

# The Effects of Additions of In & Sb on Resistivity & Sensitivity in Tin Oxide Gas Sensors

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## In과 Sb의 첨가가 Tin Oxide 가스센서에서 Resistivity와 Sensitivity에 미치는 영향

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### Abstract

To determine the effect of additions of trivalent and pentavalent ions on the electrical conductivity and sensing behaviour, indium and antimony were incorporated in tin oxide by the coprecipitation method. Antimony may be considered to enter the cassiterite structure as pentavalent ions, thermal energy could excite electrons from these ions into the conduction band. Similarly the indium ions would enter the lattice as  $In^{3+}$  but could accept electrons from the valence band, thereby becoming monovalent or divalent. These phenomena, however, how the potential barrier existing  $SnO_2$  by addition of two kinds of ions could influence on the sensing behaviour in comparison with their influence on the resistivity were observed.

### 요 약

3가와 5가이온의 첨가가 전기전도도 및 감응도에 어떤 영향을 미치는가를 확인하기 위하여, In와 Sb를 Tin Oxide에 공침법으로 첨가하였다. Sb는 5가 이온으로 cassiterite 구조에 들어가서 열에너지에 의하여 이들 이온을 여기시켜 전도대로 밀어올리리라고 여겨진다. In 이온은 결정격자 속에  $In^{3+}$ 로 들어가서 원자가대로 부터 전자를 받게 되고 그러므로써 1가나 2가가 되리라 생각한다. 그러나, 이러한 현상들이  $SnO_2$ 에 존재하는 전위장벽을 2종의 이온첨가에 의하여 일어나는 resistivity에 끼치는 영향과 비교해 볼 때 감응도에는 어떤 영향을 보이는지 고찰하였다.

### I. Introduction

Indium and antimony were incorporated on  $SnO_2$  to examine their effect on electrical conductivity and gas sensing properties. In the case of indium additions, conductivity of  $SnO_2$  is expected to decrease as also would the sensitivity. The opposite effects would be expected to occur

with antimony doping.

In general, pure  $SnO_2$  sintered material formed by calcination of  $\alpha$ -stannic acid has an appreciable conductivity in the range of  $10^{-1} \sim 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$ . The addition of the group III element, In, causes resistivity to increase while addition of the group V element, Sb, cause it to decrease.<sup>[1~4]</sup> In the case of antimony, however, resistivity was first found to decrease and then gradually increase as the doping level went beyond a certain amount. This effect on resistivity with Sb may be explained by the controlled valency mechanism.<sup>[1]</sup>

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Nonstoichiometric  $\text{SnO}_2$  may be represented by  $\text{Sn}_{1-\delta}^{4+}$ ,  $\text{Sn}_{\delta}^{2+}$ ,  $\text{O}_{2-\delta}^{2-}$ <sup>[1]</sup> by combining  $\delta$  moles of  $\text{SnO}$  with  $(1-\delta)$  moles of  $\text{SnO}_2$ . This is a semiconductor since the 2 moles of electrons formally assigned to the  $\text{Sn}^{2+}$  ions will be free to move to other  $\text{Sn}^{4+}$  sites, thus  $\delta$  moles of oxygen vacancies can donate  $2\delta$  moles of electrons for conduction.

## II. Experimental

### 1. Preparation of samples

Indium and antimony doping was carried out by coprecipitating  $\text{InCl}_3$  (99.999%) or  $\text{SbCl}_3$  (99.5%) with  $\text{SnCl}_4$  (99.999%). The  $\text{SnCl}_4$  was first diluted to about 1 : 10 with deionized water. The dopant chlorides, similarly diluted, were added to the  $\text{SnCl}_4$  and thoroughly mixed by stirring. The amount of dopant was controlled to give 0.025, 0.05, 0.1 and 1.0 w/o indium or antimony in the final product. Diluted ammonia solution was then added to the chloride solution while being stirred. The resulting precipitate was then filtered through a 10–15 $\mu\text{m}$  fritted glass filter. The precipitate was continuously washed with deionized water while being vacuum filtered. The chloride ion content of the dried precipitate was periodically checked by a colorimetric method, ASTM D512, to give a final chloride content of 0.5 w/o chloride in each sample precipitate.

The precipitates from filtration were dried in an electric oven at 110°C for 24h, the ground in an agate mortar. The sample powders were placed in alumina crucibles and fired at 650°C for 2h in air. The final dopant concentration in the heat treated  $\text{SnO}_2$  was determined by optical emission spectrography (Jarrell-Ash, U.S.A.). The  $\text{SnO}_2$  suspension was adjusted to a controlled viscosity by the drop wise addition of ethylalcohol while being ground. The electroded mullite tube was then dipped into the suspension to be coated

with a film which, when dried, was about 0.1  $\mu\text{m}$  thick. This is termed a "Thick film" in the present work. The tube was then fired under the same conditions of temperature and atmosphere as that used in the original calcination of the  $\text{SnO}_2$  powder.

The heater, which is a coil to attain the required surface temperature of the sensor, was inserted into the sensor core and arranged to the electrical connections. The test sensors were aged for at least two days before the measurements were made.

### 2. Measurements

Characteristics of the sensor evaluated changes in resistance using the circuit, Fig. 1. The total voltage applied to the sensing circuit,  $V_C$ , was applied by means of a dc power supply. The sensing element (resistance  $R_S$ ) was connected in series with a variable resistor,  $R_L$ . By adjusting the value,  $R_L$ , the total resistance of the circuit ( $R_S + R_L$ ) and hence the current could be controlled and a recorder was connected to record the output voltage from the circuit,  $V_L$ .

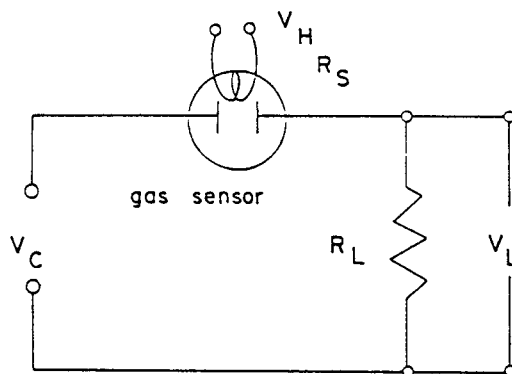


Fig. 1. Electric circuit for testing gas sensitivity.

A gas concentration was adjusted by means of injecting an adequate amount of gas into a test chamber with dimensions 25×40×18 cm where the sensor was placed. The sensor was heated in the temperature range between room

temperature and  $600^{\circ}\text{C}$ . The surface temperature of the sensor was checked with an infrared thermometer. The sensitivity of the sensor to a particular gas, therefore, at a constant temperature, is expressed by subtracting the output voltage of the sensor  $[V_L = R_L / (R_s + R_L) \times V_c]$  in air from that of the output voltage in the test gas,  $V_g - V_0 : V_0$  and  $V_g$  denote the sensor output voltage for air and for the test gas, respectively.

### III. Results

#### 1. Electrical conductivity of Sb-doped $\text{SnO}_2$

The conductivity of Sb-doped  $\text{SnO}_2$  for different sensor operating temperatures, i. e.  $300$ ,  $200$ ,  $100$  and  $25^{\circ}\text{C}$ , is shown in Fig. 2 from which it can be seen that the conductivity changes little with operating temperature but increased with the increase of Sb-doping. In the range from  $25^{\circ}\text{C}$  to  $300^{\circ}\text{C}$  the increase in conductivity may be explained on the controlled valence model, i. e. an increase of the donor electrons with increasing Sb content. Fig. 3 shows the linear increase in conductivity with doping level at  $200^{\circ}\text{C}$ . Marly<sup>[5]</sup> noted that the resistivity of  $\text{SnO}_2$  single crystal incorporating 300 ppm Sb remained constant at  $10^{-2}$  ohm $\cdot$ cm in the temperature range of 80-900 K. Loch<sup>[6]</sup> obtained similar results from polycrystalline  $\text{SnO}_2$  in that conductivity increased from 0.2 to 10 ohm $^{-1}\text{cm}^{-1}$  in the temperature range of 100-800 $^{\circ}\text{C}$  with doping from 0.00035 to 0.01 m/o Sb, and that no temperature dependence of conductivity was observed. These results also agree with the observation by Imai<sup>[7]</sup> and Paria<sup>[8]</sup> that the donor levels in Sb-doped  $\text{SnO}_2$  are fully ionized and conductivity was independent of temperature.

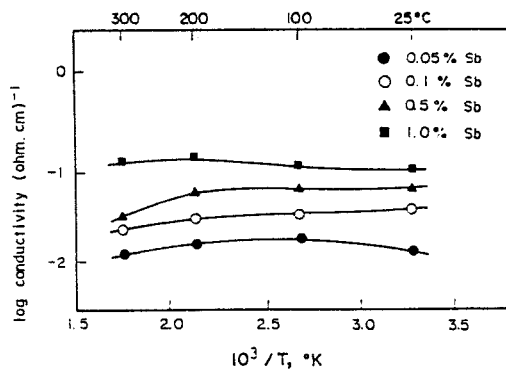


Fig. 2. Electrical conductivity of Sb-doped  $\text{SnO}_2$  sensor vs. reciprocal operating temperature.

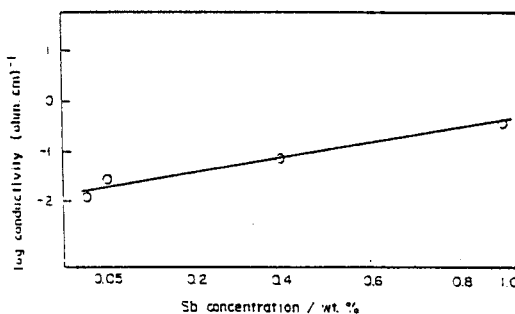


Fig. 3. Electrical conductivity dependence of Sb-doped  $\text{SnO}_2$  at  $200^{\circ}\text{C}$ .

#### 2. Electrical conductivity of In-doped $\text{SnO}_2$

Fig. 4 shows the conductivity of the In-doped  $\text{SnO}_2$  test sensors in the operating range from  $25^{\circ}\text{C}$  to  $300^{\circ}\text{C}$ . A quantitative decrease in conductivity is associated with the increase in indium doping, in contrast to the behaviour of the Sb-doped  $\text{SnO}_2$ , discussed earlier. In addition, there appears to be a small increase in conductivity with increasing operating temperature. These results indicate that the trivalent indium acts as an electron acceptor.

Antimony may be considered to enter the cassiterite structure as trivalent ions. Thermal energy could excite electrons from these ions into the conduction band, rendering the antimony pentavalent. Similarly the indium ions would enter the lattice as  $\text{In}^{3+}$  but could accept electrons from the valence band, thereby becoming mono-

valent or divalent.<sup>(1)</sup> The different effects of the two additives are clearly shown in Fig. 5 in which the logarithm of resistivity of SnO<sub>2</sub>, measured at 200°C in air, is plotted as a function of w/o of antimony or indium addition.

From Fig. 5 it can be seen that with Sb doping there is an increase and with In-doping a decrease in conductivity compared with the value for the undoped material. These observations closely agree with those of Rohatgi et. al.<sup>(9)</sup> and Carroll et. al.<sup>(3)</sup> SnO<sub>2</sub> is a typical n-type semiconductor and the extrinsic electrical properties are predominant in the lower temperature range because of the low energy of ionization of impurity centres; the intrinsic electrical properties predominate in the higher temperature range.

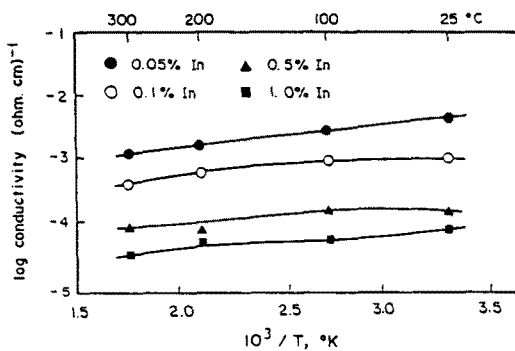


Fig. 4. Electrical conductivity of In-doped SnO<sub>2</sub> sensor vs reciprocal operating temperature.

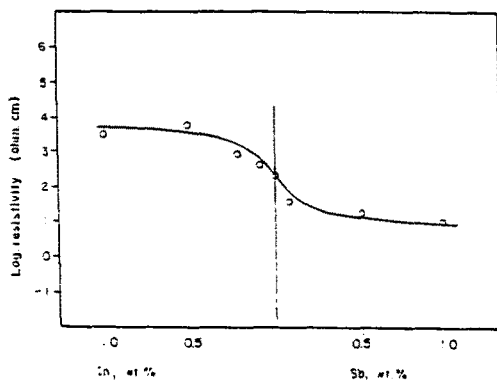


Fig. 5. The logarithm resistivity of SnO<sub>2</sub> as a function of In and Sb added concentration.

### 3. Sensitivity of Sb-doped SnO<sub>2</sub>

This particular work was undertaken to gain some information on whether or not the acceptor and donor electrons injected from Sb and In would have any influence on the potential barrier existing in SnO<sub>2</sub>.

The sensitivity of SnO<sub>2</sub> to carbon monoxide, methane and propane was examined for the pure material and SnO<sub>2</sub> doped with 1.0, 0.5, 0.1 and 0.025 w/o Sb. The sensitivities to air atmospheres with 200 ppm CO, 2000 ppm CH<sub>4</sub> and 2000 ppm C<sub>3</sub>H<sub>8</sub> of the various Sb-doped SnO<sub>2</sub> samples are shown in Fig. 6, 7 and 8, respectively. As can be seen in Fig. 6, there is no increase in sensitivity to CO of Sb-doped SnO<sub>2</sub> as compared with pure SnO<sub>2</sub>. Since small additions of Sb are known to increase the conduction electron concentration, one would expect that this increased concentration would have enhanced the sensitivity. However, the sensitivities of Sb-doped SnO<sub>2</sub> are relatively low compared with those of pure SnO<sub>2</sub>. The trends in the sensitivity of the Sb-doped SnO<sub>2</sub> to the three gases is similar to those trends observed with In-doped SnO<sub>2</sub> and both doped materials have high sensitivity to 2000 ppm propane.

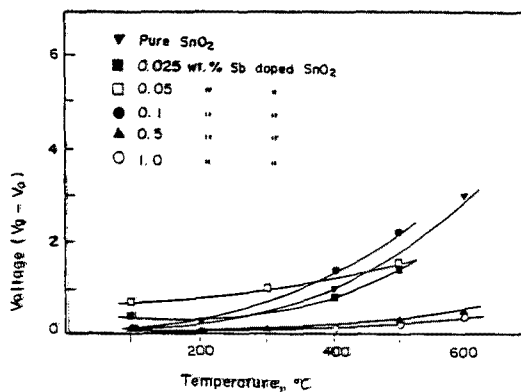


Fig. 6. Effect of Sb-doped SnO<sub>2</sub> on the sensitivity ( $V_R - V_0$ ) to 200 ppm CO.

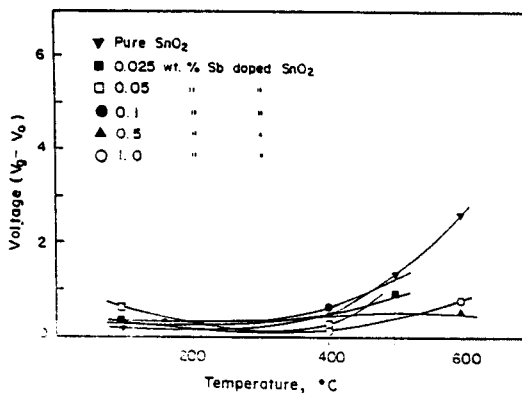


Fig. 7. Effect of Sb-doped  $\text{SnO}_2$  on the sensitivity ( $V_g - V_0$ ) to 2000 ppm  $\text{CH}_4$ .

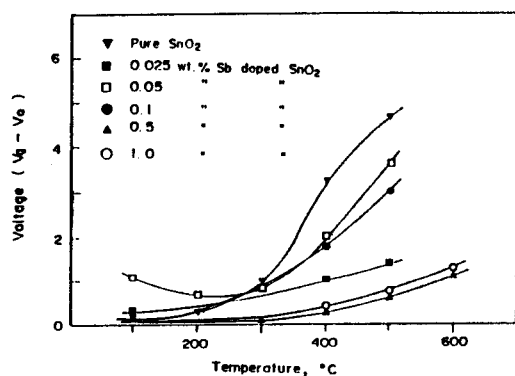


Fig. 8. Effect of Sb-doped  $\text{SnO}_2$  on the sensitivity ( $V_g - V_0$ ) to 2000 ppm propane.

#### 4. Sensitivity of In-doped $\text{SnO}_2$

Tests were carried out with carbon monoxide, methane and propane at measuring temperatures of 100 to 600°C. The contents of In were 1.0, 0.5, 0.1, 0.05 and 0.025 w/o, and tests were also made on pure  $\text{SnO}_2$  for comparison purposes. The sensitivities to air atmospheres containing 200 ppm CO, 2000 ppm  $\text{CH}_4$ , and 2000 ppm  $\text{C}_3\text{H}_8$  for the various dopant levels are shown in Fig. 9, 10 and 11 respectively. From Fig. 10 it can be seen that the sensitivity of the In-doped  $\text{SnO}_2$  is lower than that of the pure  $\text{SnO}_2$ . Although there are small fluctuations in sensitivity the general effect is a decrease in sensitivity with increasing dopant levels. In the case of methane,

with 0.5 w/o In-doped  $\text{SnO}_2$ , the unexpected increase in sensitivity, is thought to be spurious, Fig. 10. The rest of the In-doped sensors show sensitivities to the three gases lower than those of pure  $\text{SnO}_2$ . Methane is a stable compound and the activation energy for its oxidation over metal oxides is 20-23 kcal/mol. For this reason the use of In-doped materials to detect methane would not be recommended. Fig. 11 shows that propane is more readily detectable than methane. Pure  $\text{SnO}_2$  again shows higher sensi-

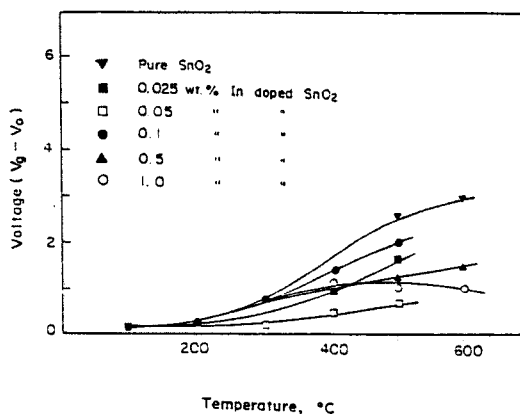


Fig. 9. Effect of In-doped  $\text{SnO}_2$  on the sensitivity ( $V_g - V_0$ ) to 200 ppm CO.

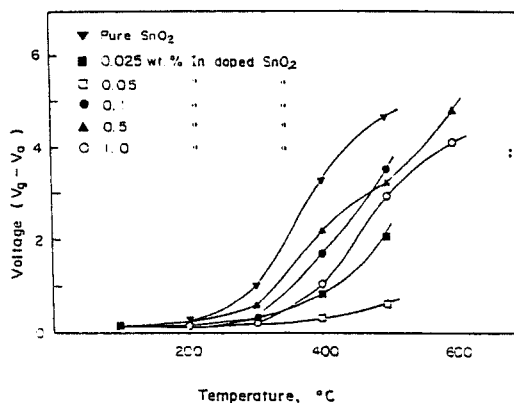


Fig. 10. Effect of In-doped  $\text{SnO}_2$  on the sensitivity ( $V_g - V_0$ ) to 2000 ppm  $\text{CH}_4$ .

vity than the doped materials. Above 400°C both doped and undoped materials show a marked increase in sensitivity to all the gases. Unfortunately, this temperature is too high for practical purposes. The increase in In doping results in a decrease in sensitivity to the three gases which parallels the decrease in conductivity with In-doping, Fig. 4. Similarly, the conductivity of the In-doped SnO<sub>2</sub> is never greater than the conductivity of pure SnO<sub>2</sub>. The more In added, the lower is the gas sensitivity.

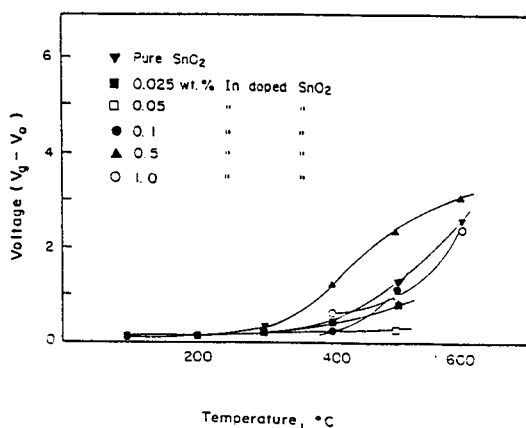


Fig. 11. Effect of In-doped SnO<sub>2</sub> on the sensitivity ( $V_g - V_0$ ) to 2000 ppm C<sub>2</sub>H<sub>6</sub>.

#### IV. Discussion

Considerable work has been carried out on tin oxide films, particularly on their electrical properties.<sup>[2,10-16]</sup> Undoped tin oxide films have n-type extrinsic conduction associated with oxygen vacancies and chloride impurity. The rise in resistivity, when these films are heat treated, is most likely due to oxidation and elimination of many of the oxygen vacancies. The n-type conduction remaining after prolonged heating is probably accounted for by the chloride ions substituting for oxygen.<sup>[3,17,18]</sup> Both of these workers observed that additions of In increased the resistance and light transmittance of SnO<sub>2</sub> films

made from the pyrolytic decomposition of SnCl<sub>4</sub>·5 H<sub>2</sub>O alcohol solution at 600°C.

Rohatgi<sup>[9]</sup> noted that the resistance increased by 4 orders of magnitude when only 3 m/o In was added and the effects of adding Sb on the sheet resistance showed minima at 3 m/o Sb. These minima in resistance coincide with maxima in the charge carrier concentration as would be expected.

Small additions of Sb caused resistivity to decrease by approximately 10 orders of magnitude compared with that of the pure material.<sup>[1]</sup>

A minimum in resistivity occurred at additions of 0.9 m/o,<sup>[19]</sup> 0.6 m/o,<sup>[20]</sup> and 3 m/o<sup>[9]</sup> Sb. Since small additions of Sb are known to increase conduction electron concentration, one would expect larger additions to do the same. However, the unexpected rise in resistivity has been attributed to impurity scattering,<sup>[19]</sup> atomic disorder<sup>[9]</sup> and precipitation of Sb<sub>2</sub>O<sub>5</sub>.<sup>[20]</sup> Indium ions, on the other hand, would be in the lattice as In<sup>3+</sup> but could accept electrons from the valence band, thereby becoming monovalent or divalent and thereby resulting in a decrease in conductivity.

The controlled valence mechanism would apply to solids with ionic bonding. A consideration of the differences in electronegativities<sup>[21]</sup> of Sn and O shows the Sn-O bond to be equally ionic and covalent. A covalent model for semiconduction would regard In (Group III) and Sb (Group V) atoms as being acceptors and donors respectively in tin (Group IV) oxide, as they do in the covalently bonded Si and Ge (Group IV) semiconductors. The controlled valency and covalent models both qualitatively predict the observed resistivity vs impurities behaviour, and both mechanisms may be operative.<sup>[3]</sup> Small additions of antimony cause resistivity to decrease by providing more donors, but large addition have caused the resistivity to increase. Carroll et al.<sup>[3]</sup> noted that the large increase in resistivity is associated with a loss in crystallinity which

becomes progressively more pronounced as more antimony is added. The loss of crystallinity results in a behaviour typical of amorphous semiconductors in which impurities do not serve as electron donors or acceptors.<sup>[22]</sup>

Carroll and Slack<sup>[3]</sup> maintained that in their SnO<sub>2</sub> thin films those with low resistivities, i. e. those with less than 3 m/o Sb, had very low activation energies for electrical conduction, which indicated that they approached or overlapped the conduction band. As resistivity rises with In additions, the activation energy rises because a number of the donors would be compensated for by the In, thereby decreasing the donor band width.

The migration of electrons associated with the adsorption and desorption of gas depends on the characteristics of the gas molecule and the surface of the solid. In the case of saturated hydrocarbon, i. e. methane and propane, these do not have a functional group in the molecular structure so that the adsorption of the molecule is followed first by dissociation on the surface of oxide<sup>[23]</sup> before reaction with adsorbed oxygen. Therefore, as can be seen in Figs. 6–11, sensitivity to methane and propane is found at the relatively higher temperatures.

## V. Conclusions

Addition of In caused resistivity to increase and small additions of Sb caused it to decrease in the temperature range from 25°C to 300°C. These results agreed with those of previous work and were consistent with the controlled valency model in both cases, the In and Sb being regarded as acceptors and donors respectively.

The decrease in conductivity with In additions, in the concentration range of 0.025 w/o and 1.0 w/o, was due to the increasing numbers of extrinsic donors being compensated by the In, thereby decreasing the donor band width. Be-

cause of this negative effect on conductivity it was decided not to use In as the sensing material. Though there was an increase in conductivity with the addition of Sb in the concentration range of 0.025 w/o and 1.0 w/o, which was predictable, there was no improvement in sensitivity to CO which was unexpected. No reason can be offered for this behaviour. It was decided not to use this dopant.

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