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Conference Paper

Effect of MgO and V_2O_5 Catalyst on the Sensing Behaviour of Tin Oxide Thin Film for SO_2 Gas

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The present work shows the SO_2 gas sensing property of SnO_2 thin film based sensor prepared by using RF sputtering technique. Different catalysts (MgO and V_2O_5) in form of nanoclusters having diameter of 600 μm have been loaded on SnO_2 surface to detect SO_2 gas. The sensing response of all these films towards SO_2 is monitored. Microstructural studies have been carried out using XRD and UV-Visible Spectrophotometer and a good correlation has been found between the microstructural and gas sensing properties of these deposited samples. Both catalysts when incorporated with SnO_2 film show high selectivity towards SO_2 gas at lower operating temperature. MgO gives a sensitivity of 317% at an operating temperature of 280°C towards 500 ppm of SO_2 gas whereas V_2O_5 catalyst gives a sensitivity of 166% at 280°C for the same amount of gas.

1. Introduction

Recently, substantial interest has arisen in terms of protecting the environment from various air pollutants generated by combustion exhausts. SO_2 is one of the most hazardous atmospheric pollutants because it directly contributes to acid rain. Several studies have shown that repeated exposure to low levels of SO_2 (<5 ppm) can cause permanent pulmonary impairment [1]. The long-term and short-term exposure limits for SO_2 gas are 2 ppm and 5 ppm, respectively. Therefore, the development of an efficient SO_2 gas sensor for environmental monitoring has become a necessary task.

There are various techniques for determining the SO_2 gas concentration in the atmosphere such as ion chromatography [2], Fourier transform infrared spectrometry [3], optical fiber sensors [4], SAW gas sensors [5], conductometry [6], and electrochemical methods [7]. Amongst all the techniques, conductometric sensors are fast, highly sensitive, reproducible, of low cost, and convenient.

Semiconducting tin oxide (SnO_2) based conductometric gas sensors have received much attention for more than four decades due to their suitable physical-chemical properties and possibility to detect wide variety of gases with high response [8–11]. SnO_2 is naturally nonstoichiometric having a rutile phase that eases the adsorption of oxygen on its surface and thus it is highly sensitive towards many toxic and harmful gases [10, 11]. The main problem with the pure SnO_2 thin film based gas sensors is their poor selectivity and high operating temperatures that can be improved to a great extent by using specific catalysts [12, 13].

The aim of this study is to develop a SnO_2 thin film based SO_2 gas sensor with MgO and V_2O_5 catalysts having efficient response characteristics.

2. Experimental

SnO_2 thin films of 90 nm thickness were deposited using RF diode sputtering technique using a metal Sn target (99.999% pure) in a reactive ambient of Ar and O_2 gas mixture as optimized in our previous work [14]. The sensing response characteristics of SnO_2 thin films were studied using Interdigital Electrodes (IDEs) of platinum (Pt) as shown in Figure 1.

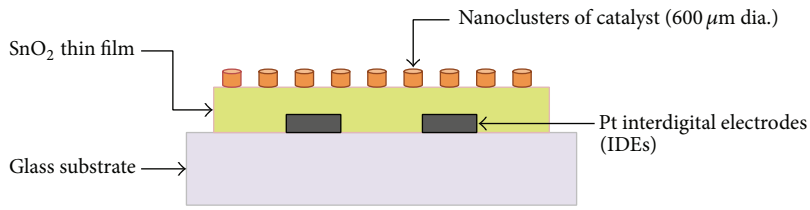

Figure 1: Cross-sectional view of the SnO_2 thin film sensor with nanoclusters of catalysts on Pt IDEs.

The sensor fabrication details are given in our previous report [14]. For the enhanced and selective gas sensing response characteristics, nanoclusters of MgO and V_2O_5 of 10 nm thickness and 600 μm diameter were dispersed uniformly over the surface of SnO_2 thin film by pulsed laser deposition technique (PLD) using a fourth harmonic (λ = 266 nm) of Nd:YAG laser with fluence ≈ 1.5 J/cm^2 using a shadow mask. Ceramic targets of MgO and V_2O_5 of 1″ diameter were used for deposition using PLD. The as-grown sensing elements (MgO/SnO_2 and V_2O_5/SnO_2) were annealed at 300°C in air for 3 h to stabilize the sensor.

Thickness and surface roughness of deposited thin films were measured using a (Veeco Dektak 150) surface profiler. Crystalline structure of SnO_2 thin films was studied using Bragg-Brentano (θ-2θ) scan of an X-ray diffractometer (Bruker D8 Discover) using the CuKα_1 source (λ = 0.154 nm). A double beam UV-Visible Spectrophotometer (Perkin Elmer, Lambda 35) was used to study the optical properties of SnO_2 thin films.

A specially designed gas sensor test rig (GSTR) has been used to study the gas sensing response characteristics of the sensing layer for SO_2 gas. The sensor was placed on a temperature controlled heating block inside the glass test chamber to measure the sensor response as a function of temperature (100 to 300°C). At each temperature, the sensor was first stabilized in air to obtain a stable resistance value. Target gas (SO_2) of specific concentration (500 ppm) was introduced into the test chamber and changes in the sensor resistance were recorded after every second using a data acquisition system consisting of a digital multimeter (model: Keithley 2700) interfaced with a computer. SO_2 is a reducing gas and the sensor response is defined as

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

where R_a and R_g are the resistance of the sensor element in the presence of atmospheric air and resistance of target SO_2 gas, respectively.

3. Results and Discussions

Figure 2 shows the X-ray diffraction (XRD) pattern of the SnO_2 sensor structure. The diffraction peaks observed at 2θ = 26.6°, 33.8°, and 51.8° can be assigned to (110), (101), and (211) planes of the rutile structure of SnO_2, respectively [15]. The observed XRD peaks are found to be broad indicating that the particles are of small size. No peaks corresponding to any

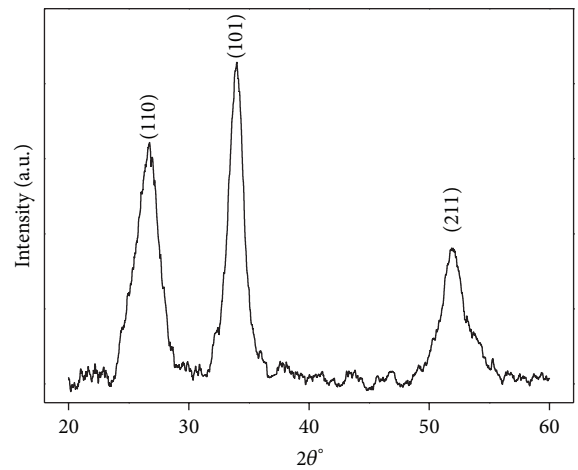

Figure 2: X-ray diffraction pattern of SnO_2 sensor structure.

secondary phase due to MgO and V_2O_5 have been observed in the XRD spectra which may be attributed to the small thickness of the nanoclusters of the catalysts. The crystallite size was estimated by fitting the width of dominant (101) diffraction peak using Scherrer's formula and is found to be ~8 nm.

Figure 3 shows the transmittance spectra of the SnO_2 thin film. The films exhibit a high transmission (>80%) in the visible region and show a sharp fundamental absorption edge at around 340 nm. The value of optical band gap was estimated from the Tauc plot and is found to be 3.9 eV which matches very well the reported value [16].

Figure 4 shows the sensing response of bare SnO_2 film and SnO_2 film having MgO and V_2O_5 as catalysts. Bare SnO_2 thin film based sensor showed no response whereas sensors having MgO and V_2O_5 catalysts are showing a response of 3.17 and 1.66, respectively. Table 1 shows the sensor response (%), response time, and recovery time of the prepared samples at their operating temperature (280°C). It can be seen from Table 1 that the sensor response (%) is low for SnO_2 thin film and gets improved with V_2O_5 as a catalyst and the maximum value of response (%) is found for the SnO_2 with MgO thin film as catalyst with a response time and recovery time of 59 s and 52 s, respectively. MgO and V_2O_5 doped SnO_2 sensors for sensing SO_2 gas have already been reported by Lee et al. [13]. However, the sensing response is reported to be poor (44%) at a high operating temperature (400°C) towards 1 ppm of SO_2 gas. Since gas sensing is a surface phenomenon, the incorporation of catalyst/modifier

Table 1: Sensing response characteristics of the prepared sensors at an operating temperature of 280°C.

Serial number	Sample	Response (%)	Response time (s)	Recovery time (s)
1	SnO_2	107	—	—
2	$SnO_2 + V_2O_5$	166	90	43
3	$SnO_2 + MgO$	317	59	52

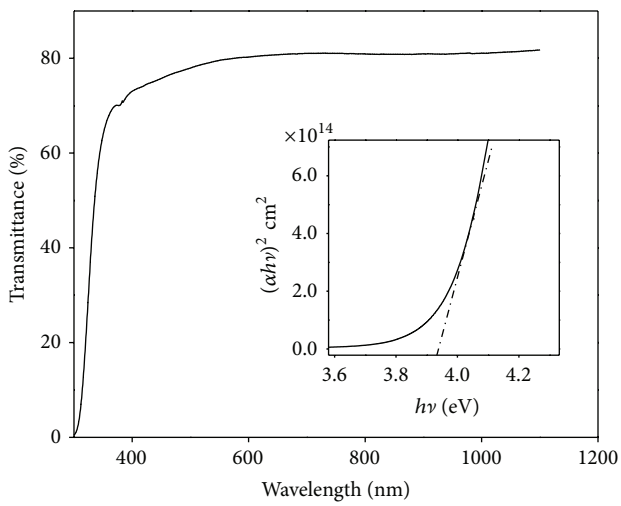

Figure 3: Transmittance spectra of SnO_2 film deposited on glass substrate. Inset: Tauc plot for the SnO_2 thin film.

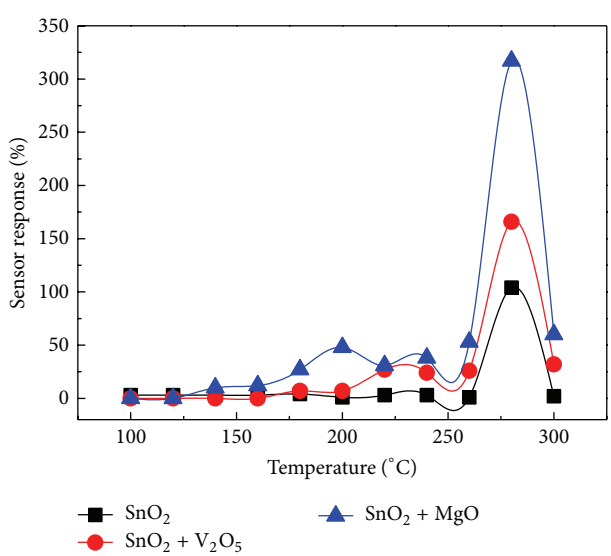

Figure 4: Sensing response of SnO_2 thin film, SnO_2 thin film having V_2O_5 catalyst, and SnO_2 thin film having MgO catalyst as a function of temperature.

in the form of nanoclusters onto the surface of SnO_2 thin film is proved to give enhanced sensing response of 317% and 166% at 280°C towards 500 ppm SO_2 gas.

4. Conclusion

SnO_2 thin films of desired morphology and higher electrical resistance have been deposited by RF sputtering for efficient detection of SO_2 gas. SnO_2 film with MgO catalyst exhibits enhanced sensor response of 317% with moderate response time of 59 s and recovery time of 52 s at an operating temperature of 280°C. The sensor response and recovery time are governed by the adsorption and desorption of SO_2 gas molecules at the sensor surface. The formation of SnO_2 thin film with desired surface morphology having moderate porosity and appropriate catalysts results in an enhanced sensing response towards SO_2 gas (500 ppm) at a low operating temperature of 280°C.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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