

Effect of Ni doping on thick film SnO₂ gas sensor

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Abstract

Ni- and/or Al-doped and undoped SnO₂ thick film gas sensors were prepared using screen printing technique and tested for their LPG gas sensitivity. Tin oxide powder was prepared using a chemical precipitation technique. The sensitivity, optimum working temperature and response time were investigated in relation to dopants as well as preparation route. The results show that the gas sensitivity is affected not only by the additive but the way it is added into the sensor material. The results indicated a reduction in grain size on Al and Ni doping. The results on resistance, response and recovery time were explained in terms of n–p junction formation between SnO₂ and NiO, which increases the depletion barrier height.

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1. Introduction

Tin oxide is the most widely used semiconductor metal oxide in gas sensing because of its capability to detect combustible gases such as methane and poisonous gases like carbon monoxide. Recently, due to increase in the usage of LPG and CNG gases, the frequency of accidental explosions due to leakage has increased. Therefore, the ability to monitor and precisely measure leakages of explosive gases is crucial in preventing the occurrence of such accidents. Accordingly, the development of sensors and systems that can selectively detect and determine various kinds and quantities of combustible gases within the ranges of explosion limits are required. Due to this, a considerable amount of current research activities have been devoted to the development of stable, pure or doped tin dioxide sensors [1–4]. SnO₂ gas sensor operates on the gas interaction involving the following processes; adsorption, chemical surface reactions with participation of chemisorbed and lattice oxygen and oxygen transport from the bulk to the surface of SnO₂

grains. The surface reactions between pre-adsorbed surface oxygen species and reducing gases cause an increase of conductance of an n-type SnO₂. This change in resistance on exposure is used to detect the concentrations of reducing gases. However, the SnO₂ sensor material is sensitive to almost all the gases though the response is different for each gas. Many approaches have been made to modify the sensing properties of these semiconductor oxide gas sensors in order to achieve high sensitivity and selectivity. In this direction different approaches are adopted such as additives, physical or chemical filters, or operating temperature, etc. Noble metals (Pt, Pd, Au) are well known for enhancing the rate of response and raising selectivity to a single gas. Chemical filters make use of this principle. They enhance the reaction to a single gas which must not be sensed. Therefore, the only gas reaching the sensor surface is the gas to be detected. Grain size reduction is another approach to enhance the gas sensitivity, and various techniques were developed to reduce the grain size. In nano-sized materials, because the surface to bulk ratio is much greater than for coarse materials, surface properties become paramount, which makes these materials particularly appealing in applications in which such properties are exploited, as in gas sensors. Further, gas sensitivity

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is expected to increase when the grain size becomes smaller than the space charge depth [5]. Controlled ultrafine and narrow distribution of particle size of ceramic powders can be obtained using chemical methods, and the first step in keeping full control of the microstructure of the material is to control the preparation method of the starting powders.

Effect of various additives was studied by Yamazoe et al. in details [6]. Some additives such as CaO, MgO, etc. were suggested to inhibit the grain growth, and therefore increase the gas sensitivity. Additives such as ZnO, CuO, MnO, etc. on the other hand, were reported to enhance densification when samples were fired at temperatures above 800 °C. Other additives such as Nb₂O₅, Sb₂O₅, etc. act on the conductivity of SnO₂, generating metal vacancies and rendering it less resistive. Sn oxide-based hydrocarbon sensor was prepared using well-dispersed 5% Pt- and Pd-supported alumina catalysts for butane and methane, respectively. The increase in sensitivity was reported to be due to the increase in dispersion of the noble metal used. Nickel addition in tin oxide gas sensor has been investigated by various researchers [7–11]. The addition of Ni oxide was reported to inhibit the grain growth and led to a small grain-sized powder due to the segregation of Ni on the surface of SnO₂ powder. Sensitivity of SnO₂/NiO films to H₂S, CO, C₂H₅OH and CH₄ have been studied and a considerable increase in gas sensitivity was reported. The electrical resistance of SnO₂ films increased upon Ni doping due to the barrier mechanism of conduction. Similar results on addition of NiO to other sensor materials were reported. NiO addition to In₂O₃ leads to increase in sensor resistance when compared to undoped In₂O₃. In the present work we have investigated the role of nickel doping on gas sensitivity further and its application in the development of LPG gas sensor.

Ni- and/or Al-doped and undoped SnO₂ thick film gas sensors were prepared using screen printing technique and tested for their gas sensitivity at various temperatures and concentration of LPG gas. Tin oxide powder was prepared using co-precipitation technique. The sensitivity, selectivity, optimum working temperature and response time were investigated in relation to nickel dopant as well as how it is added. The results show that the gas sensitivity is affected not only by the additive but the way it is added into the sensor material.

2. Experimental

Four different batches of SnO₂ powders were prepared. All the powder treatments, i.e. calcination and sintering were done in air under similar conditions. Calcination was done at 600 °C for 4 h. Undoped SnO₂ powder (batch I) was prepared using the co-precipitation route. For this 0.1 M SnCl₄·6H₂O solution was prepared and pH was adjusted to 7 by dropwise addition of diluted NH₄OH solution. The precipitate was then washed with an ammonium nitrate solution till no chloride ion was detected on AgNO₃ test. Then the precipitate was

Table 1
Preparation conditions of SnO₂

Sample no.	Preparation conditions
S1	Undoped SnO ₂ using batch I powder
S2	Al-doped SnO ₂ using batch II powder
S3	Al + Ni-doped SnO ₂ using batch III powder
S4	Al + Ni-doped SnO ₂ using batch IV powder
S5	Sample S1 dipped in Ni acetate solution
S6	Sample S2 dipped in Ni acetate solution

washed with ethanol added water to remove nitrate ions. This powder was then dried and calcined.

Batch II was prepared as follows: Sn hydrate was precipitated as above batch I. The precipitate was dried overnight and powdered. Aluminium nitrate (4 wt.%) was dissolved in a small amount of water, and the above powder was dispersed in the solution. This was then heated to remove water and calcined. In batch III, all the constituents were added together in water, i.e. 94% SnCl₄, 4% Al₂(NO₃)₃ and 2% NiSO₄. Diluted NH₃ was added to precipitate out all the constituents together. Precipitate was washed according to batch I, dried, powdered and calcined at 600 °C. In batch IV, batch II powder was further dissolved in nickel acetate 2% solution and dried and calcined at 600 °C.

After calcinations all powders were crushed and paste was prepared by adding butyl carbitol and terpeneol oil. Paste was screen printed on alumina plates on which gold electrodes (1 mm distance) were already prepared and final sintering of all the batches were done at 800 °C for 10 min. Table 1 shows the sample preparation details. The structure of calcined powder was investigated using X-ray diffraction. The sensitivity tests were carried out in a home made testing chamber that measures the change in resistance on gas exposure. Commercially available LPG gas was used for testing. The sensitivity was defined as R_a/R_g , where R_a is the resistance in air and R_g is the resistance in the presence of reducing gas.

3. Results and discussion

3.1. XRD

Fig. 1(a) and (b) shows the XRD pattern for an undoped sensor powder batch I and Ni/Al-doped powder batch IV. All the main XRD lines belong to SnO₂ with cassiterite structure and have been indexed accordingly. Ni/Al doping lowers the grain size as shown by the broadening in the XRD peaks in Fig. 1(b). XRD studies were performed on two samples S1 and S4 in the 20–70° 2θ range using Cu Kα radiation. The mean grain size of SnO₂ was evaluated by fitting the (1 0 1) diffraction peak width of SnO₂ using a Lorentz function and inserting the diffraction angle and peak full line width at half maximum (FWHM) in the Scherrer formula:

$$d = \frac{k\lambda}{\beta \cos \theta}$$

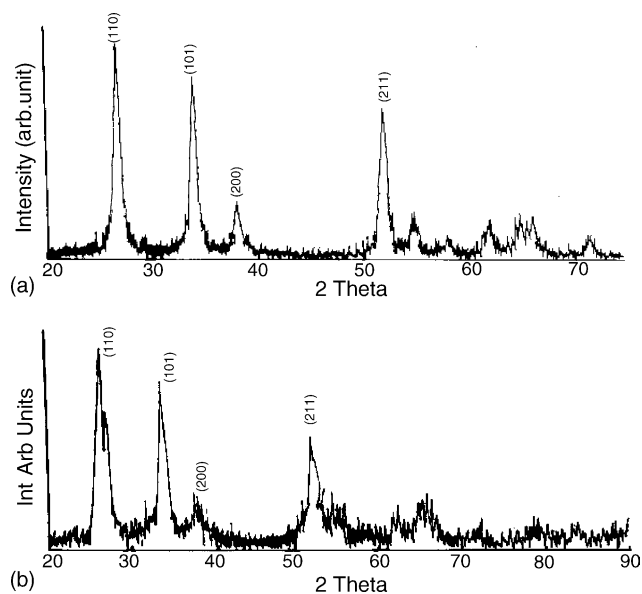


Fig. 1. (a) XRD pattern for undoped tin oxide powder and (b) XRD pattern for Ni- and Al-doped tin oxide powder.

where k is 0.9, λ the X-ray wavelength, β the peak FWHM in radiation and θ is the diffraction peak position. The grain size for batch I powder is 16 nm and for batch IV powder is 10 nm. The effect of Al as well Ni as dopants had been investigated by various researchers in the past and both Ni and Al were reported as grain growth inhibitors [6,7,10]. Our results confirm the earlier findings and show that Ni and Al combined doping also reduced the grain growth.

4. Resistance measurements

Fig. 2 shows resistance versus temperature for the sample S1, S2 and S3 in air, where $\log R$ was plotted against $1000/T$.

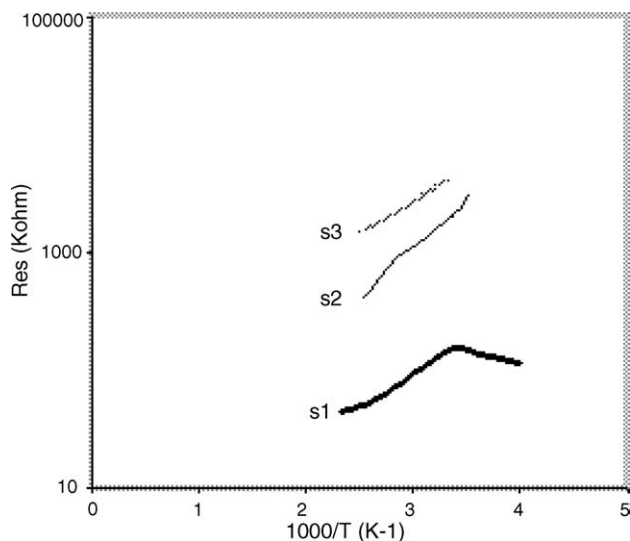


Fig. 2. Resistance vs. temperature curve for S1, S2 and S3 samples.

There is a strong increase in resistance on aluminium doping (sample S2). Electrical resistance increased further on nickel doping for sensor S3. The electrical behavior of all sensors is like n-type sensor, i.e., a drop in resistance if there is a reduction in the proportion of O_2 and exposure to a reducing gas. Earlier studies on Al doping have also shown an increased resistance on doping with Al [6,8]. This is explained to be due to increase in the depletion layer thickness. Since Al^{3+} replaces some of the Sn^{4+} sites, there is a net decrease in charge carrier concentration. This results in an increase in barrier height at the grain boundaries. Our above results indicate that the addition of Ni to aluminium-doped SnO_2 led to a further increase in resistance. This increased resistance may be caused on the one hand by the substitution of Sn(IV) ion in SnO_2 lattice with Ni(II), similar to the effect of Al(III) doping. On the other hand, such an increased sensor resistance may also be caused by the formation of n–p type junctions. It is known that the characteristics of such barriers can strongly influence electrical conductivity and sensitivity of semiconductor oxides. Such barriers are reported to form on Cu doping, i.e. on doping with Cu, pCuO–n SnO_2 forms at grain boundaries. Since NiO is also a p-type conductor, such n–p junction may form on Ni doping. Further the possibility of NiO/ SnO_2 leading to n–p junction between n-type semiconductor SnO_2 and p-type semiconductor NiO was reported by other investigations also. Formation of n–p junction electrodes made by n-type SnO_2 and p-type NiO have been studied for control of charge recombination in dye sensitized solar cell [13]. This will be discussed later in detail. Using R – T curve shown in Fig. 2, activation energy was calculated. An increase in the activation energy was obtained for doped samples as compared to undoped sample, which showed an increase from 0.23 to 0.46 eV for Al doping and to 0.36 eV for Al + Ni doping. Rumyantseva et al. [7] studied the influence of Ni doping on SnO_2 . For the films containing >0.45 at % Ni, the I – V characteristics with Au and In contacts were nonlinear which is attributed to the formation of Schottky barrier. As the Ni content increases, the $\log(R)$ versus $1000/T$ dependence becomes steeper and activation energy increases with increase in Ni content. The existence of energy barrier is attributed to pNiO–n SnO_2 junctions near grain boundaries. Electrical resistance of polycrystalline SnO_2 films increases upon Ni doping due to barrier mechanism of conduction. Further the slope of R versus T curve increased for doped samples as compared to undoped sample. Our results on polycrystalline thick films showed increased activation energy in aluminium- and Ni-doped samples.

5. Gas sensitivity

5.1. Al doping

Fig. 3 shows the gas sensitivity for 600 ppm LPG gas for sample S1 and S2 at different temperatures. A decrease in the maximum temperature at which highest sensitivity was

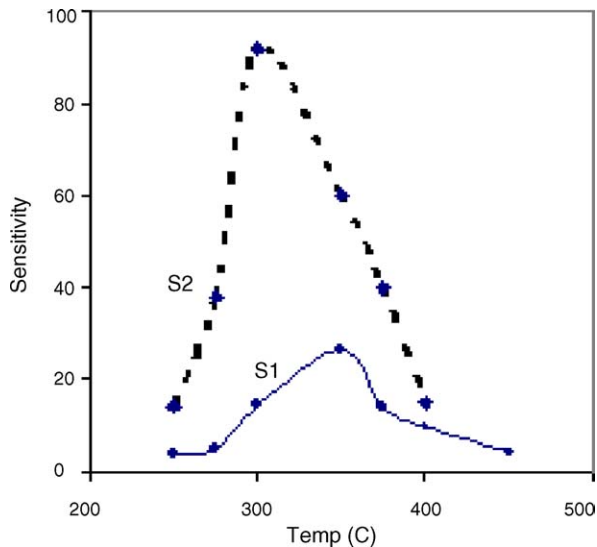


Fig. 3. Gas sensitivity for sensors S1 and S2.

observed is obtained. The maximum in sensitivity was observed at 350 °C for undoped sample S1, which reduced to 300 °C for aluminium-doped sample. Maximum gas sensitivity increased from about 25 to 92 from sample S1 to S2. Even without the noble metal catalyst additions the gas sensitivity enhancement in this case was about four times.

5.2. Al + Ni doping

Fig. 4 shows the gas sensitivity for S3 and S4 at different temperatures. The highest gas sensitivity was obtained for sample S3 at 300 °C. The gas sensitivity increased as compared to S1 and S2 on Ni addition. Further, in tin oxide gas sensors usually the dopants affect the gas sensitivity, but the way it is introduced into the sample also influences the properties. The dopant (Ni and Al) concentration for both samples (S3 and S4) was the same but in sample S3 it was added before precipitation and in sample S4, nickel is added to aluminium-doped calcined powder, during sensor fabrication. The effect

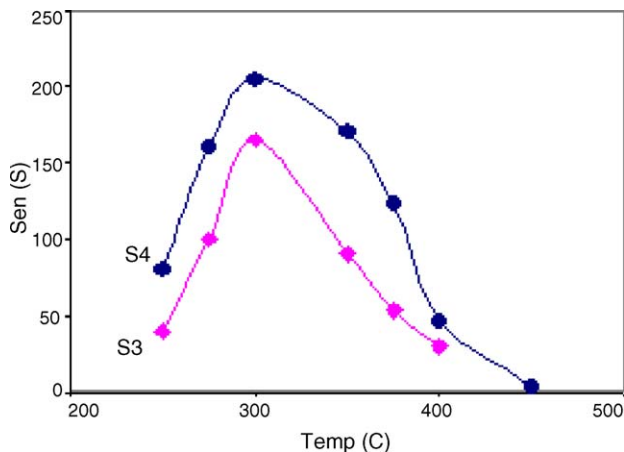


Fig. 4. Gas sensitivity for Ni and Al doping, samples S3 and S4.

of NiO was more for sample S3 since in this case the particle size was also affected by its addition. Further in this case the dopant is uniformly distributed at the molecular level, hence its effect is more. A few samples were prepared in which NiO was added as an overlayer to uncalcined powder of batch II, the increased sensitivity is observed for this case also (the results are not shown here) as compared to S1 and S2.

6. Response and recovery time

Response time was determined for LPG gas at 300 °C. All the samples sense the gas within 10–30 s. The response time for sample S3 for 600 ppm LPG is shown in Fig. 5. LPG gas response was observed instantaneously. Sensitivity increased with increasing gas concentration and saturation of gas sensitivity was observed at about 1000 ppm.

The recovery time, the time taken to return back to the normal resistance when refreshed, for undoped sensor S1 was about 10 min. However for the doped samples S2 and S3 this time is very short. It takes almost less than 10 s to recover the sample resistance back to normal. The major advantage observed using Ni dopant is that not only the response time is decreased but the recovery time is also decreased. Previously it was observed [14] that on Ru doping sensitivity increases linearly with the hydrocarbon gas concentration up to 1000 ppm and saturates for gas concentration of 1200 ppm and above. This is similar to our results on Ni doping also. However, an advantage of Ni doping is obvious when compared with earlier finding on the effect of Pd/Ru doping where even though a decrease in response time was reported but the recovery time was increased from 600 s for pure tin oxide to 1200 s for doped sensor in case of H₂ gas sensing [15]. It was shown by Lee et al. [16] that the gas reaction at 400 °C is complete after 10 s while the desorption of the gas was com-

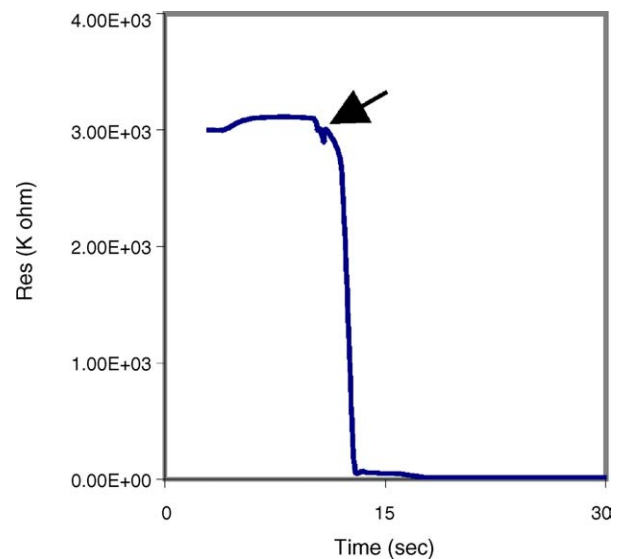


Fig. 5. Response time for LPG gas for sensor S3, arrow indicates gas in.

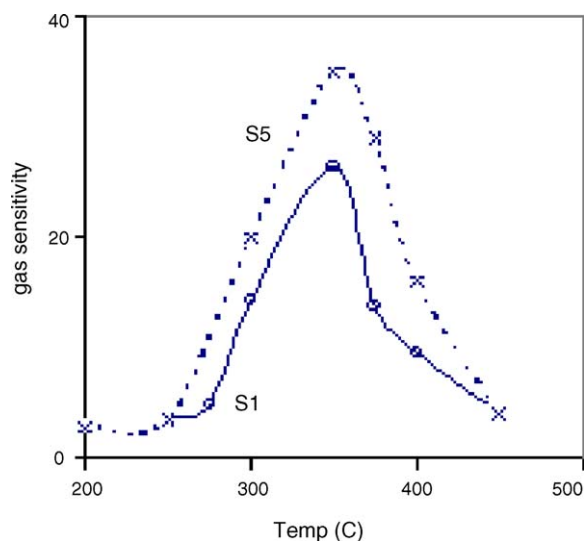


Fig. 6. Gas sensitivity for sensor S1 (○) and S5 (×).

pleted after approximately 5 min. This time is more at lower temperatures. During the recovery phase, atmospheric oxygen dissociates and adsorbs on the ceramic surface and electrons are extracted from the conduction band, which cause the resistance to rise again.

To investigate the effect of Ni doping further, samples S1 and S2 were dipped in a dilute aqueous solution of nickel acetate for 5 min and after drying, heated to 600 °C to decompose nickel acetate. Using this process a NiO layer is overcoated on the surface of the sample. These samples were again tested for gas sensitivity. Fig. 6 shows the effect of Ni overcoating on sample S1, the gas sensitivity increased from 25 to 35 for sample S5. A gas sensitivity enhancement was observed for sample S6 also for which sensitivity increased from about 92 to 136.

7. Discussion

As mentioned earlier, a large change in the resistance of oxide in presence of reducing gases is generally attributed to the changes in the potential barrier at grain boundaries. Tin oxide is an n-type semiconductor in which adsorbed oxygen reacts with a reducing gas releasing electrons into the conduction band by which conductivity increases. The degree of this depletion or accumulation depends inversely on the grain size. Stronger accumulation or depletion will occur in a smaller grain size than in a larger one. As our results indicate, samples prepared after Al and Ni dopants show lower grain size and hence decreased particle size may be responsible for the increase in gas sensitivity. Earlier investigations have shown that the gas sensitivity to H₂ and *iso*-C₄H₁₀ is promoted extensively by 1–5% Al doping [12]. It was observed that the carrier concentration is decreased with Al doping, resulting in an increase in Debye length. At the same time, the crystallite size of tin oxide was also decreased. Increased

Debye length and decreased crystallite size combined were responsible for high gas sensitivity [12]. Improved gas sensitivity for S2 sample as compared to S1 is due to aluminium doping.

In samples S3 and S4, Ni and Aluminium co-doping was used and this type of co-doping have also shown a decrease in particle size, as is evident in XRD line broadening for doped sample. Hence the observed gas sensitivity enhancement due to co-doping with Ni and Al may also be assumed to be due to similar reasons of decreased grain size. However, an increase in gas sensitivity was observed for samples for S5 and S6 on an overcoating with Ni. This enhanced gas sensitivity cannot be explained due to the decrease in grain size alone. In this case, the samples were already sintered at 800 °C, and after overcoating with Ni they were treated to 600 °C only. During this treatment at a lower temperature, not much change in grain size is expected. Hence together with a reduction in grain size, Ni must be influencing the gas sensitivity and increased resistance due to some other reason also.

NiO behaves as a p-type semiconductor. According to the existing literature, the microstructure and structure of NiO–SnO₂ system have been investigated by Castro et al. [10] and the segregation of the lower concentration component to the surface of the powder matrix was observed. The segregation of Ni on the surface of SnO₂ was observed even in specimens with 30 mol% addition. The segregation caused a decrease in the surface energy of the powders and therefore an increase in the surface area as expected by the Ostwald ripening model. The XRD measurements of SnO₂ with Ni presented only the SnO₂ tetragonal phase even with 30 mol% additive. Moreover, two important points noted were the absence of any second phase nucleated by the additive for all concentrations and no displacement of the SnO₂ reflections, indicating that there must be small or no solubility of the additives in the crystalline bulk. These results suggested that the ions must be segregated onto the surface of the powder even at high concentrations (<30%) and just an enlargement of the diffraction peaks was noticed because the crystallite size decrease. In the present work, we have added only 2% nickel and hence it is proposed from the results of previous investigations that nickel additive is segregated over the surface of SnO₂.

When pure n-type oxides are exactly stoichiometric they cannot chemisorb oxygen. However, when they are oxygen deficient they can chemisorb just as much as is needed to restore their stoichiometry or more generally until their charge averaged over the depth of the depletion layer is balanced. Therefore, it is specific for n-type oxides that the concentration of surface oxygen ions remains some orders of magnitude lower than the concentration of lattice oxygen in the uppermost surface layer. On the other hand, on p-type semiconductors, such as NiO, a full monolayer of oxygen ions typically adsorbs, because the metal ions of the lattice can be oxidized into a higher oxidation state, e.g. from Ni²⁺ into Ni³⁺ in NiO [19].

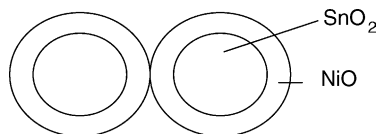
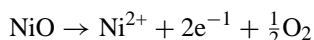


Fig. 7. Model for nickel-doped SnO₂ sensor structure.

The observed enhancement in gas sensitivity on nickel doping might be explained on the basis of this information as due to a formation of an n–p junction. Using the sensor preparation route adopted in the present work, SnO₂ particles were coated by Al₂O₃ in sample S2 and sample S2 is coated by NiO layer in samples S3 and S6. As suggested earlier Al₂O₃ may dope the lattice and an acceptor type of doping may explain its affect. Ni does not go into the lattice and segregates on the SnO₂ surface. Hence, it is proposed that p-type NiO semiconductor gets segregated over the n-type semiconductor, forming an n–p junction. Role of hetero-junction in enhanced gas sensitivity have been reported earlier. Wang et al. [17,18] have reported that a sensor composed of two successive bodies A and B whose conductivity types are different such as A is p-type and B is n-type, then under certain conditions higher sensitivity and selectivity can be observed. A hetero n–p junction model has been suggested to explain the enhanced gas sensitivity for CuO-doped SnO₂ gas sensors. Fabrication of n–p junction electrode made of n-type SnO₂ and p-type NiO increase the photocurrent and photovoltage in dye sensitized solar cells [13], the n–p junction formed between SnO₂ and NiO facilitate the efficient charge transfer.

The structure for nickel-doped sensor could be modeled as shown in Fig. 7. The defect equation as a function of NiO can be written as:



NiO present on the SnO₂ grain surface can be represented by the above equation. The resistance and the gas sensitivity of the sensor will be determined by the resistance of such p–n junctions instead of the Schottky barriers at the grain boundaries of SnO₂. In the presence of air, the electrons will be neutralized by adsorbed oxygen ion. Due to the presence of NiO overlayer a higher depletion layer width is expected, which explains the increased initial resistance for nickel-doped sensor. On exposure to reducing gas, the reducing gas will be adsorbed and react to the outer NiO layer. The electrons will be released back and tunnel through the thin NiO layer. Once the electrons are transferred to the conduction band of SnO₂, the NiO layer would act as a barrier layer for electron recombination leading to higher barrier. In addition, n–p junction would direct the electrons to travel from NiO particles to SnO₂ particles effectively. Therefore, introduction of a thin NiO layer on SnO₂ particles distinctly has two functions: (a) it acts as a barrier for the recombination of electrons in the conduction band of SnO₂ and (b) the n–p junction that formed between SnO₂ and NiO would facilitate the electron transfer

from NiO to SnO₂ [13]. Such a mechanism is able to explain the fast response on exposure to air at the time of recovery also. As mentioned earlier, NiO being a p-type semiconductor, a full monolayer of oxygen can adsorb on its surface, hence an enhancement in reactive sites is expected. Thus, more the number of reactive sites, more the diffusion rate of reducing gas/air to the adsorbing site, faster will be reaction with increased sensitivity. Hence the improvement on nickel doping is due to two reasons: (a) reduction in particle size due to nickel-doping and (b) formation of p–n junction causing increased barrier height. The oxidation–reduction reaction takes place on p-type NiO surface, hence increased reactive sites and enhanced rate of reduction–oxidation reaction.

Such a mechanism was justified further by results shown in Figs. 5 and 6, where the SnO₂ layer was formed initially and then NiO was coated on it by immersion. Higher resistance and an enhancement in gas sensitivity were observed in this case. Our results on enhanced gas sensitivity on Ni doping support n–p junction formation being the main reason for enhanced gas sensitivity and decreased recovery time. This finding is of major significance since the use of Ni instead of Pt or Pd can reduce the cost of the gas sensor. NiO behaves as a p-type semiconductor.

8. Conclusion

The LPG gas sensitivity was measured for Al- and Ni-doped SnO₂ gas sensor. The gas sensitivity of SnO₂ gas sensor is improved by Al doping, which is further improved by Ni doping. Ni and Al doping reduce the grain size. The results on resistance, response time, recovery time were explained in terms of an n–p junction formation between SnO₂ and NiO, which increases the depletion barrier height.

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References

- [1] J.G. Duh, J.W. Jou, B.S. Choi, Catalytic and gas sensing characteristics in Pd doped SnO₂, *J. Electrochem. Soc.* 136 (1989) 2740.
- [2] A. Ratna Phani, S. Manorama, V.J. Rao, Effects of additives on the response of sensors utilizing semiconducting oxide on carbon monoxide sensitivity, *Appl. Phys. Lett.* 66 (1995) 3489.
- [3] D.S. Vlachos, C.A. Papadopoulos, J.N. Avarisiotis, On the electronic interaction between additives and semiconducting oxide gas sensors, *Appl. Phys. Lett.* 69 (1996) 650.
- [4] M. Fleischer, S. Kornely, T. Weh, J. Frank, H. Meixner, Selective gas detection with high temperature operated metal oxides using catalytic filters, *Sens. Actuators B* 69 (2000) 205.

- [5] C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Grain size effects on gas sensitivity of porous SnO₂ based elements, *Sens. Actuators B* 3 (1991) 147.
- [6] N. Yamazoe, Y. Kurokuwa, T. Seiyama, Effects of additives on semiconductor gas sensors, *Sens. Actuators B* 4 (1983) 283.
- [7] M.N. Romyantseva, L.I. Ryabova, T.A. Kuznetsova, M. Labeau, G. Delabouglise, A.M. Gas'Kov, *Inorg. Mater.* 35 (1999) 54.
- [8] M. Ivanokskaya, P. Bogdanov, Effect of Ni^{II} ions on the properties of In₂O₃ based ceramic sensors, *Sens. Actuators B* 53 (1998) 44.
- [9] P. Bogdanov, M. Ivanovskaya, E. Comini, G. Faglia, G. Shervoglieri, Effect of nickel ions on sensitivity of In₂O₃ thin film sensors on NO₂, *Sens. Actuators B* 57 (1999) 153.
- [10] R.H.R. Castro, P. Hidalgo, R. Muccillo, D. Gouvea, Microstructure and structure of NiO–SnO₂ and Fe₂O₃ systems, *Appl. Surf. Sci.* 214 (2003) 172.
- [11] G. Liang, W. Li, T. Zhang, *Harbin Kexue Jishu Dexue Xuebao* 4 (1987) 49–57.
- [12] C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Promotion of tin oxide gas sensor by aluminium doping, *Talanta* 38 (1991) 1169.
- [13] J. Bandara, C.M. Divarathne, S.D. Nanayakkara, Fabrication of n–p junction electrodes made of n-type SnO₂ and p-type NiO for control of charge recombination in dye sensitized solar cells, *Solar Energy Mater. Solar Cells* 81 (2004) 429.
- [14] R.S. Niranjana, S.R. Sainkar, K. Vijaymohanana, I.S. Mulla, Ruthenium:tin oxide thin film as a highly selective hydrocarbon sensor, *Sens. Actuators B* 82 (2002) 82.
- [15] V.A. Chaudhary, I.S. Mulla, K. Vijaymohanana, Comparative studies of doped and surface modified tin oxide towards hydrogen sensing: synergistic effect of Pd and Ru, *Sens. Actuators B* 50 (1998) 45.
- [16] S.W. Lee, P.P. Tsai, H. Chen, Comparison study of SnO₂ thin and thick film gas sensors, *Sens. Actuators B* 67 (2000) 122.
- [17] Y.D. Wang, X. Wu, Z. Zhou, Novel high sensitivity and selectivity semiconductor gas sensor based on the p+n combined structure, *Solid-State Electron.* 44 (2000) 1603.
- [18] Y.D. Wang, X. Wu, Y. Li, Z. Zhou, The n+n combined structure gas sensor based on burnable gases, *Solid-State Electron.* 45 (2001) 1809.
- [19] D. Kohl, Function and application of gas sensors, *J. Phys. D: Appl. Phys.* 34 (2001) 125.