Enhanced response of SnO$_2$ based thin film sensors towards methane gas due to the collective efforts of catalytic activity and photo-activation phenomenon

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Abstract. Detection of methane is always a great cause of concern for safety productions in mines and chemical factories. The present study investigates the twin effect of UV illumination and catalytic activity on methane sensing characteristics of SnO$_2$ sensors. The sensitivity and selectivity of pure SnO$_2$ thin film sensors are improved by loading it with Pd catalyst clusters (8 nm). Further, optimizing the thickness of Pd clusters leads to an enhanced sensing response of 97% to 99% over a wider temperature range (160$^\circ$C to 240$^\circ$C) for 10 nm thick Pd clusters. The room temperature response of SnO$_2$-Pd (10 nm) sensor increases to 99.7% under UV illumination (which was around 0.6% at room temperature under no illumination) which is attributed to the efficient catalytic dissociation of methane molecules besides the spillover process at room temperature. The present study therefore investigates the effect of UV illumination on methane sensing characteristics of SnO$_2$ sensors loaded with Pd clusters. Results indicate the possibility of utilizing the sensor structure with novel dispersal of Pd catalyst clusters on SnO$_2$ film surface for efficient detection of methane at room temperature under the illumination of UV radiations.

1. Introduction

Methane is an explosive gas, used extensively at the domestic and industrial sites. It is the main constituent of natural gas, the fuel, which is supplied at homes and industries including automobiles, is often released from the walls of coal mines and when unmonitored can accumulate, causing 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 towards development of an efficient methane sensor that could work even at low temperatures. Recent concerns over the impacts of methane on global warming (it has a much greater warming effect on the climate than carbon dioxide) have resulted in an increased awareness among the research community towards the development of methane sensors. Therefore, the detection of this potent gas is essential at the environmental, industrial and domestic sites. Continuous efforts are ongoing worldwide towards the development of an efficient methane sensor that could work preferably at lower temperatures with

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enhanced response. Various analytical techniques are developed since 1990 for the detection of methane including gas chromatography (GC). Gas-chromatography is expensive, bulky, strongly affected by humidity, process limited selectivity and not well suited for on-line monitoring. Alternatively semiconductor gas sensors are becoming popular for the detection of methane gas due to their ability to alter conductance with modest detection limits, small size, low cost and on-line monitoring. Semiconducting Metal oxides have been largely exploited for the detection of such explosive and toxic gases. Among them, tin oxide (SnO₂) 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 SnO₂ to improve the selectivity and sensing response [2-4]. However a high response is observed only at high temperatures but in real time monitoring it is very difficult to monitor the gas composition in an environment having explosive species using such sensors since high temperature could trigger the explosion. Therefore there is an essential need for the development of gas sensors that can be operated at room temperature with enhanced response and selectivity. One of the additional attractive features associated with the room temperature operated semiconductor gas sensor is that it can lead to a complete integration with silicon substrate, and would not require any heating element. Therefore a new methodology or novel design approach is essentially required in order to fulfill the essential requirements of sensor market. In the present work we target mainly on achieving a high response at low operating temperature to detect low concentration of methane gas (which is below LEL) by exploring the twin effect of catalytic activity and photo-activation process.

2. Experimental

In the SnO₂ thin film of 90 nm thickness was deposited by rf sputtering technique. Palladium catalyst clusters were deposited by rf sputtering using a palladium target in pure argon ambient on the surface of sensing SnO₂ thin film for enhanced response. Pd clusters of varying thickness (2–20 nm) were deposited using a shadow mask having uniformly distributed pores of diameter 600 μm and the SnO₂–Pd sensor structures were prepared [5]. Photostimulation measurements have been carried out at room temperature by enabling a UV lamp (λ = 365 nm) as radiation source (intensity of UV light (2 μW cm⁻²)). Sensor response measurements were carried out in a home-built gas sensing test rig retrofitted with a polished stainless steel bell jar (SS 316L) with a quartz window and calibrated leaks were used for LPG introduction. The sample holder was fitted with a miniaturized heater, controlled through a temperature controller (accuracy ±0.5 °C). 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. Sensor response (S) at a given temperature T of sensing element (SnO₂) is determined by measuring change in resistance of the sensing element in absence and presence of methane. The sensor response S is defined by eq. (1)

\[ S = \left( \frac{R_a - R_g}{R_a} \right) \times 100 \]  

\( R_a \) is the sensor resistance in atmospheric air, and \( R_g \) the resistance in presence of methane.

3. Results and discussion

The response characteristics of pure SnO₂ thin film and SnO₂–catalyst cluster sensors were studied over a wide temperature range of 60 to 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 both sensor structures were obtained for 200 ppm methane gas and is shown in figure 1 as a function of temperature. The sensing response of both 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 SnO₂ film (without any catalyst) with a maximum value (S=57%) was observed at an operating temperature of 200°C. The presence of catalyst on the surface of SnO₂ sensing layer and its nature was identified to be crucial for the enhanced response. A high response (S=97.2%) was observed for SnO₂–Pd clusters (8 nm thin) sensor structure at an operating temperature of 220°C (figure 1). 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 SnO₂ film.

**Figure 1.** Variation of sensor response with operating temperature.

Thickness of the Pd clusters are varied from 2 to 20 nm. The variation of sensor response as a function as a function of the thickness of Pd catalyst cluster loaded on SnO₂ surface at their operating temperature for 200 ppm methane is shown in figure 2.

**Figure 2.** Variation of sensor response vs thickness of Pd clusters at the operating temperature for 200 ppm methane.

It may be noted from figure 2 that the response characteristics depends strongly on the thickness of the Pd clusters loaded on the surface of SnO₂ thin film. The response was found to be relatively higher for the sensor structures having Pd clusters in the thickness range 8–10 nm. The response
increases continuously from 52% - 99.2% with increasing thickness of Pd metal clusters from 2 nm to 10 nm. However, response start decreasing with further increase in thickness of the Pd cluster (>10 nm). The maximum response obtained at 10 nm thickness of Pd clusters indicates the importance of the presence of an optimum quantity of catalyst on the surface of the sensing SnO2 layer. Since the response of all sensor structures was poor at room temperature, the photostimulation process (under exposure of UV photons) was implemented simultaneously. The sensor structures were exposed initially with UV light and subsequently methane was introduced into the test gas chamber. Figure 3 compares the response of SnO2-Pd clusters sensor structures (having 8 nm, 10 nm and 12 nm thickness of Pd clusters) obtained with and without UV exposure at room temperature for 200 ppm methane. UV illumination has immensely enhanced the response at room temperature for all prepared sensors. Tremendous increase in the room temperature response 0.19 (=0.6%) to 252.3 (=99.7%) could be seen to occur with dispersal of 10 nm thin Pd clusters over the surface of SnO2 thin film which is same as that obtained without UV illumination at elevated temperature of 220°C (figure 3). The enhanced response of sensor at room temperature under UV illumination is attributed to the photo-catalytic behavior of SnO2 towards breakdown of a range of organics.

UV assisted photosensitive activation convert the chemisorbed oxygen available on the surface of SnO2 film into photoinduced oxygen which has low thermal stability and therefore is amenable to desorption at room temperature. CH4 gas molecules after interaction with Pd catalyst clusters get dissociated under UV illumination and interact with photoinduced oxygen species available on the uncovered surface of SnO2 thin film, which thereby briefly explains the gas sensing mechanism.

4. Conclusion
The sensing characteristics of rf-sputtered SnO2 thin film (90 nm) loaded with palladium catalyst clusters has been studied for methane detection. The SnO2-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 SnO2 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. Methane detection has been shown to be possible at room temperature under UV illumination using SnO2-Pd-cluster sensor structure. Room temperature response of the sensor with 10 nm thin Pd clusters is seen to be about 99.7% for 200 ppm methane under UV illumination. UV illumination plays the role of activating reversible adsorption-desorption property in SnO2-Pd-cluster sensor akin to their operation at elevated temperatures. Obtained results are encouraging for
commercial realization of room temperature SnO$_2$ based thin film sensor for CH$_4$ gas with enhanced response.

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