Gas sensing properties of undoped and antimony doped tin oxide films prepared by spray pyrolysis and electron beam evaporation method

K S Shamala & L C S Murthy
Department of Physics, Jnanabharathi, Bangalore University, Bangalore 560 056
and
K Narasimha Rao*
Department of Instrumentation, Indian Institute of Science, Bangalore 560 012
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The thin films of undoped and antimony doped tin oxide films were prepared on glass substrates by spray pyrolysis and electron beam evaporation techniques. The substrate temperature was varied between 300 and 370°C in case of spray pyrolysis and 200°C in case of electron beam evaporation. The films were tested as gas sensors in the presence of liquid petroleum gas (LPG) and compressed natural gas (CNG). Undoped and antimony doped tin oxide films prepared by spray pyrolysis were more sensitive to LPG. Sensitivity of spray deposited ATO film in the presence of 1000 PPM of LPG was found to be 0.86 at an operating temperature of 400°C and it was 0.23 for undoped film. Undoped tin oxide films prepared by electron beam evaporation showed a maximum sensitivity of 0.79 at an operating temperature of 375°C on its exposure to 1000 PPM of LPG. The performance of the sensor has been explained on the basis of the structure and conduction mechanism of the tin oxide film.

Keywords: Tin oxide films, Spray pyrolysis, Vacuum evaporation, Gas sensors
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1 Introduction
Metal oxide semiconductors have potential applications as gas sensors\(^1\)\(^-\)\(^3\). Among metal oxide gas sensors, tin oxide has been an attractive candidate due to its high selectivity and sensitivity to several gases like H\(_2\), CO, NO\(_2\), H\(_2\)S, ethanol etc\(^4\)\(^,\)\(^5\). Sensing mechanism of tin oxide films has been explained by Bittencourt et al\(^6\). Sensitivity can be defined as the ratio of the change in resistance due to the presence of test gas to the resistance in the presence of air.

Sensitivity (S) is given by the equation:

\[
S = \frac{(R_a - R_g)}{R_a} \quad \ldots (1)
\]

where \(R_a\) is the resistance of the film in the presence of air and \(R_g\) is the resistance in the presence of test gas.

Behzoed et al\(^7\) prepared SnO\(_2\)-CuO sensors by spin coating method over platinum electrodes and they were exposed to H\(_2\)S gas. They have observed a high sensitivity of 2.15\(\times\)10\(^6\) \((R_a/R_g)\) for 10 PPM of H\(_2\)S at a temperature of 85°C for 5% CuO doped tin oxide sensor. Rao et al\(^3\) fabricated tin oxide sensors and studied the sensing properties in the presence of fluorocarbons. They used metal catalyst salts like Pd, Pt, Ag, etc for doping purpose. They reported an excellent sensitivity for SnO\(_2\)-Pt based sensor, with high selectivity and fast response.

Ireneusz Kocemba et al\(^8\) reported the effects of evaporated metal films like Pd, Pt, Ag on the surface of SnO\(_2\) sensors. The sensors were exposed to H\(_2\), CO, CH\(_4\)/air.

In this paper, we report the preparation of undoped and antimony doped tin oxide films prepared by spray pyrolysis and electron beam evaporation and their gas sensing properties to gases like compressed natural gas (CNG) and liquid petroleum gas (LPG).

2 Experimental Details
Undoped tin oxide films were prepared by spray pyrolysis method by spraying a solution of tin tetra chloride (SnCl\(_4\)) dissolved in iso-propyl alcohol on to the heated glass substrates at two different temperatures of 300 and 370°C. Molarity of the solution was 0.75 M. Antimony doped tin oxide (ATO) films were prepared by adding antimony trichloride (SbCl\(_3\)) to the solution. The details of the
method of film preparation and the characterization of
the films have already been published in our earlier
paper.9

Undoped tin oxide films were prepared by electron
beam evaporation method by evaporating metallic tin
of purity 99.999% on to the heated glass substrates at
a temperature of 200°C. The deposition rate was kept
at 2.5 Å/S and the deposition was carried out in the
presence of ionized oxygen. Partial pressure of 10⁻⁴ m
bar of oxygen was maintained at the time of
deposition. The film thickness and rate of deposition
were controlled using a quartz crystal monitor.

Figure 1 shows a schematic view of a dynamic
system of gas sensing. This consists of a bank of mass
flow controllers to provide a fixed flow of gases
which are mixed and passed on to the device under
test. There is an independent temperature control
which permits the determination of the sensitivity at
different temperatures. The chamber is connected to a
residual gas analyzer through a leak valve to permit
an independent confirmation of the gas composition.
The resistance of the sensor was measured using a dc
resistance meter.

3 Results and Discussion

Figure 2 shows the sensitivity of undoped tin oxide
films prepared by spray pyrolysis. The sensitivity of
spray deposited tin oxide film, when exposed to LPG
of concentration 1000 PPM, increases with the
increase in operating temperature and shows a
maximum value of 0.23 at an operating temperature
of 325°C (Fig. 2). Sensitivity decreases with further
increase in the operating temperature. When the same
film was exposed to 1000 PPM of CNG, the response
was very low. However, at higher concentration (6000
PPM) of CNG, the film showed a better response (not
shown here). The maximum sensitivity was found to
be around 0.023 at 375°C, which is very low
compared to the sensitivity of the film with LPG.

Figure 3, curve (a) shows the sensitivity of a tin
oxide film deposited by electron beam evaporation. It
is observed from Fig. 3 that the sensitivity of the film,
when exposed to LPG of 1000 PPM, increases with
increase in the operating temperature and attained a
high value of 0.59 at 300°C. The sensitivity was
observed to be maximum of 0.79 at 350°C and this is
similar to what is reported in the literature3,10. The
comparison of [Figs 2 and 3(a)] shows that the

![Fig. 1 — Schematic diagram of dynamic method of gas sensor
set-up used for sensor measurements]

![Fig. 2 — Plot of sensitivity versus operating temperature for
undoped tin oxide film prepared by spray pyrolysis]

![Fig. 3 — Sensitivity of tin oxide films exposed to LPG versus
operating temperature (a) undoped tin oxide film prepared by
electron beam evaporation; (b) spray deposited ATO films with
(Sb/Sn) = 0.065]
sensitivity of spray deposited tin oxide film was found to be very much less compared to that of evaporated films. This may be due to the porous nature of the evaporated films deposited at lower substrate temperatures.

Figure 3, curve (b) shows the variation of sensitivity of spray deposited antimony doped tin oxide film (Sb/Sn = 0.065) which is prepared at a substrate temperature of 370°C when exposed to 1000 PPM of LPG. It is seen from Fig. 3 that the sensitivity of the film increases with the increase in operating temperature, reaches a value of 0.66 at 300°C and it decreases with further increase in the operating temperature. Beyond 350°C, sensitivity increases once again and it shows a maximum value of 0.86 at 400°C. Figure 4 shows the variation of the sensitivity of the same antimony doped tin oxide film when exposed to 6000 PPM of CNG. The sensitivity increases with the increase in operating temperature and a high value of 0.08 at 450°C (Fig. 4). It was observed from the plot that the sensitivity was almost constant with a value of 0.7 for different PPM of the test gas.

4 Conclusion

Undoped and antimony doped tin oxide films were prepared by spray pyrolysis and electron beam evaporation methods. These films were tested as selective gas sensors for the detection of gases like LPG and CNG. Undoped tin oxide films prepared by evaporation method exhibited good response to LPG. Among spray deposited films, ATO films were more sensitive to LPG, compared to undoped films. Spray deposited tin oxide films, both undoped and antimony doped showed very low response to CNG.

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References