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Influence of Lattice strain and Dislocations on the LPG Sensing Performance of Praseodymium Doped SnO₂ Nanostructured Thin Films

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Abstract: Spray pyrolysed SnO₂ thin films doped with Praseodymium are prepared and analysed for LPG detection. X-Ray diffraction analyses are administered which suggests that the addition of Praseodymium weakens the crystalline growth leading to enhanced sensor response with improved response time. FESEM micrographs show polygonal grain features along with voids in between the grains. HRTEM presents the crystallite size of 1 wt.% Pr-doped tin oxide films in the range of 12-18 nm. The tetragonal rutile structure obtained from XRD has been confirmed in HRTEM. It is observed that 1 wt.% Praseodymium doped sample exhibits fastest response and recovery time of 10 sec. with good sensor response of 98.8 % for 500 ppm of LPG. The microstructural analysis of the Pr-doped material instigates that when the lattice strain is lowest and dislocations are in a moderate concentration, the gas response is found to be maximum.

Keywords: SnO₂ thin film, doping, Spray Pyrolysis, LPG, Sensor Response

I. INTRODUCTION

Gas sensors based on solid state semiconductor materials offer considerable advantages in comparison to other gas sensing methods. At present, there are several approaches to enrich gas sensitivity of polycrystalline semiconductor oxide [1]. Doping has been proved to be one of the most effective ways to enhance the properties of gas sensing by altering the structure, grain size variation, introduction of impurity defects or surface defects. Literature shows that doping by noble metals is the traditional approach used often for this purpose [2].

Rare earth elements have attracted the attention of many researchers due to their doping homogeneity, interesting structural, catalytic, transport properties and high chemical activity which make them suitable for application in areas of gas sensors. In particular, it is found that the introduction of rare earth metals in gas sensing matrix can contribute in the decrease of operating temperatures, increase of sensor response, selectivity and improvement of the response time. Praseodymium (Pr-59) is one from a set of seventeen rare earth elements in the periodic table. Praseodymium oxide has a special position within the series of the rare-earth oxides, as it forms a homologous series with a large number of stoichiometrically defined oxides Pr_nO_{2n-2}, with n = 4, 7, 9, 10, 11 [3]. Praseodymium is different from the other trivalent rare earths, as it forms compounds wherein it is in tetravalent status.

The present work illustrates how the incorporation of Pr into the SnO₂ matrix improves the LPG sensor response of SnO₂ thin film prepared by spray pyrolysis technique. To account the variation, undoped and Pr-doped SnO₂ thin films are prepared at deposition temperature of 320°C. The improvement in sensitivity, response time and reduction in operating temperature has been clearly observed.

II. EXPERIMENTAL TECHNIQUES

All the reagents (analytical-grade purity) are procured from Sigma-Aldrich and used as received without any further purification. In a typical synthesis, 10 g. SnCl₄ · 5H₂O is dissolved in a mixture of isopropanol and distilled water (2:3, v/v), followed by vigorous stirring to form a homogeneous solution. Total volume of the solution is divided into 3 parts, then calculated amount (1 and 3 wt.%) of Praseodymium oxide (Pr₂O₃) added to the said solution. The solution is then transferred into the atomizer and sprayed ultrasonically onto preheated substrates maintained at 320°C at the spray rate of 0.3 ml/min. The Pr-doped SnO₂ films are obtained by the mentioned deposition process, but for undoped films solution not including Praseodymium oxide have been used. Visibly uniform films with smooth surface are obtained and taken for detailed characterisations and sensor response studies.

X-Ray power diffraction (XRD) analysis conducted on a Rigaku MiniFlex 600 X-Ray diffractometer with Cu-Kα radiation (λ = 1.5418Å) as X-Ray source (at 20kV and 20mA) in the scanning angle (2θ) range from 20° to 80°. The mean crystallite size

calculated using Debye-Scherrer formula, $D = 0.95\lambda / (\beta \cos \theta)$, where λ is the X-Ray wavelength, θ is the Bragg diffraction angle and β (in radians) is the full width at half maximum. The Morphological analysis is done by Field Emission Scanning Electron Microscopy (FESEM) by Carl Zeiss microscopy. The High resolution transmission electron microscopy measurements are obtained on JEOL JEM-2100 microscope operated at 200 kV.

Gas response measurements of the samples are carried out as follows: The films are loaded in the sensing chamber with four probe leads attached. The film is heated in the chamber with atmospheric air as ambient and then in the ambience of LPG. Resistance measurement and gas sensing response of the samples are carried out at different temperatures using Keithley 2400 source meter. The sensor response to a particular gas concentration is defined as

$$S (\%) = \frac{(R_a - R_g)}{R_a} \times 100 \quad (1)$$

where R_a and R_g are the resistances of the sample in the absence and presence of the test gas respectively.

III.RESULT AND DISCUSSION

A. Structural and Morphological Analysis

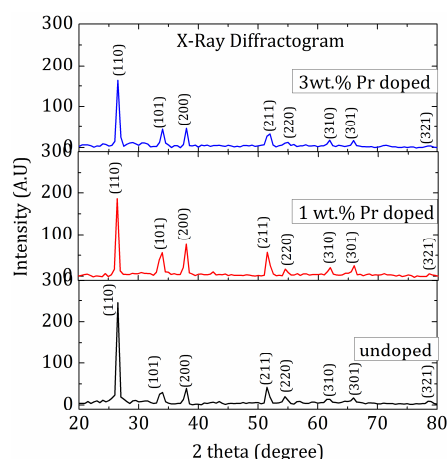


Fig. 1 XRD Spectra of undoped, 1 wt.% and 3 wt.% Pr-doped SnO₂ thin films

Typical XRD patterns of the as-prepared SnO₂ samples are shown in figure 1, where one can see that they are identically similar except in peak intensities. The cassiterite phase is identified, having no evidence of impurity regardless of dopant concentration. The diffraction peaks corresponding to Pr₂O₃ cannot be seen in XRD patterns, in the studied Pr concentration range less than 3 wt.%. It can be seen that the diffraction peaks become weaker and broader with the increasing amount of dopant, which indicate that Pr³⁺ doping suppress the growth of large SnO₂ crystallites.

Table I: Crystallite Size, Lattice Parameters And Strain Of Undoped And Pr- Doped SnO₂ Thin Films

Sample	Crystallite size (nm)	Crystallite size from W-H plot	Cell volume (Å) ³	a/c (Å)	Strain	Strain from W-H plot	Dislocation density (x10 ¹⁵ nm ⁻²)	Stacking fault
Undoped SnO ₂	18.4	20.98	71.7426	1.4884	0.010207	0.00698	9.85	0.006168
1 wt% Pr-doped SnO ₂	12.5	13.79	71.7722	1.4867	0.008041	0.00079	7.02	0.005135
3 wt% Pr-doped SnO ₂	11.2	13.79	71.4728	1.4871	0.009983	0.00079	1.61	0.006606

Table 1 gives the information about lattice related parameters of pure and Pr-doped SnO₂ obtained from XRD data, where the crystallite size calculated from using the Scherrer formula. It is observed that the crystallite size decreases with increasing Pr-doping concentrations up to 3 wt.% under the study. This may be because of the fact that the dopant atoms exert a drag force on boundary motion and grain growth [4]. Hence addition of Pr element decreases the particle mobility on formation and thereby inhibits the growing-up of SnO₂ crystallites. The crystallite size is calculated from Scherrer formula, for undoped, 1 wt.% and 3 wt.%, films are

18.4, 12.5 and 11.2 nm respectively, agree nearly with the values calculated from Williamson-Hall method. When the crystallite size becomes less in the range of nano-scale, it is likely that the defects get introduced is found to be more in undoped films.

On doping with Pr^{3+} , the cell volume shows a tendency to increase up to 1 wt.% Pr, although the lattice ratio (a/c) exhibits a lower value in 1 wt.%, in contrast with undoped SnO_2 . The cell volume is increased to 71.7722 \AA^3 at 1 wt.% doping, which is higher than the bulk standard value of 71.57 \AA^3 as well as undoped film value 71.7426. This can be substantiated by considering the higher ionic size of Pr. Considering the fact that the Pr^{3+} (0.101 nm) is somewhat large than Sn^{4+} (0.071 nm), soft substitution is possible with minor lattice disruption in the cassiterite structure.

But at a higher doping concentrations of 3 wt.% Pr in SnO_2 the cell volume decreases, possibly for the reason that large strain cannot be accommodated with the lattice and the dopant is expected to come out of the lattice as segregation. However the cell volume decreases to 71.4728 for 3 wt.% Pr, may be as a result of partial inclusion and lattice reformation. In our experiments, lattice distortion caused by 1 wt.% Pr-doped sample giving the lattice ratio is 1.4867 which is less than the undoped SnO_2 value, suggesting that Pr-doping result in a distortion in the crystal structure of the host compound, thereby causing change in cell volume. This implies that limited amount of Pr^{3+} addition does introduce sufficient lattice distortion and more oxygen vacancies in the film matrix to enhance gas sensing to a maximum level. On doping, the strain and the amount of stacking faults decrease up to 1 wt.% Pr content, but shows a tendency to increase thereafter. However the dislocation density shows continued lowering with increase of doping amount. The increase in cell volume with increasing Pr-doping level and the observed reduction of defect density indicates the quenching of inherent defects in the films by the incorporation of Pr.

B. Microstructure and morphology

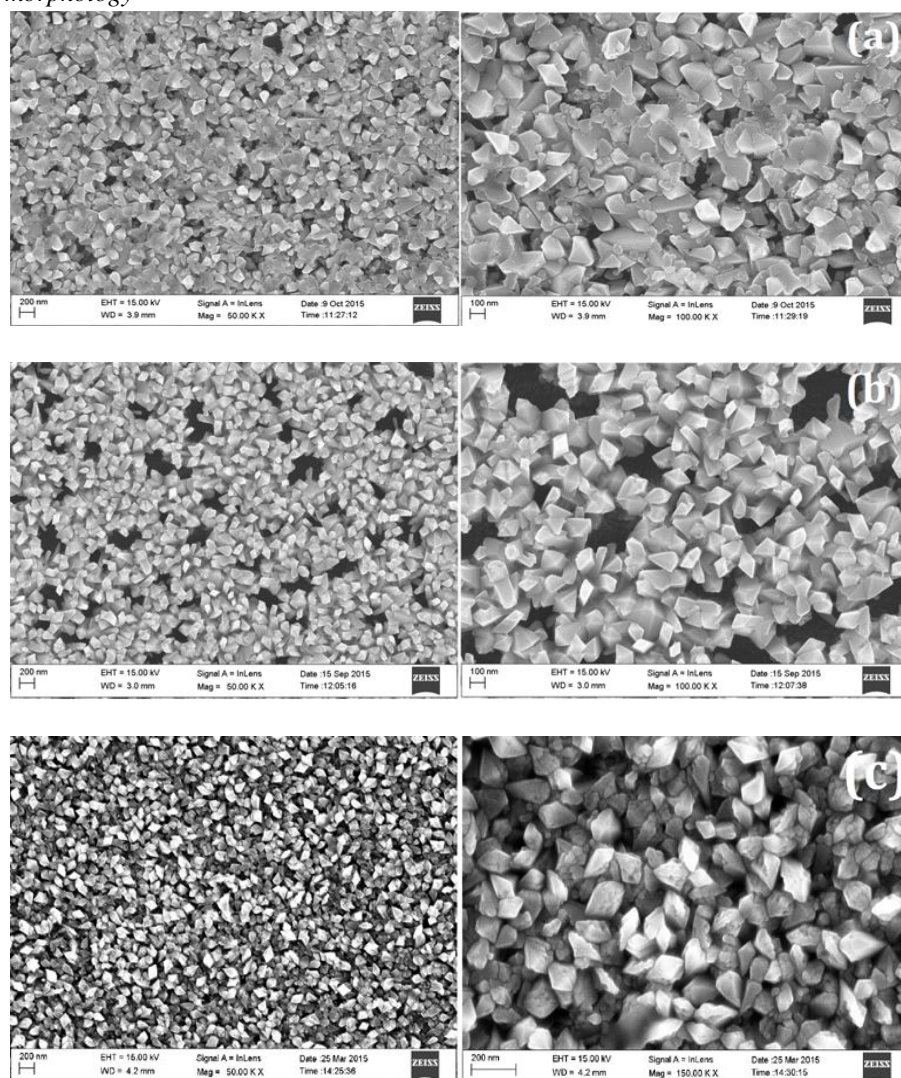


Fig. 2 FE-SEM image of pure and Pr-doped SnO_2 : (a) 0% (b) 1% (c) 3%

Figure 2(a-c) illustrate typical representatives FE-SEM images of as-prepared samples which illustrates the morphological features of the undoped, 1 wt.% and 3 wt.% Pr-doped films respectively. Undoped SnO_2 film shows closely packed, jumbled up polygonal grains with less number of pores in between. But, in 1 wt.% Pr-doped SnO_2 film, well-defined huddled polygonal grains are seen which are composed of aggregates of nanoparticles. These films show a large surface irregularity and voids could be located in between the grains. When dopant amount is 3 wt% (Fig 2(c)), clear polygonal shaped nano-grain growth observed with finer dispersive nanoparticles.

To get further information about the microstructure and crystallinity of the 1 wt.% Pr-doped SnO_2 thin film, TEM and HRTEM analysis are performed. The typical TEM image of 1 wt.% doped sample shows the nanocrystalline nature of the crystallites having domain size 13 nm (Fig. 3(a)), in conformity with the XRD estimation from the peak broadening. The lattice fringes are clearly visible in the HRTEM image (Fig. 3(b)) and the lattice spacings determined are 0.356 and 0.278 nm. They found to correspond to the d-spacing of the (110) and (101) planes of rutile SnO_2 lattice, respectively. The selected-area electron diffraction (SAED) of bright spots and rings (Fig. 3(c)) indicate that the nanoweb structure consists of randomly orientated crystals. The reciprocal lattice 'rings' spacings in the SAED pattern are directly proportional to the *d*-spacings and is well indexed to the tetragonal unit cell.

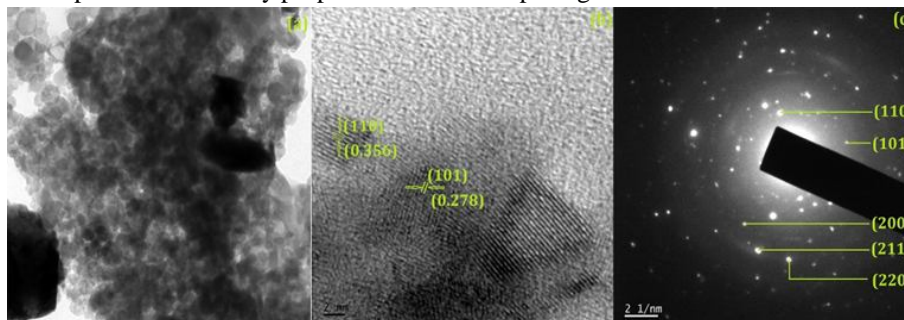


Fig. 3 Typical TEM image of 1 wt% Pr-doped SnO_2 thin film (a) TEM (b) HR-TEM image and (c) SEAD pattern

C. Gas Sensing Properties

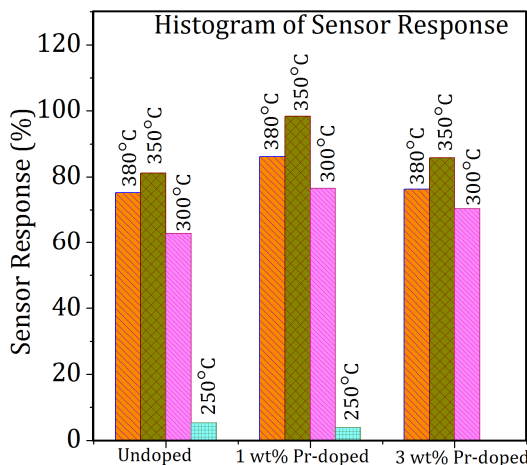


Fig. 4 Response of undoped and Pr-doped SnO_2 thin film toward 500 ppm of LPG at different operating temperature

The effect of Pr-doping on gas sensing properties of the films are studied by making ohmic contacts using high conducting silver (Ag) paste electrodes. The sensors at various operating temperatures are tested for 500 ppm of reducing gas LPG. The sensor resistance is determined, and utilized as the measure of response. At each temperature, before starting the measurements, the sample resistance is measured without the test gas. The resistance of the sensors decreases on exposure to reducing gas.

By comparing the responses of different amount of Pr-doped and undoped SnO_2 samples at different operating temperature in Fig. 4, it can be unambiguously understandable that the response of SnO_2 is improved by adding of Pr. LPG gas sensor response measured at 350°C get increased from 81.2% to 98.8 %, when 1 wt.% Pr is incorporated into the SnO_2 thin film. However, the response value fails to persist and declines in the magnitude with the increasing dopant concentration.

It can also be seen that for all the samples the sensor response increases with operating temperature up to 350°C, thereafter the response decreases. With increase of LPG concentration, the response % increases steadily but saturates more or less above 300 ppm (Fig. 5).

It has been depicted that the Pr-doping is effective in forming grain-linked microstructure. As it is known, resistance of polycrystalline SnO₂ is mostly controlled by inter-grain potential barrier [5]. Taking this into account, one can conclude that the addition of Praseodymium in small concentration lowers the growth of potential barrier height at the inter grain interface, by increasing the chemisorbed oxygen at the SnO₂ grain surface. Based on that, incorporation of Pr-ion favour adsorption of atmospheric oxygen species on the surface and thus creates more sensing site to respond [6]. This also contributes to gas sensing enhancement. On the other hand, deep quenching of defects accompanied by heavy doping exerts strong negative influence on gas sensing properties. Besides, the surface disorder introduced by the heavy Pr-doping is accompanied inevitably by the increase of surface state density [7] which could lead to pinning of surface Fermi level and the decrease of sensor response [8].

Figure 6 present the dynamic gas response and recovery behaviour for undoped and 1 wt.% Pr-doped SnO₂ sample for different gas concentration which is measured at 350°C. The sensor shows fast response and recovery time (defined as the time required to reach 90% of the final equilibrium value) of 10-15 sec in the concentration range 500 ppm to 50 ppm of LPG. In contrast, the pure SnO₂ exhibits comparably slow response and recovery towards LPG especially below 200 ppm of gas concentrations. Thus incorporation of praseodymium as Pr³⁺ can significantly reduce the response and recovery time and subsequently, it is reasonable to conclude that the capability of adsorbing oxygen at the surface get enhanced in SnO₂ by Pr-doping, for the observed fast response.

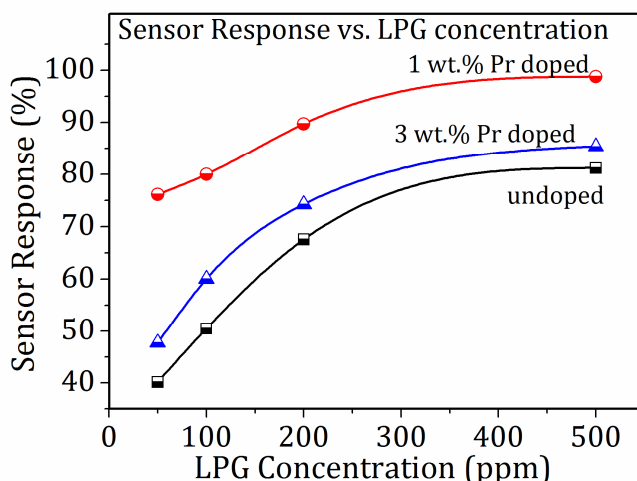


Fig. 5 Response of pure and Pr-doped SnO₂ sensor to different LPG concentration tested at 350°C

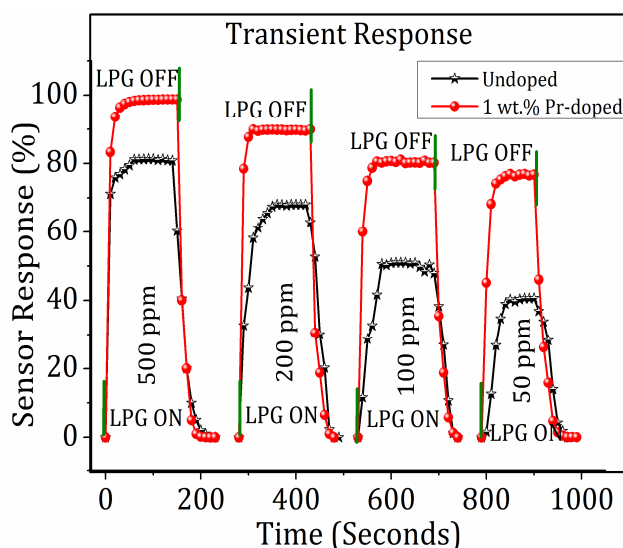


Fig. 6 Response – recovery characteristics of pure and Pr-doped SnO₂ sensors towards different concentration of LPG at 350°C

The enhance of gas response parameters can further pursued from the following aspects: (1) doping of Pr^{3+} results in creating more vacant oxygen sites in the matrix, which is helpful in adsorbing oxygen at the surface from the atmosphere; (2) it is considered that Pr^{3+} catalytically activates the dissociation of molecular oxygen to increase the quantity of oxygen adsorption while the praseodymium itself has a good oxygen storage capacity [9]; (3) The lattice strain and defect density are significantly less on doping with Pr, leading to more carrier density and surface oxygen adsorption. Furthermore the low gas sensor response time depends on the speed of chemical reaction on the surface which gets boosted up by abundantly adsorbed surface oxygen.

IV. CONCLUSIONS

In this study, Pr-doped SnO_2 nanostructured thin films with different dopant amounts are synthesized by spray pyrolysis. By using X-ray diffraction and electron microscopy studies, it is found that Pr^{3+} doping can suppress the growth of large SnO_2 crystallites and assist in a uniform growth of agglomerated polygonal shaped grains. The gas sensing properties to LPG is tested and found that 1 wt. % Pr-doped SnO_2 exhibit the best gas sensing properties which can be attributable to enhanced capability of adsorbing oxygen by Pr on the surface. Thus the Pr-dopant exhibit excellent sensor response characteristics with fast response and recovery time of 10 sec, even at low LPG concentration of 50 ppm. This implies a good potential of the Pr-dopant in SnO_2 films, for practical LPG sensing applications.

V. ACKNOWLEDGMENT

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