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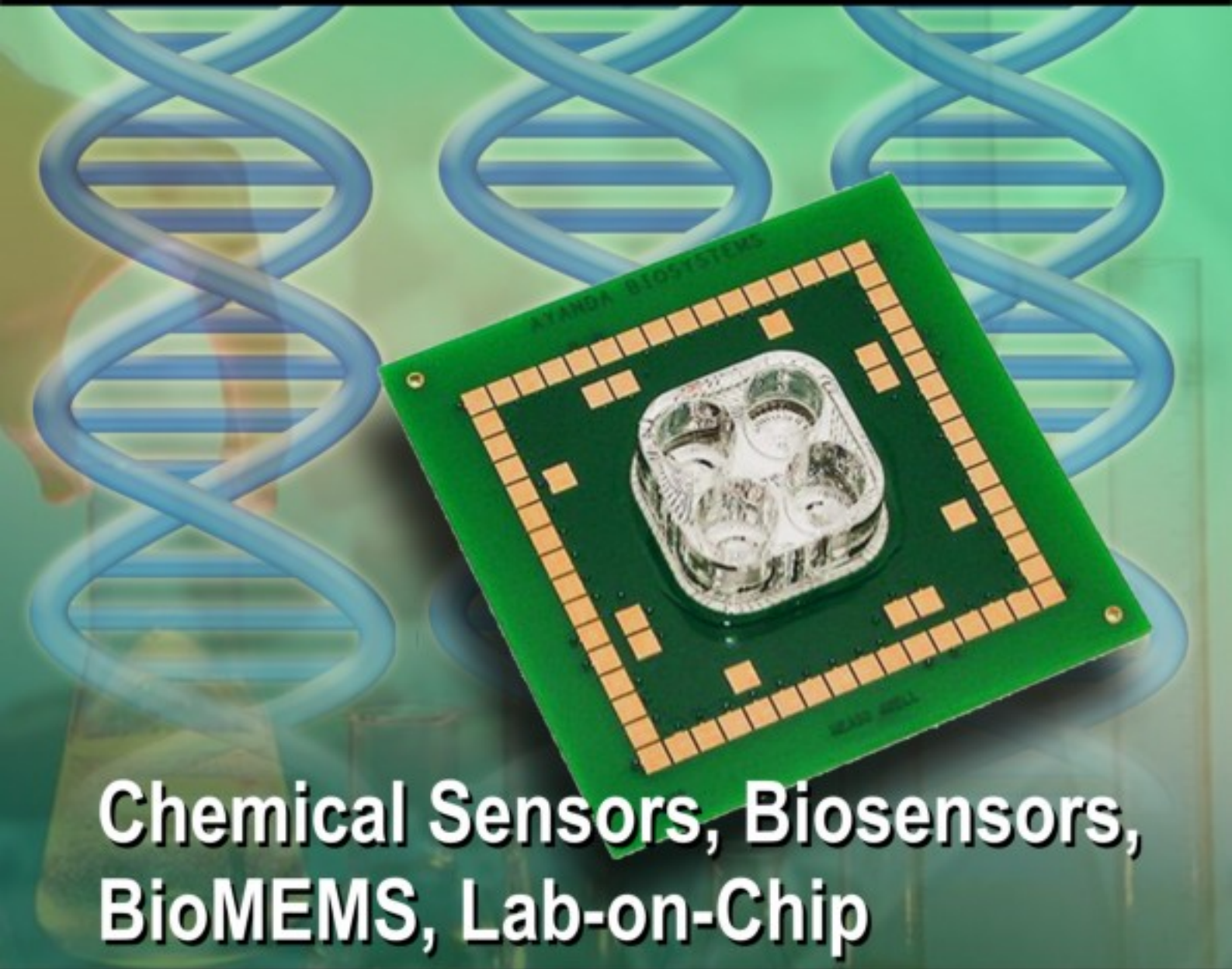

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Cobalt Doped SnO_2 Thick Film Gas Sensors: Conductance and Gas Response Characteristics for LPG and CNG Gas

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Abstract: Cobalt doped thick films tin oxide sensors were studied for their LPG and CNG gas sensitivity. SnO_2 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_2 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

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_2, and TiO_2 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_2 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^{4+}ions with Zn^{2+}, Co^{2+}, Co^{3+}, Fe^{3+}, Mn^{2+} and Mn^{3+}, enhances material densification through the activation of diffusion and material transport mechanisms [6,7]. Among various transition metal oxide dopants, Fe-substituted SnO_2 has been widely studied for sensing of reducing gases such as methane, butane, and CO by different groups [8, 9]. Synthesis of SnO_2 powders mixed with NiO and Fe_2O_3 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_2–Fe_2O_3 nano-crystalline powders [11]. Depending on the oxygen concentration and operating temperature, both p- and n-type behavior of Fe doped SnO_2 has been observed by Galatsis et al. [12]. On the other hand, the gas sensing properties of Co-doped SnO_2 thick films have been studied for CO and H_2 [13, 14], but the sensing characteristics of Co-doped SnO_2 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_2 gas sensor specifically for applications to LPG/CNG detection. In earlier studies, Co_3O_4 - based isobutene sensor operating at low temperature has been reported by Choi and Min [15]. The addition of 2 mole% of $CoSO_4$ was reported to promotes the densification of SnO_2 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_2, promoting an increase of diffusion through the SnO_2 lattice [16]. $CoSO_4$ in solutions within the SnO_2 structures acts as an acceptor, leading to creation of additional oxygen vacancies in the SnO_2, and thus increasing the densification rate of this oxide. $CoSO_4$ segregates at the SnO_2 grain boundaries and creates a large oxygen vacancy concentration there. Co_3O_4 has been reported to enhance CO sensitivity for the In_2O_3-based CO sensor [17]. SnO_2 (n)-Co_3O_4 (p) composites were of n- or p-type depending on whether they were SnO_2-rich or Co_3O_4-rich [14]. The observed better sensing properties have been attributed to the active role played by Co_3O_4 grains and porosity in the film. The Co_3O_4 grains combine with SnO_2 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_3O_4 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_2) thick film sensors.

In this paper we report the sensing characteristics of cobalt doped tin oxide (Co–SnO_2) thick film sensor for LPG and CNG gas sensitivity. SnO_2 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 $CoSO_4$. The transient response characteristics were determined at different temperatures and concentrations.

2. Experimental

Undoped SnO_2 powder was prepared using the precipitation route [18]. For this 0.1 M $SnCl_4{\cdot}6H_2O$ solution was prepared and pH was adjusted to 7 by drop wise addition of diluted NH_4OH solution. The precipitate was then washed with an ammonium nitrate solution till no chloride ion was

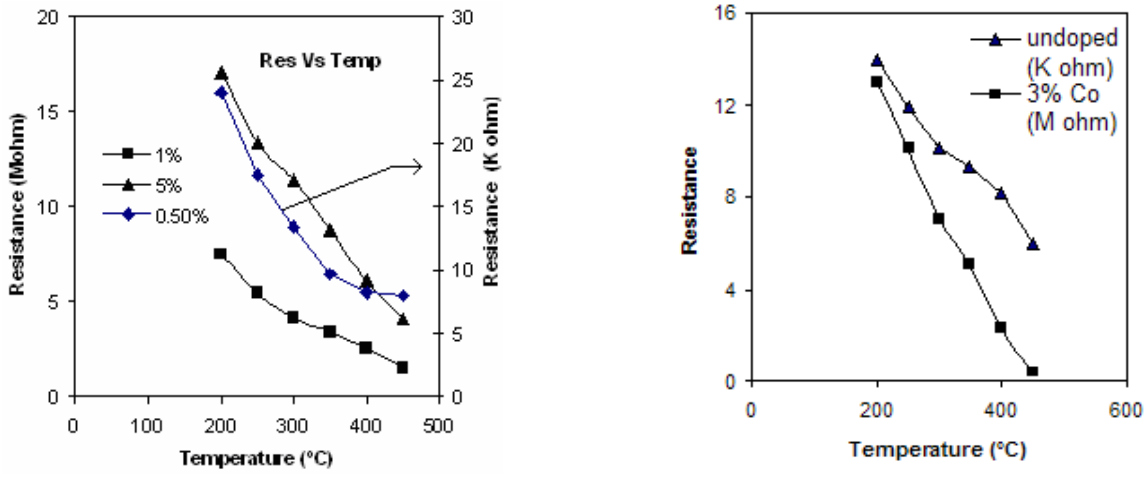
detected on $AgNO_3$ test. Then the precipitate was washed with ethanol - added water to remove nitrate ions. This powder was then dried and calcined at 600 °C for 4 h. Cobalt doped sensors were prepared by the impregnation method, i.e., the metal salt ($CoSO_4$) in required amount was dissolved in water. Calcined tin oxide powder was dispersed in this metal salt solution, and then dried. This dried powder containing different concentrations (0 to10 wt %) of dopant was used to prepare gas sensors. Thick paste was prepared using α-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 °C for 1 h. These sensors were finally fired at 800 °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_{air}) to resistance in gas environment (R_{gas}). Sensor devices were annealed at 450ºC 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 ºC at steps of 50°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_{air} is seen to increase sharply by about four orders of magnitude after cobalt doping. Such a sharp increase in R_{air} with increasing amount of cobalt addition had been reported earlier and was considered as reflecting electronic interactions taking place between SnO_2 and cobalt [14].



(a) (b)

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

Fig. 2 shows a representative ln(R) verses 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.

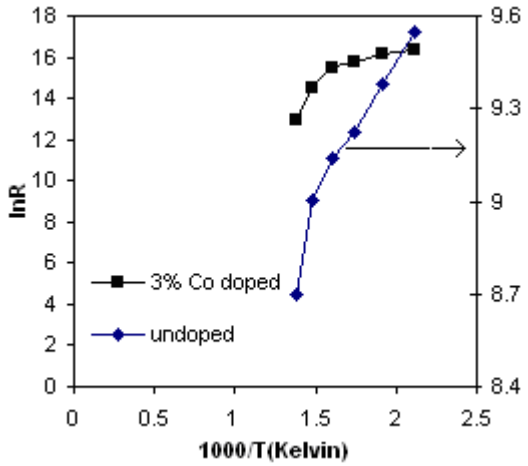
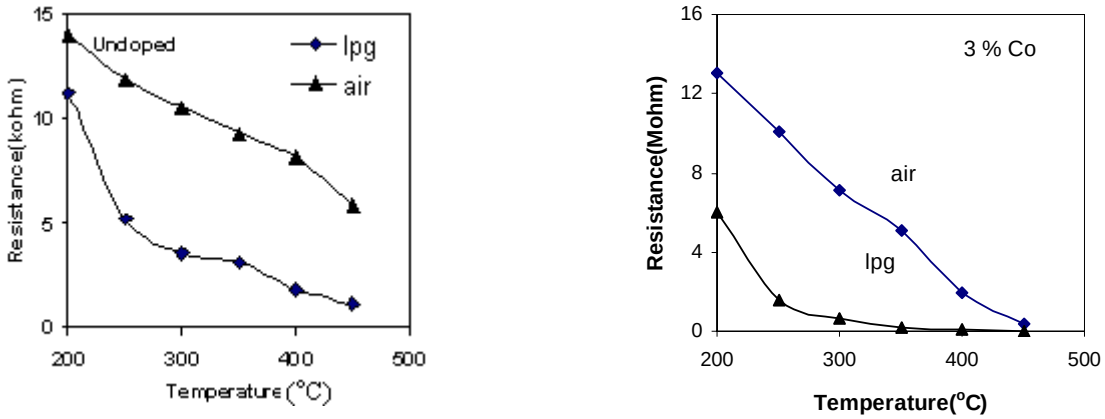


Fig. 2. Variation of ln(R) of undoped and 3% Co-doped tin oxide gas sensor for different temperature.



(a) (b)

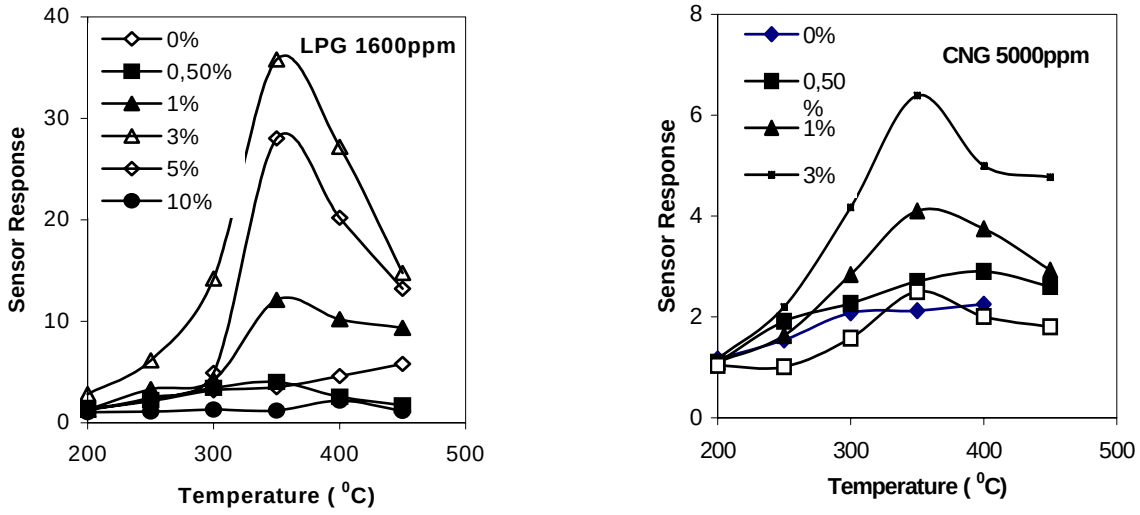
Fig. 3. Change in resistance with temperature (a) Undoped and (b) 3 % Co-doped tin oxide sensor in air and 1600 ppm LPG.

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_2 to 35.3 for 3 % Co-doped SnO_2. 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_2 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 350ºC 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_2 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_2-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_3O_4 (p) has larger work function than SnO_2. When SnO_2–Co_3O_4 heterocontacts are formed, conduction electrons of SnO_2 grains are drawn toward Co_3O_4, increasing the electrical resistance in air (R_{air}) as actually observed. Upon exposure to reducing gas, Co_3O_4 is reduced more preferentially than SnO_2, so that the conduction electrons are given back to SnO_2, leading to large sensor response. This mechanism of promotion (electronic sensitization) is essentially the same as has been observed in the PdO-loaded SnO_2 sensor [19]. As was so for the PdO loading, the optimum Co_3O_4 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].



(a) (b)

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

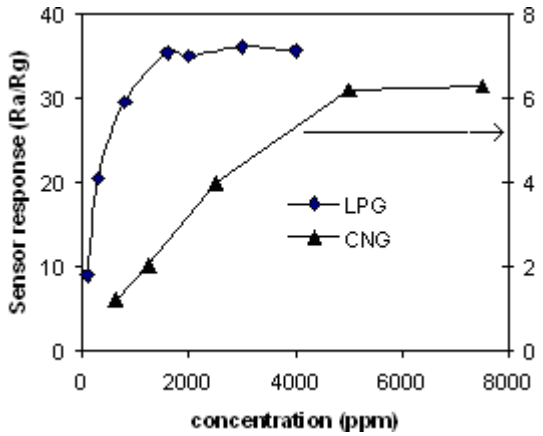


Fig. 5. Sensor response concentration of LPG and CNG for 3% Co doping at 350^{0}C.

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_2 sensor at 350°C. The speed of response of pure SnO_2 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.

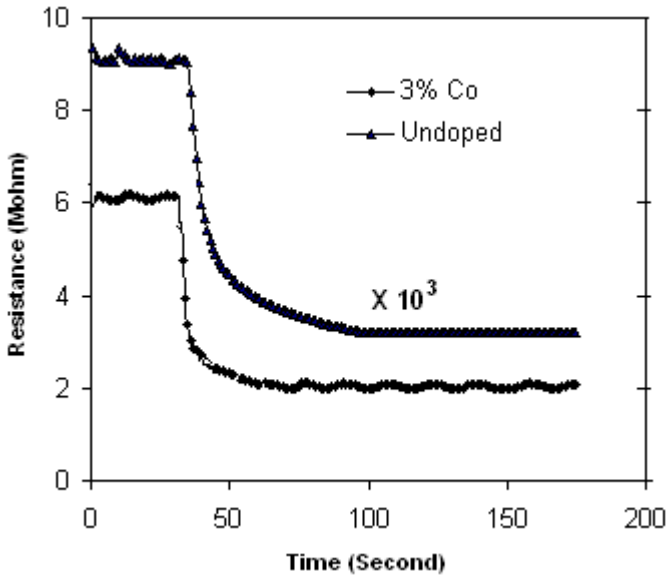
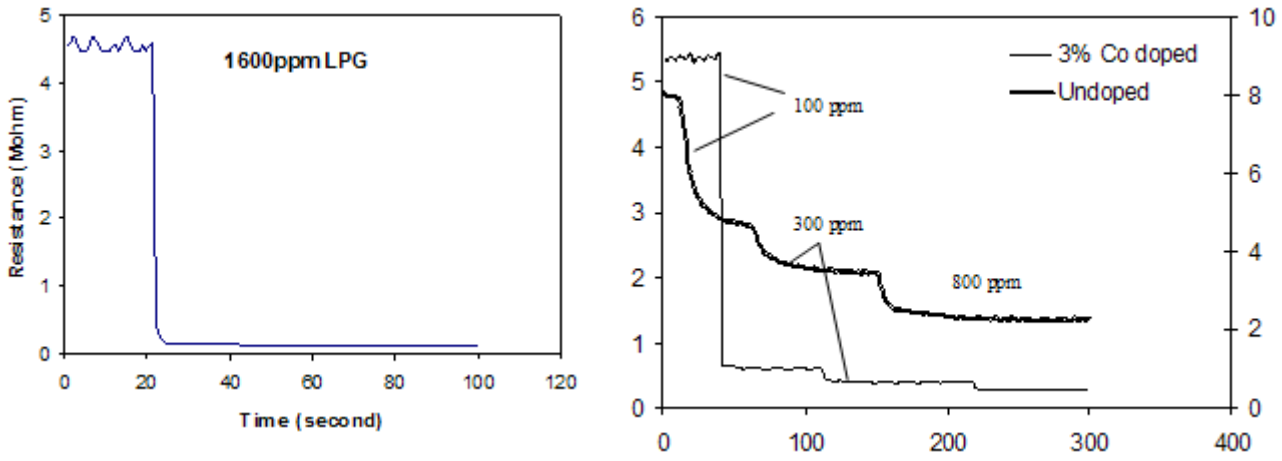


Fig. 6. Response time curve at 350^{0}C for 3 % Co-doped and undoped tin oxide gas sensor for 5000 ppm CNG.



(a) (b)

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

Fig. 7 (a) shows the transient response curve for 3 wt % Co-doped SnO_2 sensors to 1600 ppm LPG at 350ºC. 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 350ºC 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_2 using SILD method and found an appreciable improvement in the rate of response to H_2 gas. This finding is similar to the present report, where faster response to LPG and CNG has been established for Cobalt-doped SnO_2 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).

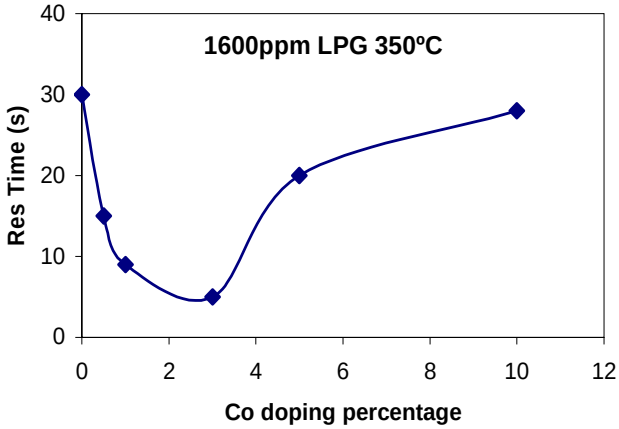
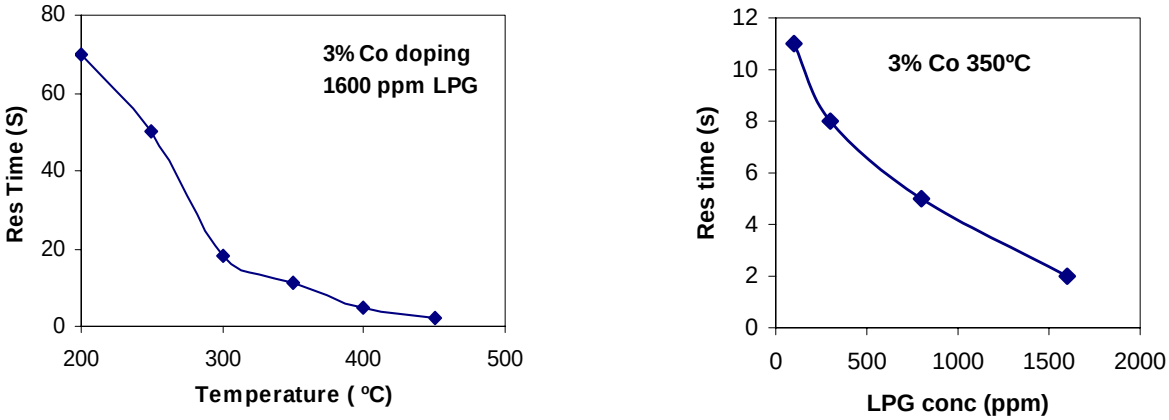


Fig. 8. Variation of response time with cobalt doping percentage.



(a) (b)

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 verses 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_2 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_3O_4 or CoO at the surface of SnO_2. 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^{+2} substituting at Sn^{+4} sites increases the oxygen vacancies. The high densification of Co-doped SnO_2 is promoted by enhancing solid state diffusion from oxygen vacancy creation near to the grain boundaries of the SnO_2 grains. These large oxygen vacancy concentrations get filled by chemical adsorption of oxygen and hence increase the resistance of SnO_2 samples. Another effect of dopant addition may be the reduction in the grain size. In the present work, the cobalt compound wad 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_2, when exposed to air, adsorbs oxygen ions O_2^- or O^- 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_2, 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^- 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 (Vs) when hopping from one grain to another. In this hypothesis, the conductance of the sensing layer can be expressed by [22, 23]

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

where σ_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.

$$eV_s = \frac{e^2 N_s^2}{2\varepsilon_r \varepsilon_0 N_d}, \quad (2)$$

where N_s is the surface density of adsorbed oxygen ions (O_2^- or O^-), $\varepsilon_r\varepsilon_0$ 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.

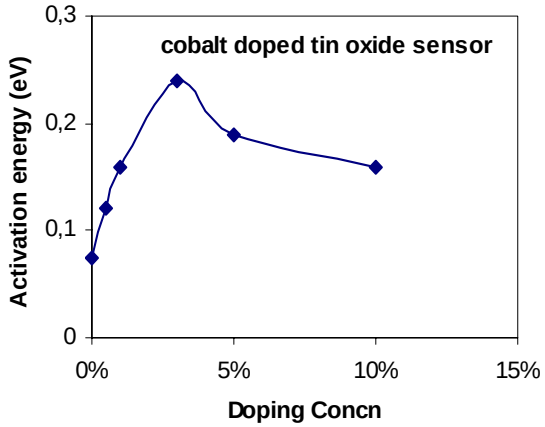


Fig. 10. Dependence of Activation energy on doping concentration.

On increasing the dopant concentration, the Schottky barrier height increases up to x ≤ 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_2 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_4 with all the second row transition metal cations (M^+) by ab. initio methods [25] and demonstrated the very strong stabilization of M^+-CH_4 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_2–CoO (n-p) heterocontacts are formed, conduction electrons of SnO_2 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_2, so that the conduction electrons are given back to SnO_2, leading to large sensor response. In reducing environment CoO is converted to Co and resistance decreases (similar to Cu-SnO_2 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_2 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_2 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_2 sensor.

5. Conclusion

The response of SnO_2 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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Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

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