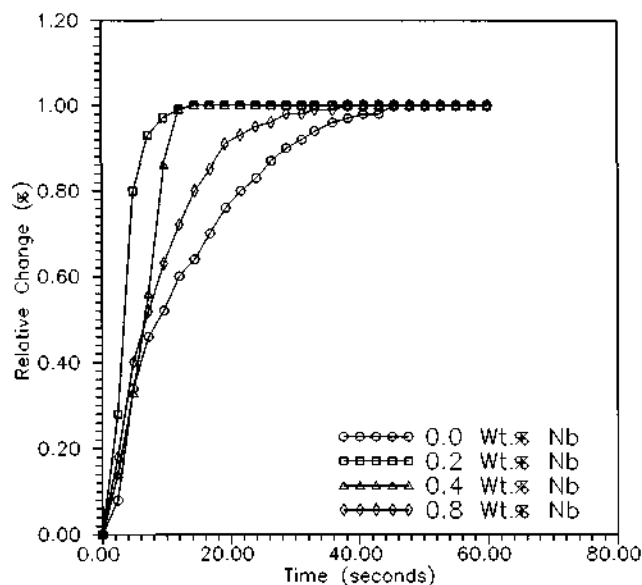


Fig. 6. Response time of 0.0, 0.2, 0.4 and 0.8 wt.% Nb doped sensors at 500°C at 1200 ppm oxygen partial pressure.

position, FWHM, spin-orbit (s-o) splitting (ΔE) for Ti 2p and Nb 3d and intensity ratio ($2p_{1/2}/2p_{3/2}$) of Ti 2p and intensity ratio of ($3d_{3/2}/3d_{5/2}$) of Nb 3d peaks, are listed in Table 2. The spectra show that B.E. of Ti 2p_{3/2} in TiO₂ is 458.6 eV, whereas in Nb doped materials it varies from 458.3 to 458.5 eV. It has been observed that s-o splitting ΔE of Ti 2p decreases from 5.8 to 5.6 eV on Nb doping. The change in s-o splitting indicates that oxidation state of titanium changes to its lower state [21,22]. It has also been observed that as the Nb concentration increases, the peak intensity ratio ($2p_{1/2}/2p_{3/2}$) in Ti increases, while peak intensity ratio of ($3d_{3/2}/3d_{5/2}$) peaks in Nb decreases. These results imply that there is a charge transfer taking place from Nb⁵⁺ to Ti⁴⁺. Due to the charge transfer the number of electrons increases in the conduction band of the host material, therefore, the work function of the host material decreases [13]. Because of the lowering of work function higher sensitivity and shorter response time of the sensing material has been observed. In these sensors chemical sensitization mechanism is suggested because oxygen molecules get adsorbed at the TiO₂ sites, where the excess electrons are available in the conduction band of Ti due to Nb doping.

4. Mechanism

A model for sensitization mechanism in TiO₂ based oxygen gas sensor has been proposed. The pentavalent dopants such as Nb, Ta etc. act as donor to host material, therefore excess charge carriers are available at TiO₂ site. When an oxygen molecule comes across

the sensor surface, it gets adsorbed/dissociated at TiO_2 site after exchange of electrons from sensor material to oxygen molecule. The reported bond strength of Ti-O and Nb-O are 159.3 ± 1.5 and $180 \pm 3 \text{ D}_{298}^\circ/\text{kcal mol}^{-1}$, respectively, therefore, dissociation energy of Nb-O is much higher than Ti-O . Since Nb donates electrons to conduction band of TiO_2 , hence the barrier/potential to the incoming oxygen molecules is reduced as compared with pure TiO_2 . In chemical sensitization mechanism the metal additive interacts with sensing gas/vapor indirectly and finally the sensing gas/vapor gets adsorbed at semiconductor site. Here the authors have also found that the chemical sensitization mechanism is prominent as oxygen molecules get adsorbed at the TiO_2 sites because of lower dissociation energy of Ti-O and the number of electrons increases in the conduction band of TiO_2 due to Nb doping. After this dissociated oxygen diffuses in the bulk and interacts with oxygen vacancies. The model of chemical sensitization mechanism is also shown in Fig. 9. The role of Nb additives is to donate electrons to the conduction band of host TiO_2 material. The change in the initial value of resistivity is due to extraction of electrons from the conduction band of TiO_2 material by the oxygen molecule, which gets dissociated at the sensor surface.

As soon as oxygen molecule comes across sensor surface it gets dissociated in the form of $\text{O}_{2\text{ads}}^-$ which is less reactive. Further dissociation of this atom in the form of highly reactive O_{ads}^- take place on diffusion into the bulk.

The enhancement in the sensitivity in Nb doped TiO_2 sensor can be explained by this model. The Nb dopants

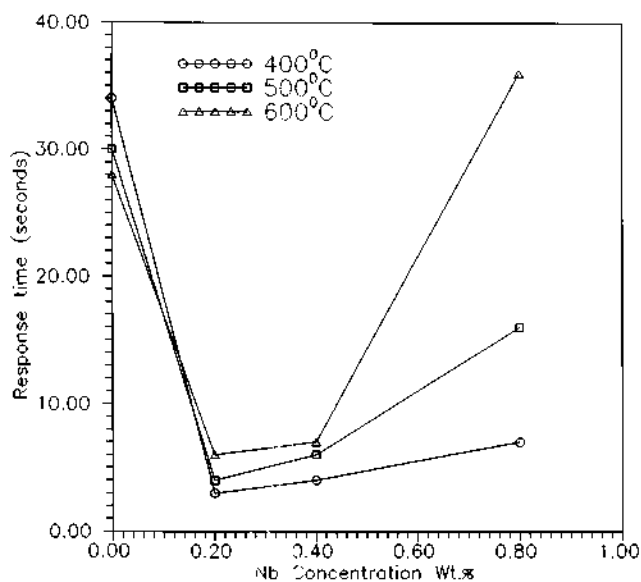


Fig. 7. Variation of response time as a function of Nb concentration at 400, 500 and 600°C.

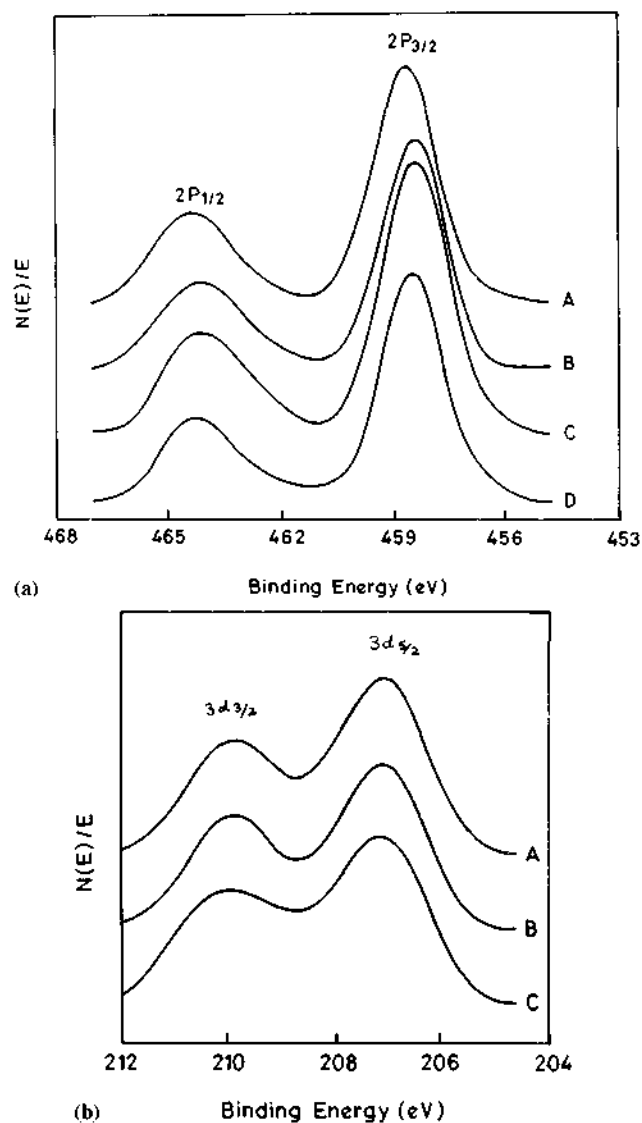
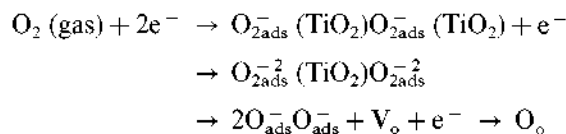


Fig. 8. (a) The core level spectra of Ti_{2p} at a different Nb concentration. A = 0.0, B = 0.2, C = 0.4 and D = 0.8 wt.% Nb in TiO_2 . (b) Core level spectra of Nb_{3d} . A = 0.2, B = 0.4 and C = 0.8 wt.% Nb in TiO_2 .

play an important role as a catalyst in TiO_2 matrix and promote the sensitivity by producing adsorption sites for incoming oxygen gas molecules, which can react with the TiO_2 surface. The reactions which are occurring at the sensor surface are as follows.



In this case the oxygen gas molecules get dissociated at lower temperature because of lower bond formation energy of Ti-O in Nb doped TiO_2 sensor material. Due to this the dissociation and adsorption becomes faster and therefore, sensitivity increases. After this adsorbed

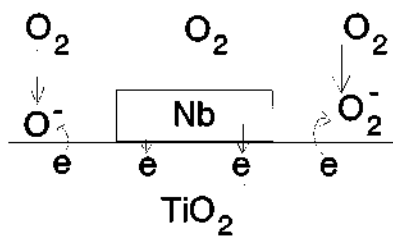


Fig. 9. A model for sensitization mechanism of TiO_2 oxygen gas sensor.

oxygen species diffuses into the material and interacts with interstitial oxygen and oxygen vacancies. Porosity measurements which are reported elsewhere [23] show that Nb doping increases the porosity of the TiO_2 material. The higher porosity of the sensor material is required for attaining faster equilibrium and shorter response time [20]. The movement of oxygen vacancies decides the response time of the sensor. Fast movement of oxygen vacancies leads to faster response of the sensor.

5. Conclusions

In conclusion, it has been observed that the Nb doped TiO_2 oxygen gas sensor shows higher sensitivity and shorter response time as compared with pure TiO_2 sensor at significantly low operating temperatures. It has been found that 0.2 and 0.4 wt.% Nb incorporated sensor shows the maximum sensitivity and the shortest response time of 3 s at 400°C , whereas in the case of pure TiO_2 , the shortest response time of 28 s could be achieved at 600°C . The increase in sensitivity and reduction in response time has been attributed to increase in diffusivity of oxygen molecule at these operating temperatures. The XRD and SEM results have shown an increase in the porosity of the material on Nb doping. The XPS has revealed that maximum electronic interaction is taking place at 0.2 wt.% of Nb doping. The coincidence between gas sensing behavior and B.E. shifts suggests that electronic interaction is very important in Nb doped TiO_2 gas sensor. The XPS results has also indicated that the transfer of charge from Nb metal ions to Ti, which leads to change in the oxidation state of titanium.

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