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Improved response characteristics of SnO_2 film based NO_2 gas sensor with nanoscaled metal oxide catalysts

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Abstract:
Gas sensor structure based on rf sputtered SnO_2 thin film is found to be highly sensitive ($1.4x10^4$) towards 100 ppm NO_2 gas, but with slow response (~4min.) and recovery (~33min.) times. To improve the response and recovery speeds of the sensor, different catalysts (WO_3, TeO_2, Al_2O_3, NiO, CuO and In_2O_3) in the form of nanoclusters have been deposited over SnO_2 surface and their effect towards sensing response characteristics of NO_2 gas has been studied. Amongst all the catalysts WO_3 nanoclusters are found to be yielding a high response ($5.1x10^4$) for low concentration of NO_2 gas at a low operating temperature of 100°C with a fast response and recovery times of 67sec and 17 min respectively.

Key words: *Tin oxide, NO_2 gas, Semiconductor, sensor, sputtering*

Introduction

Gas sensors based on semiconducting metal oxides have attracted the attention of environmentalist and many others. Now a days, air pollution by nitrogen oxides (NO_x), mainly NO and NO_2, is becoming an important environmental issue. NO_2 associated with other pollutants like volatile organic compounds (VOC) is responsible for the formation of ozone in lower atmosphere, smog in urban areas and also chemical reaction of NO_2 gas with water vapour causes acid rain [1]. Therefore, as a first step, the development of a NO_2 gas sensor for environmental monitoring has become a necessary task. Among a variety of semiconducting metal oxides, tin oxide (SnO_2) is the most preferred material for gas sensor application because of its enhanced ability to adsorb oxygen on its surface and thus is highly sensitive towards many toxic and harmful gases [2]. However, requirement of lower operating temperature (< 200 °C) is the major objective. Currently, worldwide efforts are towards the development of inexpensive, compact and maintenance free NO_2 gas sensors exhibiting higher response at low operating temperature. Pure SnO_2 is sensitive to many gases, and some degree of selectivity can be conferred by the use of appropriate materials and additives and/or the careful choice of working temperatures [3]. There are few reports on the detection of NOx gas using semiconducting metal oxide thin films of SnO_2 and SnO_2 doped with suitable metal/metal oxide catalysts but the operating temperatures are reported to be quite high [4,5,6] and a systematic comparison of different catalysts for NO_2 gas detection is missing. In the present work, an effort has been to study the effect of different catalysts in reducing the operating temperature of SnO_2 based sensor structure along with improving the rate of adsorption and desorption of target gas on the sensor surface.

Experimental

Tin oxide thin films were deposited using RF diode sputtering technique on Pt inter digital electrodes (IDEs) patterned corning glass substrates using a metallic tin target (99.999% pure) in Ar + O_2 gas ambient. The SnO_2 film of 430 nm was deposited at an optimized sputtering pressure of 16 m Torr in reactive ambient of 30% oxygen and 70% argon gas in the sputtering chamber [2]. The target to substrate distance was kept fixed at 7.5 cm and a power of 150Watt was supplied to the target. The ultrathin (thickness 8-16 nm) metal oxide catalysts of WO_3, TeO_2, Al_2O_3, NiO, CuO and In_2O_3 were loaded in the form of nanoclusters on the surface of the sensing SnO_2 layer using a shadow mask (600 μm pore size). The TeO_2 and NiO catalysts were deposited by RF sputtering using their respective metal targets in Ar + O_2 gas ambient, whereas WO_3 and CuO catalysts were deposited using Pulsed Laser Deposition technique. Nanoclusters of Al_2O_3

and In_2O_3 were fabricated over SnO_2 thin films by depositing nano-thin Aluminum and Indium thin films using E-beam evaporation technique followed by annealing in oxygen environment at 300°C for 3 hours. All the prepared sensor structures were stabilized by annealing them in air at 300 °C for 2 hours. Crystalline structure of the deposited SnO_2 film was studied using X-Ray diffractometer (Bruker D8 Discover). Scanning electron microscope (SEM) (Zeiss Ultra Plus) was employed to examine the surface morphology of the sensor structures. A Double Beam UV-Visible Spectrophotometer (Perkin Elmer, Lambda 35) was used to study the optical properties of SnO_2 thin film.

Gas sensing characteristics were performed in the specially designed Gas sensor test rig (GSTR). The GSTR was used with a glass bell jar to serve the twin purposes of mixing of target gas with the atmospheric gas and as the test chamber. The gas to be sensed (10 ppm NO_2) was introduced in the bell jar with calibrated leaks using needle valves. Changes in the resistance values of sensor structure on interaction with the target NO_2 gas were recorded using a data acquisition system consisting of a digital multi-meter (DMM model: Keithley 2700) interfaced with a computer. This way the fast changing resistance values were logged on the computer every second.

NO_2 is an oxidizing gas and the sensor response for the same is defined as

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

Where, R_a and R_g are the resistances of the sensor element in the presence of atmospheric air and target gas respectively.

Results and Discussions

The as deposited SnO_2 film was found to be smooth, transparent and strongly adherent to the substrate surface. The as grown film was amorphous in nature which became polycrystalline when annealed at 300 °C for 3 hrs in air. Figure 1 shows the XRD pattern of annealed SnO_2 film deposited at 16 mTorr sputtering pressure. Broad and well defined reflections corresponding to (110), (101) and (211) planes of SnO_2 were observed at 2θ= 26.54°, 34.1° and 51.54° respectively which are in good agreement to the reported values for rutile structure [7]. The crystallite size of annealed SnO_2 thin film was evaluated to be 10nm by fitting the FWHM of (110) XRD reflection using Scherrer's formula.

When the XRD pattern of SnO_2 thin film loaded with various catalysts was carried out, no peak corresponding to any other metal oxide catalyst was observed. This may be due the very low thickness (8 to 18 nm) of metal oxide catalysts considered in the present work. Inset of figure 1 shows a low resolution SEM image of WO_3 nanoclsuters loaded over SnO_2 thin film. Smooth circular structures of catalyst on the surface of SnO_2 film can be easily seen confirming the presence of thin catalyst clusters on the surface of SnO_2 thin film.

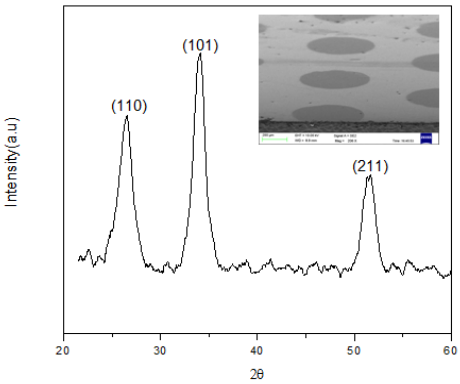

Figure 1: X-ray diffractogram of the SnO_2 thin film annealed in air at 300°C. Inset: SEM image of WO_3 nanoclusters loaded over SnO_2 thin film

A transmittance spectrum of the SnO_2 thin film has also been studied which shows that the SnO_2 thin film exhibits a high transmission (> 80%) in the visible region with well defined interference fringe pattern and show a sharp fundamental absorption edge at around 340 nm. The presence of well defined interference fringes pattern in the optical transmittance spectra indicates the growth of good quality SnO_2 thin films free from any type of inhomogenity. The value of optical bandgap (E_g) was estimated from the Taue plot (linear portion of the plot between $(\alpha h\upsilon)^2$ with photon energy ($h\upsilon$) where, α is absorption coefficient and υ is the optical frequency) and was found to be 3.8 eV which is close to the reported value (3.4 eV to 4.0 eV) for SnO_2 thin film by other workers [8].

Figure 2 shows the variation in sensor response with temperature for pure SnO_2 thin film and SnO_2 thin films loaded with different nanoclustered metal oxide catalysts (WO_3, TeO_2, Al_2O_3, CuO, In_2O_3, NiO) towards 10 ppm NO_2 gas. It could be observed from figure 2 that for all the sensor structure, with increasing the temperature, the sensor response first increases, attains a maxima at a temperature called the operating temperature and then reduces with further increase in temperature. It may be seen that the incorporation of WO_3 and TeO_2 catalysts, improves the sensing response, Al_2O_3 gives almost similar response and other

catalysts reduce the sensor response compared to the pure SnO_2 thin film based sensor structure. There is a slight reduction in the operating temperature also when TeO_2 (90°C) and CuO (80°C) catalysts are incorporated with the SnO_2 sensing layer. Sensing response characteristics (response, response time, recovery time, operating temperature) of all the sensor structures i.e. pure SnO_2 and SnO_2 thin film loaded with metal oxide catalysts, are summarized in table I. It may be seen from Table I that the pure SnO_2 thin film based sensor structure shows the maximum response of 1.4 $x10^4$ at an operating temperature of 100 °C but with poor response and recovery times of 4 mins and 33 mins. respectively. Sensor structures with WO_3, TeO_2 and Al_2O_3 nanoclusters show the improved gas sensing response with faster response and recovery times. However, with the incorporation of NiO, CuO and In_2O_3 catalysts the sensor response reduces, but the response and recovery times are improved (Table 1).

A maximum response of $5.1x10^4$ is obtained for the sensor structure loaded with WO_3 nanoclusters at a comparatively low operating temperature of 100 °C with fast response and recovery speeds of 67 sec and 17 min. respectively. With the incorporation of TeO_2 the maximum sensor response is obtained at an operating temperature of 90 °C with response and recovery times of 1.6 min and 16 min respectively. This may be attributed to the modulation of junction formed at the semiconducting SnO_2 and catalyst interface on interaction with the target NO_2 gas (10 ppm) along with the possible spill over mechanism.

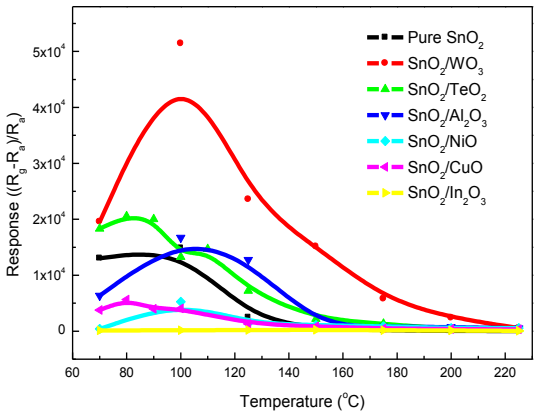

Fig 2: Variation in response with temperature of SnO_2 sensors covered with various catalysts

Figures 3 and 4 show the variation of sensor resistance in presence of atmospheric air (R_a) and 10 ppm of NO_2 gas (R_g) respectively with temperature for all the sensor structures. It can be observed from figure 3 that pure SnO_2 and SnO_2 loaded with WO_3 catalyst shows the minimum starting resistance which increases for other catalysts. CuO and NiO nanoclusters loaded sensor structures show a high starting resistance of 49 kΩ and 23 kΩ respectively. The higher resistance values are attributed to the formation of depletion width at the catalyst-SnO_2 interface. With increasing the temperature, the sensor resistance of all the sensor structures decreases and is in accordance with the semiconducting nature of the sensing layers.

When 10 ppm of NO_2 gas was exposed to different sensor structures, sensor resistance increases drastically from R_a to R_g due to the oxidizing nature of NO_2 gas. Sensor structures exhibiting low initial resistance (R_a) and high resistance in the presence of target gas (R_g) result in higher sensing response. Sensor structure with TeO_2 and CuO shows the maximum increase in R_g (Figure 4) but due to higher initial value of resistance R_a (Figure 3) the sensor response does not show appreciable enhancement (Table I). On the other hand, for WO_3 catalyst the value of R_g does not increase much but due to lower R_a value, it shows the maximum sensor response as compared to other metal oxides catalysts. Thus the cumulative values of R_a and R_g decides the maximum sensor response.

Sensor Structure	Response	Response time	Recovery time	Operating temperature
Pure SnO_2	$1.4x10^4$	4 min	33 min	100 °C
SnO_2/WO_3	$5.1x10^4$	67 sec	17 min	100 °C
SnO_2/TeO_2	$2.0x10^4$	1.6 min	16 min	90 °C
SnO_2/Al_2O_3	$1.6x10^4$	1.5 min	20 min	100 °C
SnO_2/NiO	$5.2x10^3$	1.4 min	22 min	100 °C
SnO_2/CuO	$5.6x10^3$	1.2 min	4.2 min	80 °C
SnO_2/In_2O_3	$1.6x10^2$	6.7 min	6.8 min	100 °C

Tab. 1: Summarized sensing parameters obtained for various sensor structures

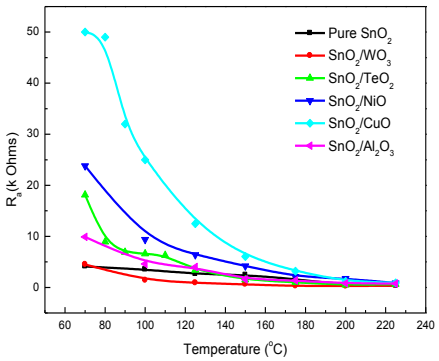

Fig 3: Variation in Resistance in presence of air with temperature of SnO_2 sensors covered with various catalysts

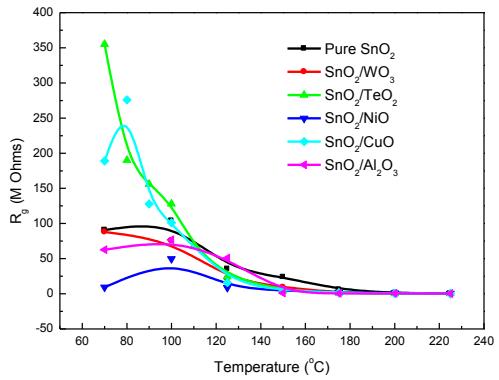

Fig 4: Variation in Resistance in presence of 10 ppm NO_2 gas with temperature of SnO_2 sensors covered with various catalysts

Conclusion

The sensing response characteristics of the RF-sputtered SnO_2 thin film sensor having metal oxide catalysts in the form of nanoclusters have been studied towards 10 ppm NO_2 gas. The SnO_2 thin film based sensor structure having WO_3 catalyst exhibits enhanced response ($5.4x10^4$) at a lower operating temperature of 100 ^oC. The possible spillover of dissociated NO_2 gas molecules leads to fast response and recovery times of 67 sec and 17 min respectively.

Acknowledgements

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