Bull. Mater. Sci., Vol. 31, No. 3, June 2008, pp. 397–400. © Indian Academy of Sciences.

Enhanced catalytic activity of nanoscale platinum islands loaded onto SnO_2 thin film for sensitive LPG gas sensors

DIVYA HARIDAS, VINAY GUPTA* and K SREENIVAS

Department of Physics and Astrophysics, University of Delhi, Delhi 110 007, India

Abstract. In the present study, different catalysts (~10 nm thick) including metals, noble metals and metal oxides, were loaded in dotted island form over SnO_2 thin film for LPG gas detection. A comparison of various catalysts indicated that the presence of platinum dotted islands over SnO_2 thin film deposited by r.f. sputtering exhibited enhanced response characteristics with a high sensitivity, ~742, at an operating temperature of ~280°C. Different characterization techniques have been employed such as atomic force microscopy, X-ray diffraction and UV–vis spectroscopy, to study the surface morphology, grain size and optical properties of the deposited thin films. The results suggest the possibility of utilizing the sensor element with the present novel method of catalyst dispersal for the efficient detection of LPG.

Keywords. Pt–SnO_2; gas sensor; LPG; thin film.

1. Introduction

The recent emergence of concern over environmental pollution and accidental leakages of explosive gases has increased awareness for efficient detection and constant monitoring of such gases. To meet this demand, considerable research into the development of sensors with novel design using tailored material properties is underway. Consistent efforts have been made to enhance the performance of semiconductor metal oxide gas sensors through nano-engineering. Besides metal oxides, metal nanoparticles as catalysts have attracted much attention for gas-sensing applications. Semiconducting tin oxide (SnO_2) is known to be sensitive to various reducing gases and provides good selectivity for different gases with appropriate metal additives (Ihokura and Watson 1994; Chowdhuri *et al* 2003). Hydrocarbon gases are being used as fuel for domestic and industrial purposes. Increasing usage of liquefied petroleum gas (LPG) has increased the frequency of accidental explosions due to leakage. Thus the requirement for reliable and sensitive gas detecting instruments have increased for safety at home and industry. The normal constituents of LPG are propane (C_3H_8), propylene (C_3H_6), butane (C_4H_{10}) and butylenes (C_4H_8). They are not pure chemical hydrocarbons, but commercial quality products marketed as butane and propane, which also contain trace quantities of other similar gases. Many researchers have worked on propane or butane gas sensor but little work has been done on LPG gas sensor. From the literature (Phani *et al* 1998; Reddy and Chandorkar 1999; Gupta *et al* 2004; Pourfayaz *et al* 2005; Baruwati *et al* 2006; Chaudhari *et al* 2006; Jain *et al* 2006; Senguttuvan *et al* 2007; Shinde *et al* 2007; Srivastava *et al* 2007; Wagh *et al* 2007; Waghulade *et al* 2007), it is inferred that presently available sensors have two major shortcomings, one, low sensitivity (ranging from 2–20) and two, its operation at a high temperature (320–800°C). One has to compromise with either the sensitivity or the operating temperature. A highly sensitive sensor mostly works at a very high operating temperature thus increasing the power consumption. On the other hand, other sensors which operate at low temperature are not sensitive enough for trace level detection of LPG. The present investigation describes the fabrication and characterization of a LPG sensor exhibiting a higher sensitivity of $\sim 7{\cdot}4 \times 10^2$ for trace level detection of 50 ppm of LPG at a relatively low operating temperature (~280°C).

2. Experimental

Tin oxide (SnO_2) thin film (~90 nm thick) was deposited by a r.f. sputtering technique using a metallic tin target (99·999% pure), in a reactive gas mixer of Ar and O_2 (50 : 50). The film was deposited over platinum interdigital electrodes patterned over borosilicate glass substrates using conventional photolithography technique. Electrodes were placed under the SnO_2 thin film so that the actual changes in the resistance occurring in the bulk of SnO_2 layer could be measured. The surface morphology and crystallographic orientation of the films were analysed by X-ray diffraction (XRD) and atomic force microscopy (AFM). UV-vis spectrometer (Perkin Lamda 25) was used for optical characterization of thin film. The nanoscale thin (10 nm) overlayers of various metal catalysts (Pd, Pt, Ag, Pb) and their oxides in the form of dotted islands were deposited on the surface of SnO_2 thin film

*Author for correspondence (vgupta@physics.du.ac.in)

(figure 1), using a shadow mask of 0·6 mm pore size. The platinum and palladium catalysts were deposited by r.f. sputtering using their respective metal targets in pure argon ambient, whereas silver and lead catalysts were thermally evaporated. The prepared Pt–SnO_2 dotted sensor was also annealed in air at 300°C for 2 h to convert ultrathin catalyst dotted islands to its respective oxide. Thus 10 nm thick catalyst dots with 0·6 mm diameter were loaded over SnO_2 thin film. Sensitivity and response speed characteristics for 50 ppm LPG were measured in the temperature range 60–250°C using an automatic data acquisition system. At each temperature the sensor was first stabilized in air to obtain a stable resistance value. The sensitivity factor is defined as

$$S = R_a/R_g,$$

where R_a is the resistance of the sensor in the absence of detecting gas, and R_g the corresponding resistance in the presence of the reducing gas. The time required to attain 90% of the stabilized value of sensitivity after the sensing gas interacts with the surface of sensing element is the response speed of the sensor.

3. Results and discussion

The tin oxide (SnO_2) thin film deposited under optimized sputtering condition was found to be uniform, transparent and strongly adherent to the substrate. As-grown SnO_2 thin film on borosilicate glass substrates were found to be amorphous. The post-deposition annealing treatment at 300°C in air for 2 h was found to transform the amorphous film into polycrystalline structure (figure 2). Broad characteristic peaks in the XRD spectra of post-deposited annealed SnO_2 thin film were observed at $2\theta = 26{\cdot}5°$, 33·9° and 51·8° corresponding to reflections from (110), (101) and (211) planes, respectively. The estimated values of lattice constants were found to be $a = b = 4{\cdot}789$ Å and $c = 3{\cdot}164$ Å, and are in good agreement with the reported values. The mean value of the crystallite size of deposited SnO_2 thin film was evaluated by fitting the (110) diffraction peak width using Scherrer's formula

$$d = K\lambda/\beta\cos\theta,$$

where K is 0·9, λ the X-ray wavelength, β the peak FWHM, and θ the diffraction peak position. The crystallite size of the annealed thin film is about 12 nm. All as grown and annealed SnO_2 thin films were found to be

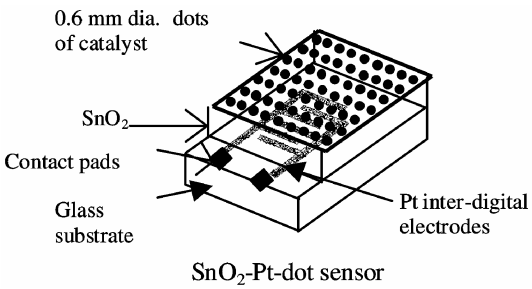

Figure 1. Design of dotted metal/SnO_2 LPG sensor.

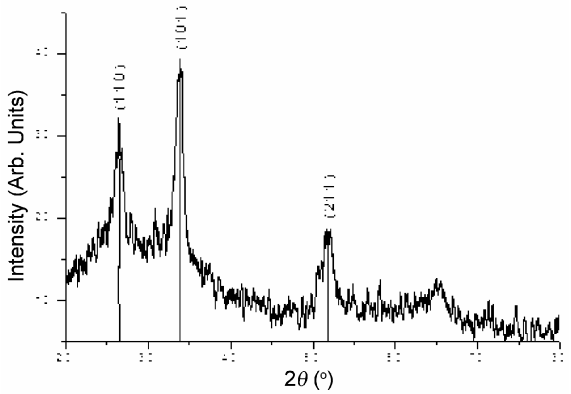

Figure 2. XRD pattern of post deposition annealed SnO_2 film (90 nm thick) in air.

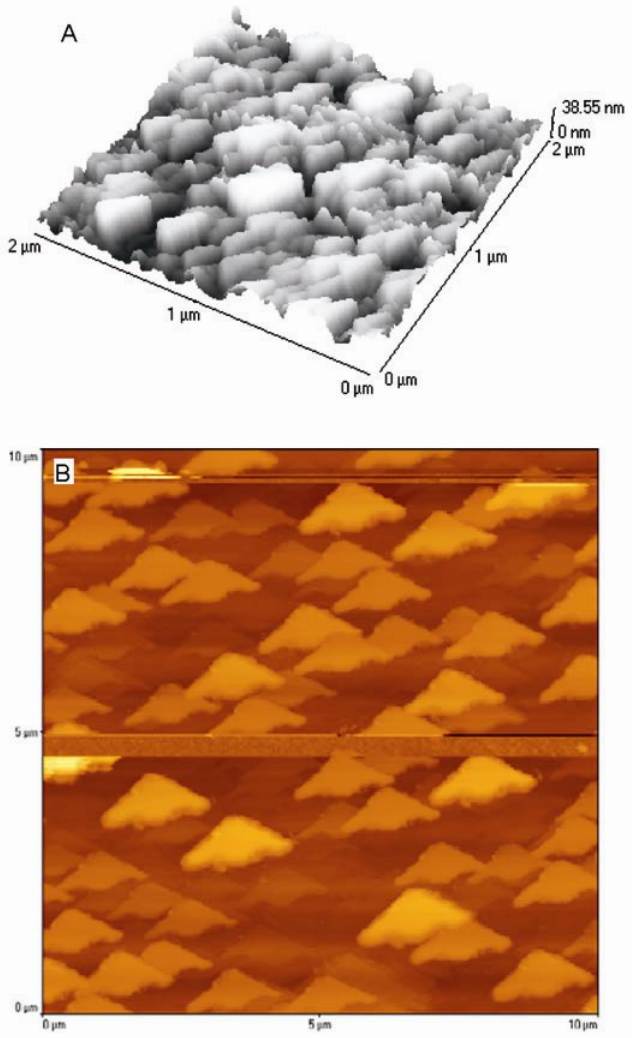

Figure 3. **A**. AFM image of post deposition annealed SnO_2 film and **B**. AFM image of SnO_2–Pt dotted sensor structures.

highly transparent around 90% in the visible region. The presence of a sharp fundamental absorption edge at around 4·13 eV confirmed the formation of a single phase SnO_2 material. The surface morphology of the as-deposited and annealed films was examined by AFM. The spherical grains observed in the as grown thin film were found to be transformed into smooth elongated structures with channel formation after annealing treatment in air (figure 3A), leading to an effective increase in the surface to volume ratio. Figure 3B shows surface morphology of SnO_2–Pt dotted sensor structure, clearly depicting the distributed dotted island structure of catalyst over the surface of SnO_2 thin film.

Pure SnO_2 thin film was found to exhibit very low sensitivity to LPG, and therefore, different catalysts (~10 nm thick) including metals, noble metals and metal-oxides were loaded in dotted islands form over the sample. Figure 4 shows the variation of sensitivity as a function of temperature obtained with different catalysts loaded onto SnO_2 sensor for 50 ppm LPG. The presence of Pt catalyst in dotted island form on the surface of SnO_2 sensor was found to enhance the sensitivity to a large extent in comparison to other catalysts (figure 4). The maximum sensitivity was obtained at a particular operating temperature and is strongly influenced by the nature of the catalyst. A maximum sensitivity of ~742 is obtained at 280°C for Pt dotted SnO_2 thin film followed by platinum oxide (sensitivity, ~379). It is important to point out that the pure SnO_2 thin film without any catalyst exhibited a very poor sensitivity (~3), and the presence of nanoscale thin catalyst on its surface enhanced the sensitivity by one to two orders of magnitude. It was of interest to understand the sensing mechanisms that influence the response characteristics of the SnO_2–Pt-dot sensor. The observed increase in the sensitivity (R_a/R_g) could be related either due to a large resistance in air (R_a), and a substantial change in resistance in the presence of the LPG gas, resulting in low value of R_g. For an enhanced performance, it is desired that both the changes occur effectively. The variation of resistance of Pt loaded SnO_2 sensor in air (in terms of $\log R_a$) with temperature is shown in figure 5. The sensor resistance decreases continuously with increase in temperature up to 160°C which is due to the semiconducting nature of SnO_2 thin film. The increase in the value of R_a at higher temperatures is due to the enhanced activation of the chemisorbed oxygen on the surface of SnO_2 thin film thereby decreasing the concentration of free charge carrier. The chemisorbed activity is expected to vary according to the equations (Bonasewicz *et al* 1986; Heiland 1988)

$$O_2(g) \rightarrow O_{2\,(ads)} + e^- \xrightarrow{T \le 500\ K} O^-_{2(ads)},$$

$$O^-_{2(ads)} + e^- \xrightarrow{T > 500\ K} 2O^-_{(ads)}.$$

The most probable species at 300°C is $O^-_{(ads)}$ which is formed from $O^-_{2(ads)}$. The stabilization is achieved when an equilibrium concentration of adsorbed species is obtained. Figure 6 shows the variation in the sensor resis-

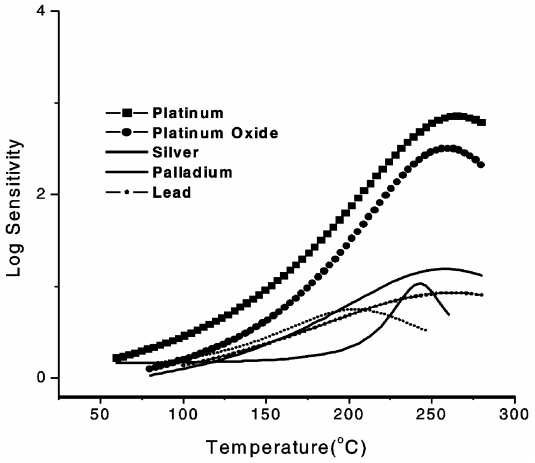

Figure 4. Variation of sensitivity of LPG sensor using various catalysts.

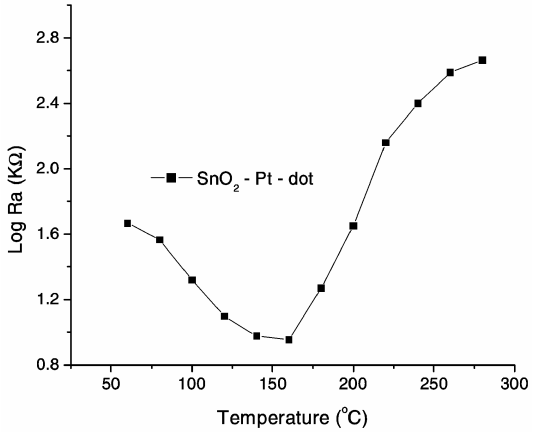

Figure 5. Variation of $\log R_a$ of LPG sensor with temperature.

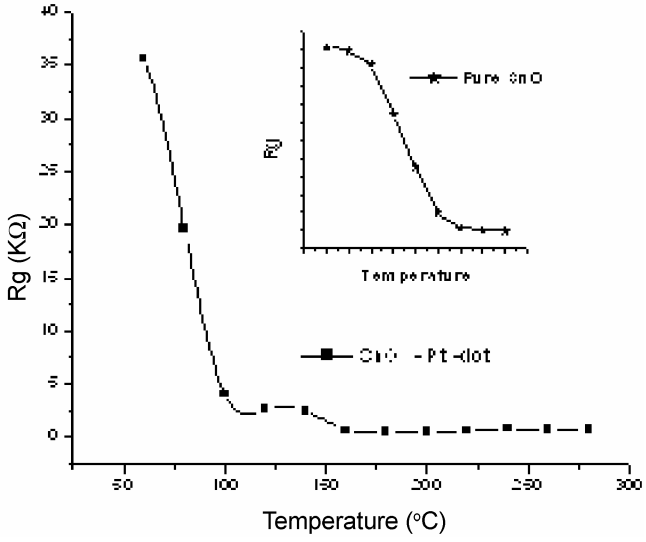

Figure 6. Variation of $\log R_g$ of LPG sensor with temperature.

tance (R_g) under the presence of LPG with temperature. The corresponding variation in R_g for pure SnO_2 sensor is shown in the inset of figure 6 for comparison. The value of R_g is found to decrease continuously with increase in temperature for both the sensors. However, the decrease in resistance (R_g) with the interaction of sensing gas (LPG) molecules was more for the Pt loaded SnO_2 sensor in comparison to the pure SnO_2 thin film (figure 6), indicating the effectiveness of the presence of nanoscale thin Pt as a catalyst in dotted islands form for enhancing the sensitivity. Response time of the sensor is also found to decrease with the presence of platinum dots. Response time for pure SnO_2 is found to be 400 s whereas with the SnO_2–Pt-dot sensor the response time reduces to 100 s.

SnO_2–Pt dotted islands sensor was tested for three different gases, H_2S, methane and LPG. The sensitivity for H_2S and methane at 260°C was found to be low indicating good selectivity of the prepared sensor for LPG.

Gas	Sensitivity	Operating temperature (°C)
H_2S	4	150
Methane	3	200
LPG	742	260

3.1 *Mechanism*

The observed increase in the sensitivity (R_a/R_g) could be related either due to a large resistance in air (R_a) or a very small resistance (R_g) in the presence of LPG, and for an enhanced performance it is desired that both the changes occur accordingly. The increase in R_a value is dependent on the nature of the catalyst being loaded on the SnO_2 film. The difference between the work function of catalyst and SnO_2 thin film is expected to play a crucial role in defining the enhanced resistance, R_a value (Yadav *et al* 2007). Work function of Pt (6·3 eV) is much higher in comparison to that of pure SnO_2 (4·18 eV) (Sahm *et al* 2006), and therefore, creates a Schottky barrier at metal–semiconductor interface.

The formation of barrier at interface is due to reduction in the concentration of conduction electron in sensing SnO_2 film via Fermi energy exchange control mechanism and thereby, results in an increase in the value of R_a for SnO_2–Pt dotted sensors. When the impinging molecules of LPG interact with the prepared sensor structure, its resistance decreases. The constituent hydrocarbons of LPG dissociates over catalysts islands and activates the spill over process. The dissociated atoms spill over onto the surface of underneath sensing SnO_2 layer and interacts with the adsorbed oxygen. This interaction leads to the release of trapped electrons thereby, increasing the concentration of electron in the conduction band of SnO_2 film. Therefore, the resistance (R_g) of the prepared sensor structure decreases in the presence of reducing gas (LPG).

4. Conclusions

A novel sensor structure has been fabricated for enhanced sensitivity and low operating temperature for the detection of LPG, using nanoscale thin platinum catalysts (~10 nm) dispersed in the form of dotted islands on r.f. sputtered SnO_2 thin film (~90 nm thick). The response speed of the sensor becomes fast by loading platinum dots over SnO_2 sensing element, and exhibit a high sensitivity (~742) at a relatively low operating temperature of 280°C. The developed sensor with improved sensing response characteristics is promising for efficient detection of LPG.

Acknowledgements

Authors thank the Department of Science and Technology (DST), India, for financial support under NSTI program. One of the authors (DH) is also thankful for a fellowship.

References

Baruwati B, Kumar D K and Manorama S V 2006 *Sens. Actuators* **B119** 676

Bonasewicz P, Hirschwald W and Neumann G 1986 *J. Electrochem. Soc.* **133** 2270

Chaudhari G N, Bende A M, Bodade A B, Patil S S and Manorama S V 2006 *Talanta* **69** 187

Chowdhuri A, Gupta V and Sreenivas K 2003 *Sens. & Actuators* **B93** 572

Gupta S, Roy R K and Pal Chowdhury M 2004 *Vacuum* **75** 111

Heiland G, Kohl D and Seiyama T (eds) 1988 *Chem. Sens. Technol.* **1** 15

Ihokura K and Watson J 1994 *The stannic oxide gas sensor, Principles and applications* (Boca Raton, FL: CRC Press)

Jain K, Pant R P and Lakshmikumar S T 2006 *Sens. Actuators* **B113** 823

Phani A R, Manorama S and Rao V I 1998 *Mater. Chem. & Phys.* **58** 101

Pourfayaz F, Khodadadi A, Mortazavi Y and Mohajerzadeh S S 2005 *Sens. Actuators* **B108** 172

Reddy M M H and Chandorkar A N 1999 *Thin Solid Films* **349** 260

Sahm T, Gurlo A, Bârsan N and Weimar U 2006 *Sens. Actuators* **B118** 78

Senguttuvan T D, Rai R and Lakshmikumar S T 2007 *Mater. Letts* **61** 582

Shinde V R, Gujar T P and Lokhande C D 2007 *Sens. Actuators* **B123** 701

Srivastava A, Rashmi and Jain K 2007 *Mater. Chem. & Phys.* **105** 385

Wagh M S, Jain G H, Patil D R and Patil D R 2007 *Sens. Actuators* **B122** 357

Waghulade R B, Patil P P and Pasricha R 2007 *Talanta* **72** 594

Yadav H K, Sreenivas K and Gupta V 2007 *Appl. Phys. Lett.* **90** 172113