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LPG sensing properties of platinum doped nanocrystalline SnO_2 based thick films with effect of dipping time and sintering temperature

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ABSTRACT

Synthesized nanophase SnO_2 powder is used to fabricate thick film resistors using screen printing technology. The surfaces of the thick film resistors were modified by dip coating in platinum chloride ($PtCl_2$) solution of optimized 1.5 M for different time periods of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 minutes. Sintering of the films is carried out at different temperatures of 550, 600, 650, 700, 750 and 800°C. The films were tested for 400 ppm of LPG. Thick films which were dip coated for 5 minutes and sintered at 750°C show the highest sensitivity towards LPG which is ten times higher than undoped SnO_2 sensors. The characterization of the sensors was done using XRD, EDX and SEM. The sensors were found to be extremely stable and repeatable with a response and recovery time of 10 and 22 s with a minimum detection limit of 5 ppm of LPG.

Keywords: Thick film; LPG sensor; Pt doping; SnO_2.

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Introduction

Nanocrystalline metal oxide based thick film resistors as gas sensing devices have attracted great attention for a long time due to their low cost, ease of fabrication and high sensitivity towards toxic gases **[1-2].** A good chemical and thermal stability under operating conditions along with high mobility of conduction electrons are the important features of the SnO_2 based gas sensors **[3].** Most of the sensors based on commercially available bulk tin oxide is severely affected by the small surface to volume ratio and also operate at relatively high temperatures of over 573 K **[4].** On the other hand nanosized tin oxide have a high surface to volume ratio hence more surface area is available for gas sensing **[5].** Low level gas detection via surface modifications of senors is a recent area of thrust. Metal additives such as Pd, Pt are dispersed on the oxide as activators or sensitizers to improve the gas selectivity and to lower the operating temperature **[6].** The method used to introduce the additives and the subsequent thermal treatments performed play an important role in distribution of the additives on the surface of SnO_2. The additives modify the microstructure of the base material and introduce donor or acceptor levels which cause the variation the resistivity of metal oxide **[7]** .Dipping a film in chloride solution of noble metals ($PtCl_2$, $PdCl_2$) and then decomposing at or slightly above the decomposition temperature of the additive causes the doping of respective noble metal on the film **[8].** In the present work, nanocrystalline tin oxide based thick films were fabricated

by screen printing technology. The films were doped with platinum by dip coating in $PtCl_2$ solution for different time periods and then sintered at various temperatures for 5 hrs. The effects of dipping time and sintering temperature on LPG sensing properties of SnO_2 based thick films have been investigated.

Experimental

Synthesis of nanocrystalline SnO_2

1 gm of tin powder (99.9 % pure, AR grade, Qualigens, Mumbai, India) is taken in an alumina boat [99.8 % alumina, ANTS advanced materials,Nashik, India) and thermally oxidized at 900°C for 1 hour in air atmosphere using muffle furnace. The crystallites were ground into powder using mortar and pestle for 20 min. Bulk XRD analysis of the synthesized powder was carried out using Philips X-ray generator (Holland Model 1729) and Philips diffractometer PW 840 using CuKα radiation (λ = 1.542 Å); voltage of 30 kV and a current of 3 mA. The crystallite size was determined by using Scherrer formula

$$D = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta} \qquad (1)$$

Where, D is crystalline size, $\lambda = 1.541$ Å, the wavelength of X- ray radiation used and β is the angular width of the diffraction peak at the half maximum (FWHM) for diffraction angle 2θ.

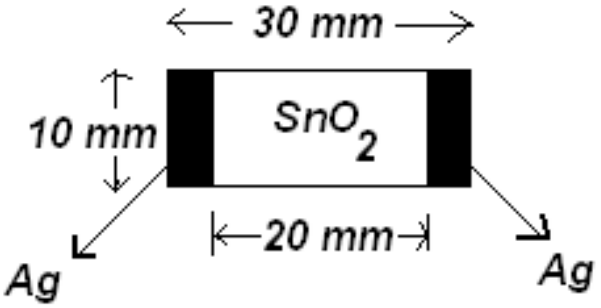

Fig. 1. Structure of TFR.

Fabrication of thick film resistor (TFR)

The synthesized nanophase tin dioxide along with lead borosilicate glass frit is used as a functional material for the preparation of the thick film resistors using screen printing technology .The dimensions of the samples were 20 mm X 10 mm as shown in **Fig. 1**. Silver paste was printed on the substrate for the electrical contacts. The printed samples were dried under IR lamp at 150°C for about 20 minutes to remove the organic vehicle and fired at optimized 550°C for better adhesion. Thickness of the samples was maintained as 30 μm (± 2 μm) as measured by the light section microscope (Carizeisss Jena, Model Bk 70 X 50).

Structural characterization

The fabricated TFR's were are dip coated in platinum chloride solution of optimized 0.15 M **[8]** for different time periods of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 minutes (Referred as S1 to S10) and then sintered at various temperatures 550, 600, 650, 700, 750 and 800°C for 5 hrs in a muffle furnace. The phase of SnO_2 and Pt was identified by structural characterization (XRD) of the sintered samples S1-S10. In addition, further information about the microstructure and morphology of samples S1-S10 after sintering was gained by examining them under scanning electron microscope JOEL JSM 63608. The % mass of Pt deposited on films was determined using energy dispersive X-ray spectroscopy (EDX) of the samples.

Sensor performance

The performance of sensors was checked using a static system [**9**] under laboratory conditions (40 % RH). The samples were characterized for 400 ppm concentration of LPG. The percentage sensitivity factor (S_f) at various temperatures is calculated as,

$$S_f(\%) = \frac{R_{air}}{R_{gas}} \; X \; 100 \qquad (2)$$

where R_{air} and R_{gas} are values of the resistance of the sensor in air and test gas plus air respectively at the same operating temperature. The response and recovery time along with calibration of the LPG sensors was determined.

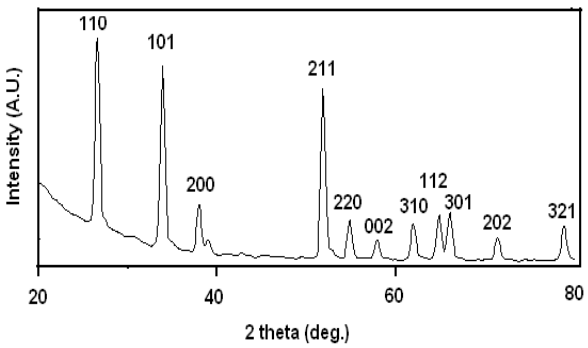

Fig. 2. Bulk XRD pattern of synthesized SnO_2 powder

Results and discussion

XRD analysis of synthesized SnO_2

A typical bulk XRD pattern of synthesized SnO_2 powder is shown in **Fig.2**. From XRD it is observed that all peaks belongs to tetragonal phase (JCPDS file no. 18-1381), with Δd variation < 1% and the average particle size is of 10 nm (±2 nm).

EDX analysis

Table 1 gives the data for amount of mass % of Pt on the surface of samples S1-S10 before sintering. It is clear from the table that the mass percentage of platinum increases

with dipping time, reaches to a maximum (S5) and then decreases with a further increase in dipping time.

Table 1. Mass % of Pt detected using EDX analysis of S1-S10.

Sample	Pt Mass %	O Mass %	Sn Mass %
Undoped	-	4.15	95.85
S1	9.37	27.12	**63.51**
S2	19.97	24.72	**55.31**
S3	28.38	18.23	53.39
S4	35.94	8.38	55.68
S5	45.67	3.15	51.18
S6	44.17	3.68	52.15
S7	43.12	3.76	53.12
S8	41.38	4.77	53.85
S9	38.28	5.63	56.09
S10	32.94	8.34	58.72

The sample S5 was observed to have an oxygen deficiency of 3.15 mass %. Oxygen deficiency would be favorable for adsorption of more oxygen species. The sample S5 was preferred to use for the further experimental work. A typical EDX of sample S5 is presented in **Fig. 3.**

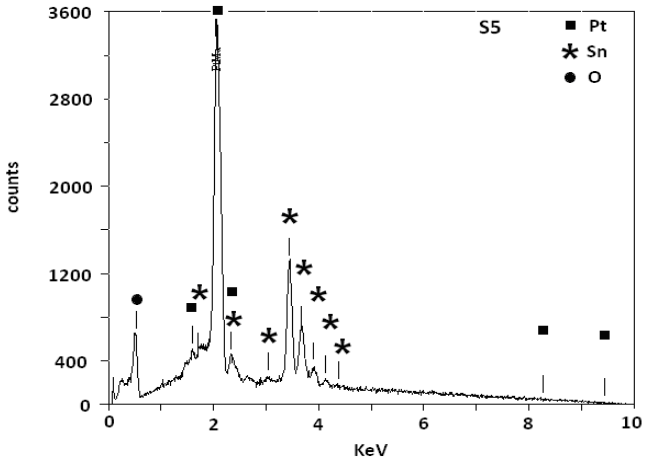

Fig. 3. A typical EDX of sample S5.

Table 2. Relative presence of tetragonal phase of SnO_2 and platinum for the sample S5 after sintering.

Sintering Temp.(oC)	Tetragonal Phase (%)	Platinum Phase (%)	Other Avg. Crystallite size (±2nm)		
			(Al2O3)	SnO2	Pt
550	30.53	63.35	6.12	18	12
600	32.61	60.99	6.4	20	14
650	36.12	58.12	5.76	22	16
700	38.23	56.26	5.51	24	18
750	42.85	51.68	5.47	26	20
800	36.33	57.82	5.85	28	24

XRD analysis

Fig. 4(a) depicts a typical XRD for undoped and unsintered sample S5 while **Fig. 4(b)** represents XRD for Pt doped and sintered (750°C) sample S5. **Table 2** shows the relative presence of tetragonal phase of SnO_2 and platinum for the samples S1-S10 after sintering. First the relative intensities of all observed peaks in a diffractogram were calculated considering the highest peak as with intensity 100%. The normalized intensity of each peak was weighed (multiplied) by the respective full-width at half-maximum (FWHM) of the same peak. This represented the area under the peak. Total of such areas in a particular diffractogram was calculated. From this the relative presence of each phase was derived considering all the peaks assigned to that phase **[10].**

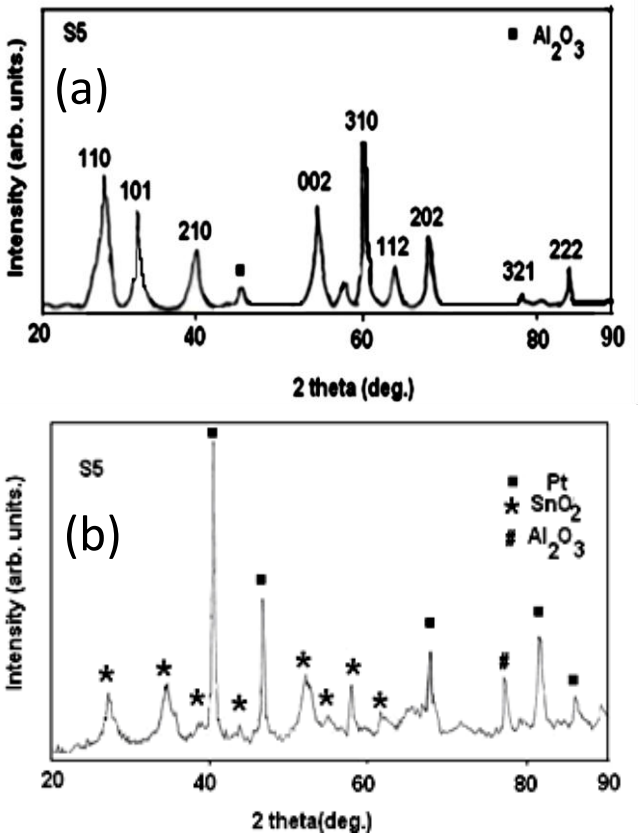

Fig. 4. A typical bulk XRD pattern of (a) undoped S5 and (b) Pt doped S5 sintered at 750°C.

It is also observed that with increase in sintering temperature, the major contribution towards tetragonal phase increases upto 750°C. The tetragonal phase of SnO_2 plays an important role in gas sensing. A slight increase in mass% of Pt after 750°C may be attributed to the homogeneous distribution of Pt on the surface of film due to subsequent thermal treatment above the decomposition temperature of $PtCl_2$.A peak of Al_2O_3 is due to alumina substrate. The increase in particle size with increase in sintering temperature is in good agreement with the previous reported work **[11].**

Surface morphological studies

A typical SEM image for S5 before and after sintering at 750°C is shown in **Fig.5 (a-b)**. The average particle size observed in SEM is larger than estimated from X-ray diffraction data indicating agglomeration of the particles. However there is some non –uniformity in the shape and size of the particles and the maximum particle size in all cases is < 50 nm.

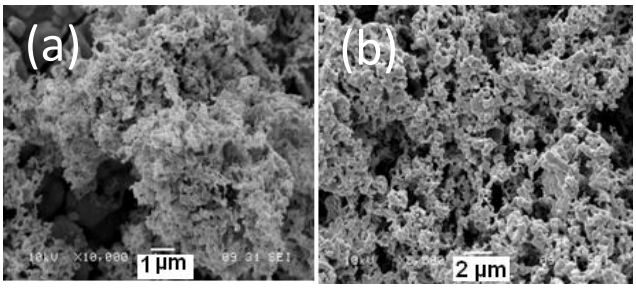

Fig. 5. (a) A typical SEM for the sample S5 before sintering and (b) A typical SEM for the sample S5 after sintering at 750°C.

LPG sensing mechanism

The change in resistance of semiconductor oxide thick film sensor in the presence of toxic gases takes place according to following two reactions. In the first reaction atmospheric oxygen molecules are physiosorbed on the surface sites, which while moving from site to site, get ionized by taking an electron from the conduction band and is thus ionosorbed on the surface as O^-_{ads}. This leads to increase in resistance of the sensor material. The resulting equation is,

$$O_{2(atm)} + 2e^-_{(cb)} \rightarrow 2O^-_{ads} \qquad (3)$$

The nanocrystalline SnO_2 provides high surface to volume ratio results in high quantity of surface atoms which leads to high surface energy. The film surface becomes highly active resulting in further adsorption of oxygen in the ambient atmosphere. In the second reaction when the sensors are exposed to the reducing gases, for instance LPG, reacts with the chemisorbed oxygen, thereby releasing the trapped electron back to the conduction band and decreasing the resistance of the sensor material.

$$R + O^-_{ads} \rightarrow RO + e^- \qquad (4)$$

Desorption of RO takes place at higher temperature known as optimal temperature. At the optimal temperature, the activation energy may be enough to complete the chemical reaction [Eq.3.1] which results in the maximum adsorption of the LPG. At higher temperature, the adsorbed oxygen ions would desorbs from the surface of the sensor. Hence there would be a less number of oxygen ions present on the surface of the SnO_2 to react with the reducing gas and therefore the response falls at higher operating temperature. The increase and decrease in the sensitivity factor observed in the graph indicates the adsorption and desorption phenomenon of the LPG. The reaction may be takes place as follows:

$$C_nH_{2n+2} + 2\,O^- \rightarrow C_nH_{2n} - O + e^- \qquad (5)$$

where, C_nH_{2n+2} represents CH_4, C_3H_{10} and C_4H_{10}. Platinum acts as a catalyst for oxygenation and allows more oxygen species to be adsorbed on the surface than on pure tin oxide **[1, 6, 8]** at low temperature. The oxygen species are chemisorbed on Pt-SnO_2 film surface, leading to the transfer of electrons from the conduction band to the chemisorbed oxygen, because of which a depletion region is formed on the film surface and the grain boundaries. The depletion region extends towards the substrate. The depletion of electrons leads to a decrease in the conductance (an increase in potential barrier) of the film. It reacts with the oxygen ions and releases electrons back to the conduction band, leading to an increase in conductance (a decrease in potential barrier). The larger the depletion region generated in the sensor film, larger is the change in conductance and hence the response. Thus Pt doping with SnO_2 leads to obtain more sensitivity at relatively low operating temperature.

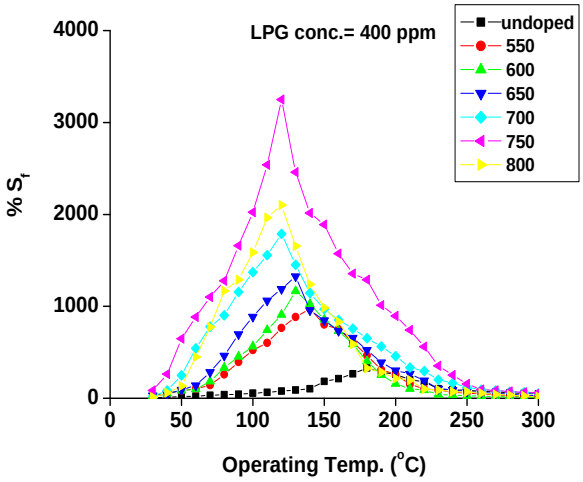

Fig. 6. LPG response of S5 sintered at different temperatures.

LPG sensing performance

Fig. 6 illustrates the sensitivity factor variation with operating temperature of the sensors sintered at 750°Ctested for 400 ppm concentration of LPG. The variation in S_f (%) with operating temperature tested for 400 ppm concentration of LPG is depicted in **Fig. 6**.The sample S5 shows highest sensitivity factor of 3.2 x 10^3 at an optimal temperature of 120°C. This may be attributed to the low particle size (26 nm) and highest % relative presence of tetragonal phase for the sample S5 sintered at 750°C. In spite of the low particle size the low sensitivity at sintering temperatures of 550-700 is due to the low relative presence of tetragonal phase of SnO_2. The tetragonal phase of tin oxide is the most stable structure amongst other phases .The orthorhombic phase of SnO_2 is detrimental to the reducing gas sensing **[12].**

In SnO_2 combustion gas sensor oxygen species acting on the sensor surface are O^{2-}, O^- and O_2^-. The O_2^- species related to orthorhombic phase do not contribute to

sensing properties of the SnO_2 sensor towards reducing gas. The enhanced LPG response at 750°C is may be due to the distribution of Pt atoms on the surface as well as stuck up in the inner portion of pores which is responsible for large surface area. The larger the effective surface area available, the larger the number of Pt sites available for adsorption – desorption process of Oxygen, giving high gas response as in case of S5. The low value for S_f (%) for the sintering temperatures 550-700°C may be attributed to the discontinuous distribution on the surface causing insufficient catalytic activity. At higher temperature, the carrier concentration increases and the Debye length decreases. This may be one of the possible reasons for the decrease in response at 800°C. As observed from the XRD analysis the grain size increases with the increase in sintering temperature may be responsible for the low sensitivity at 800°C.In present work, lead and boron oxides used in the glass as permanent binders - may work as modifiers, promoting gas sensing properties by acting as a catalyst in grain boundaries. In the present work, a noticeable change in optimal temperature from 180°C (undoped) to 120°C (Pt doped) is observed. This decrease in optimal temperature is due to the role of Pt as a catalyst **[13].**

The subsequent thermal treatment above the decomposition temperature of $PtCl_2$ causes the homogeneous distribution of Pt on the surface of film **[14].** It would be optimum to adsorb the maximum amount of oxygen on the surface. This oxygen would then be beneficial to reduce LPG fastly.

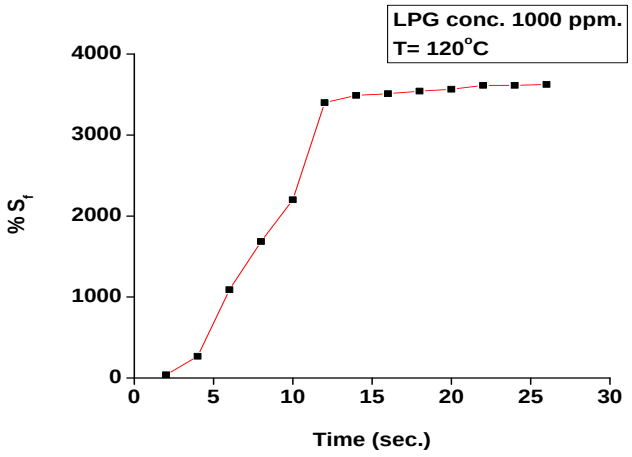

Fig. 7. Response time for S5 sintered at 750°C.

Response and recovery time

The response time and calibration curve for S5 sintered at 750°C is shown in **Fig.7-8.** The response time is of ~ 10 s for LPG while the recovery time is ~ 22 s .For measuring recovery time, the sensor is exposed to air ambient by maintaining the optimal temperature constant and then time was noted till it achieves at least 90 % of its original value. The response and recovery times of sensors reported in present work are comparable with earlier reported values those of the Pt doped SnO_2 based sensors **[15].** A typical calibration curve for the sensor S5 sintered at 750°C is represented in **Fig. 8**. Three regions are seen in the calibration curve, region I from 10-400 ppm, region II from 400-2000 ppm and region III 2000-10000 ppm. The sensitivity is highest for the region 10-400 ppm.

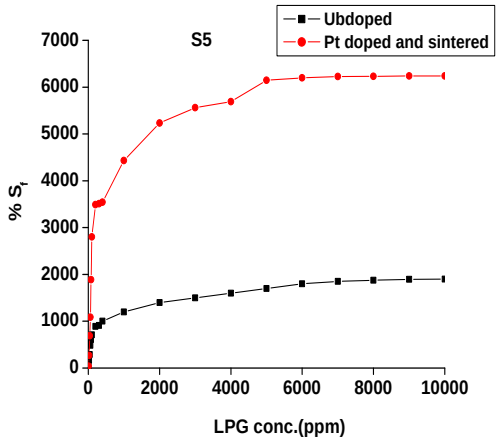

Fig. 8. Calibration curve for S5 sintered at 750°C

Repeatability and aging effect

The repeatability in the sensor performance is checked by testing five samples dip coated in $PtCl_2$ solution for 5 min. and sintered at 750°C. A slight decrease of 5% in the sensitivity factor along with deviation of 5°C in the optimal temperature is observed. The aging effect for the LPG sensors was checked by investigating the response to LPG for 1 month. The measurements are not stable during initial 5 days, but after that they are consistent around the value with a variation of less than ±1 %. These results show that Pt doped SnO_2 based LPG sensors gives a stable LPG sensor.

Conclusion

The sensors dip coated for the time of 5 min. and sintered at 750°C for 5 hrs are highly sensitive towards LPG at 120°C, with a remarkable increase in sensitivity ten times higher than the earlier reported for undoped SnO_2 sensors. The response and recovery time is 10 and 22 sec respectively which are in good agreement with the earlier reported values. The calibration range of the LPG sensor is found to be 10-10000 ppm. Optimization of dipping time (5 min.) and sintering temperature (750°C) along with low operating temperature of 120°C for LPG sensor is the achievement of this work.

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