

Enhanced Room Temperature Response of SnO₂ Thin Film Sensor Loaded with Pd Catalyst Clusters Under UV Radiation for Methane

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Abstract:

Room temperature response characteristics of SnO₂ thin film sensors loaded with palladium catalyst clusters of varying thickness are investigated for methane under the exposure of ultraviolet radiation. The SnO₂-Pd cluster sensor structures have been prepared using rf sputtering. Combined effect of UV radiation exposure (wavelength=365 nm) and presence of Pd catalyst clusters (10 nm thick) on SnO₂ thin film sensor surface is seen to lead to an enhanced sensing response (252.3) for the detection of methane (200 ppm) at room temperature which is similar (158) to that obtained without UV illumination at elevated temperature of 220°C. Obtained results are encouraging for commercial realization of room temperature SnO₂ based thin film sensor for CH₄ gas with enhanced response.

Key words: methane, room temperature response, SnO₂ thin film, palladium catalyst and ultraviolet radiation.

Introduction

SnO₂ is one of the popular materials used for gas sensing but still endure from few limitations because of its low response, high operating temperature and poor cross-sensitivity. Various catalysts are used to enhance the response of SnO₂ based sensors besides improved selectivity towards a particular gas [1]. 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.

Few reports are available in the literature towards improving the room temperature sensing response of metal oxide gas sensors by photo-stimulation [2-4]. In the present work

we have examined the response characteristics of SnO₂ thin film based methane sensor loaded with varying thickness of Pd catalyst clusters (2–12 nm) under the exposure of UV light, and an enhanced sensing response ($S \sim 252.3$) was demonstrated at the room temperature for the sensor structure loaded with 10 nm thick palladium clusters. Hence photostimulation of SnO₂ thin film sensor loaded with Pd catalyst clusters has been shown to exhibit potential for realization of room temperature operated methane sensor.

Experimental

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 [1]. Photostimulation measurements have been carried out at room temperature by enabling a UV lamp ($\lambda = 365$ nm) as radiation source (intensity of UV light $(2 \mu\text{Wcm}^{-2})$). 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)

$$S = \frac{R_a}{R_g} - 1 \approx \frac{R_a}{R_g} \quad (1)$$

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

Results and discussion

The sensing response characteristics of all prepared sensor structure having varying thicknesses of Pd clusters have been studied and the variation of sensor response as a function of the thickness of Pd catalyst cluster loaded on SnO_2 surface at their operating temperature for 200 ppm methane is shown in Fig. 1.

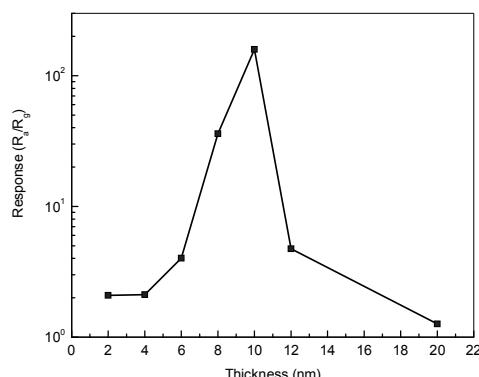


Fig. 1. Graph of sensor response vs thickness of Pd clusters at the operating temperature for 200ppm methane.

It may be noted from Fig. 1 that the response characteristics depends strongly on the thickness of the Pd clusters loaded on the surface of SnO_2 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 2.0×10^0 to 1.5×10^2 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 SnO_2 layer.

Enhanced response of SnO_2 thin film towards methane gas is achieved by integrating palladium catalyst clusters on SnO_2 thin film surface but still high operating temperature is major cause of concern. Room temperature operation of the gas sensors is an attractive proposition for the industry since it not only

holds a promise to cut down the costs but also overcome technological limitations of miniature heaters of high wattage. One of the additional attractive features associated with room temperature operated semiconductor gas sensor is that it can lead to a complete integration with well established Si based micro-electronics technology. Photosensitive activation of semiconducting metal oxides is a relatively new field with a bright future since it shows a way to develop commercial sensors with a promise of very low power consumption. UV illumination has immensely enhanced the response at room temperature for all prepared sensors. Fig. 2 compares the response of all the SnO_2 -Pd clusters sensor structures, 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 to 252.3 could be seen to occur with dispersal of 10 nm thin Pd clusters over the surface of SnO_2 thin film which is same as that obtained without UV illumination at elevated temperature of 220°C (Fig. 2). The enhanced response of sensor at room temperature under UV illumination is attributed to the photo-catalytic behavior of SnO_2 towards breakdown of a range of organics

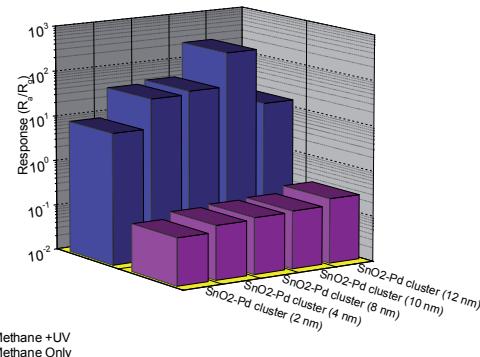


Fig. 2. Graph of sensor response for all prepared sensor structures (varying thickness of Pd catalyst) at room temperature.

The observed result obtained in present study shows the assistance of UV illumination towards sensing response. As gas sensing is a surface phenomenon and photostimulation explores this aspect and enhances the gas sensing response. Photosensitive activation process on the surface of SnO_2 is the main cause of conversion of chemisorbed oxygen ions into photoinduced oxygen ions at room temperature which has low thermal stability and therefore is amenable to desorption at room temperature. Afterwards methane molecules gets dissociated by the Pd clusters are spilled

over the bare surface of SnO_2 thin film and interact with the adsorbed oxygen thereby increasing conductivity and further increases the sensing response. The observed result obtained in present study shows that the assistance of UV illumination towards sensing response of SnO_2 thin film based sensors is manifold. (i) Photosensitive activation process on the surface of SnO_2 and therefore conversion of chemisorbed oxygen ions into photoinduced oxygen ions at room temperature (ii) Dissociation of reducing CH_4 gas by Pd catalyst cluster at room temperature.

In general, these activities on the surface of metal oxides are reported to occur at elevated temperature, but the presence of UV light even of very low intensity ($2\mu\text{W}/\text{cm}^2$) activates these processes at room temperature and provide a way towards the realization of room temperature operated SnO_2 thin film based sensors for efficient detection of CH_4 gas with enhanced response.

Conclusion

Methane detection has been shown to be possible at room temperature under UV illumination using SnO_2 -Pd-cluster sensor structure. Room temperature response of the sensor with 10 nm thin Pd clusters is seen to be about 252.3 for 200 ppm methane under UV illumination, which is same as that obtained without UV illumination at elevated temperature of 220°C . UV illumination plays the role of activating reversible adsorption-desorption property in SnO_2 -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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