Enhanced LPG response characteristics of SnO_2 thin film based sensors loaded with Pt clusters

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ABSTRACT

RF sputtered SnO_2 thin films (90 nm thick) loaded with clusters of nanoscale (8 nm) metal catalysts (Pt, Ag, Ni, Pb, Al, Pd) are investigated for LPG detection. SnO_2 film loaded with Pt catalyst clusters exhibits enhanced response (~ 7.5×10^2) to 200 ppm of LPG at a relatively low operating temperature (185^oC) with a fast response time of 100s. Variation of thickness of Pt clusters in the nanoscale range (2 to 20 nm) is seen to significantly influence the sensor response characteristics. Enhanced performance is observed for SnO_2 thin films loaded with 10 nm thick platinum clusters that exhibited a high response (~ 5×10^3) at an operating temperature, of 220^oC. Preliminary results indicate the potential application of prepared sensor structure of Pt clusters (10nm)/SnO_2 (90 nm)/IDE/glass substrate for efficient detection of LPG at relatively low temperature.

Keywords: Gas Sensor, Pt clusters-SnO_2, Thin films, Sputtering, LPG

1. INTRODUCTION

Gas sensors based on semiconducting metal oxides have attracted the attention of environmentalist and many other researchers [1-10]. Hydrocarbon gases, including liquid petroleum gas (LPG) find useful applications, as a clean source of energy at both the domestic and industrial sites [9]. However the explosive nature of LPG makes requirement of reliable and efficient gas sensors indispensable. Major constituents of LPG include butane (70%-80%), propane (5%-10%) and propylene, butylene, ethylene and methane (1%-5%). Tin dioxide (SnO_2) in thin film form is found to be the most promising for gas sensing applications due to advantages such as high sensitivity, low cost, fast response and recovery speed [1]. SnO_2 exhibits sensitivity to various gases, and therefore catalysts are introduced to make the sensor selective [2]. Besides improving the selectivity, catalysts also modulate the electron transport properties of the sensing SnO_2 layer and enhanced response characteristics are obtained. The

introduction of catalysts influence grain size, the shape of crystallites, bulk and surface stoichiometry, properties of intercrystalline barriers, and bulk electro-physical properties [3-5]. Additional possible effects of metal oxide catalysts include the formation of p-n junctions, the appearance of transitional areas and layers acting as catalytic filters, the changes in the valency of metal state, etc. [6-8]. Therefore various additives are used to enhance the sensor response as well as selectivity [3-8].

Literature indicates that various metal catalyst including Pt, Pd, Ni etc. have been introduced in the SnO_2 for realization of LPG sensors with enhanced response for LPG [10-11]. Various processing techniques like chemical co-precipitation method [12], chemical bath deposition method [13], screen printing of SnO_2 and further doping it with RuO_2 [14], e-beam evaporated Pt–SnO_2 and Pd–SnO_2 [15], surface Ru-doped SnO_2 [16], Ni doping on thick SnO_2 film [17], evaporating a thin layer of Pd over sputtered SnO_2 film [18] were used to prepare LPG sensor with improved response. Further, dispersal of catalyst and its content [4-18,30] is identified to be crucial for sensing response, and its presence on the surface of sensing layer in the nanoscale range seems to give enhanced response [19]. The response magnitude of LPG sensors are reported over the range 2–200 and operating temperature is very high (350–800◦C) [9-22]. Efforts are continuing towards the enhancement of sensitivity of LPG sensors along with the reduction in operating temperature by developing good quality SnO_2 thin films using reproducible technique and integrating appropriate catalysts in different manner. However, no attempt has been made towards the comparison between the various metal catalysts loaded on SnO_2 thin film for LPG detection. In the present work LPG sensing properties of SnO_2 thin films loaded catalytic clusters in nanoscale range (10 nm) of various metal catalysts including platinum, palladium, silver, nickel, lead and aluminium are investigated. It has been observed that the Pt-loaded SnO_2 sensor exhibits enhanced response (~5×10^3) for 200 ppm LPG at a relatively low operating temperature (~220 ◦C) with fast response and recovery times.

2. EXPERIMENTAL

SnO_2 thin films were deposited by rf sputtering under reactive ambient (50%Ar+50%O_2) on the Corning glass substrates using 99.999% pure tin target. A 90 nm thin film of SnO_2 was grown at a sputtering pressure of 14 mTorr with rf power of 150W. The substrate was kept at room temperature at a distance of about 7.5 cm from the target surface. The glass substrates were

patterned by inter-digital electrodes (IDE) of sputtered platinum using conventional photolithography technique. The sensing response characteristics were recorded by depositing the SnO_2 thin films onto the entire IDEs protecting the contact pads using a shadowmask, as shown in Fig. 1. The crystallographic structure and surface morphology of the sensing layer has been investigated using a Philips (model PW 1830) X-ray diffractometer. The optical characterization of SnO_2 thin films was made using a double beam UV–vis spectrometer (PerkinElmer Model LAMBDA35) over a range 190–1100 nm. Clusters of various metal catalysts (Pt, Ni, Ag, Pb, Al, Pd) were deposited on the surface of SnO_2 thin films to make the sensor structures using a shadow mask (600 μm pore size). Catalytic clusters of 8 nm thin platinum, palladium and nickel were deposited by rf sputtering whereas thermal evaporation was used for silver, lead and aluminium catalysts. Post deposition annealing of all prepared sensor structures (Metal Clusters / SnO_2 Film/ IDE / Glass) was carried out in air ambient at 300^{o}C for 2 h to improve the stability.

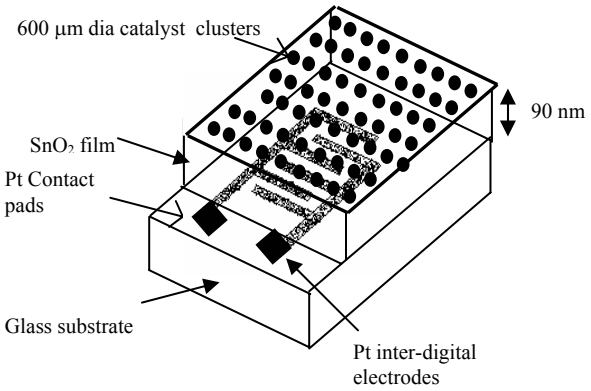

Fig. 1: SnO_2-catalyst cluster sensor

The sensor was placed in a special designed gas test rig chamber on a temperature controlled heating block and spring loaded platinum contacts were used to measure the sensing response characteristics. The response characteristics of the prepared sensor structures were measured over the temperature range 60 to 280^{o}C for 200 ppm of LPG. At each temperature the sensor was first stabilized in air to obtain a stable resistance (R_a) value. LPG (200 ppm) was injected into the

test rig chamber and sensing response characteristics were recorded using a Keithley Digital multimeter (model-2700) interfaced with a personal computer. Sensor response is defined as $S= R_a/R_g$, where R_a is the sensor resistance in air and R_g is the resistance in the presence of reducing gas (LPG).

3. RESULTS AND DISCUSSION

As-grown SnO_2 films on corning glass substrates were found to be transparent, strongly adherent to substrate and amorphous. Annealing at 300 ^oC in air for two hours transformed the amorphous SnO_2 film into a poly-crystalline structure. Figure 2 shows the typical X-ray diffraction pattern of a 90 nm thin SnO_2 film annealed at 300 ^oC in air. The broad and well defined reflections were observed at 2θ = 26.50, 33.89 and 51.79 corresponding to (1 1 0), (1 0 1) and (2 1 1) planes, respectively, in the XRD spectrum of the annealed SnO_2 thin film, which are in good agreement to the reported values for rutile structure [1], confirming the formation of a polycrystalline SnO_2 thin film. The estimated value of lattice constants were found to be $a = b$ = 4.789 Å and c=3.164 Å, which are in close agreement to the reported values for bulk SnO_2 [1].

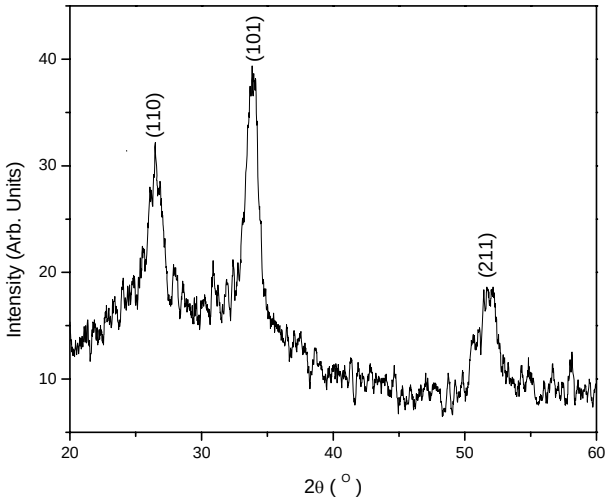

Fig. 2: X-Ray diffractogram of the SnO_2 thin film annealed in air at 300^{o}C.

The optical properties of the annealed SnO_2 thin film were studied, and a high transmission >85 % was obtained in the visible region. The onset of sharp absorption edge at around 350 nm was observed in the transmission spectra of SnO_2 thin film. The optical bandgap (Eg) of film was evaluated by extrapolating the Taut plot between $(\alpha h\nu)^2$ versus $h\nu$ to α=0, where α is the

absorption coefficient and hv is the photon energy. The estimated value of the bandgap was found to be 4.13 eV for the annealed film and is in agreement to the value reported by other workers for SnO_2 thin film [23].

The sensing response characteristics of the SnO_2 catalyst cluster sensor structure were studied over a wide temperature range 60 to 280°C. The resistance of the sensor was measured in air and in the presence of LPG at each temperature. Figure 3 shows the variation of sensor resistance (R_a) measured in air as a function of temperature for SnO_2 thin film and SnO_2 catalyst-cluster structures having metal catalysts of Pt, Pd, Ag, Ni, Pb and Al.

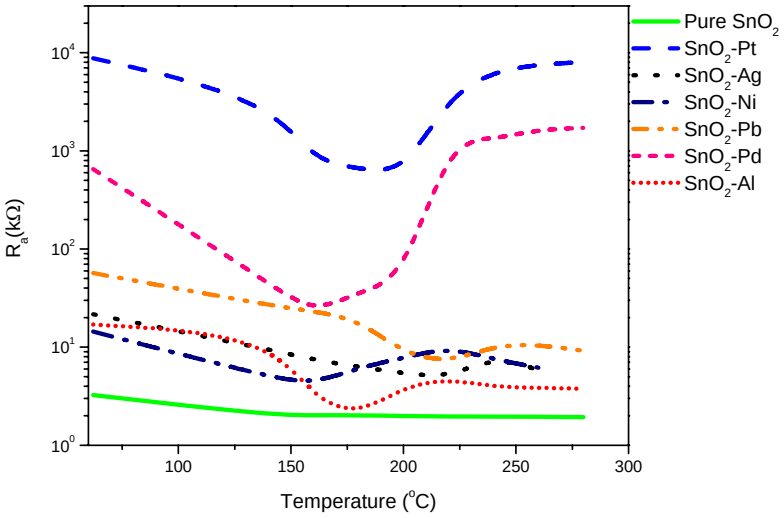

Fig 3. Variation of resistance (*R*a) measured in air with temperature.

The SnO_2 sensing film shows a continuous decrease in R_a value with increasing temperature and is in accordance with its semiconducting behavior. It is interesting to note that resistance (R_a) of SnO_2/metal catalyst clusters sensors shows higher value compared to bare SnO_2 film sensor over the entire temperature range (Fig. 3). Maximum increase in R_a was noted for sensor structure having Pt catalyst clusters followed by Pd clusters. It was also interesting to found that the value of R_a increase with increase in temperature at higher temperature (>180°C) for all SnO_2/metal-cluster sensors in contrary to bare SnO_2 thin film sensor (Fig.3).

Variation of resistance (R_g) of SnO_2 film sensor and SnO_2/catalyst-clusters sensor structures measured in the presence of LPG (200 ppm) is shown in Figure 4 as a function of temperature. The values of Rg could be seen to decrease (in comparison to R_a) for all sensor

structures after interaction with LPG therefore showing the reducing nature of the interacting gas. However, the quantum of fall observed for SnO_2/metal-clusters sensor structures was much higher compared to the corresponding value for uncoated SnO_2 film [Figs. 3 and 4]. Value of R_g for uncoated SnO_2 film was found to decrease rapidly at lower temperatures (< 180 ^oC) and then shows a sign of saturation (Fig 4). However, a much rapid fall in the R_g value with temperature is distinctly seen for SnO_2 film/Pt cluster sensor at lower temperature [Fig. 4].

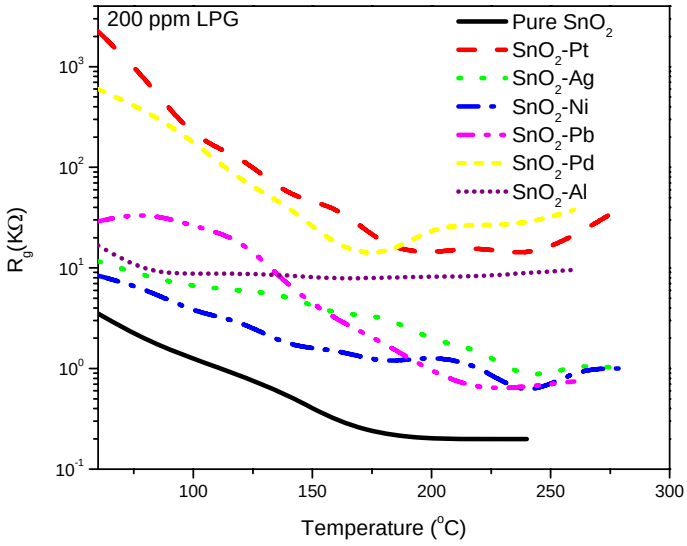

Fig. 4 Variation of resistance (R_g) measured in the presence of LPG with temperature

Variation in the sensing response as a function of temperature for SnO_2 film and SnO_2 film/catalyst clusters (catalyst = Pt, Ag, Pb, Ni, Al, Pd) to 200 ppm of LPG is shown in Fig. 5

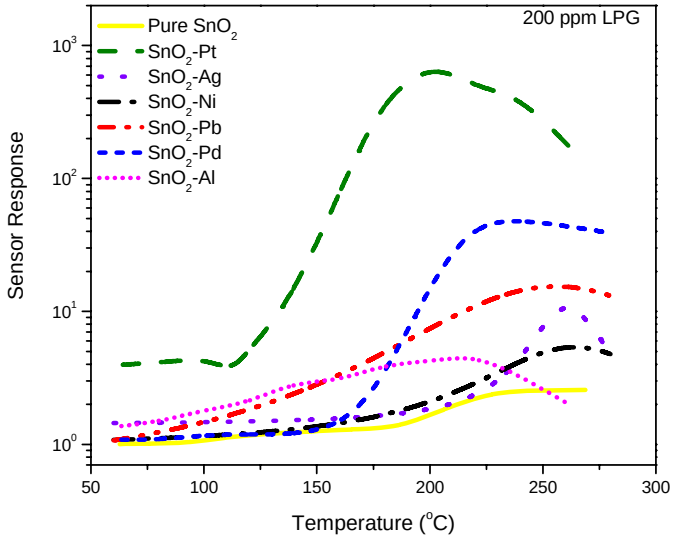

Fig. 5: Variation of sensor response with temperature of SnO_2 sensors covered with various catalysts in islands form.

Response of all the sensor structures prepared in the present study was found to increase with increasing temperature and shows a maximum value at a particular temperature. A relatively poor response for uncoated SnO_2 film sensor was obtained (S = 3) even at an elevated temperature of 280°C and no well defined peak was observed. A high response ($S \sim 7.5 \times 10^2$) was observed for SnO_2/Pt clusters (8 nm thin) sensor structure at a relatively lower operating temperature (~ 185 °C). Other sensor structures having different metal catalysts were found to exhibit poor sensing response (S < 50) and at relatively higher operating temperature (> 220 °C). Therefore it can be inferred that for efficient detection of LPG, clusters of Pt catalysts on the surface of sensing SnO_2 thin film could be utilized to obtain an enhanced response at a relatively lower operating temperature. The observed enhanced response characteristics for LPG may be attributed to the activation of spill-over of sensing gas molecules by the presence of Pt catalyst clusters on to the surface of sensing SnO_2 layer. The enhanced interaction of spill-over of reducing gas molecules with the adsorbed oxygen available on SnO_2 thin film surface leads to the significant reduction in the value of R_g thereby giving maximum sensing response (Fig. 5). Looking at the promising results obtained in the present study with SnO_2/Pt cluster sensor structure the effect of thickness of Pt clusters on the LPG response characteristics has also been investigated. The thickness of Pt catalyst clusters grown on SnO_2 thin film was varied in the

nanoscale range from 2 nm to 20 nm. The sensing response of the SnO_2/Pt cluster sensor was found to increase from 6×10^1 to 5×10^3 with an increase in thickness of Pt cluster from 2 nm to 10 nm, and shows a decrease thereafter. The initial increasing trend in sensor response is attributed to the fact that spillover of sensing gas molecule on the surface of SnO_2 thin film increases with an increase in the content of Pt catalysts. The sensor having 10 nm thin Pt clusters gives an enhanced sensing response of 5×10^3 at an operating temperature of 220 ^oC. It may be noted from the literature that SnO_2 based LPG sensors either exhibits high sensing response (~ 333) at much higher operating temperature (350^oC) [21] or a relatively lesser response (~45) with lower operating temperature (150^oC) [29]. The sensor structure prepared in the present study having effective dispersal of 10 nm thin Pt catalyst in the cluster form on the surface of SnO_2 film (90 nm) shows promising application for LPG detection.

Mechanism

It was observed that simple metal oxide could not comply with all demands, made to perfect gas sensing matrix. Addition of various catalyst would enhance the sensor response of the gas sensing matrix. The enhanced response observed in the present work for all the SnO_2/catalyst island structures in comparison to pure SnO_2 sensor is attributed to an increase in sensor resistance measured in air (R_a). The value of R_a is found to depend significantly on the nature of catalyst used in the study and may be correlated with the difference in their work function (ϕ_m) with respect to SnO_2. The work function of the metal catalysts of Pt, Ag, Ni, Pb, and Pd are in the range between 4.25 to 6.35eV, and are generally higher (except for Aluminium where ϕ_m= 4.08eV) than the corresponding value (4.18 eV) reported for a semiconducting SnO_2-sensing layer [33]. The integration of a 10nm thin metal catalyst in the form of islands having a relatively higher work function with a SnO_2 thin film may lead to the formation of a space charge barrier at the metal–semiconductor interface due to the transfer of electrons from the SnO_2 layer to the metal catalyst. The reduction in concentration of conduction electrons in the SnO_2 film due to formation of the Schottky barrier results in an increase in the value of R_a at room temperature for all the SnO_2/metal catalyst structures (Fig. 3). The increase in R_a was found to be in agreement with the difference in the work function of SnO_2 with the metal catalyst used in the present study except for the Al catalyst.

The resistance of the prepared samples decreases as soon as the sensor surface interacts with impinging gas (LPG) molecules. Hydrocarbons are known to dissociate on metal oxide

surfaces before reacting with adsorbed oxygen. The presence of a catalyst on the SnO_2 surface in the form of islands may dissociate the impinging LPG molecules and activate the spillover mechanism. The dissociated molecules then spillover onto the surface of the sensing SnO_2 semiconductor and interact with the adsorbed oxygen. The overall reaction of LPG molecules with adsorbed oxygen can be explained as follows :

$C_nH_{2n+2} + 2O^- \leftrightarrow H_2O + C_nH_{2n}–O + e–$

The interaction of the reducing gas species with the chemisorbed oxygen results in the release of trapped electrons, thereby increasing the electron carrier concentration in the bulk of sensing SnO_2 layer. The increase in the concentration of electron in the conduction band of SnO_2 layer accounts for the decrease in sensor resistance (R_g) in the presence of reducing gas. It was observed that the SnO_2/Pt-islands structure exhibits a three to four orders higher response comparison to that seen for pure SnO_2 sensor. The observed large response is due to the coexistence of Fermi energy control and spillover mechanism. The large difference in the work function of catalyst and enhanced oxygen adsorption activity on the surface of SnO_2 film at elevated temperature due to the presence of ultrathin Pt islands results in the higher value of R_a. The Pt catalyst is also known to activate the spillover process after dissociation of hydrocarbons (LPG) on the surface of the sensing SnO_2 layer, leading to a much lower value of sensor resistance (Rg) in the presence of LPG.

The sensing response characteristic of SnO_2/Pt-catalyst structure was also studied as a function of Pt thickness. Whenever the thickness of the Platinum islands is less than 10 nm, the dispersal of catalysts on the SnO_2 film surface may be poor and the gas response would be decreasing. At lower thickness of catalyst(less than 10 nm) there is a reduction in the concentration of adsorbed oxygen on the SnO_2 film surface leading to a lower value of R_a and hence giving a lower sensing response. Therefore sensing response increases with increase in the thickness of the catalyst. On the other hand, if the thickness of the Pt catalyst increases beyond 10 nm, response of the sensor again decreases. The Pt catalyst are known to activate the spillover process after dissociation of hydrocarbons (LPG) on the surface of sensing SnO_2 layer leads to decrease in the resistance (R_g) value. At higher Pt thickness (>10 nm) there is excess leftover adsorbed oxygen after the interaction of spilled over hydrocarbons, and as a result the resistance R_g does not fall to a low enough value, and giving a lower response. Therefore for an enhanced performance of the sensor it is desired that the changes in both the resistances (higher

R_a and lower R_g) occur simultaneously. A critical thickness of 10 nm for the Pt islands allows the spill over mechanism to be more effective besides the activation of adsorbed oxygen activity and a Fermi-level type of interaction in the SnO_2/Pt-cluster sensors for efficient and reliable detection of LPG.

4. CONCLUSIONS

Sensing characteristics of rf sputtered SnO_2 thin films loaded with various metal catalysts in the form of nanoscale thin clusters are investigated for LPG (200 ppm) sensing. Amongst all the SnO_2/metal-cluster structure hetero-structures tested, SnO_2 thin films loaded with 10 nm thin clusters of Pt catalyst exhibit highest sensor response (~ 5 x 10^3) at relatively lower operating temperature (~ 220 ^oC). The onset of oxygen adsorption activity from atmosphere and spillover of dissociated hydrocarbons (LPG) on the surface of the sensing SnO_2 thin film due to the presence of nanoscale thin (10 nm) Pt islands results in enhanced sensing response characteristics with a fast response speed (~100 s) and a fast recovery (~120 s).

ACKNOWLEDGEMENTS

The authors wish to thank Department of Science and Technology (DST), Govt. of India for a sponsored research project.

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