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ANTIMONY DOPED TIN OXIDE THIN FILMS: CO GAS SENSOR

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Tin dioxide (SnO_2) serves as an important base material in a variety of resistive type gas sensors. The widespread applicability of this semicoducting oxide is related both to its range of conductance variability and to the fact that it responds to both oxidising and reducing gases. The antimony doped tin-oxide films were prepared by spray pyrolysis method. The as-deposited films are blackish in colour. Addition of antimony impurity showed little increase in the thickness. The X-ray diffraction pattern shows characteristic tin oxide peaks with tetragonal structure. As the doping concentration of antimony was increased, new peak corresponding to Sb *was observed. The intensity of this peak found to be increased when the* Sb *concentration was increased from* 0.01 % *to the* 1 % *which indicates the antimony was incorporated into the tin oxide. For gas sensing studies ohmic contacts were preferred to ensure the changes in resistance of sensor is due to only adsorption of gas molecule. The graph of I-V shows a straight line in nature which indicates the ohmic contact. The sensitivity of the sensor for* CO *gas was tested. The sensitivity of antimony doped tin oxide found to be increased with increasing* Sb *concentration. The maximum sensitivity was observed for* Sb = 1 % *at a working temperature of* 250 °*C.*

Keywords: *SPRAY PYROLYSIS, THIN FILM, XRD, SENSITIVITY FOR CO-GAS.*

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1. INTRODUCTION

Tin oxide SnO_2 has attracted much attention as candidate materials for next generation devices such as gas sensors, optical devices, Lithium batteries [1-3], etc. Various nano structures including nanowires, nanorings, grains, flakes, plates, meshes and columnar thin films were synthesized [4-8]. SnO_2 is one of the most studied n-type wide gap 3.6 eV semiconductor of fairly high electrical conductivity ranging from 10° to 10^2 $\Omega^{-1}cm^{-1}$ were observed [9].

It is well known that gas sensing mechanism of SnO_2 consists of the interaction of gas species with the surface that causes the changes in concentration of oxygen vacancies near the surface which act as n-type donors localized below the bottom of conduction band. For this reason, a significant density of electronic state is observed in the band gap close to Fermi level. Their occupation causes a change in the concentration of free carriers in the surface space charge region, and then a charge in electrical conductivity within the space charge layer responsible for gas sensing mechanism. It is

generally accepted that the selectivity and sensitivity of SnO_2 type gas sensors depends on surface chemical reactions between the dominant type of surface oxygen and chemisorbed gas. Since oxygen rich atmosphere is a standard environment for the operation of SnO_2 type gas sensors.

In this study we have successfully deposited SnO_2: Sb thin films by spray pyrolysis technique, and the physical properties of SnO_2 have been investigated. The gas sensing properties of antimony doped tin oxide films were investigated. The sensing gas employed was carbon monoxide.

2. EXPERIMENTAL TECHNIQUES

2.1 Deposition of Antimony doped thin films

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 °C using a compressed air as automisation gas. The nozzle size, distance from glass substrate rate of motion of nozzle is properly controlled to obtain a good quality adhesive films. For antimony doped sample, antimony trichloride solution (Sb_2Cl_3) is added to the starting as a solution. The concentration of antimony was varied from 0.01 % to 1 %.

2.2 Structural Analysis by XRD

The X-ray diffraction patterns were obtained for all these samples by using Bruker D8 advanced instrument with source $CuK_{\alpha 1}$ with $\lambda = 1.5406$. The angle 2θ is varied in the range between 10° to 100°. The data shown in Table 1.

Table 1 *– XRD Analysis of Antimony doped tin oxide thin films*

Peak No.	Observed data		ASTM data		Plane
	Angle-2θ	Intensity	Angle-2θ	Intensity	
I	**II**	**III**	**IV**	**V**	**VI**
Sb = 0%					
1	26.54	100	26.61	100	[110]
2	36.90	075	37.95	021	[200]
3	37.90	038	37.95	021	[200]
4	51.72	060	51.78	057	[211]
5	64.63	050	64.71	012	[112]
Sb = 0.01%					
1	14.29	054.54	14.34	100	*[011]
2	20.11	052.27	20.04	070	*[014]
3	26.61	100.00	26.611	100	[110]
4	33.90	068.18	33.893	075	[101]
5	42.78	061.36	42.635	001	[210]
6	51.72	050.00	51.781	057	[211]
7	64.63	045.54	64.719	012	[112]
Sb = 0.1%					
1	14.29	063.00	14.34	100	*[011]
2	20.11	059.00	20.04	070	*[014]
3	26.61	100.00	26.61	100	[110]

I	II	III	IV	V	VI
4	33.90	068.18	33.89	075	[101]
5	42.78	061.36	42.63	001	[210]
6	51.72	050.00	51.78	057	[211]
7	64.63	045.54	64.71	012	[112]
Sb = 0.5%					
1	14.29	060	14.34	100	*[011]
2	20.11	052	20.04	070	*[014]
3	26.61	100	26.61	100	[110]
4	33.90	050	33.89	075	[101]
5	42.78	054	42.63	001	[210]
6	51.72	044	51.78	057	[211]
7	64.63	040	64.71	012	[112]
Sb = 1%					
1	14.29	088.00	14.34	100	*[011]
2	20.11	066.00	20.04	070	*[014]
3	26.61	100.00	26.61	100	[110]
4	33.90	082.22	33.89	075	[101]
5	42.78	064.44	42.63	001	[210]
6	51.72	071.11	51.78	057	[210]
7	78.80	048.80	78.71	009	[321]

2.3 Gas Detection experiments

The gas sensor element (shown in Fig. 1). Silver paste contacts were made at the end of sensor. To find the type of contacts, the I-V characteristics are plotted [10].

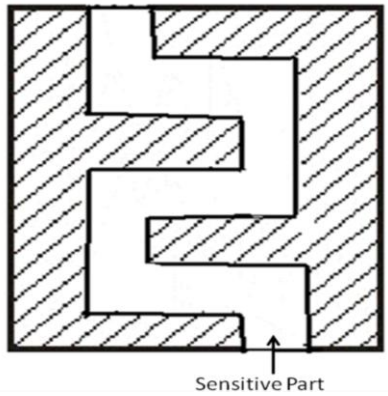

Fig. 1 *– The Gas Sensor Element*

The gas sensitivity chamber (Fig. 2) was used to study the sensitivity of antimony doped tin oxide thin films. The gas sensitivity test were carried out for carbon monoxide gas.

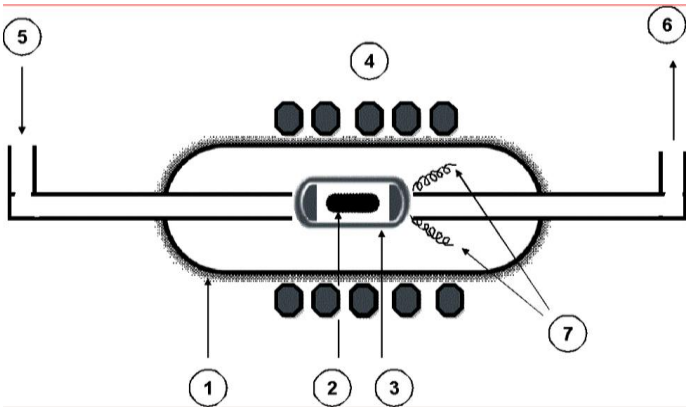

Fig. 2 *– The Gas Sensitivity Chamber (1. Quartz Tube, 2. Sample Holder, 3. Quartz Cup, 4. Heater, 5. Gas Inlet, 6. Gas Outlet, 7. Electrical lead)*

The resistance of the sensor was measured by applying a constant voltage. The current flowing through the sensor was recorded by using digital multimeter. The samples were heated by using a heating resistance from room temperature to 400 °C. The sample temperature was monitored and controlled by thermocouple attached to the substrate. A constant amount of CO (500 ppm) was injected to the testing chamber. The sensing characteristics of the sensors were then recorded by using the change in the electrical resistance. The film resistance in presence of gas was calculated at different temperature. The sensitivity is calculated by using a standard formula,

$$S = (R_{air} - R_{gas})/R_{gas}.$$

3. RESULT AND DISCUSSION

The as-deposited films are blackish in colour. The films are well adherent to the substrate. The thickness of the films are in the range of micrometer. Addition of antimony impurity shows little increase in the thickness.

3.1 X-ray Diffraction Analysis

Fig. 3 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 41-1445 [11], 5.562 [12].

The results were given in the Table 1. 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. Similar results were observed by Jaehyeong Lee [13] and T. Becker et al. [14].

3.2 Gas Sensing Properties

For gas sensing studies ohmic contacts are preferred to ensure the changes in resistance of sensor is due to only adsorption of gas molecule. If the work

function of contact metal is lower than the electron affinity of semiconductor an ohmic contact is obtained [10]. An ohmic contact imples that there is no accumulation of charge carrier in interface of contact. Fig. 4 shows I-V characteristics, the straight line nature of graph indicates that the contact with SnO_2 film is ohmic [10].

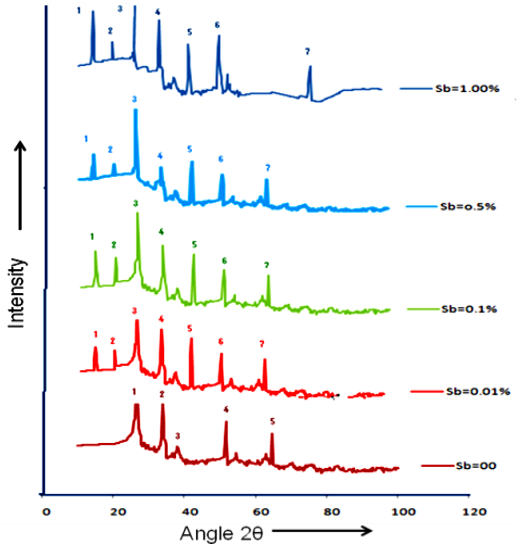

Fig. 3 *– X-ray diffraction pattern for antimony doped tin-oxide thin films*

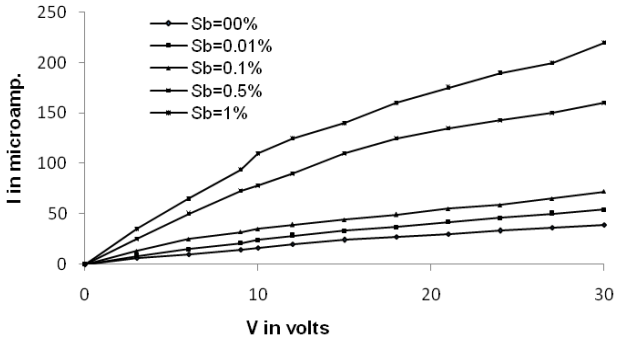

Fig. 4 *– I-V Characteristics of sensor*

The gas sensing is surface phenomenon and is mainly controlled by the adsorbed oxygen species. Doping with Sb give rise to various oxygen species and surface state causing in enhancement at the gas sensing.

The Resistance of tin oxide films depends mainly on various oxygen-deficient sites present after deposition as well as on the doping level. Antimony was found to reside on the grains and at the grain boundaries of SnO_2 films. Presence of antimony in the film generate surface states and provide excess electron to them. When such films are heated at higher temperature, oxygen is adsorbed by the tin oxide layers and abstract electron from surface states thereby increasing the film resistance. This

results in the formation of ionic species such as O^{2-}, O_2^- and O^-. Desorption of oxygen species at the surface due to presence of Sb would culminate in an increase in conductance of the SnO_2 layer significantly in presence of sensing gas (CO). Additionally, an increase in conductivity is also due to the reduction of electronic potential barrier in the grain boundary of SnO_2 when oxygen is adsorbed by its surface. The adsorption/desorption of oxygen causes change in Fermi level of the grains and hence changes in grain boundary potential barrier [15]. The reaction at the surface of film would be as follow,

$$O_2 + e^- \rightarrow O_2^-$$

$$O_2 + e^- \rightarrow 2O^-$$

$$CO + O^- \rightarrow CO_2$$

Fig. 5 shows sensitivity to CO gas as a function of operating temperature for SnO_2 doped with different Sb concentration.

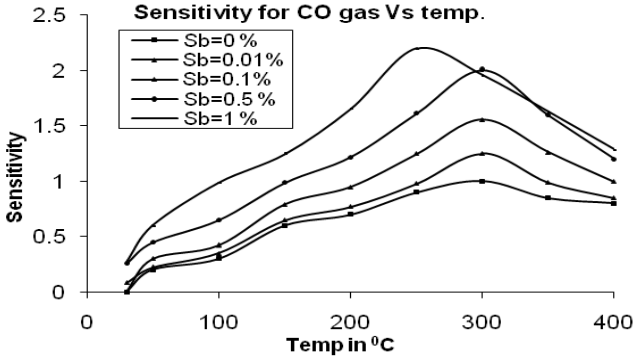

Fig. 5 *– Sensitivity of CO gas vs temperature*

It is seen that sensitivity of SnO_2 incresed with increasing Sb concentration. Addition of antimony shows higher surface area This translate into improved dynamic gas sensing properties and also improved responses to gases It was found that the sample with 1 % Sb showed highest sensitivity for CO gas operated at 250 °C. Similar type of results were observed by [14-16].

4. CONCLUSION

The spray deposited thin film of antimony doped tin oxide are adherent to the substrate The diffraction pattern shows characteristic tin oxide peaks with tetragonal structure. It can be seen that sensitivity of SnO_2 increased with increasing Sb concentration. It is found that the sample with 1 % Sb shows highest sensitivity for CO gas operated at 250 °C.

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