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Enhanced response characteristics of SnO_2 thin film based sensors loaded with Pd clusters for methane detection

Divya Haridas [a],*, Vinay Gupta [b]

[a] Keshav Mahavidyalaya, University of Delhi, Delhi 110034, India
[b] Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

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ABSTRACT

This paper reports the response characteristics of rf-sputtered SnO_2 thin films (90 nm thin) loaded with nanoscale catalytic clusters for detection of methane. Ultrathin (8 nm) metal and metal-oxide catalysts (Pt, Ag, Ni, Pd, Au, NiO, Au_2O_3) clusters are loaded over the surface of SnO_2 thin film. The SnO_2–Pd cluster structure is found to exhibit an enhanced response (97.2%) for 200 ppm of methane at a relatively low operating temperature (220 °C). The enhanced response is shown to be primarily due to the dominant roles played by both Fermi level energy control mechanism and spillover mechanism. Thickness of the Pd catalyst clusters in the nano-scale range (2–20 nm), influences significantly the sensor characteristics. Optimized performance is observed with 10 nm thick Pd catalyst clusters showing a high response (~99.2%) at a relatively low operating temperature of 160 °C. Thickness of the Pd clusters is shown to influence the amount of adsorbed oxygen present on the uncovered SnO_2 film surface and also activates the spillover mechanism. The results suggest the possibility of utilizing the sensor structure having novel dispersal of Pd catalyst clusters (10 nm thickness) on the surface of SnO_2 thin film for efficient detection of methane gas.

1. Introduction

Methane gas is found in environment, industrial and domestic areas. It is the main constituent of natural gas which is the fuel supplied to homes and industries. Natural gas is often released from the walls of coal mines and when unmonitored, it can accumulate resulting in dangerous explosions. Methane gas is highly volatile in nature and can cause explosion due to inflammability. It has a lower explosion limit (LEL) of 4.9% and an upper explosion limit (UEL) of 15.4% [1]. Thus, trace level detection of methane gas in the environment is very important to avoid any accidental explosion due to its leakage from automobiles. Continuous efforts are ongoing worldwide toward development of an efficient methane sensor that could work even at low temperatures.

Semiconducting metal oxides have been largely exploited for the detection of such explosive and toxic gases. Among them, tin oxide (SnO_2) is the most explored material as chemical gas sensors, due to its ease in processing and good response to a number of gases at low operating temperature. However, there are problems associated with tin oxide related to its poor selectivity to various gases. In general, suitable catalysts are incorporated with SnO_2 to improve the selectivity and sensing response [2–8]. The effect of addition of various metallic particles (catalysts) on the gas sensing response of metal oxides has been widely studied. The two major mechanisms involved in gas sensing are chemical and electronic mechanisms [9]. Platinum, palladium, gold, silver are found to be well-known catalysts required to enhance the sensing response of SnO_2 for reducing gases [8–11]. Palladium or silver metal catalysts are typically considered to be related with an electronic mechanism, whereas platinum catalyst supports chemical mechanism [12,13].

Palladium is a suitable oxidation catalyst for SnO_2 based sensor for methane (CH_4) gas [14–17]. The reported values of sensor response for methane is about 10–80% (the sensor response is defined in percentage as $S\,(\%) = (R_a - R_g)/R_a \times 100\%$ where R_a is the resistance of the sensor in air (i.e. in the absence of methane), and R_g is the resistance of the sensor in the presence of the methane gas) and operating temperature is very high (250–600 °C) (Table 1) for a moderate concentration ($\leq$1000 ppm) of methane gas. Sensor response is observed to be good only for higher concentration of methane ($\geq$1000 ppm), presence of which may lead to accidental explosions. Efforts are continuing toward the enhancement of sensing response of methane sensors along with the reduction in operating temperature either by fabricating good quality SnO_2 thin films or by incorporating an appropriate catalyst in various manners. Still, appreciable efforts need to be made toward the study of

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* Corresponding author. Tel.:+91 9868331663.
E-mail address: divya_h14@rediffmail.com (D. Haridas).

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Table 1
Brief summary of results reported on SnO_2 based methane sensors.

Year	Sensing material	Technique used	Gas cons.	Response	Temp (°C)	Ref.
1996	SnO_x and InO_x thin films/Al_2O_3 + Pd	rf sputtering	10,000 ppm	2.55 (=R_a/R_g)	420	[9]
1997	SnO_2 thick film	Screen-printing technology	10,000 ppm	700%	450	[21]
1999	SnO_2/Os thin film	Sol–gel	1000 ppm	620 (=R_a/R_g)	250	[38]
2000	MgO into SnO_2–In_2O_3–TiO_2	Catalytic combustion	5000 ppm	3.4 (=R_a/R_g)	300	[3]
2000	SnO_2 thin film	Sol–gel	500 ppm	27%	400	[16]
2000	SnO_2/Au thick film	Co precipitation method	3000 ppm	82%	400	[4]
2002	SnO_2 nanopowders	Sol–gel	1000 ppm	35%	325	[17]
2005	Nanostructure tinoxide powder	Low temperature catalyst adding (LTCA) method	3500 ppm	1%	400	[39]
2005	Fe doped SnO_2 thick films	Precipitation technique	1000 ppm	65%	350	[5]
2006	Pd loaded SnO_2 thin film	Sol–gel	1000 ppm	4%	350	[7]
2006	Iron doped tinoxide	Precipitation method	1000 ppm	66%	350	[6]
2007	Tin dioxide thick film	Precipitation method	1000 ppm	85%	350	[22]
2008	Pd loaded SnO_2 nanoparticles	MEMS technique	5000 ppm	34 (=R_a/R_g)	450	[14]
2010	Nanoporous SnO_2	Nano-casting	4000 ppm	0.6 (=R_a/R_g)	600	[40]
2011	Pd doped SnO_2	Chemical method	6500 ppm	21 (=R_a/R_g)	600	[41]

the effect of various catalysts on the sensing response characteristics of SnO_2 thin film for methane gas. Furthermore the content of catalyst incorporated into the sensing layer is very crucial for the enhanced response characteristics; therefore a dedicated effort is needed to optimize the catalyst content for an efficient detection of methane gas.

In the present work, we have loaded the surface of rf-sputtered SnO_2 thin film with uniformly distributed ultrathin clusters of catalysts of different metals and their oxides for detection of methane gas. A significant improvement in the sensor response was observed using a structure consisting of palladium clusters on the surface of SnO_2 thin film. The thickness of palladium clusters dispersed on the surface of SnO_2 thin film has been varied over the range from 2 to 20 nm, to understand its influence on the response characteristics for methane sensing. The SnO_2 sensor loaded with 10 nm thin Pd clusters exhibits a response of about 99.2% at an operating temperature of 160 °C for 200 ppm methane gas and is relatively better in comparison to many other methane sensors that have been reported so far (Table 1).

2. Experimental

SnO_2 thin film (90 nm) was deposited by rf sputtering using a metallic Tin target (99.99% pure) in a reactive atmosphere (50%Ar and 50%O_2) at 14 mTorr. Interdigital electrodes of platinum/titanium were patterned on corning glass substrates using photolithography technique prior to the deposition of SnO_2 film. The catalyst of various metal including platinum (Pt), palladium (Pd), nickel (Ni), silver (Ag), gold (Au) of 8 nm thickness each were loaded on the surface of SnO_2 thin film using a shadow mask of 600 μm pore size (Fig. 1) [18]. The gap between the pores in the shadow mask is around 1000 μm and thereby leaves no possibility of short-circuits among the clusters. The three catalysts namely Pd, Ni and Pt were deposited onto SnO_2 thin film using rf sputtering (Nordiko NM 1250) and the thickness of the clusters were being optimized, where the deposition rate of Pt, Pd and Ni are 2.5 nm/min, 2 nm/min and 1 nm/min respectively. Further the thickness of the deposited clusters (using rf sputtering technique) was measured using surface profiler (Dectak 150A). The thickness of the catalyst film deposited by evaporation technique (Au and Ag) was monitored using a quartz crystal based thickness monitor (Hind-Hivac, India, Model No. DTM 101), having calibration features like acoustic impedance correction, film density and tooling factor parameters for enhanced accuracy. The prepared SnO_2-catalyst cluster sensors were also heated in air at 400 °C for 2 h so as to transform ultrathin metal catalysts to their respective oxides.

Thickness of palladium islands loaded on SnO_2 surface has been varied in the range from 2 to 20 nm. Sensor response (sensor response is defined in percentage as $S\,(\%) = (R_a - R_g)/R_a \times 100\%$ where R_a is the resistance of the sensor in air (i.e. in the absence of methane), and R_g is the resistance of the sensor in the presence of the methane gas) of all the prepared structures was measured over the temperature range of 60–260 °C. Sensor response

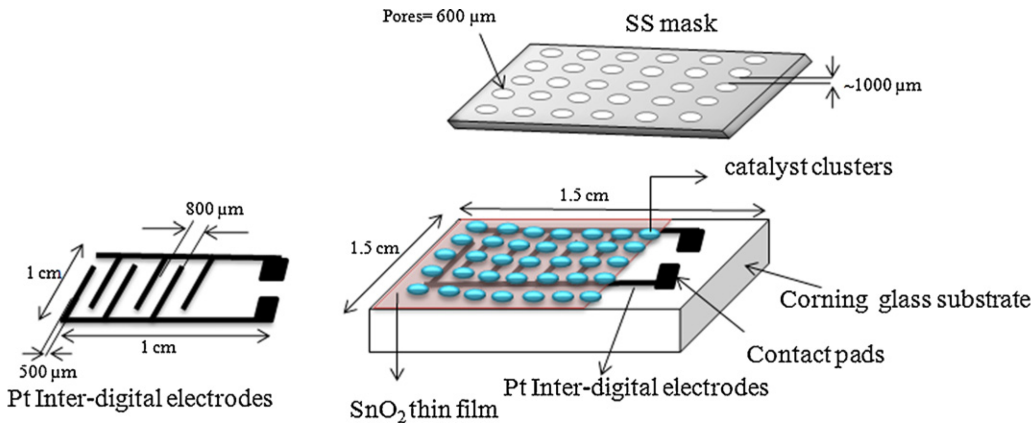

Fig. 1. Top view of the SnO_2-catalyst cluster sensor structure on Pt IDEs.

measurements were carried out in a home-built gas sensing test rig retrofitted with a glass bell jar and calibrated leaks were used for methane introduction. The humidity in the test chamber was about 30%RH while doing the sensing measurements. Volume of the test chamber was taken to be 11.0 L and target methane gas was injected in the test chamber through a syringe of 2 mL at the time of taking response for 200 ppm of methane gas. Vacuum of the order of $\sim 10^{-3}$ Torr was first created in the test chamber and subsequently a mixture of the known concentration of target gas and clean synthetic air was introduced till the test chamber acquired the atmospheric pressure to ensure that the target gas was free from any other interfering gases. In our case the target gas is pure methane gas which is introduced into the test chamber along with clean synthetic air. The measurements were carried out in static mode. At the time of recovery of the senor resistance, target gas was flushed out of the test chamber (by creating vacuum again) and the clean dry air was introduced into the chamber. The surface of porous SnO_2 are generally covered with chemisorbed and physisorbed water at room temperature in normal laboratory condition (ca. 40–60%RH) and then shows ionic (H+) conductivity, and the effect of polarization on sensor resistance cannot be ruled out. However, these effects are expected to be low in the SnO_2 thin film having low resistivity as observed in the present work, therefore we neglect the polarization effect in our case. It may be noted that the resistance of SnO_2 sensor prepared in present study was unstable at room temperature and become stable only after a thermal treatment at 300 °C in air for 2 h. Therefore, all prepared sensor structures were refreshed at a temperature of 300 °C prior to loading catalyst clusters.

A piezo-sensor (Provac A100) was used to monitor gas pressure inside the test chamber. The sample holder was fitted with a miniaturized heater, controlled through a temperature controller (accuracy ±0.5 °C), which was used to measure the sensor response as a function of temperature (60–260 °C). At each temperature the sensor was first stabilized in air to obtain a stable resistance value. Target gas (methane) of specific concentration was introduced into the test chamber and the change in resistance was measured using Pt coated spring electrodes fitted to probes of Digital Multimeter DMM (Model No.: Keithley 2002) interfaced to a computer which acted as the data acquisition system. The sensing results (response at respective operating temperature) of these sensor structures were found to be reproducible within an accuracy of ±3%.

The crystallographic orientation of the deposited films has been studied using X-ray diffraction (XRD) using a Philips X-ray diffractometer. The X-ray source used is Cu Kα1 radiation (λ = 1.5405 Å). 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. Atomic force microscope (VECCO DI multimode SPM), was used to study the surface morphology of SnO_2 thin films grown on glass substrates. Surface morphology of the films was examined over an area of 2 μm × 2 μm in the non contact mode.

3. Results and discussions

The SnO_2 thin film deposited on corning glass substrate was found to be uniform, transparent and strongly adherent. No Bragg reflection corresponding to any plane of SnO_2 was observed in the XRD pattern of as grown SnO_2 thin film indicating the growth of amorphous film. However film becomes polycrystalline after an annealing treatment at 300 °C in air for 2 h. Tin oxide (SnO_2) thin films deposited in the present study are polycrystalline with rutile crystallographic structures. The surface morphology of the sensing layer was studied using an atomic force microscope (AFM). AFM studies of the as-grown SnO_2 thin film revealed the formation of a rough surface morphology with randomly distributed channels (Fig. 2a). The post-deposition annealing treatment of the film at 300 °C resulted in the formation of rough microstructure with well elongated channels (Fig. 2b). Thereby confirming the preparation of a good quality film which can be used for gas sensing application as the formation of channels on the surface of the sensing layer seems to be advantageous for efficient detection of gas molecules.

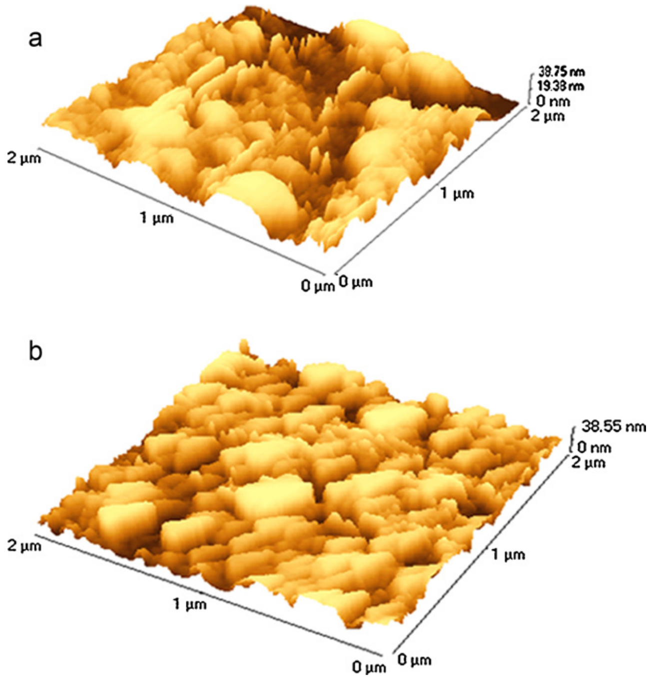

Fig. 2. AFM images of 90 nm thin SnO_2 films: (a) as-deposited and (b) post-deposition annealed in air at 300 °C.

Fig. 3(a)–(h) shows the XRD patterns of all the samples. Fig. 3(a) corresponds to XRD pattern of SnO_2. The diffraction peaks observed at around $2\theta = 26.6°$, 33.9° and 51.8° are ascribed to the reflections corresponding to (1 1 0), (1 0 1) and (2 1 1) planes of tetragonal SnO_2 respectively which are in good agreement to the reported values for rutile structure, JCPDS 41-1445, confirming the formation

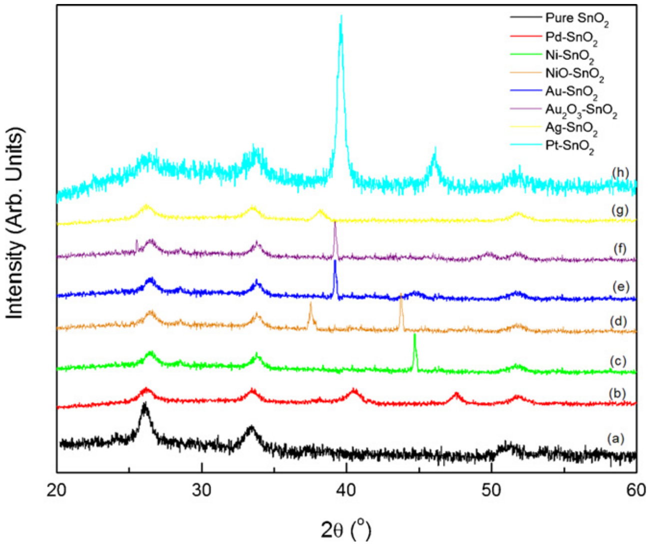

Fig. 3. X-ray diffractogram of all sensor structures (a) pure SnO_2 thin film (b) Pd—SnO_2 thin film, (c) Ni—SnO_2 thin film, (d) NiO—SnO_2 thin film, (e) Au—SnO_2 thin film, (f) Au_2O_3—SnO_2 thin film, (g) Ag—SnO_2 thin film, (h) Pt—SnO_2 thin film.

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. The value of crystallite size of the annealed SnO_2 thin film was evaluated by fitting the width of (1 1 0) reflection using Scherrer formula $d = K\lambda/\beta \cos\theta$, where K is 0.94, λ is the X-ray wavelength, β the peak full width half maxima (FWHM) and θ is the diffraction peak position. The estimated value of crystallite size of the sensing layer is found to be about 10 nm. Fig. 3(b)–(h) represents XRD pattern of SnO_2 sensor structure loaded with various catalyst. Thereby diffraction peaks corresponding to SnO_2 is observed for all the samples along with the diffraction peaks of the respective catalyst loaded over SnO_2 thin film. XRD peaks (Fig. 3b) around $2\theta = 40.7^\circ$ and 47.3° are associated with (1 1 1) and (2 0 0) planes of FCC palladium respectively (JCPDS file of ICDD Pattern: 00-002-1439). A strong XRD peak (Fig. 3c) around $2\theta = 44.3^\circ$ is associated with (1 1 1) plane of FCC nickel (JCPDS file of ICDD Pattern: 00-001-1258). XRD peaks (Fig. 3d) around $2\theta = 37.4^\circ$ and 43.4° are associated with (1 1 1) and (2 0 0) planes of FCC nickel oxide (NiO) respectively (JCPDS file of ICDD Pattern: 00-001-1239). XRD peaks (Fig. 3e) around $2\theta = 38.3^\circ$ and 44.7° are associated with (1 1 1) and (2 0 0) planes of FCC gold respectively (JCPDS file of ICDD Pattern: 00-001-1172). The prepared SnO_2–Au cluster sensor structure was heated in air at 400 °C for 2 h. The annealing treatment was given to transform ultrathin metal dotted islands into their respective oxides [19,20]. Gold oxide primarily obtained in two forms Au_2O_3 and AuO. The characteristic diffraction peaks of Au_2O_3 is normally observed at 25.5°, 32.5° and 49.7° (JCPDS file of Pattern: 00-024-0462). Fig. 3f shows the XRD peaks around $2\theta = 25.5^\circ$ and 49.5° which are associated with planes of gold oxide (Au_2O_3) (JCPDS file of ICDD Pattern: 00-024-0462) along with the characteristic Au peak at 39.1°. Though diffraction peak at 32.5° is not observed in the XRD pattern as characteristic SnO_2 peak at 33.4° has probably suppressed it, but the observation of other two peaks confirms the formation of Au_2O_3 phase. Further the presence of a small peak at 49.7° also confirms the presence of Au_2O_3 phase only as no such diffraction peak is observed for AuO phase at 49.7° (JCPDS file of ICDD Pattern: 00-023-0278). XRD peak (Fig. 3g) around $2\theta = 38.1^\circ$ is associated with (1 1 1) plane of FCC silver (JCPDS file of ICDD Pattern: 00-001-1167). XRD peaks (Fig. 3 h) around $2\theta = 39.6^\circ$ and 46.3° are associated with (1 1 1) and (2 0 0) planes of FCC platinum respectively (JCPDS file of ICDD Pattern: 00-001-1190).

UV–visible transmittance spectra showed the well defined interference fringes with a strong adsorption edge at around 309 nm indicating that the as grown SnO_2 thin film is free from in-homogeneity [18]. A brief review of the results on semiconductor SnO_2 sensors reported by different workers for methane gas is summarized in Table 1.

The response characteristics of all prepared SnO_2-catalyst cluster sensors were studied over a wide temperature range of 60–260 °C. The resistances of the sensors were measured in both air and in the presence of methane gas at each temperature. The variation of sensing response of SnO_2-catalyst cluster sensors (catalyst = Pt, Ag, Pd, Ni, NiO, Au, Au_2O_3) obtained for 200 ppm methane gas is shown in Fig. 4 as a function of temperature. The sensing response of all the sensor structures prepared in the present study was found to increase with increasing temperature and ultimately reaches the maximum value at a particular temperature (operating temperature). A relatively poor response for sensor having pure SnO_2 film (without any catalyst) with a maximum value ($S = 57\%$) obtained at an operating temperature of 200 °C. The presence of catalyst on the surface of SnO_2 sensing layer and its nature was identified to be crucial for the enhanced response. A high response ($S = 97.2\%$) was observed for SnO_2–Pd clusters (8 nm thin) sensor structure at an operating temperature of 220 °C (Fig. 4). The improved response characteristics of the sensor in the present study may be attributed to the interaction of sensing gas molecules with both the palladium catalyst (dispersed in the form of uniformly distributed clusters) and the uncovered surface of sensing SnO_2 film.

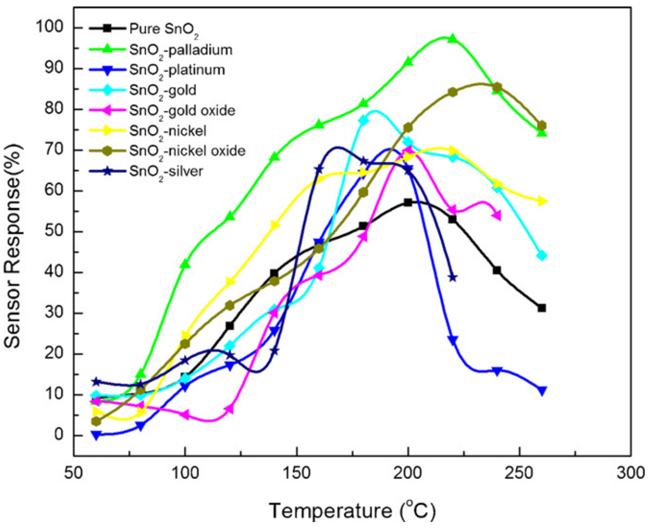

Fig. 4. Variation of sensor response with temperature of SnO_2 sensors covered with various catalysts in cluster form, under 200 ppm methane gas balanced with air.

The SnO_2–NiO cluster sensor structure showed good response (~85.6%) at an operating temperature of 240 °C (Fig. 4). It is important to point out that the sensor structure loaded with clusters of gold also exhibited a reasonably good response (~77.3%) at a much lower operating temperature of 180 °C. Therefore, it is a trade off between the sensing response and the operating temperature, and depending upon the requirement one could select either SnO_2–Pd cluster structure or SnO_2–Au cluster sensing structure for efficient detection of methane gas.

It may be noted from Table 1 that SnO_2 thick film grown by screen printing technology showed an enhanced response at high operating temperature (450 °C) for 1% methane concentration [21]. SnO_2 thick film prepared by precipitation technique also showed a good response of 85% at 350 °C for the detection of 1000 ppm of methane [22]. The incorporation of gold or palladium into SnO_2 film is reported to enhance response for methane gas (Table 1) at 400 °C for 3000 ppm methane [4]. However it is observed that sensors showed a good response at high temperatures only, thus one needs to maintain a high operating temperature (>325 °C) and/or high concentration of methane gas (≥1000 ppm) to achieve a high response. A higher response (>75%) at a relatively low operating temperature (180–240 °C) (comparing with other sensors reported in Table 1) was observed in the present study for Pd, Au and NiO catalyst clusters for 200 ppm methane gas. It clearly indicates that the nature of catalyst on the surface of sensing SnO_2 layer plays a crucial role.

Fig. 5 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 catalysts of Pt, Pd, Ag, Ni, NiO, Au, Au_2O_3. Pure SnO_2 thin film sensor shows a continuous decrease in the value of R_a with increasing temperature, which is in accordance with its semiconducting nature. The SnO_2 catalyst cluster structures (except Au and Au_2O_3 catalyst) showed higher values of R_a in comparison to the corresponding value obtained for pure SnO_2 thin film sensor over the entire temperature range (Fig. 5). 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 with respect to SnO_2. The work function of the metal catalysts of Pd, Pt, Ag, Ni and Au are 5.12, 6.35, 5.1, 4.55, 4.25 and 5.1 eV respectively, and are higher than the corresponding value (4.18 eV)

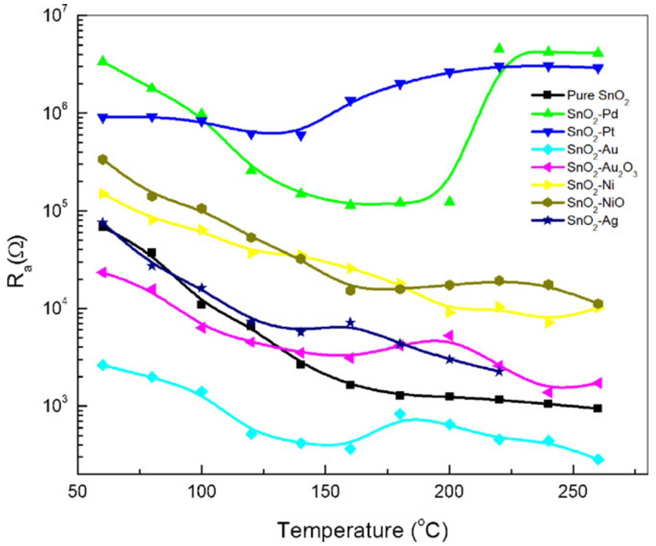

Fig. 5. Variation of sensor resistance (R_a) with temperature for various sensor structures.

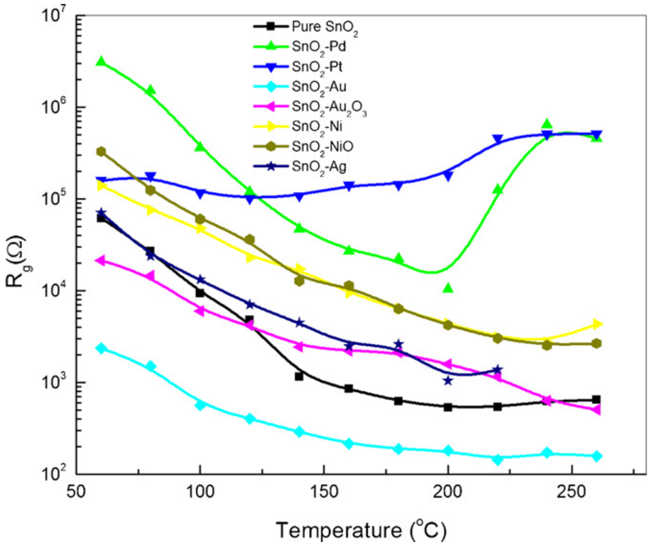

Fig. 6. Variation of sensor resistance (R_g) with temperature for various sensor structures, under 200 ppm methane gas balanced with air.

for a semiconducting SnO_2-sensing layer. The integration of an ultrathin metal catalyst in the form of clusters having a relatively higher work function with a SnO_2 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 to the metal catalyst. The reduction in concentration of conduction electrons in the SnO_2 film due to formation of the Schottky type barrier results in an increase in the value of R_a at room temperature for all the SnO_2–metal catalyst structures (except for gold). The value of R_a for sensors having metal oxide catalysts (such as NiO) are higher in comparison to that obtained with corresponding metal catalysts (such as Ni). Such an increase may be attributed to the formation of the depletion region at the interface of n-type SnO_2 with p-type metal oxide catalysts and the reduction in the volume of semiconducting SnO_2 available for carrier conduction. However the unexpected decrease in R_a induced by the Au and Au_2O_3 loading is still an observation subjected to further studies. Similar observation is observed by Bierwagen et al. [23] where they reported Au loading over SnO_2 as non-ohmic and had low rectification and high reverse leakage current. This non-Schottky behavior was attributed to an increased near surface free electron concentration and thereby leading to an enhanced conductivity.

It was also interesting to found that at higher temperature range the value of resistance R_a for all SnO_2-catalyst cluster structures, increases with increase in temperature. The same trend was not observed for pure SnO_2 thin film. The SnO_2—Pd cluster structure showed a significant increase in resistance (R_a) after 200 °C. The initial decrease in R_a with temperature is due to the semiconducting nature of the sensing SnO_2 layer in all prepared sensor structure. The presence of catalysts (metal or metal oxide) in the form of clusters is probably enhancing the adsorption activity of oxygen from atmosphere on the uncovered surface of the SnO_2 thin film at elevated temperatures. Such an adsorption activity is already been reported in the literature [24,25]. Guo et al. reported that a monolayer of oxygen is rapidly adsorbed at temperatures above 200 K, the temperature for the onset of dissociative adsorption of O_2 on Pd, and that bulk oxidation begins above 473 K [26]. The adsorbed oxygen captures the free electrons from the bulk of SnO_2 thin film thereby resulting in an increase in the value of sensor resistance (R_a) with temperature (Fig. 5).

The resistance (R_g) of the prepared sensor structures measured in the presence of the methane gas is shown in Fig. 6 as a function of temperature. The value of the resistance was found to decrease for all prepared sensor structures after interaction with methane molecules in the measured temperature range indicting the reducing nature of the interacting gas. The value of R_g for uncoated SnO_2 film was found to decrease rapidly with temperature (<150 °C) and thereafter it gets saturated (Fig. 6). However, an increase in the value of R_g with temperature (Fig. 6) is distinctly seen for SnO_2—Pd cluster sensor at higher temperatures (>200 °C). With increasing temperature the chemisorption phenomena reaches a maximum where the interaction between the adsorbed oxygen and the methane gas molecules enhances. Thereafter it becomes a competing process between the chemisorption and re-oxidation of the catalyst due to the presence of air in the background. The rapid decrease in the value of R_g along with higher values of R_a obtained for SnO_2–Pd cluster sensor led to the maximum sensing response (~97.2%) in comparison to other sensor structures. In order to evaluate the gas response speed, the time required to attain 90% of the stabilized value of sensor resistance (R_g) after the target gas comes in contact with the sensing element at a particular temperature T_{opt} which is called as the response time of the sensor ($\tau_{res\text{-}90}$) and keeping the sensing element at the same temperature T_{opt} and removing the sensing gas, the time required by the sensor to attain 90% of its original sensor resistance value (R_a) is referred to as the recovery time ($\tau_{recov\text{-}90}$), were obtained from the gas sensing response transients. Fig. 7 shows the response and recovery time of SnO_2—Pd sensor with temperature. On an average the response time of SnO_2—Pd sensor varies between 87 and 26 s and recovery time varies between 110 and 70 s. The response transients of SnO_2—Pd sensor structure for temperatures lower than 100 °C are shown in the inset of Fig. 7. The decrease in resistance of the sensor structure was not appreciable at low temperatures (<100 °C) when methane gas interacts with the sensing surface and therefore recovers to the original value of the resistance quickly when the gas is flushed out. Usually the recovery of the sensors is very slow at lower temperatures, however in the present study, fast recovery was observed. It may also be noted that four samples of SnO_2–Pd cluster structure were prepared under similar processing conditions in different batches and tested for methane detection. The sensing results (response and operating temperature) of different samples were found to be reproducible within an accuracy of ±2%.

Among proposed catalytic systems the superiority of palladium as a catalyst for complete oxidation of methane to carbon dioxide

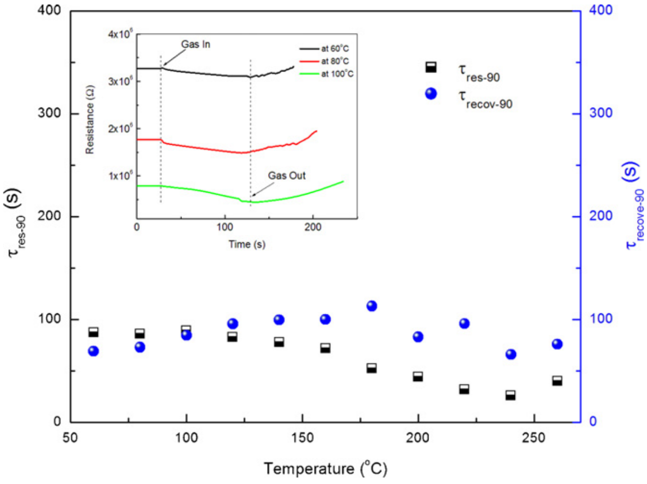

Fig. 7. Variation of response time (τ_{res-90}) and recovery time ($\tau_{recov-90}$) of SnO_2—Pd sensor with temperature under 200 ppm methane gas balanced with air.

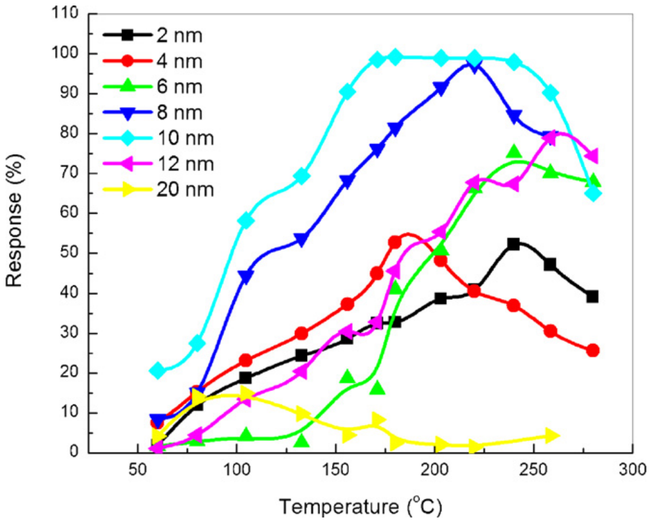

Fig. 8. Variation of sensor response with temperature for different thickness of Pd clusters loaded on SnO_2 thin film, under 200 ppm methane gas balanced with air.

and water has been well known for years. High efficiency of palladium may be related to its ability to dissociate oxygen molecules by forming a surface oxide. It has been shown that periodic decomposition of palladium oxide to metallic Pd and re-oxidation occurred during the [27] catalytic methane combustion over Pd catalysts. The ability to activate the C—H bond in a hydrocarbon is a crucial step. This activation is very efficient on metallic palladium where such processes as the dissociation of molecular hydrogen or C—H bonds in hydrocarbons may easily occur. Engel and Kuipers [28] found that at room temperature O_2 adsorbs dissociatively on Pd (1 1 1) with a saturation coverage of $\theta = 0.25$ in a 2×2 surface mesh. The d orbitals of metallic Pd transfer electronic charge into antibonding levels of the adsorbate, facilitating dissociation. Therefore, oxygen spillover from Pd to the SnO_2 surface can become an important source of atomic oxygen for CH_4 catalytic oxidation on the SnO_2 surface at T_{oper}-200 °C. Solymosi et al. reported the methane decomposition on supported palladium above 473 k to yield hydrogen, ethane and surface carbon [29]. The hydrogen produced in the methane decomposition exhibited a high tendency to be dissolved into palladium crystallites and thereby an enhancement in the decomposition is observed for increasing temperature and methane concentration [29]. Similar behavior was observed by Wang et al. [30] following the decomposition of methane on a Pd surface at 500–600 K, which was also attributed to the dissolved hydrogen. A high dissociation probabaility S_{Tot} (defined as a ratio of the number of dissociatively chemisorbed CH_4 molecules to the total number of CH_4 molecules incident on the surface) on clean Pd (1 1 0) cluster for CH_4 was reported by Valden et al. [31]. Su et al. [32] proposed a mechanism of CH_4 reduction on Pd surface. They worked on ZrO_2 supported by Pd thin films. At an elevated temperature Pd is oxidized and then PdO is reduced in presence of methane. Very rapid oxidation occurs as a consequence of electric field-driven transport of oxygen anions through the oxide film. Once the film thickness exceeds about 15 nm, oxidation occurs more slowly via diffusive transport of oxygen through the oxide film. The reducing gases diffuse to the metal oxide boundary where reduction of the oxide occurs. After the reduction of PdO continuous diffusion of H through Pd to Pd/metal oxide junction takes place and a dipole layer is formed. Dissociative adsorption of methane followed by water formation occurs almost simultaneously due to reaction of hydrogen with the chemisorbed oxygen. Broclawik et al. [33] reported the electronic structure of bare PdO and Pd dimers with their interaction with a methane molecule for various adsorption geometries by means of quantum chemical density functional methodology. It has been found that the strongest non-dissociative adsorption of methane occurs in a bridging position on a palladium dimer accompanied by very strong activation of a C—H bond and a negligible energy barrier for the bond scission. This could be ascribed to the absence of repulsive 5 s electrons in the case of palladium dimer. In the case of palladium atom with closed-shell d^{10} electronic structure no repulsive 5 s electrons are present thus the adsorption complex is relatively stable [33]

Since SnO_2–Pd cluster structure is giving good response characteristics for methane detection, the effect of quantity of palladium catalyst clusters loaded on the surface of SnO_2 thin film on the sensor response has been investigated. The thickness of palladium catalyst clusters was varied in the nanoscale range from 2 nm to 20 nm. The variation of sensing response of SnO_2—Pd cluster sensor structures as a function of temperature obtained with different thickness of Pd catalyst clusters are shown in Fig. 8. The response was found to increase with increase in temperature and exhibits a maximum value at a certain temperature (T_{opt}), and shows a decrease thereafter (Fig. 8). Sensor structures also showed response at low temperatures (<100 °C), though they were relatively very small. The possible reason for the response at substantially low temperature may be mentioned as due to the increased surface free energy of the nanocrystalline SnO_2 surface [2]. In a nanocrystalline material, smaller particles with increased molar free energy are more prone to adsorb molecules or ions per unit area onto their surfaces in order to decrease the total free energy and to become more stable. Also the presence of Pd clusters over the SnO_2 surface further reduces the adsorption activation energy and hence, adsorption onto smaller particles has a higher adsorption coefficient, thereby giving enhanced response toward methane gas even at low temperatures. As a result the sensors respond at considerably low temperature. Similar observation was also reported by Basu et al. for 1% methane gas (in synthetic air) sensing response at very low temperatures around 20–80 °C [2]. The response was found to be relatively higher for the sensor structure having Pd clusters in the thickness range 8–10 nm. Furthermore the operating temperatures of these sensors were also relatively low (160–220 °C). Fig. 9 shows the variation in response of the SnO_2—Pd cluster sensor obtained at their operating temperature for 200 ppm methane concentration as a function of the thickness of Pd metal cluster loaded on SnO_2 surface. The sensor response was found to increase from 52% to 99.2% with an increase in thickness of Pd cluster from 2 nm to 10 nm and shows a decrease with further increase in Pd thickness (Fig. 9).

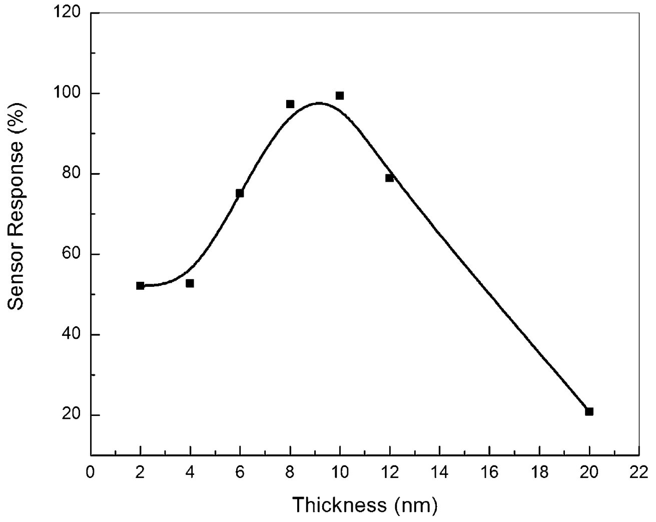

Fig. 9. Variation of sensor response with thickness of Palladium cluster loaded over the SnO_2 thin film, under 200 ppm methane gas balanced with air.

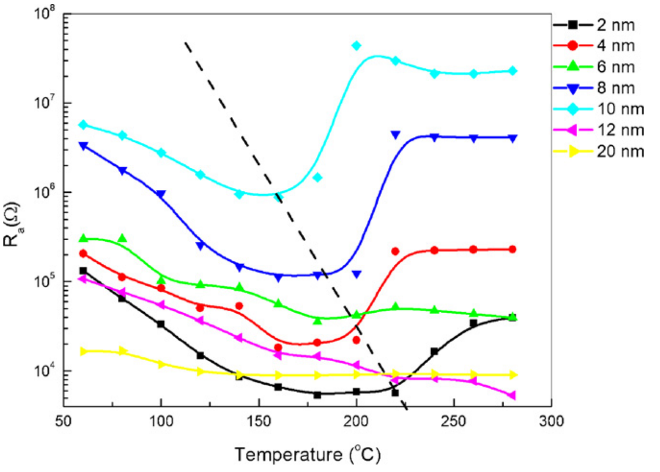

Fig. 10. Variation of sensor resistance (R_a) with temperature for different thickness of Pd clusters.

Fig. 10 shows the variation in resistance measured in air (R_a) for all prepared sensor (SnO_2—Pd cluster) structures. The resistance of the sensor was found to increase with loading of Pd clusters on the surface of SnO_2 thin film. The low temperature (60 °C) value of R_a was found to increase from 1.3×10^5 Ω to 5.7×10^6 Ω with increase in thickness of Pd clusters from 2 nm to 10 nm, and shows a decrease to 1.6×10^4 Ω with further increase in Pd thickness to 20 nm. The integration of Pd clusters (having relatively higher work function) with SnO_2 thin film (low work function) is expected to create a Schottky type surface barrier at the interface due to transfer of electron from semiconducting SnO_2 to Pd metal, thereby giving a higher value of resistance in comparison to pure SnO_2 film (without Pd catalyst) as observed in the present study. The increase in thickness of Pd from 2 nm to 10 nm results in the transfer of more and more electrons from the semiconducting SnO_2 film to Pd and therefore an increase in R_a with Pd thickness was observed. It is expected that the presence of Pd clusters of larger thickness results in an increase in the value of R_a. However, a decrease in the value of R_a is observed at higher thickness of Pd (>10 nm), and may be attributed to the higher oxygen affinity of Pd with respect to Sn [34]. The thicker Pd cluster may pull off oxygen from underneath SnO_2 thin film and becomes partially PdO_X. Therefore, the presence of oxygen vacancies in the surface of SnO_2 thin film results in an increase in carrier concentration in the conduction band of SnO_2, and decrease the sensor resistance (R_a) as observed in the present study for higher thickness (>10 nm) of Pd. The value of R_a for all SnO_2—Pd-clusters sensor structures having different thickness of Pd clusters shows a continuous decrease with increasing temperature (Fig. 10) up to a particular temperature (160–220 °C), and is attributed to the semiconducting behavior of sensing SnO_2 layer. However, above that particular (160 °C) temperature an increase (or small hump) in the R_a with temperature was observed indicating that some other mechanism is also playing important role in determining the senor resistance in air. It may be noted from Fig. 10 that the temperature where R_a begins to increase with temperature is strongly depend on the thickness of Pd clusters, and shifts toward lower temperature with increase in Pd thickness (dashed line). The observed behavior of sensor resistance in air confirms the temperature dependent physisorption and chemisorption process on the surface of SnO_2 film [35]. The activity of adsorbed oxygen on the surface of semiconducting SnO_2 thin film is enhanced at the moderate temperatures (160–220 °C) due to the presence of Pd catalyst in the form of clusters, thereby resulting in an observed increase in R_a with temperature (Fig. 10). The spillover process of adsorbed oxygen is activated at elevated temperature by the presence of suitable catalyst clusters. Furthermore the oxygen activity is expected to increase with increase in the quantity (thickness) of Pd clusters present on the surface of SnO_2 layer. The combined effect of enhanced oxygen activity and its dissociation into atomic oxygen (>160 °C) is attributed to the maximum resistance (R_a) obtained for SnO_2—Pd-clusters sensor structure having 10 nm thin Pd catalyst (Fig. 10). The reduction in spillover of adsorbed oxygen (Fig. 10) due to partial conversion of Pd cluster to PdO_X may be responsible for significant decrease in the value of R_a at higher temperatures for higher thickness (>10 nm) of Pd catalyst. Similar sharp increase in conductivity was observed by Batzill and Diebold for SnO_2 loaded with palladium clusters of higher thickness (>5 monolayer) which is attributed to the formation of a contiguous Pd ad-layer. This indicates the formation of a PdSn alloy at high Pd coverage. For a diluted Sn–Pd alloy ([Pd]/[Sn] > 6) the Pd—Sn bonds are quite strong (over 60 kcal/Sn atom) and thus may favor the alloy formation which are conducting in nature [36]. Fryberger et al. also observed a similar increase in the sheet conductance of Pd/SnO_2(1 1 0) surface for 7–8 monolayers of palladium clusters. This rapid rise of conductance was observed, as each of the growing islands takes on metallic character [37].

The variation of sensor resistance (R_g) in the presence of 200 ppm methane is shown in Fig. 11 as a function of temperature. The value of resistance at all measured temperature was found to decrease for all sensor structures after interaction with sensing gas molecules. The resistance, R_g of all the sensor structure decreases to minimum at a particular temperature (160–200 °C) and thereafter increases slowly. The observed behavior clearly suggest that initially (below operating temperature) the process of chemisorption is irreversible, and the reaction become reversible at higher temperature (>T_{opt}) due to enhanced oxygen activity at higher temperatures.

The decrease in sensor resistance with interaction of sensing gas is mainly due to the spillover of dissociated methane molecules. The dissociated molecules desorbed the adsorbed oxygen from the uncovered SnO_2 surface, thereby releasing the trapped electrons and resulting in an observed decrease in sensor resistance. Methane dissociates on the Pd surface to a methyl group and a hydrogen adatom [9], which then reacts with adsorbed atomic oxygen to produce water and free electrons which justifies the observed increase in conductivity. As the operating temperature of the sample is

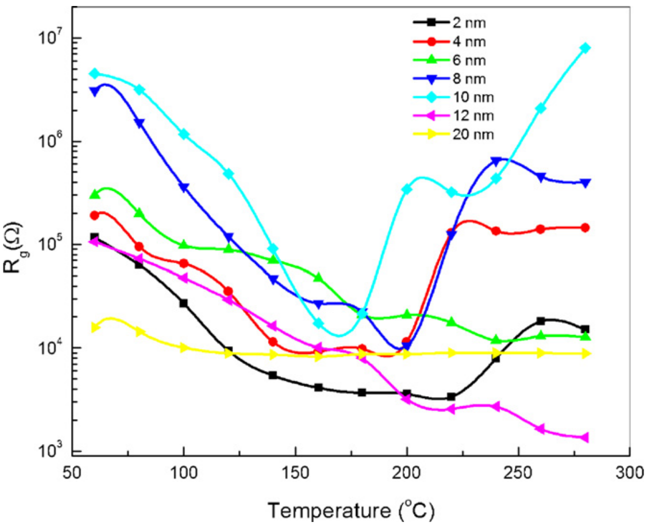

Fig. 11. Variation of sensor resistance (R_g) with temperature for different thickness of Pd clusters, under 200 ppm methane gas balanced with air.

above 100 °C, the water molecules formed will rapidly desorb from the surface. The reaction mechanism can be briefed as:

$$CH_4 \rightarrow CH_3(ads) + H(ads) \tag{1}$$

$$CH_3 + H + 4O^- \rightarrow CO_2 + 2H_2O + 4e^- \tag{2}$$

$$CH_4 + 4O^- \rightarrow CO_2 + 2H_2O + 4e^-(\text{completereaction}) \tag{3}$$

The enhanced response exhibit by SnO_2—Pd cluster sensor is attributed to the catalytic behavior of Pd toward dissociation of CH_4 gas molecules besides the activation of adsorbed oxygen activity on the uncovered surface of SnO_2 layer. Therefore the interaction of methane with SnO_2 layer leads to a substantial decrease in the resistance (R_g) value due to desorption of adsorbed oxygen thereby increasing the concentration of electron in the conduction band of SnO_2 after releasing the trapped electrons. Therefore the sensor with 10 nm thick Pd islands offers optimum sensitivity (99.2%) at a low temperature of 160 °C. Since the sensor structure having 10 nm thin Pd catalyst cluster exhibits maximum R_a and relatively low R_g at the operating temperature; the maximum response (99.2%) was observed.

4. Conclusions

The sensing characteristics of rf-sputtered SnO_2 thin film (90 nm) has been studied for methane detection after loading with various metal and metal-oxide catalysts in the form of clusters. The SnO_2—Pd cluster structure exhibit enhanced response (97.2%) at a relatively low operating temperature of 220 °C. The influence of the thickness of Pd clusters on the response characteristics of SnO_2 thin film for methane is also being studied. The enhanced response (99.2%) at an operating temperature of 160 °C was obtained with the presence of 10 nm Pd clusters. A critical thickness of 8–10 nm for the Pd clusters allows the enhanced catalytic activity for adsorbed oxygen besides the spill over mechanism in the SnO_2–Pd cluster sensors.

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Biographies

Divya Haridas received her MSc and PhD degree in physics in 2005 and 2011, respectively, from the University of Delhi, New Delhi. Presently she is an assistant professor at the Department of Physics in Keshav Mahavidyalaya, University of Delhi. Her research work is in the area of condensed matter physics and is focused on gas sensors which involve the development of LPG and CNG sensors and also actively working in the field of E-Nose. Her other research interest are in the growth and characterization of metal oxide films for their structural and optical properties.

Vinay Gupta received the BSc, MSc, and PhD degrees in physics in 1987, 1989, and 1995, respectively, from the University of Delhi, New Delhi, India. In 1995, he worked as a senior lecturer in physics at Deen Dayal Upadhyaya College, University of Delhi. Presently, he is Professor in the Department of Physics and Astrophysics, University of Delhi. His current research interests are in piezoelectric thin films and layered structures, semiconductor and surface acoustic wave (SAW) sensors, ferroelectric films for electrooptic applications, and nanostructured oxide materials for multifunctional application.