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Highly sensitive ZnO–SnO_2 nanocomposite H_2 gas sensor

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Abstract:

Thin film sensors based on SnO_2, ZnO and ZnO–SnO_2 nanocomposite have been fabricated using pulsed laser deposition technique. The prepared sensors were studied for their response characteristics towards 500 ppm H_2 gas. The nanocomposite sensor structure (ZnO–SnO_2) shows an enhanced response of about 8.8×10^2 as compared to that obtained (7 and 8) for bare ZnO and SnO_2 thin film sensors respectively at a relatively lower operating temperature of 160°C. The nanocomposite sensor shows an improvement in response and recovery speeds compared to that of pure ZnO film sensor, though the results are slightly degraded in comparison to the bare SnO_2 thin film based sensor structure. The origin of enhanced response of ZnO–SnO_2 composite sensor is attributed to the modulation of depletion region width at the n–n heterojunction besides the enhanced oxygen adsorption. The high sensing response obtained at low operating temperature for ZnO–SnO_2 composite sensor is attractive for efficient detection of H_2 gas.

Key words: ZnO–SnO_2 nanocomposite, thin film, H_2 sensor, and pulsed laser deposition

Introduction

H_2 gas is utilized extensively in scientific research, glass and steel manufacturing industries, refining of petroleum products, medicine, space exploration, production of industrial chemicals, food products etc. As H_2 is a colourless, odourless and tasteless flammable gas it cannot be detected by human senses. Therefore, rapid and accurate detection of hydrogen gas in the surroundings is essential to prevent the risk of explosion. Semiconductor sensors are the most popular amongst various sensors employed for detection of H_2 gas due to simple construction, easy operation, low cost and portability [1]. It is also reported that the gas sensors based on composite sensing element result in improved sensing characteristics, since they tend to be porous and contain many heterogeneous interfaces [2-5]. Especially, SnO_2 thin film, which is widely used as gas sensing element, can be made porous with the addition of small amount of ZnO and results in the availability of larger effective area for interaction with the sensing gas molecules [2]. Some composites also have the unique properties that are not observed in each of the constituent components. Efforts are continuing towards the development of ZnO–SnO_2 composite structures and exploration of their sensing properties for various target gases.

Amongst various techniques used for the fabrication of thin film sensors, chemical methods are widely explored, though reproducibility and stability are major issues [1]. Pulsed laser deposition (PLD) is a well known physical deposition technique to produce high quality thin films with controlled surface morphology and reproducible properties which could be easily controlled. Furthermore, in our earlier work, it is identified that PLD grown SnO_2 thin film gives better gas sensing response characteristics compared to the one deposited using rf sputtering technique [5]. In the present work, an effort has been made to prepare sensor structures based on bare SnO_2, bare ZnO and ZnO–SnO_2 nanocomposite thin films deposited using PLD technique. The sensor structures were studied for their gas sensing response characteristics towards 500 ppm H_2.

Experimental

Thin films of bare SnO_2, bare ZnO and ZnO–SnO_2 nanocomposite structures were deposited using pulsed laser deposition (PLD) technique under O_2 ambient at 100 mT pressure. Interdigital electrodes (IDEs) of platinum (Pt) were patterned prior to the deposition of sensing layer, on the corning glass substrates using conventional photolithographic technique. The Pt layer of 90 nm thickness was deposited by rf sputtering

technique in argon ambient after depositing a buffer layer of Ti (20 nm thin) for improvement in its adhesion on corning glass substrate. For the deposition of thin films of SnO_2, ZnO and ZnO–SnO_2 composite, ceramic pellets of SnO_2 and ZnO were prepared by pressing their high purity powders (99.99% pure) using a dye (2.5 cm diameter) by applying a pressure of 110 MPa. The SnO_2 and ZnO pellets were sintered at 1350°C and 1000°C respectively for 4 hours in a temperature controlled furnace. The fourth harmonic of Nd:YAG laser (λ= 266 nm) at a pulse rate of 5 Hz and fluence of 1.2 Jcm^{-2} was used to ablate the ceramic targets. Thickness of sensing element in all structures was kept at 90 nm. The nanocomposite structure consisted of 1:1 proportion of ZnO and SnO_2. The films were post-deposition annealed at 300°C in air for 2 hours for the stabilization in sensor resistance and improvement in the crystallinity of the films. The films were characterised for structural and optical properties using XRD and UV-Visible spectroscopy respectively. The sensing response characteristics of the prepared sensors were obtained in a special design test gas chamber over a wide temperature range (80°C to 240°C). The sensor resistance was measured using Keithley 4200 SCS (Semiconductor Characterisation System). The sensing response is defined as $S = R_a/R_g$, where R_a is the sensor resistance measured in the atmospheric air, and R_g is the sensor resistance in the presence of 500 ppm of target H_2 gas .

Results and Discussion

As-deposited SnO_2 thin films were found to be strongly adherent to the substrate, optically transparent and amorphous. The films became polycrystalline after post deposition annealing treatment at 300°C for 2 hours (Fig. 1). ZnO thin films were preferred (002) oriented with c–axis normal to the substrates (Fig. 1).

It may be noted from Fig. 1 that the XRD peaks corresponding to SnO_2 were present in the XRD pattern of ZnO–SnO_2 film. However, the peak corresponding to ZnO was missing, also observed by Moon et. al [3]. The crystallinity of all deposited films was found to improve significantly with post deposition annealing treatment. The grain size of the ZnO, SnO_2 and ZnO–SnO_2 thin films estimated from the FWHM of the dominant XRD peak were found to be about 15 nm, 20 nm, and 18 nm respectively.

The UV-visible spectra of ZnO, SnO_2 and nanocomposite ZnO-SnO_2 thin films are shown in Fig. 2. The onset of sharp fundamental absorption band edge was observed in the range 300–350 nm, for all deposited thin films. The values of bandgap of the bare ZnO, bare SnO_2 and ZnO–SnO_2 nanocomposite thin films was evaluated by extrapolating the linear portion of Tauc plot between $(\alpha h\nu)^2$ versus $h\nu$ to $\alpha = 0$, where α is the absorption coefficient and $h\nu$ is the energy of the photon. The estimated values of bandgap of ZnO, SnO_2 and nanocomposite ZnO–SnO_2 thin film was found to be 3.37 eV, 3.98 eV, and 3.64 eV respectively.

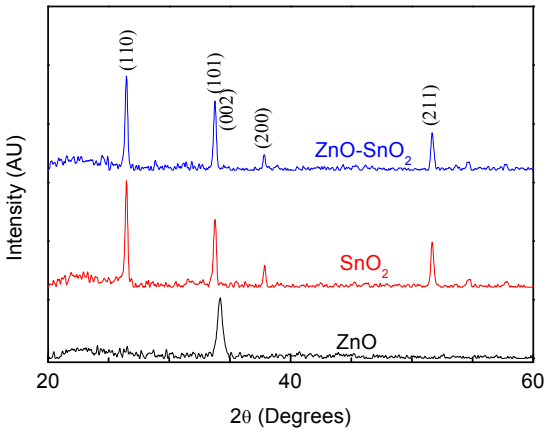

Fig. 1. XRD spectra of bare ZnO, bare SnO_2 and ZnO–SnO_2 nanocomposite thin films.

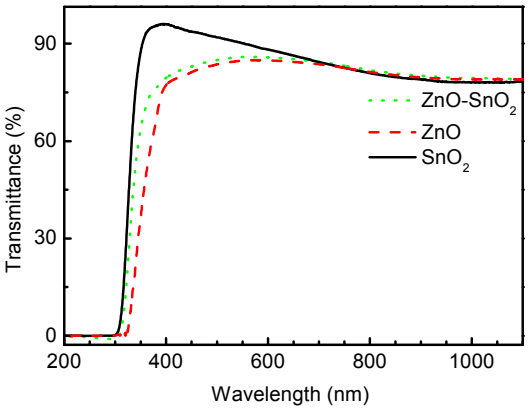

Fig. 2. UV-Visible spectra of ZnO, SnO_2 and ZnO–SnO_2 nanocomposite thin films annealed annealed at 300°C.

Sensing Response Characteristics

Fig. 3 shows the sensing response characteristics of all the prepared sensor structures towards 500 ppm H_2. It is noted from Fig. 3 that the sensing response of bare SnO_2 and bare ZnO thin film sensors was almost similar and quite low even at a high operating temperature (T_{opt}) of 180°C. The sensing response and operating temperature of all the prepared sensors are summarized in Table I. The SnO_2–ZnO nanocomposite sensor shows a remarkable enhancement in the sensing response over the measured temperature range giving a maximum response of about 8.8×10^2 at an operating temperature of 160°C. The

obtained value of response was found to be much higher (two orders of magnitude) in comparison to the corresponding values observed for sensors based on bare SnO_2 or bare ZnO thin fims (Fig. 3). The enhanced response of ZnO–SnO_2 sensor towards H_2 gas is attributed to the presence of high porosity (not shown) and the formation of heterojunctions (ZnO–SnO_2) in the nanocomposite thin film sensor. The enhanced porosity of the nanocomposite films (not shown) in the nanocomposite thin film sensor and heterojunction formed plays a significant role in the sensing behavior of the films.

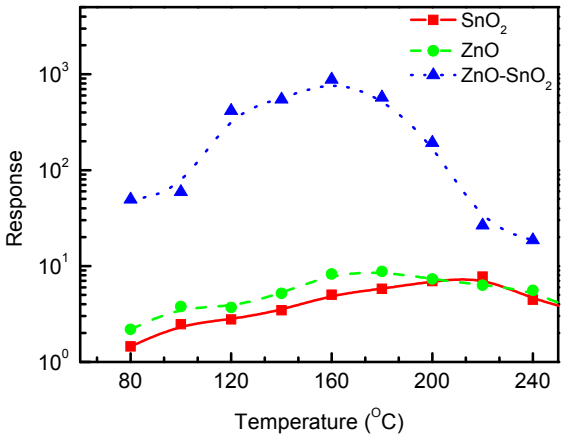

Fig. 3. Variation of sensing response of bare SnO_2, bare ZnO and nanocomposite ZnO–SnO_2 thin film sensors towards 500 ppm H_2 with temperature.

Tab. 1: The sensing response parameters of prepared sensors.

Sample	Operating Temp.(°C)	Response
SnO_2	220	7.7×10^0
ZnO	180	8.7×10^0
ZnO–SnO_2	160	8.8×10^2

The variation of resistance in air (R_a) of all the prepared sensors is shown in Fig. 4 as a function of temperature. Both ZnO and SnO_2 thin film sensors show a decrease in sensor resistance in air with increase in temperature, which is in consistence with their semiconducting behaviour. The resistance of the ZnO-SnO_2 nanocomposite thin film sensor is found to be much higher in comparison to the corresponding values obtained for both ZnO and SnO_2 thin film sensors. The observed higher value of R_a for ZnO–SnO_2 composite sensor is attributed to the formation of n–n junction. The heterogeneous interface of ZnO with SnO_2 in the nanocomposite sensor structure, results in the formation of depletion region at the hetero-junction (n–n type junction) due to the difference of the work function of the two materials [4]. It is interesting to note from Fig. 4 that the ZnO-SnO_2 nanocomposite sensor shows an initial rise in resistance with increasing temperature. This may be attributed to enhanced oxygen adsorption from the atmosphere on the sensor surface with increasing temperature. The higher concentration of adsorbed oxygen captured the free electrons in large amount from the bulk of sensing elements, thereby giving a higher value of R_a. However, at higher temperature (>160°C), the sensor resistance falls with increasing temperature due to the increase in the concentration of charge carriers.

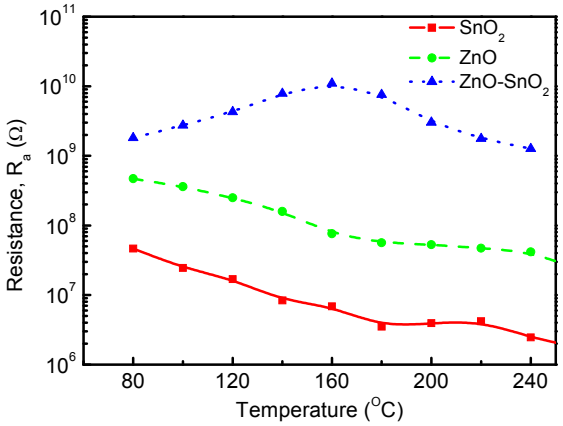

Fig. 4. Variation of resistance (R_a) in air of all the prepared sensors (bare SnO_2, bare ZnO and nanocomposite ZnO–SnO_2).

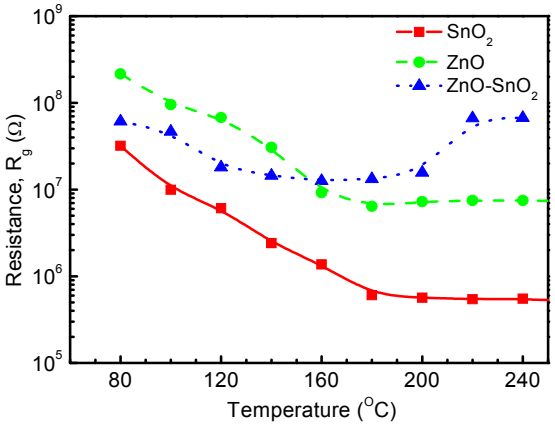

Fig. 5. Variation of resistance (R_g)with temperature for all the prepared sensors (bare SnO_2, bare ZnO and nanocomposite ZnO–SnO_2) in the presence of 500 ppm H_2 gas.

The variation of resistance in the presence of 500 ppm H_2 for all the prepared sensors is shown in Fig. 5 as a function of temperature. The resistance of all the sensors falls from initial higher value (R_a) to low resistance value (R_g) in the presence of 500 ppm of target H_2 gas. The decrease in resistance was found to be about of one order for bare ZnO and bare

SnO_2 thin film sensors at their respective operating temperatures. However the decrease in resistance of the ZnO–SnO_2 nanocomposite thin film sensor from R_a to R_g was about two orders in magnitude at T_{opt} = 160°C. The much higher fall in the resistance of composite sensors is due to the availability of higher concentration of adsorbed oxygen species on its surface for interaction with the target H_2 gas molecules. A large amount of adsorbed oxygen molecules are desorbed from the sensor surface, thereby liberating the trapped electrons and increasing the conductivity.

Conclusion

Thin film ZnO–SnO_2 nanocomposite sensor showed an enhanced response of 8.8×10^2 towards 500 ppm H_2, at a relatively low operating temperature of 160°C. The enhanced response is due to the twin effect of enhanced porosity of the nanocomposite films and the formation of space charge regions at the n–n type hetero–junction. The modulation of depletion region at n–n heterojunction besides enhanced activity of adsorbed oxygen results in a significant decrease in the sensor resistance (R_a to R_g) in the presence of target H_2 gas.

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