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# SPRAY DEPOSITED $SNO_2$: SB THIN FILMS FOR OXIDIZING AND REDUCING GAS SENSORS

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**ABSTRACT**
Metal-oxide based thin film gas sensors have found wide applications for the control of different industrial processes. Tin-oxide demonstrates high thermal and chemical resistivity and sensitivity to different gases. Among the various methods available, Spray Pyrolysis is preferred for the preparation of $SnO_2$:Sb thin films. The as-deposited films are blackish in color. There is little increase in thickness with increase in addition of antimony doping. The X-ray diffraction pattern shows characteristic tin-oxide peaks with tetragonal structure. As doping concentration of antimony was increased new peak corresponding to Sb is observed. The concentration of antimony was varied from 0.01% to 1%. Ohmic contacts are preferred for the gas sensing studies. The gas sensing properties were studied for CO and $NO_2$ gases. The maximum sensitivity was observed for Sb=1% at a working temperature of $250^0$C.

**KEY WORDS: $SnO_2$:** Sb, Sensitivity for CO and $NO_2$ gases, Spray-pyrolysis.

## INTRODUCTION

$SnO_2$ is one of the promising candidate materials for gas sensing applications. $SnO_2$ serves as an important base material in a variety of resistive type gas sensors. The widespread applicability of this semiconducting oxide is related both to its range of conductance variability and to the fact that it responds to both oxidizing and reducing gases. It has also peculiar properties of large surface area and small grain size which is expected to exhibit a high sensitivity to the detected gases [Shen *et al*., 2009]. Gas sensing mechanism of $SnO_2$ consists of the interaction of gas species with the surface that cause the changes in concentration of oxygen vacancies near the surface which acts as n-type donors localized below the bottom of conduction band. Because of this, a significant density of electronic state is observed in the band gap close to Fermi level. Due to this, there is a change in the concentration of the free carriers in the surface space charge region which in turn changes the electrical conductivity. In the present work, $SnO_2$: Sb thin films were successfully deposited by spray pyrolysis technique, and the physical properties of $SnO_2$ had been investigated .Also the gas sensing properties of $SnO_2$:Sb films were studied. The gases employed were Nitrogen Dioxide [Sutrave. *et al*., 2011] and Carbon Monoxide.
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## EXPERIMENTAL DETAILS

### a. Deposition of Antimony doped thin films:

Structured properties of the films are mainly dependent on deposition techniques and deposition parameters. In addition, doping also has a large influence for improving sensing properties of the films [Wang *et al*., 2010]. The undoped tin oxide films were prepared by spray pyrolysis method by spraying a solution of tin tetrachloride ($SnCl_4.5H_2O$) dissolved in isopropyl alcohol on to the heated glass substrate at $375^0$C using a compressed air as atomization gas. The nozzle size, distance from glass substrate rate of motion of nozzle was properly controlled to obtain a good quality adhesive films. For antimony doped sample, antimony trichloride solution ($Sb_2Cl_3$) was added to the starting as a solution. The concentration of antimony was varied from 0.01% to 1%.The experimental set up for deposition can be diagrammatically represented as shown in figure.1.

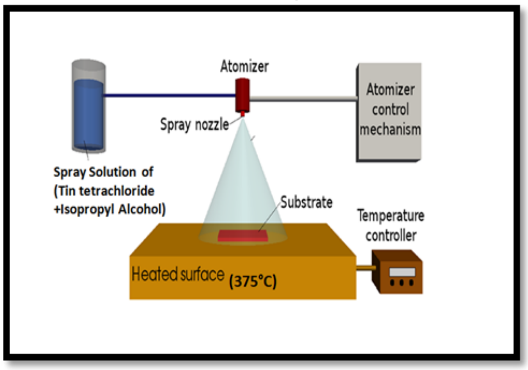


**Figure 1. Experimental set up for deposition of thin films.**

**a.Structural Analysis by XRD:**

The x-ray diffraction patterns were obtained for all these samples by using Bruker D8 advanced instrument with source CuKα1 with λ =1.5406 . The angle 2θ was varied in the range between $10^0$ to $100^0$.

**b.Gas detection experiments:**

The gas sensitivity chamber using quartz tube was constructed to study the sensitivity of antimony doped tin-oxide thin films and details were published Elsevier [Joshi *et al*., 2011] Figure. 2. Shows the gas sensor element. Silver paste contacts were made at the end of sensor.

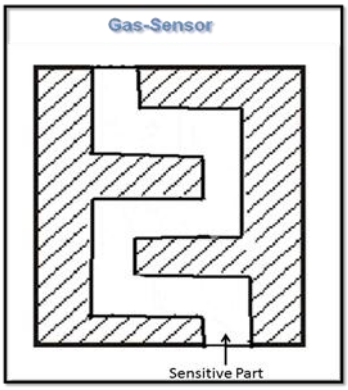


**Figure 2. The Gas Sensor Element**

The gas sensitivity tests were carried out for CO and $NO_2$ gases. By applying a constant voltage, the resistance of the sensor was recorded. The current through the sensor was measured. The I-V characteristics were plotted to find the type of contacts. The samples were heated from room temperatures to $400^0$C by using a heating resistance. The sample temperature was monitored and controlled by thermocouple attached to the substrate. A constant amount of CO and $NO_2$ (550 ppm) was injected to the testing chamber. The sensing characteristic of the sensors were then recorded by the change in the electrical resistance. The film resistance in the presence of gas was calculated at different temperatures. The sensitivity, in the case of resistive gas sensors is defined as the ratio of the resistance of the sample measured in air to the target gas containing atmosphere.[Lee *et al*., 2002]

Hence, Sensitivity for oxidizing gas can be calculated by the formula as equation (1),

$$S=(R_O-R_G)/R_O \quad \text{------------------------------------(1)}$$

Sensitivity for reducing gas can be calculated by the formula as in equation (2),

$$S=(R_G-R_O)/R_O \quad \text{-------------------------------(2)}$$

**RESULTS AND DISCUSSIONS**

The as-deposited films are blackish in color. The films are well adherent to the substrate. The thickness of the as deposited films was calculated by weight –difference method. The thicknesses of the films are in the range of micrometer. It has been reported that the thickness of the sensitive layer does play a role in determining the sensitivity of the sensor for different gases. Thus sensitivity of metal oxide sensor is directly influenced by the size of the oxygen induced depletion layer at the film surface relative to the thickness of bulk semiconductor Variation of thickness of the film with increasing concentration of Antimony is shown in Figure. 3.

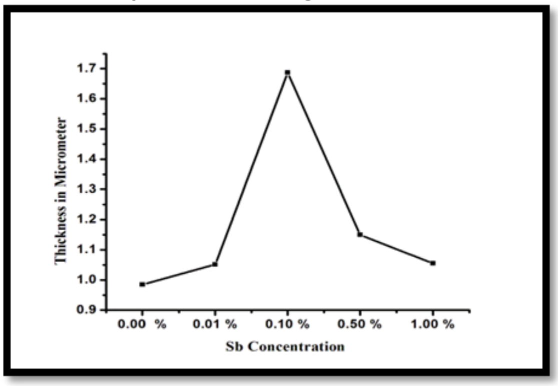


**Figure 3 . Variation of Thickness with increasing Sb concentration**

**A. X-Ray Diffraction Analysis**

Figure. 4. Shows the X-ray diffraction pattern for the tin oxide thin films with doped and un-doped antimony. The observed data is compared with ASTM/JCPDA data card [JCPDS card 41-1445; JCPDS card 5-562]. All the diffraction pattern shows characteristic tin oxide peaks with tetragonal structure. The dominating peak correspond to the [110] plane. The addition of antimony impurity give rise to a new peak corresponding to [011] plane of Sb .The intensity of this peak was increased when the Sb concentration was increased from 0.01% to the 1% which indicates the antimony was incorporated into the tin oxide.

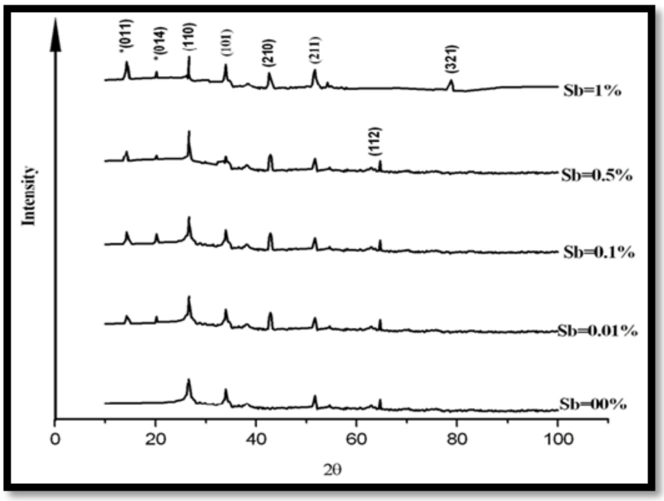


**Figure. 4. X-ray Diffraction Pattern for Antimony Doped Tin-Oxide Thin Films.**

**B. GAS SENSING PROPERTIES**

Ohmic contacts were preferred for gas sensing studies. The changes in resistance of sensor are due to only adsorption of gas molecules. An ohmic contact represents that there is no accumulation of charge carriers in interface of contact [Ray *et al*., 2010] The I-V characteristics were plotted as in fig 5. shows the straight line nature of graph which implies that the contact with $SnO_2$ film is ohmic.

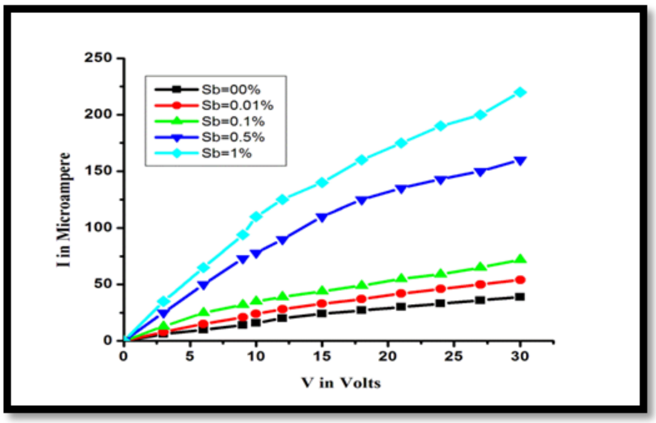


**Figure 5. I-V Characteristics of Sensor**

Depending on the temperature, the bond between the gas molecules and the sensor surface are broken at certain rate. For a given concentration of gas, the molecules leaving the surface are replaced by new molecules, producing a steady state situation. Hence for the working of gas sensors a certain temperature is required [Thokura. *et al*., 1994].When such films are heated at higher temperatures, oxygen is absorbed by $SnO_2$ layers and abstract electrons from surface states thereby increasing the film resistance. This results in the formation of ionic species such as $O_2^-$,$O^{2-}$ and $O^-$.

The adsorption/desorption of oxygen species at the surface due to presence of Sb causes change in Fermi level of the grains and hence changes the grain boundary potential barrier.

Figure.6.shows variation of Current with Temperature of sensor without sensing gas. The graph shows linear increase in current with temperature.

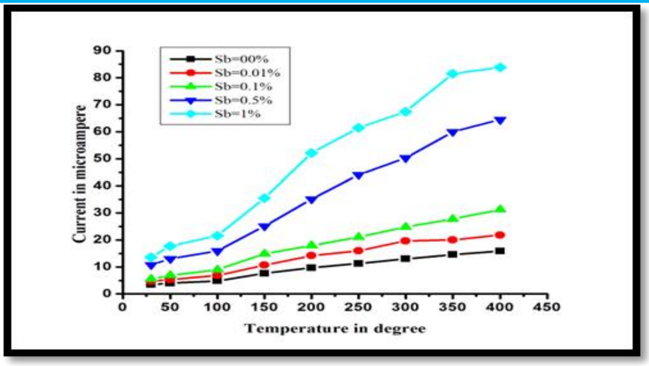


**Figure 6. Variation of Current with Temperature without Sensing Gas**

In the present work, the sensing gas used is $NO_2$ which is oxidizing gas. As oxidizing gas, increases the charges in the system algebraically, it increases oxygen from the surface, proportion to its concentration, there by injecting the electrons into the metal oxide and increasing the resistance. The oxidizing gas will react with adsorbed $O^-$ and inject into the semiconductor, tending to increase the barrier for the electrons through grains. Thus, the conductivity of the material decreases.[Rantala *et al*, 1998] Due to this gas, the adsorption of oxygen causes change in Fermi level and in turn potential barrier.
Figure. 7.Shows the Current Vs Temperature profile in the presence of sensing gas. Due to the presence of oxidizing gas( $NO_2$ ) the conductivity decreases abruptly.

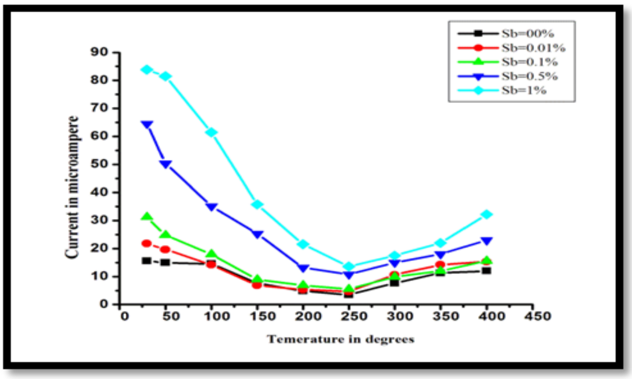


**Figure 7. Current Variation with Temperature in presence of sensing gas $NO_2$**

Atmospheric oxygen extracts the electron from near-surface region that leaves positively charged donor ions and negatively charged oxygen ions on the surface. Due to this, resistance of the film increases which in turn is related with sensitivity of the gas sensor.
Figure. 8. Shows the sensitivity to $NO_2$ gas as a function of operating temperature for the $SnO_2$ doped with different Sb concentration.

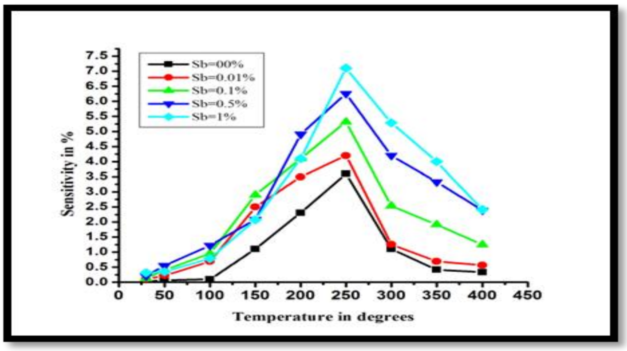


**Figure 8. Sensitivity of $NO_2$ gas Vs Temperature**

It can be seen that the sensitivity of $SnO_2$ films was increased with Sb concentration.. It was found that the sample containing 1% of Sb concentration has the highest sensitivity at operating temperature 250 $^0$C for $NO_2$ gas. Similar types of results were observed by [Ray *et al*., 2010: Shamala *et al*., 2006; Hamd *et al*., 2009]. A reducing gas removes oxygen from the surface, in proportion to its concentration, thereby re-injecting the electrons into the metal oxide and decreasing the resistance. Hence the conductivity of the material increases [Boshta *et al*., 2010].

Figure. 9 shows the sensitivity to CO gas as a function of operating temperature for the $SnO_2$ doped with different Sb concentration. It was observed that the sample containing 1% of Sb concentration has the highest sensitivity at operating temperature 250 $^0$C for CO gas.

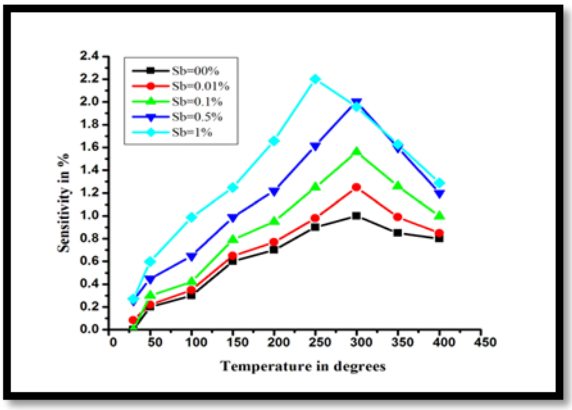


**Figure 9. Sensitivity of CO gas Vs Temperature.**

## CONCLUSIONS

The spray deposited thin film of antimony doped tin oxide were adherent to the substrate. The color of pure (undoped) sample was black. Addition of antimony in tin oxide changes the color to slighly gray. The thicknesses of all the samples were around micrometer. The diffraction pattern showed characteristic tin oxide peaks with tetragonal structure. Antimony doped sample showed new peak [011] corresponding to the pure Sb. The sensitivity of $SnO_2$ increased with increasing Sb concentration. It was found that the sample with 1% Sb shows highest sensitivity for $NO_2$ as well as for CO gases operated at 250$^0$C.

## ACKNOWLEDGMENT

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## REFERENCES

**Boshta, M., Mahmoud, F., Sayed, M., (2010),** Characterization of Sprayed $SnO_2$:Pd Thin Films For Gas Sensing Applications, Journal of Ovonic Research

**Joshi, P.S., Sutrave, D. S., Jogade, S. M., Jamadar, B. N. (2011).** Structural And Gas Sensing Properties of Sprayed Antimony Doped Tin Oxide Thin Films, *Proc. of SPIE*
**Vol. 85490Y-1**

**Joshi, P., Jogade, S., Lohar,P., Sutrave, D, (2011).** Antimony Doped Tin Oxide Thin Films: CO Gas Sensor. , Journal of Nanoelectron Physics.

**Shen, Y., Yamazaki, T., Liu,Z., Meng, D.,Kilkuta, T.,2009** Hydrogen Sensing Properties of Pd-Doped SnO2 Sputtered Films with Columnar Nanostructures, *Thin Solid Films*

**Wang, C., Yin, L., Zhang, L.,Xiang, D.,Gao, R. (2010).** Metal Oxide Gas Sensor: Sensitivity and Infulencing Factors, *Sensors*

**Lee, D.,Kim, Huh, J., Lee,D., (2002).** Fabrication and Characteristics of SnO2 Sensor Array For Volatile Organic Compounds Recognition, *Thin Solid Films* **JCPDS Data Card 41-1445**

**Ray, S., Gupta, P., Singh, G., (2010),** Electrical and Optical Properties of Sol-Gel Prepared Pd-doped $SnO_2$ Thin Films: Effect of Multiple Layers and Its Use as Room Temperature Methane Gas Sensor, *Journal Of Ovonic Research*

**Thokura, K.,Watson, J.,(1994),** The Stannic Oxide Gas Sensors: Principles and Applications , *CRC Press*, Boca Ratson

**Ihokura, H., Okino, K., (1983)**, *Sensor Technol*

**Morrison, (1987),** Selectivity in Semiconductor Gas Sensors, *Sensors and Actuators*

**Rantala,L., Lanto,V., Rantala,T., (1998),** Computational Approaches to the Chemical Sensitivity of Semiconducting Tin-Oxide , *Sensors and Actuators*

**Shamala, K., Murthy, L.Rao, K., (2006),** Gas Sensing Properties of Undoped and Doped Tin Oxide Films Prepared by Spray Pyrolysis and Electron Beam Evaporation Method , *Indian Journal of Pure and Applied Physics*

**Hamd,W., Wu,V.,Boulle, A.,Thune,E., Guine Bretiere,R., (2009),** Microstructural Study of $SnO_2$ Thin Layers Deposited on Sapphire by Sol-Gel Dip Coating , *Thin Solid Films.*