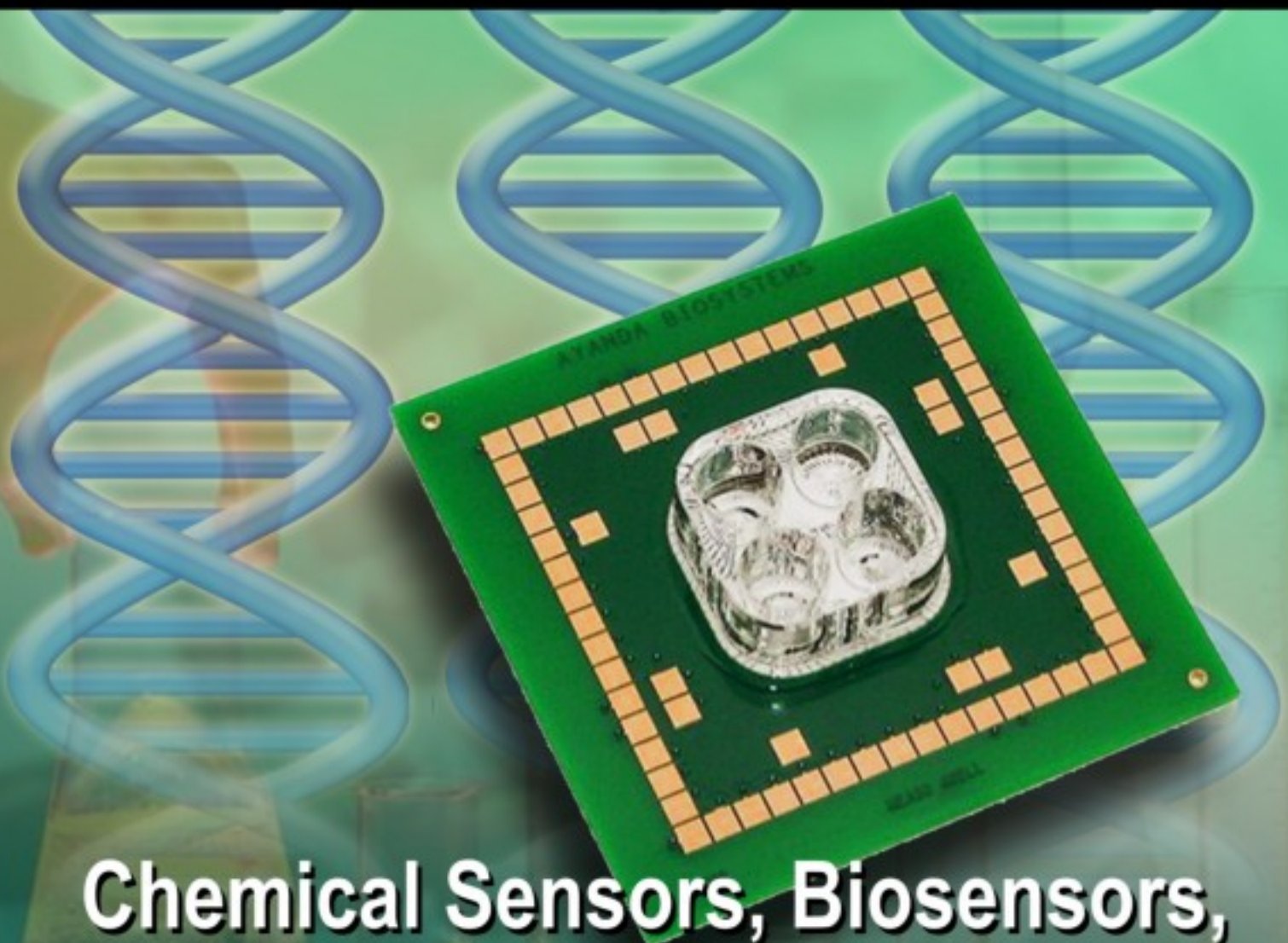


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## Cobalt Doped SnO<sub>2</sub> Thick Film Gas Sensors: Conductance and Gas Response Characteristics for LPG and CNG Gas

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**Abstract:** Cobalt doped thick films tin oxide sensors were studied for their LPG and CNG gas sensitivity. SnO<sub>2</sub> powder was synthesized by precipitation technique and doped with cobalt sulphate (0 to 10 wt %) by impregnation technique. The sensing characteristics were found to depend on the cobalt concentration and operating temperature. Best performance for LPG and CNG detection was obtained for 3 wt % addition of cobalt sulphate. Cobalt doped SnO<sub>2</sub> sensors showed a decrease in the optimum temperature for CNG detection from 450°C to 350°C. The transient response characteristics were determined at different temperatures and doping concentrations to understand the effect of doping on the rate kinetics. A correlation was established between response time, sensor response and the intergranular potential barriers. *Copyright © 2009 IFSA.*

**Keywords:** Metal oxide, Tin oxide, Gas sensor, LPG sensor, Cobalt-doping, Transient response characteristics

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### 1. Introduction

The properties of metal oxides have received a great deal of interest for many years, due to applications in various fields such as solar cells, optical devices and oxidation catalysts. Numerous metal oxide semiconductor materials have been reported to be usable as gas sensor, such as ZnO, SnO<sub>2</sub>, and TiO<sub>2</sub> and so on [1, 2]. These materials have non-stoichiometric structure, so free electron, originating from oxygen vacancies contribute to electrical conductivity. The interaction of

different gas compounds with an oxide surface may lead to changes in the lattice oxygen content at the surface in addition to changes in the amount of adsorbed species.

Sensitivity and selectivity of the sensors are influenced by many factors, among which foreign additives dispersed on the semiconducting oxides are of particularly importance [3, 4]. It is well known that surface adsorption of thin Pd /Pt sensitizers on semiconductor chemical sensors could promote the sensitivity to reducing gases and response time of tin oxide based sensors. Transition metal oxides are known to enhance surface adsorption sites by inhibiting crystallite growth in the basic SnO<sub>2</sub> matrix [5]. The role of the oxygen vacancies generated by these transition metal oxides as the driving force for densification has been thoroughly treated in the literature [5]. It has been proved that the oxygen vacancies created by substitution of Sn<sup>4+</sup> ions with Zn<sup>2+</sup>, Co<sup>2+</sup>, Co<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup> and Mn<sup>3+</sup>, enhances material densification through the activation of diffusion and material transport mechanisms [6,7]. Among various transition metal oxide dopants, Fe-substituted SnO<sub>2</sub> has been widely studied for sensing of reducing gases such as methane, butane, and CO by different groups [8, 9]. Synthesis of SnO<sub>2</sub> powders mixed with NiO and Fe<sub>2</sub>O<sub>3</sub> additives have been reported to enhance the surface area [10]. Tan et al. have reported the size effect and ethanol sensing properties of mechanically alloyed SnO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> nano-crystalline powders [11]. Depending on the oxygen concentration and operating temperature, both p- and n-type behavior of Fe doped SnO<sub>2</sub> has been observed by Galatsis et al. [12]. On the other hand, the gas sensing properties of Co-doped SnO<sub>2</sub> thick films have been studied for CO and H<sub>2</sub> [13, 14], but the sensing characteristics of Co-doped SnO<sub>2</sub> films have never been reported for LPG and CNG gases. The present work was undertaken with an aim to examine the gas sensing properties of cobalt doped SnO<sub>2</sub> gas sensor specifically for applications to LPG/CNG detection. In earlier studies, Co<sub>3</sub>O<sub>4</sub> - based isobutene sensor operating at low temperature has been reported by Choi and Min [15]. The addition of 2 mole% of CoSO<sub>4</sub> was reported to promote the densification of SnO<sub>2</sub> significantly, due to the formation of a non-reactive liquid which is responsible for the rearrangement during the initial stage of calcination and for the formation of lattice defects in SnO<sub>2</sub>, promoting an increase of diffusion through the SnO<sub>2</sub> lattice [16]. CoSO<sub>4</sub> in solutions within the SnO<sub>2</sub> structures acts as an acceptor, leading to creation of additional oxygen vacancies in the SnO<sub>2</sub>, and thus increasing the densification rate of this oxide. CoSO<sub>4</sub> segregates at the SnO<sub>2</sub> grain boundaries and creates a large oxygen vacancy concentration there. Co<sub>3</sub>O<sub>4</sub> has been reported to enhance CO sensitivity for the In<sub>2</sub>O<sub>3</sub>-based CO sensor [17]. SnO<sub>2</sub> (n)-Co<sub>3</sub>O<sub>4</sub> (p) composites were of n- or p-type depending on whether they were SnO<sub>2</sub>-rich or Co<sub>3</sub>O<sub>4</sub>-rich [14]. The observed better sensing properties have been attributed to the active role played by Co<sub>3</sub>O<sub>4</sub> grains and porosity in the film. The Co<sub>3</sub>O<sub>4</sub> grains combine with SnO<sub>2</sub> electronically by forming p-n junctions, resulting in an increase in electrical resistance of the device. Upon exposure to the gas environment, reduction of Co<sub>3</sub>O<sub>4</sub> molecules, results in destruction of the p-n junctions, thereby exhibiting sensing action. These encouraging results have motivated us to examine the gas sensing properties of cobalt doped tin oxide (Co-SnO<sub>2</sub>) thick film sensors.

In this paper we report the sensing characteristics of cobalt doped tin oxide (Co-SnO<sub>2</sub>) thick film sensor for LPG and CNG gas sensitivity. SnO<sub>2</sub> powder was synthesized by precipitation technique and doped with cobalt by impregnation technique. The sensing characteristics were found to be dependent on the cobalt concentration and operating temperature. The best performance was obtained for 3 wt % doping of CoSO<sub>4</sub>. The transient response characteristics were determined at different temperatures and concentrations.

## **2. Experimental**

Undoped SnO<sub>2</sub> powder was prepared using the precipitation route [18]. For this 0.1 M SnCl<sub>4</sub>·6H<sub>2</sub>O solution was prepared and pH was adjusted to 7 by drop wise addition of diluted NH<sub>4</sub>OH solution. The precipitate was then washed with an ammonium nitrate solution till no chloride ion was

detected on  $\text{AgNO}_3$  test. Then the precipitate was washed with ethanol - added water to remove nitrate ions. This powder was then dried and calcined at  $600\text{ }^\circ\text{C}$  for 4 h. Cobalt doped sensors were prepared by the impregnation method, i.e., the metal salt ( $\text{CoSO}_4$ ) in required amount was dissolved in water. Calcined tin oxide powder was dispersed in this metal salt solution, and then dried. This dried powder containing different concentrations (0 to 10 wt %) of dopant was used to prepare gas sensors. Thick paste was prepared using  $\alpha$ -terpineol – ethyl cellulose and butyl carbitol in the pestle mortar and brush painted on two gold lines with 1-2 mm separation (pre-fired for contacts) followed by drying at  $150\text{ }^\circ\text{C}$  for 1 h. These sensors were finally fired at  $800\text{ }^\circ\text{C}$  for 10 minutes. This firing is expected to convert cobalt sulphate to cobalt oxide.

Gas sensing experiments were carried out in a static system equipped with heating facilities. The sensor resistance was measured using a two-probe method. The sensing characteristics were measured under a controlled test gas/vapour ambience, created by introducing a known quantity of gas into the chamber. A fixed quantity of LPG or CNG was injected into the chamber through a micro-syringe. The sensing characteristics were investigated at least for three samples synthesized under identical experimental conditions. Sensor response (S) is defined as the ratio of resistance measured in air ( $R_{\text{air}}$ ) to resistance in gas environment ( $R_{\text{gas}}$ ). Sensor devices were annealed at  $450\text{ }^\circ\text{C}$  for 2 h in air prior to sensitivity or resistance measurement to stabilize the sensor. The sensitivity was measured in the temperature range  $250 - 450\text{ }^\circ\text{C}$  at steps of  $50\text{ }^\circ\text{C}$ . The resistance was measured while cooling down sample from the elevated temperature, thereby securing a good reproducibility in resistance temperature characteristics.

### 3. Results

#### 3.1. Resistance

Temperature dependence of resistance of tin dioxide thick film sensors in air containing different amounts of cobalt sulphate is shown in Fig. 1. The resistance of samples increased on increasing the cobalt concentration. From Fig. 1, it is clearly seen that the resistance increases on increasing the cobalt concentration 'x' from 0 to 10 mass %,  $R_{\text{air}}$  is seen to increase sharply by about four orders of magnitude after cobalt doping. Such a sharp increase in  $R_{\text{air}}$  with increasing amount of cobalt addition had been reported earlier and was considered as reflecting electronic interactions taking place between  $\text{SnO}_2$  and cobalt [14].

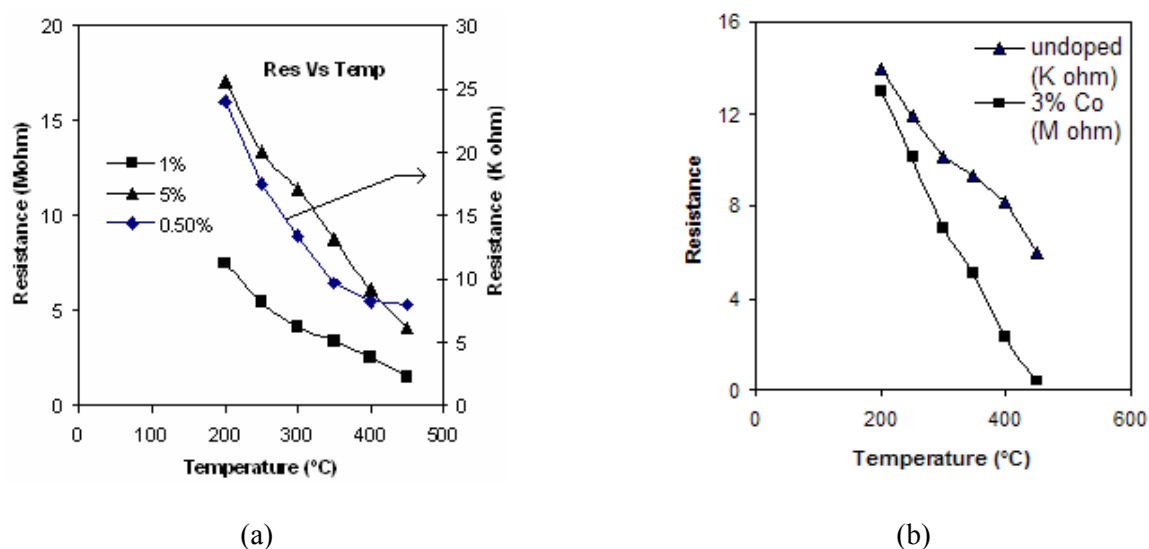


Fig. 1 (a, b). Variation of resistance with temperature for different concentrations of Cobalt addition.

Fig. 2 shows a representative  $\ln(R)$  versus  $1000/T$  curve for undoped and Co doped sensor. As shown in figure, in general the slope of such Arrhenius curve can be used to calculate the activation energy for conduction. Figs. 3 (a) and (b) show variations in resistance with temperature of an undoped and 3 % Co doped sensor in air and in presence of 1600 ppm LPG. It is observed that for the films doped with 3% Co, the change in resistance is much higher than that for undoped sensor.

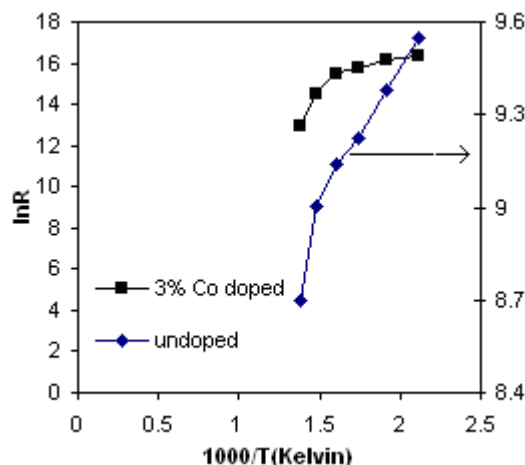


Fig. 2. Variation of  $\ln(R)$  of undoped and 3% Co-doped tin oxide gas sensor for different temperature.

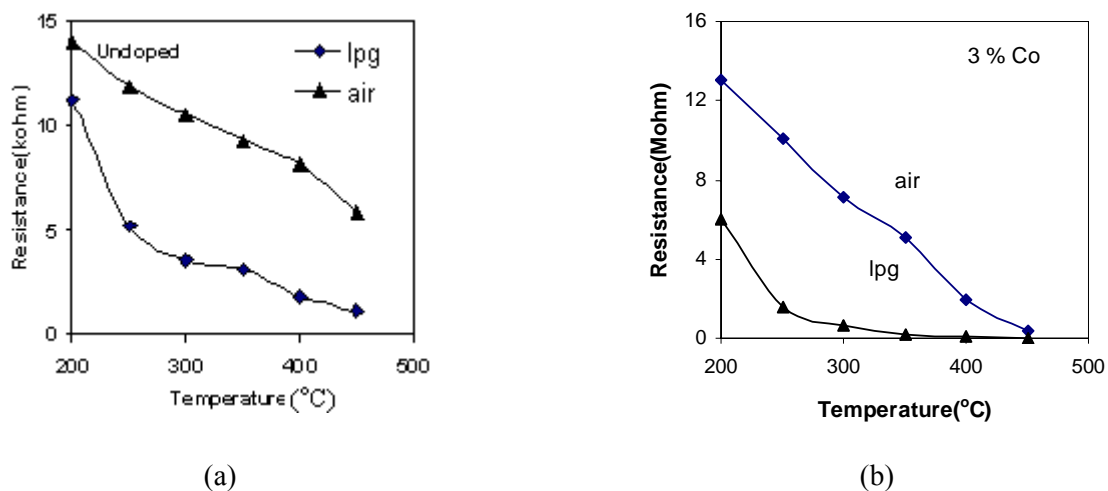


Fig. 3. Change in resistance with temperature (a) Undoped and (b) 3 % Co-doped tin oxide sensor in air and 1600 ppm LPG.

### 3.2. Sensor Response

The sensor response (as defined by  $R_{air}/R_{gas}$ ) was measured at temperatures from 200 to 450°C. The resistance of the sensing material decreases on exposure to reducing gases such as LPG or CNG for all samples; this shows that tin oxide behaves like an n-type material for cobalt doping up to 10 wt %  $CoSO_4$ . Fig. 4 (a) shows the variation of sensitivity to LPG gas as a function of temperature for the  $SnO_2$  films with different Co concentrations. For very low cobalt concentrations (0.5-1 wt %), the sensor response was low even at higher operating temperatures. The sensor response improved on increasing the doping concentration, and for 3 wt % cobalt doping the response was highest. On

increasing the cobalt concentration further, the sensor response degrades again. The response to 1600 ppm LPG increased from 3.4 for pure SnO<sub>2</sub> to 35.3 for 3 % Co-doped SnO<sub>2</sub>. The observed degradation of the sensor response at higher cobalt concentrations is in agreement with the results obtained by other researchers [14]. High Co concentration might have reduced the relative number/strength of favorable adsorption sites for LPG, which causes a decrease in the sensitivity. The optimum operating temperature for LPG detection for cobalt doped SnO<sub>2</sub> sensors is 350°C. Cobalt doping affected not only the sensor response, but also the temperature at which the response reached a maximum ( $T_M$ ). Fig. 4 (b) shows the gas sensitivity for 5000 ppm CNG (main component methane) at different temperatures. The optimum temperature for CNG detection was 350°C for 3 wt % cobalt doping wherein a response magnitude of about 6.3 was observed. Response to methane for pure tin dioxide does not go above 2 due to presence of agglomerates in the powder and absence of catalysts like platinum or palladium in the composition. Methane sensitivity increases continuously on increasing temperature up to 450°C for pure tin oxide, but for cobalt-doped samples, maximum response was observed at 350°C. This reduction in optimum temperature can be attributed to the optimization between the enhancement of reaction kinetics of oxidation of methane with adsorbed oxygen species and increased desorption of the oxygen species from the surface of tin dioxide with increasing temperature, the mechanism will be discussed later. Gas sensitive metal oxide materials (MOX) usually show a bell shaped variation of the response with sensor operation temperature  $T$  as observed in Fig. 4 (a, b). Our results on cobalt doping suggest that addition of cobalt oxides can enhance the gas response of SnO<sub>2</sub> materials, leading to a lowering of  $T_M$  (temperature at which maximum response was observed) and an increase in response  $S$ . The operating temperature of 350°C for best performance is lower than that reported for undoped SnO<sub>2</sub>-based CNG sensors, which lies in the range of 450°C for pure tin oxide samples [18]. This is quite advantageous for device application since the power required for operation may be lowered. Interestingly, CNG sensitivity also decreases on increasing the Co-doping level to 10 wt %, similar to a decreased sensitivity for LPG on higher cobalt concentration. Fig. 5 shows the variation in response with concentration of LPG and CNG for 3 % Co-doped sensor at 350°C. The response increases on increasing the LPG /CNG concentration and at high concentrations, saturation in response was observed. Almost linear variation in gas response was observed up to 2000 ppm LPG and 5000 ppm CNG, after that, the sensor saturates. The saturation of response  $S$  may be due to the total coverage of the film surface by the adsorbed gas molecules. The response variation with respect to gas type (LPG or CNG) is caused by a difference in reducing power of gas. The decrease in gas sensitivity above 350°C for cobalt-doped tin dioxide coatings may be related to enhanced desorption (probably due to some catalytic activity arising out of cobalt doping) of adsorbed gases from the sensor surface because of their higher kinetic energy at high temperature [14, 15].

The cobalt doping was expected to form a p-n type heterojunction [13]. Co<sub>3</sub>O<sub>4</sub> (p) has larger work function than SnO<sub>2</sub>. When SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> heterocontacts are formed, conduction electrons of SnO<sub>2</sub> grains are drawn toward Co<sub>3</sub>O<sub>4</sub>, increasing the electrical resistance in air ( $R_{air}$ ) as actually observed. Upon exposure to reducing gas, Co<sub>3</sub>O<sub>4</sub> is reduced more preferentially than SnO<sub>2</sub>, so that the conduction electrons are given back to SnO<sub>2</sub>, leading to large sensor response. This mechanism of promotion (electronic sensitization) is essentially the same as has been observed in the PdO-loaded SnO<sub>2</sub> sensor [19]. As was so for the PdO loading, the optimum Co<sub>3</sub>O<sub>4</sub> loading in the present study is small (e.g. 1 wt %). Excessive loadings degrade sensor response sharply, because increasing highly reactive sites too much makes it more difficult for gas molecules to diffuse into the inner part of thick films, as illustrated by the reaction-diffusion equation-based analysis of gas sensing properties [11].

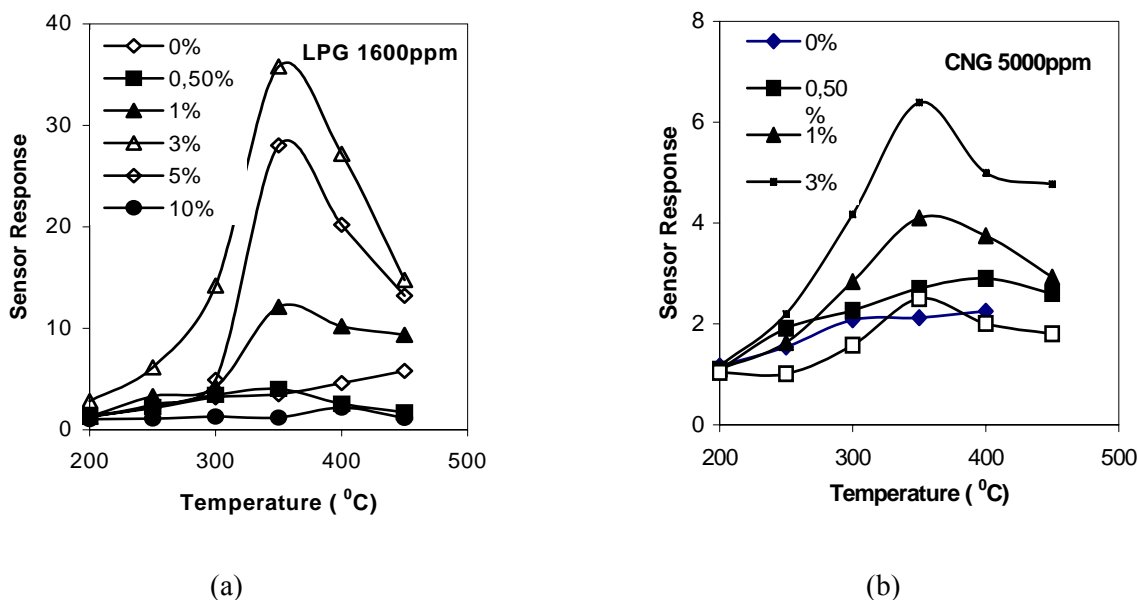


Fig. 4. Co-doped gas sensor (a) LPG (b) CNG sensitivity.

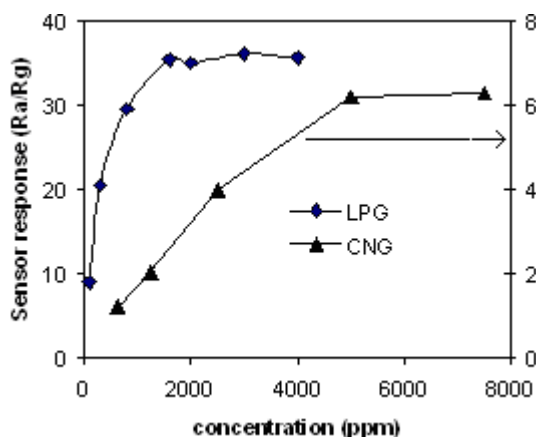


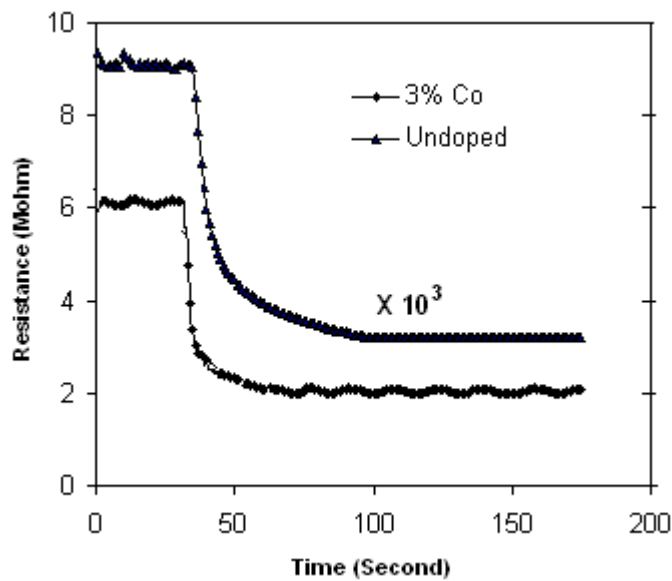
Fig. 5. Sensor response concentration of LPG and CNG for 3% Co doping at 350°C.

### 3.3. Transient Response Characteristics

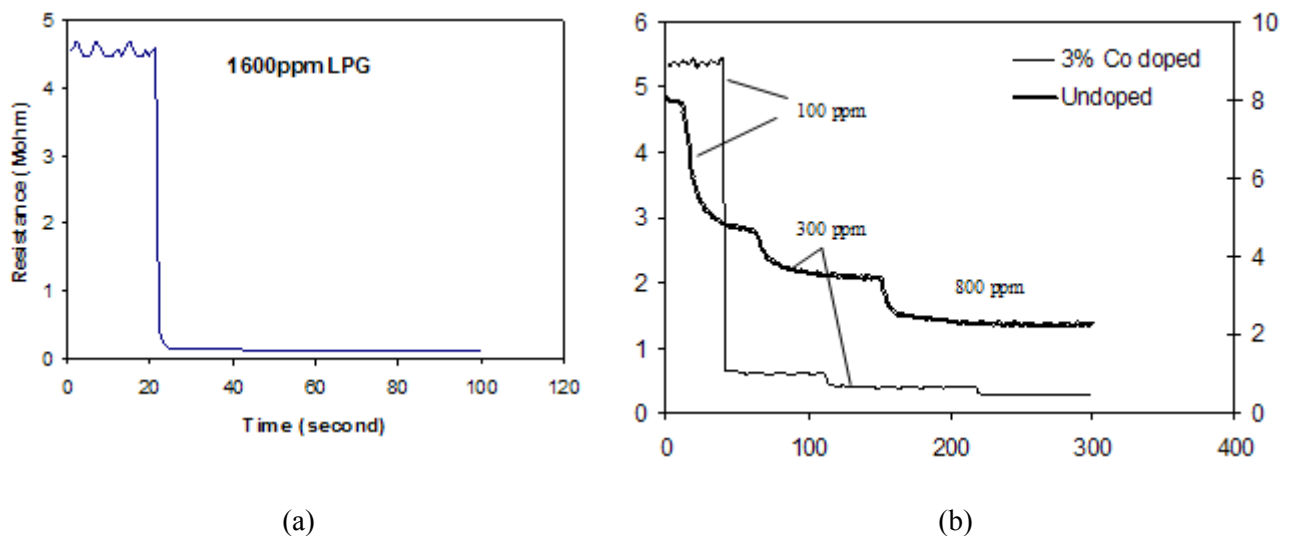
Addition of a dopant can modify the rate parameters and the characteristics of the sites in which the reaction occurs. Such modifications of the metal oxide surface results in a change of the kinetic characteristics of the response to gas. The degree of the change will be determined by the amount of the impurity and therefore it is important to investigate the correlation between the amount of the impurity and the rate parameter of the reaction. To study the effect of cobalt doping on rate reaction, we measured the transient response characteristics of these sensors. Electrical resistance was measured after a time interval of 1 s using a Keithley multimeter interfaced with a computer. Required amount of gas was inserted into the chamber after starting the experiment for about a minute. The length of the measured transient was similar in all the tests and equal to about 300 s. At the end of this period, the resistance tended to the constant value in all the tests. The sensors were again exposed to the gas when the initial resistance was restored in the sensors after switching back to the clean air. The sensors were functioning at fixed temperatures during single test. In different tests, the temperature of a sensor was set at individual values within the interval from 200 to 450°C long before the measurements. To measure response at different concentrations, the time interval

for transient was increased to 1000 sec. and after every 2 to 3 min., the concentration was increased to the next value.

The response characteristics of all the sensors were measured at different temperatures and for different concentrations. The response characteristics of the undoped and 3% cobalt doped tin oxide gas sensor for LPG and CNG respectively are shown in Fig. 6 and 7. Cobalt addition was found to accelerate the speed of response of a sensor material to LPG and CNG gases. The response time is defined as the time required for the sensor response to reach 90 % of the saturation value after the test gas contacts the surface of the sensor. As shown in Fig. 6, the response time for CNG decreased from 40 s to 12 s for Co-doped SnO<sub>2</sub> sensor at 350°C. The speed of response of pure SnO<sub>2</sub> to CNG is much slower than that of co-doped tin oxide, due to the lack of the catalytic activation. On comparing Figs. 6 and 7 we can see that the response time is more for CNG as compared to LPG gas.



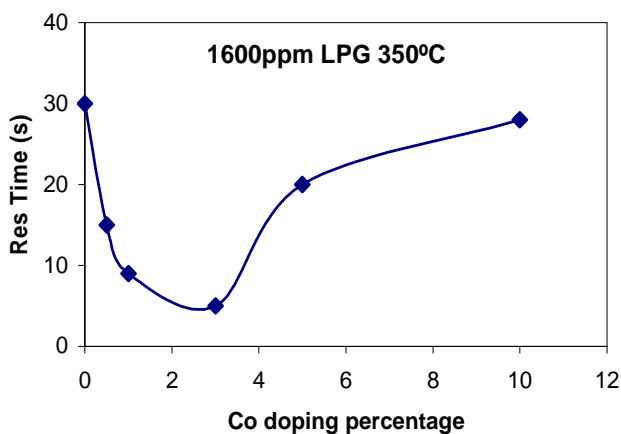
**Fig. 6.** Response time curve at 350°C for 3 % Co-doped and undoped tin oxide gas sensor for 5000 ppm CNG.



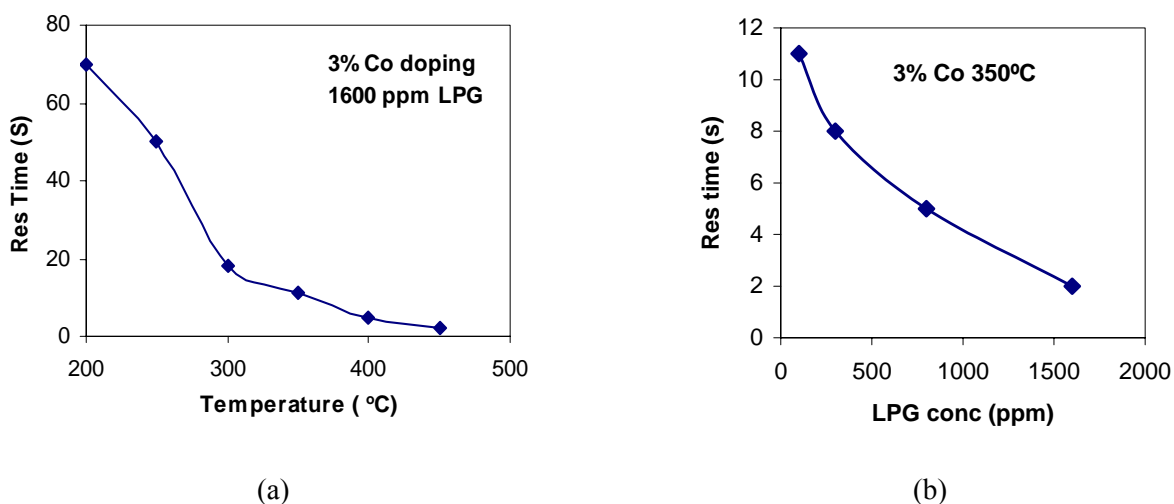
**Fig. 7.** Response time curve for (a) 1600ppm LPG (b) different concentration of LPG at 350°C.

Fig. 7 (a) shows the transient response curve for 3 wt % Co-doped SnO<sub>2</sub> sensors to 1600 ppm LPG at 350°C. As shown, the response was quite fast and took about 5 sec. Fig. 7 (b) shows the response characteristics at different concentrations of LPG at 350°C for undoped and Co-doped sensor, which clearly shows the effect of cobalt addition on response time. Co-doped sensor showed fast response, while the undoped sensor showed a slow response. Korotcencov et. al. [19] investigated the influence of surface modification by Cobalt oxide on gas sensing characteristics of SnO<sub>2</sub> using SILD method and found an appreciable improvement in the rate of response to H<sub>2</sub> gas. This finding is similar to the present report, where faster response to LPG and CNG has been established for Cobalt-doped SnO<sub>2</sub> sensor.

Response characteristics depend on cobalt concentration. The dependence may be described as shown in Fig. 8. Minimum response time was observed for 3 % Co-doping, and on increasing cobalt concentration further, response time increased again. In addition to the cobalt concentration present in the films, the response time was found to depend on the operating temperature and gas concentration as shown in Fig. 9 (a, b).



**Fig. 8.** Variation of response time with cobalt doping percentage.



**Fig. 9.** Response Time variation to LPG with (a) temperature and (b) concentration.

At lower operating temperature the response time was large and it decreases with increase in temperature. It is interesting to note that, at higher temperatures, the films with various cobalt

concentrations have the response and recovery times of the order of 10 s. The response time versus operating temperature characteristics can be attributed to the saturation time and mean residence period of the gas molecules on the film surface. It is expected that at low temperature the saturation time (the time required for complete coverage of the film surface by the gas molecules) is large, leading to a large response time. As the temperature is increased, the thermal energy of the adsorbed gas will be more and as a result the average residence time will be small. Thus, at higher operating temperatures the response time is smaller and the film exhibits better sensing characteristics. Response characteristics depended on LPG concentration, and for higher concentration, response time decreases.

#### **4. Discussion**

The results show that cobalt addition to SnO<sub>2</sub> sensors brings an increase in air resistance  $R_{air}$ . At optimum doping, an enhanced gas response was observed which was accompanied with an increase in the rate of response. There are several mechanisms used to explain the sensitivity enhancement through doping. Addition of another element in the tin oxide matrix may result in a new material with different features-, in stabilization of the active sensing material (grain growth inhibition), in grain size control within dimensions comparable to the Debye length; one of the two phases could act as a filter and the other one as a sensing material, or one of the two phases could perform the receptor function (being chemically active) while the other one could perform the transducer (in electrical signal) function (this is more effective in the case of the metallic phases added).

Enhancement in gas sensitivity for cobalt doping is associated with the presence of cobalt oxide, probably Co<sub>3</sub>O<sub>4</sub> or CoO at the surface of SnO<sub>2</sub>. There are many studies on cobalt doping in tin oxide in literature [13, 14, 19-21]. Accordingly, the doping with a lower valency cation i.e. Co<sup>+2</sup> substituting at Sn<sup>+4</sup> sites increases the oxygen vacancies. The high densification of Co-doped SnO<sub>2</sub> is promoted by enhancing solid state diffusion from oxygen vacancy creation near to the grain boundaries of the SnO<sub>2</sub> grains. These large oxygen vacancy concentrations get filled by chemical adsorption of oxygen and hence increase the resistance of SnO<sub>2</sub> samples. Another effect of dopant addition may be the reduction in the grain size. In the present work, the cobalt compound was added to an already calcined tin oxide powder. It is expected that dopant addition through such process suppresses the effect of dopant on grain size.

The adsorption / desorption processes and catalytic reactions on the surface determine the gas sensing properties. SnO<sub>2</sub>, when exposed to air, adsorbs oxygen ions O<sub>2</sub><sup>-</sup> or O<sup>-</sup> on the surface, leaving a positively charged metal cation below the particle surface. This creates a space charge layer at the particle surface, which increases the potential barrier for the electron conduction. Exposure to a reducing gas (such as LPG, CNG), the reducing gas reacts with the surface- adsorbed oxygen ions, thus releasing the electron back to the conduction band of SnO<sub>2</sub>, which reduces the potential barrier. The first step is adsorption followed by catalytic reaction at active sites. LPG had faster response as compared to CNG having methane as main constituent. For alkane oxidation, the initial step of the reaction consists of C-H bond breaking, which is considered as the rate limiting step, then hydrogen atom is adsorbed onto the surface and reacts with O<sup>-</sup> sites. In general, faster gas response will be expected in the molecule rich in C-atoms; in agreement with the higher reactivity of heavier alkanes (LPG, consisting of propane as main component) as compared to CNG (main component methane).

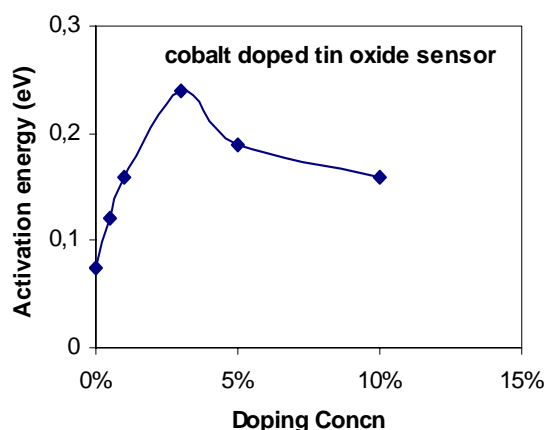
For a porous layer, the free conduction electrons have to overcome the surface potential barrier ( $V_s$ ) when hopping from one grain to another. In this hypothesis, the conductance of the sensing layer can be expressed by [22, 23]

$$\sigma = \sigma_0 \left( \frac{-eV_s}{kT} \right), \quad (1)$$

where  $\sigma_0$  is a factor that includes the bulk intragranular conductance,  $k$  the Boltzmann's constant,  $T$  the absolute temperature, and  $eV_s$  the potential energy barrier at the interface between two neighboring grains.

$$eV_s = \frac{e^2 N_s^2}{2\epsilon_r \epsilon_0 N_d}, \quad (2)$$

where  $N_s$  is the surface density of adsorbed oxygen ions ( $O_2^-$  or  $O^-$ ),  $\epsilon_r \epsilon_0$  the permittivity of the semiconductor, and  $N_d$  the volumetric density of the electron donors. Clearly, the energy barrier is a function of temperature, atmosphere (oxygen partial pressure), and dopant concentration; each of these parameters affects the energy barrier, the conductivity, and thus the sensitivity. Effective activation energies i.e. Schottky barrier height for conduction was derived from the slopes of the  $\ln(R)$  versus  $1000/T$  Arrhenius-type plots using data from Fig. 2 and shown in Fig. 10. For 3 wt % Co-doped  $SnO_2$  sensor, the activation energy is maximum and response time is minimum. On comparing Fig. 8 & Fig. 10, an inverse relationship between activation energy and response time was observed. Hence, more is the activation energy lesser will be the response time.



**Fig. 10.** Dependence of Activation energy on doping concentration.

On increasing the dopant concentration, the Schottky barrier height increases up to  $x \leq 3$  wt % and on further increase in cobalt concentration, the barrier height starts to decrease, thus the Schottky barrier height is maximum at 3% cobalt doping, as shown in Fig.10. Defect formation by donors and acceptors in the tin oxide material should be responsible for the origin of potential barriers at grain boundaries. The concentration of the free charge carriers at the surface depend on the height of the intergranular barrier ( $V_s$  is proportional to  $N_s^2$ ), hence increased barrier height means an increased adsorbed oxygen ion sites at the grain boundary region. As discussed earlier, the oxygen defects originated through the substitution of  $Sn^{+4}$  by  $Co^{+2}$  will be partly absorbed at  $SnO_2$  grain boundaries and the absorbed oxygen will capture electron from the negatively charged defects to form  $O^-$  or  $O_2^-$ . The increased concentration of  $O^-$  and  $O_2^-$  leads to an increase of grain resistance as well as increased intergranular barrier. Increase in activation energy or the Schottky barrier is directly related with the increased rate of reaction, as well as maximum response magnitude. This is not unexpected, since more are the number of surface sites i.e.  $O^-$  and  $O_2^-$  ions present, more will be the barrier height and faster will be the reaction. The other part of gas detection is linked with

transducer function. As pointed out earlier, cobalt doping increases the number of oxygen vacancies. More vacancies will increase the rate of diffusion of oxygen ions inside the grains. This suggests a faster charge transfer action. In this way the cobalt addition increases the reaction kinetics by improving receptor as well as transducer function. In the present work, a direct correlation between maximum Schottky barrier height with maximum response as well as minimum response time was observed. Further, response time depends on the type of the gas. CNG took more time as compared to LPG. This means that the rate of response is limited by the rate of reaction of the reducing gas, and oxygen adsorption /desorption is quite fast on Co-doped SnO<sub>2</sub> surface.

Another reason that can improve gas response after cobalt doping is formation of n-p junction. The transition metals such as cobalt oxide are known to be p-type semiconductors and themselves act as good sensing materials for alkanes such as butane or methane [15, 24]. Blomberg et al. investigated the reaction of CH<sub>4</sub> with all the second row transition metal cations (M<sup>+</sup>) by ab. initio methods [25] and demonstrated the very strong stabilization of M<sup>+</sup>-CH<sub>4</sub> complexes compared to their neutral analogues. Therefore the cobalt ions present in the grain boundary region may directly be involved in the reaction and the adsorption–desorption reaction. When SnO<sub>2</sub>–CoO (n-p) heterocontacts are formed, conduction electrons of SnO<sub>2</sub> grains are drawn toward CoO, increasing the electrical resistance in air ( $R_{air}$ ) as actually observed (Fig. 1). Upon exposure to LPG and CNG, CoO is reduced more preferentially than SnO<sub>2</sub>, so that the conduction electrons are given back to SnO<sub>2</sub>, leading to large sensor response. In reducing environment CoO is converted to Co and resistance decreases (similar to Cu-SnO<sub>2</sub> mechanism). Increased dopant concentration beyond 3 % Cobalt does not increase the intergranular barrier height, even though resistance of the sensor increases. The decrease in sensitivity on further increase in dopant concentration may be explained due to (i) at higher doping concentration the dopant is segregated at the grain boundaries, (ii) in p-n junction model a monolayer coating over the metal oxide will be sufficient and higher concentration of dopant will reduce the sensor property.

The resistance increase with increased cobalt doping as observed in Fig.1 can be associated with a decrease in the carrier concentration through cobalt doping. This will reflect in increase in the Debye length since

$$L_D \propto (1/N_d)^{1/2},$$

where  $N_d$  is the carrier concentration of SnO<sub>2</sub> crystallites.

According to the grain size effect model brought up by Xu et al. [26], depending on the grain size ( $D$ ) relative to the Debye length  $L_D$  (space charge layer thickness), the transducer function is operated by a mechanism of grain boundary control, neck control or grain control. Hence if the grain size does not change with doping, addition of a lower valence cation, that is increasing the resistance thereby decreasing the carrier concentration, would increase the effective sensor area taking part in the gas sensing action. The gas sensitivity is largest when the depletion (or space charge) region generated by the chemisorbed oxygen extends entirely through the sensor.

Further, the rate of response increased as the CNG/LPG concentration was increased. The larger the  $V_s$  is, the slower the rate of charge transfer. Thus with increased reducing gas concentration that causes decrease in potential barrier, the rate of charge transfer increased and hence decrease in response time. The increase in temperature caused a decrease in response time due to increased rate of diffusion. In short, the optimum dopant concentration leads to highest inter granular potential barrier correlated to increase in number of oxygen defect sites, responsible for increase in hydrocarbon gas response. A model for the electronic interaction between cobalt and SnO<sub>2</sub> gas sensor was presented. The electrical measurements on doped and undoped samples revealed an enhanced barrier height for cobalt-doped sample. Cobalt doping improves the gas response through

increased receptor as well as transducer function. An appreciable improvement of the reaction kinetics, rate of response was observed. This represents a great advantage of cobalt doping in SnO<sub>2</sub> sensor.

## 5. Conclusion

The response of SnO<sub>2</sub> gas sensors was increased through Co doping for detection of LPG gas. This type of sensor can also be used in the detection of CNG at 350°C. A low operating temperature of 350°C would result in low power consumption. The studies revealed that optimum doping concentration for best LPG and CNG sensor performance is 3 wt % addition of cobalt sulphate. A possible mechanism for the effect of cobalt doping on the sensing properties is explored. The increased gas sensitivity can be explained through an increased Schottky barrier height. Dependence of response time on concentration, temperature and doping concentration was investigated. The minimum response time was observed for the optimum doping concentration giving best sensitivity.

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## References

- [1]. N. Yamozoe and N. Mura, Environmental gas sensing, *Sens. Actuators B*, 20, 1994, pp. 95-102.
- [2]. W. Gopel, D. Schierbaum, SnO<sub>2</sub> sensors: current status and future prospects, *Sens. Actuators B*, 26/27, 1995, pp. 1-12.
- [3]. K. D. Schierbaum, J. Geiger, U. Weimar, W. Gopel, Specific palladium and platinum doping for SnO<sub>2</sub> based thin film sensor arrays, *Sens. Actuators B*, 13, 1993, pp. 143-147.
- [4]. B. Kamp, R. Merkle and J. Maier, Chemical diffusion of oxygen in tin dioxide *Sens. and Actuators B*, 77, 2001, pp. 534-542.
- [5]. M. L. Margionte, A. Z. Simoes, C. S. Riccardi, A. Ries, F. M. Filho, L. Perazolli, J. A. Varela, Nonlinear characteristics of Cr<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, ZnO and CoO doped SnO<sub>2</sub> varistors, *Mat. Let.* 60, 2006, pp. 142-146.
- [6]. M. S. Castro, C. M. Aldao, Characterization of SnO<sub>2</sub>-Varistors with different additives, *J. Eur. Cer. Soc.*, 18, 1998, pp. 2233-2239.
- [7]. M. S. Tong, G. R. Dai, D. S. Gao, Gas-sensing properties of PdO-modified SnO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> double-layer thin-film sensor prepared by PECVD technique, *Vacuum*, 59, 2000, pp. 877-884.
- [8]. D. Kotsikau, M. Ivanovskaya, D. Orlik, M. Falasconi, Gas sensitive properties of thin and thick film sensors based on Fe<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> nanocomposites, *Sen. Actuators B*, 101, 2004, pp. 199-206.
- [9]. M. N. Rumyantseva, V. V. Kovalenko, A. M. Gaskov, T. Pagnier, D. Machon, J. Arbiol, J. R. Morante, Nanocomposites SnO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>: wet chemical synthesis and nanostructure characterization, *Sens. Actuator B*, 109, 2005, pp. 64-74.
- [10]. R. H. R. Castro, P. Hidalgo, R. Muccillo, D. Gouvea, Microstructure and structure of NiO-SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>, *Appl. Surf. Sci.*, 214, 2003, pp. 172-177.
- [11]. O. K. Tan, W. Zhu, Q. Yan, L. B. Kong, Size effect and gas sensing characteristics of nanocrystalline xSnO<sub>2</sub>-(1-x)-Fe<sub>2</sub>O<sub>3</sub> ethanol sensors, *Sens. Actuator B*, 65, 2000, pp. 361-365.
- [12]. K. Galatsis, L. Cukrov, W. Wlodarski, P. McCormick, K. Kalantarzadeh, E. Comini, G. Sberveglieri, p- and n-type Fe doped SnO<sub>2</sub> gas sensors fabricated by the mechanochemical processing technique, *Sens Actuator B*, 93, 2003, pp. 562-565.

- [13].U. S. Choi, G. Sakai, K. Shimano, N. Yamazoe, Sensing properties of Au-loaded SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composites to CO and H<sub>2</sub>, *Sens. Actuators B*, 107, 2005, pp. 397-401.
- [14].U. S. Choi, G. Sakai, K. Shimano and N. Yamazoe, Sensing properties of SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composites to CO and H<sub>2</sub>, *Sens. Actuators B*, 98, 2004, pp. 166-173.
- [15].S. D. Choi, B. K. Min, Co<sub>3</sub>O<sub>4</sub> based isobutene sensor operating at low temperatures, *Sens. Actuators B*, 77, 2001, pp. 330-334.
- [16].B. Kamp, R. Merkle and J. Maier, Microstructural evolution during sintering of CoO doped SnO<sub>2</sub> ceramics, *Ceramics International*, 25, 1999, pp. 253-256.
- [17].H. J. Lee, J. H. Song, Y. S. Yoon, T. S. Kim, K. J. Kim, W. K. Choi, Enhancement of CO sensitivity of indium oxide based semiconductor gas sensor through ultra thin cobalt adsorption, *Sens. Actuator B*, 79, 2001, p. 200.
- [18].A. Srivastava, K. Jain, Rashmi, A. K. Srivastava, S. T. Lakshmikummar, Study of structural and microstructural properties of SnO<sub>2</sub> powder for LPG and CNG gas sensors, *Mat. Chem. Phys.*, 97, 2006, pp. 85-90.
- [19].G. Korotcenkov, V. Macsanov, V. Brinzari, V. Tolstoy, J. Schwank, A. Cornet and J. Morante, Influence of Cu-, Fe-, Co-, and Mn-oxide nanoclusters on sensing behavior of SnO<sub>2</sub> films, *Thin Solid Films*, 467, 2004, pp. 209-214.
- [20].J. A. Cerri, E. R. Leite, D. Gouvea, E. Longo, J. A. Varela, Effect of cobalt (II) Oxide and Mn (IV) oxide on sintering of tin (IV) oxide, *J. Am. Cer. Soc.*, 79, 1996, pp. 799-804.
- [21].M. A. Ponce, R. Parra, M. S. Castro, C. S. Aldao, Conductance analysis of (Co, Nb, Fe)-doped SnO<sub>2</sub> thick film gas sensors, *J. Mater. Sci, Mat. Elec.*, 18, 2007, pp. 1171-1177.
- [22].H. Windischmann and P. Mark, A model for the operation of a thin film SnO<sub>x</sub> conductance modulation carbon monoxide sensor, *J. Electrochem. Soc.*, 126, 1979, pp. 627-633.
- [23].R. K. Srivastava, P. Lal, R. Dwivedi, S. K. Srivastava, Sensing mechanism in tin oxide based thick film gas sensors, *Sens. Actuator B*, 21, 1994, pp. 213-218.
- [24].S. F. Tahir, C. A. Koh, Catalytic oxidation of ethane over supported metal oxide catalysts, *Chemosphere*, 34, 1997, p. 1787.
- [25].C. Hall, R. N. Perutz, Transition Metal Alkane Complexes, *Chem. Rev.*, 96, 1996, pp. 3125-3146.
- [26].C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Grain size effect on gas sensitivity of porous SnO<sub>2</sub> based elements, *Sens. Actuators B*, 3, 1991, pp. 147.

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