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Research Article

Preparation, Characterization, and H_2S Sensing Performance of Sprayed Nanostructured SnO_2 Thin Films

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Nanostructured SnO_2 thin films were prepared by spraying tin chloride dihydrate onto the heated glass substrate at 250°C. The films were fired at 500°C. As-prepared thin films were studied using XRD and FESEM to know crystal structure and surface morphology. The average crystallite and grain size observed from XRD and FF-SEM was found to be less than 33 and 67 nm, respectively. The films sprayed for 30 min were observed to be most sensitive to H_2S at 250°C. The results are discussed and interpreted.

1. Introduction

The n-type semiconductor material has been widely used in the gas detecting field during the last decades. The sensing properties of various semiconductor oxides, especially the SnO_2-based material, have been extensively studied [1]. Gas sensing applications demand materials that have a quick response-recovery time and high response for trace level detection of various gases. Semiconducting tin oxide is found useful for various gas sensing applications and improves its sensitivity and selectivity with appropriate catalysts [2]. Several potential applications have been reported previously, such as a transparent conductive electrode for solar cells [3], a gas sensing material for gas sensors devices [4], photochemical and photoconductive device, liquid crystal display [5], gas discharge display, and lithium-ion batteries. There has been intensive research on improving the gas response and selectivity by controlling the particle size [6], nanostructures [7], sensing temperature [8], surface structure [9], and catalysts [10].

A variety of techniques have been used to prepare tin oxide (SnO_2) thin films. These include spray pyrolysis [11], ultrasonic spray pyrolysis [12], chemical vapour deposition [13], activated reactive evaporation [14], ion-beam-assisted deposition [15], sputtering [16], and sol-gel [17] methods. Among these techniques, spray pyrolysis has proved to be simple, reproducible, and inexpensive, as well as suitable for large area applications. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make it useful for industrial as well as solar cell applications. In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nanometer range. As demonstrated [18] spray pyrolysis is a versatile technique for deposition of metal oxides.

Hydrogen sulfide is a toxic gas, often produced in coal, coal oil, or natural gas manufacturing. Even at low concentration it produces severe effects on the nervous system. Therefore, reliable sensors with low cost, low energy consumption having high sensitivity, selectivity, and

operability in ppm range of H_2S are in high demand for environmental safety and industrial control purposes. In general, SnO_2 response towards H_2S is reported at the higher temperatures; however, there are few references where a response at room temperature is also reported [19, 20].

We have tried to improve the H_2S gas response by making nanostructured SnO_2 thin film sensor and found that nanostructured SnO_2 thin film gas sensor gives maximum response to H_2S gas. In the present investigations, nanocrystalline SnO_2 thin films with different spraying time of the solution were prepared by spray pyrolysis technique. Structural properties and grain sizes were studied using X-ray diffraction. Microstructure was studied using FESEM. These nanostructured SnO_2 thin films were tested for sensing different gases and were observed to be most sensitive to H_2S at 250°C.

2. Experimental

2.1. Preparation of Nanostructured SnO_2 Thin Films. Figure 1 shows spray pyrolysis technique for preparation of nanostructured SnO_2 thin films. Set-up consists of spraying chamber, spray nozzle (gun), compressor for carrier gas, heating system, and temperature indicator.

Nanostructured SnO_2thin films were prepared from aqueous solution of tin (II)chloride dehydrate ($SnCl_2 \cdot 2H_2O$), Purified Merck) dissolved in deionized water to a concentration of 0.05 M for the preparation of thin films. The spray produced by nozzle was sprayed onto the ultrasonically cleaned glass substrates heated at 250 ± 5°C. Various parameters such as nozzle-to-substrate distance, deposition time and flow rate of solution, deposition temperature, and concentration were optimized to get good-quality films. Thus the films with different spraying time of 10 min, 20 min, 30 min and 40 min were obtained and were referred to as sample S1, S2, S3, and S4, respectively. The as-prepared samples were annealed in air at 500°C for 1 h.

2.2. Characterization. In the present study nanostructured SnO_2 thin films were characterized by X-ray diffraction (Miniflex Model, Rigaku, Japan). The microstructure of the films was analyzed using a field emission scanning electron microscope (FESEM, JEOL·JED 6300). Gas sensing properties were measured using a static gas sensing system. The sensor performance on exposure of LPG, carbon dioxide, hydrogen, ammonia, ethanol, chlorine, and H_2S was examined.

3. Results

3.1. X-Ray Diffraction Analysis. Figure 2 shows the X-ray diffractogram of nanocrystalline SnO_2 thin film. The observed peaks are matching well with the standard JCPDS data of SnO_2 [21]. The broad peaks may be due to the nanocrystalline nature of SnO_2. The average grain size is calculated from Scherer's formula, $D = 0.9\lambda/\beta\cos\theta$, where D is average crystallite size, λ is X-ray wavelength (1.5418 Å),

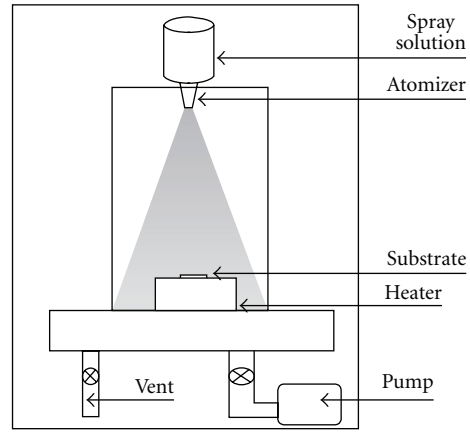

Figure 1: Schematic diagram of spray pyrolysis system for the preparation of nanostructured SnO_2 thin films.

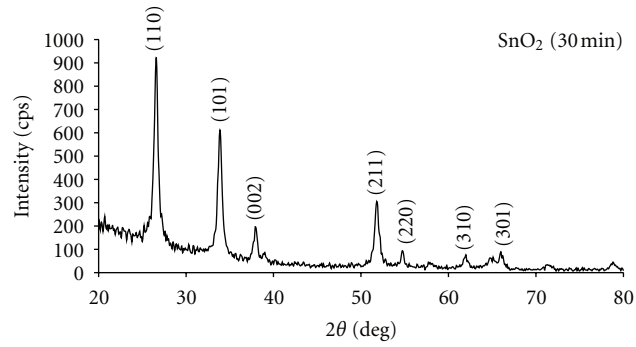

Figure 2: X-ray diffractogram of pure SnO_2 thin film (30 min).

β is FWHM of the peak, and θ is diffraction peak position. It was found to be 33 nm.

3.2. Surface Morphology. The microstructure of the prepared film was analyzed using a field emission scanning electron microscope (FE-SEM, JEOL.JED 6300).

Figure 3 shows the FESEM images, showing surface topography of most sensitive thin film samples. The morphology of the grains was roughly spherical in shape. The observed grain size was 67 nm.

3.3. Gas Sensing Performance of the Sensors

3.3.1. Gas Response with Operating Temperature. Gas response is defined as the change in conductance of the sample on exposure to gas to the original conductance. It is given by the relation

$$S = \frac{G_g - G_a}{G_a}, \tag{1}$$

where G_a is the conductance of sensor in air and G_g is the conductance of sensor in presence of gas.

Figure 4 shows the variation in response with the operating temperature to 600 ppm of H_2S for S1, S2, S3, and S4 samples. For all the samples the H_2S gas response increases

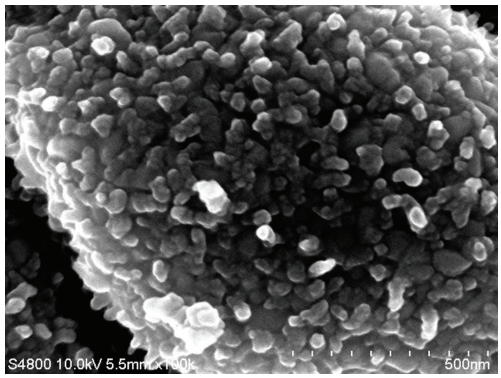

Figure 3: FESEM images of most sensitive thin films.

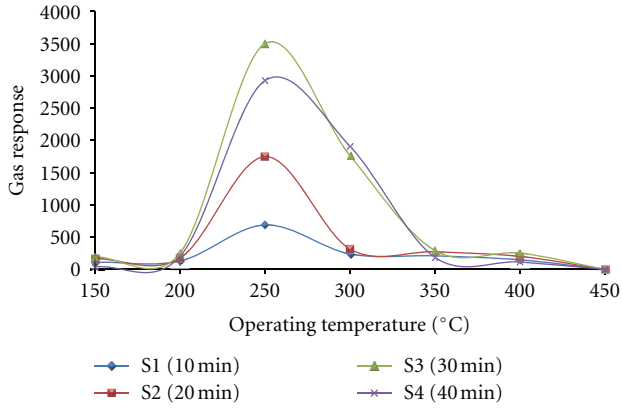

Figure 4: Gas response of pure nanostructured SnO_2 thin films with operating temperature.

with increase in operating temperature, reaches maximum ($S = 3499$ for sample S3) at 250°C, and falls with further increase in operating temperature.

Response of sensors depends on two factors, namely, the speed of chemical reaction on the surface of the grains, and the speed of the diffusion of gas molecules to that surface. These are activation processes, and the activation energy of chemical reactions is higher. At low temperatures the sensor response is restricted by the speed of chemical reactions. At higher temperature the sensor response is restricted by the speed of the diffusion of gas molecules to that surface. At some intermediate temperature the speed values of two processes become equal, and at that point the sensor response reaches its maximum. According to this mechanism for every gas there is a specific temperature at which the sensor response attains its peak value.

Thus, in the present case the optimum operating temperature for nanostructured SnO_2 films was 250°C. The temperature, which corresponds to a certain peak value, is a function of the kind of target gases and the chemical composition of the oxide, including additives and catalysts, and pure oxides are generally stable at lower temperatures.

3.3.2. Gas Response to H_2S at Various Gas Concentrations. Figure 5 shows the gas response against H_2S concentration

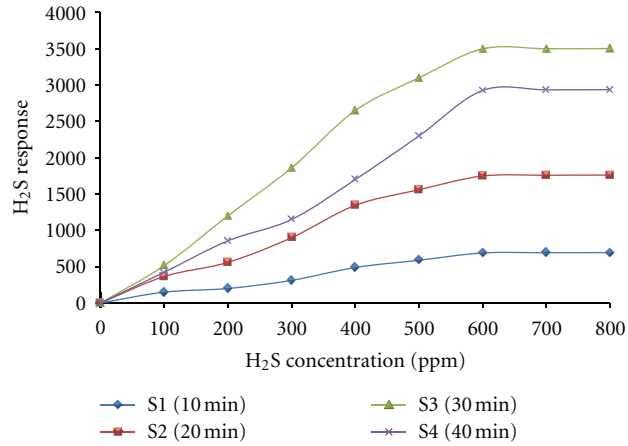

Figure 5: Variation of response with gas concentration.

at 250°C. It is observed that the response increases linearly as the H_2S concentration increases from 100 to 600 ppm and then remains nearly constant with further increase in the H_2S concentration. The linear relationship between the response and the H_2S concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the H_2S. The low gas concentration implies a lower surface coverage of gas molecules, resulting into lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in the gas concentration increases the surface reaction due to a large surface coverage. Further increase in the surface reaction will be gradual when saturation of the surface coverage of gas molecules is reached. Thus, the maximum sensitivity was obtained at an operating temperature of 250°C for the exposure of 600 ppm of H_2S.

3.3.3. Response and Recovery of the Sensor. The time taken for the sensor to attain 90% of the maximum decrease in resistance on exposure to the target gas is the response time. The time taken for the sensor to get back 90% of original resistance is the recovery time. The response and recovery of the nanostructured SnO_2 thin film (S3) sensor on exposure of 600 ppm of H_2S at 250°C are represented in Figure 6. The response is quick (4 s) and recovery is fast (9 s). The high oxidizing ability of adsorbed oxygen species on the surface nanoparticles and high volatility of desorbed by-products explain the quick response to H_2S and fast recovery.

3.3.4. Comparison of H_2S Sensing Performance of Reported SnO_2 Sensor with sensors Prepared in the Present Work. (See Table 1).

4. Discussion

The gas response of any metal oxide semiconductor to a particular gas increases with the decrease in the size of nanocrystallites [28, 29] due to an increase in surface-to-volume ratio and therefore the reactivity. Grain sizes and microstructures of the sensor affect the gas sensing

Table 1

Form of SnO_2 sensor	Temperature (°C)	Gas conc. (ppm)	H_2S response	References
Thin	250	600	3499	Present work (Sample S3)
Thin	100	80	96	[22]
Thick	—	50	106	[23]
Thin	150	100	2500	[24]
Thin	27	5	4	[25]
Thin	30	3.4	81	[26]
Thin	300	20	809	[27]

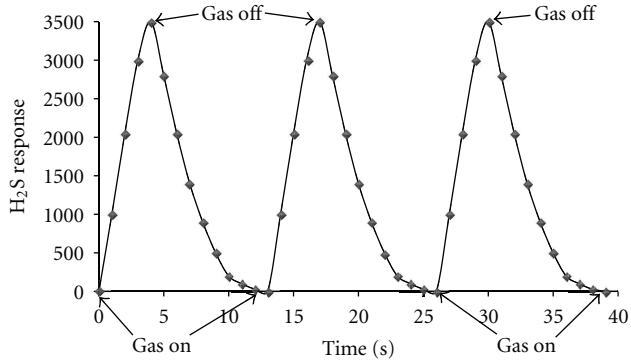

Figure 6: Response and recovery of the sensor.

performance of the sensor. It was found that, if the grain size of the sensor material is sufficiently small, the area of active surface sites is larger, and the sensitivity and selectivity for a particular gas enhance largely. Nanostructured materials would be expected to show much better gas sensing performance as compared with the sensor fabricated from bulk materials [30, 31].

The resistance of the nanostructured SnO_2 thin films decreases as gas flows into the test chamber and is adsorbed on the surface of the nanostructured SnO_2. However, when nanostructured SnO_2 thin films consist of nanograins in absence of H_2S, the depletion layer would extend throughout the entire layer of nanostructured SnO_2 on the film and its resistance would become strikingly large. In a H_2S gas environment the depleted layer would shrink quickly as it obtains conduction electrons due to reaction between H_2S adsorbed oxygen, and the resistance of the nanostructured SnO_2 would experience a large change. The response to H_2S can be explained in the following reaction:

$$H_2S + 3O_{(ads)}^{-} \longrightarrow H_2O_{(g)} + SO_{2(g)} + 3e^{-} \quad (2)$$

5. Conclusion

Nanostructured SnO_2 thin films could be prepared by simple and inexpensive spray pyrolysis technique. The structural and microstructural properties confirm that the as-prepared SnO_2 thin films are nanostructured in nature. The SnO_2 thin film of sample (S3 = 30 min spray time) was most sensitive to H_2S gas and exhibited the response of S = 3499 to the gas concentration of 600 ppm at the temperature of 250°C. The sensor has good selectivity to H_2S against different gases. The nanostructured SnO_2 thin films exhibit rapid response–recovery, which is one of the main features of this sensor.

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References

[1] J. Liu, X. Huang, G. Ye et al., "H_2S detection sensing characteristic of CuO/SnO_2 sensor," *Sensors*, vol. 3, no. 5, pp. 110–118, 2003.

[2] V. Gupta, S. Mozumdar, A. Chowdhuri, and K. Sreenivas, "Influence of CuO catalyst in the nanoscale range on SnO_2 surface for H_2S gas sensing applications," *Pramana*, vol. 65, no. 4, pp. 647–652, 2005.

[3] S. Chappel and A. Zaban, "Nanoporous SnO_2 electrodes for dye-sensitized solar cells: Improved cell performance by the synthesis of 18 nm SnO_2 colloids," *Solar Energy Materials and Solar Cells*, vol. 71, no. 2, pp. 141–152, 2002.

[4] G. E. Patil, D. D. Kajale, D. N. Chavan et al., "Synthesis, characterization and gas sensing performance of SnO_2 thin films prepared by spray pyrolysis," *Bulletin of Materials Science*, vol. 34, no. 1, pp. 1–9, 2011.

[5] S. Gnanam and V. Rajendran, "Luminescence properties of eg-assisted SnO_2 nanoparticles by sol-gel process," *Digest Journal of Nanomaterials and Biostructures*, vol. 5, no. 3, pp. 699–704, 2010.

[6] C. Xu, J. Tamaki, N. Miura, and N. Yamazoe, "Grain size effects on gas sensitivity of porous SnO_2-based elements," *Sensors and Actuators B*, vol. 3, no. 2, pp. 147–155, 1991.

[7] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, and Z. L. Wang, "Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts," *Applied Physics Letters*, vol. 81, no. 10, pp. 1869–1871, 2002.

[8] Y. Wang, X. Jiang, and Y. Xia, "A solution-phase, precursor route to polycrystalline SnO_2 nanowires that can be used for gas sensing under ambient concentrations," *Journal of the American Chemical Society*, vol. 125, no. 52, pp. 16176–16177, 2003.

[9] Y. Shimizu, E. Di Bartolomeo, E. Traversa et al., "Effect of surface modification on NO_2 sensing properties of SnO_2 varistor-type sensors," *Sensors and Actuators B*, vol. 60, no. 2, pp. 118–124, 1999.

[10] T. Maekawa, J. Tamaki, N. Miura, and N. Yamazoe, "Sensing behavior of CuO loaded SnO_2 element for H_2S detection," *Chemistry Letters*, vol. 25, no. 4, pp. 575–578, 1991.

[11] K. Murakami, K. Nakajima, and S. Kaneko, "Initial growth of SnO_2 thin film on the glass substrate deposited by the spray pyrolysis technique," *Thin Solid Films*, vol. 515, no. 24, pp. 8632–8636, 2007.

[12] L. A. Patil, M. D. Shinde, A. R. Bari, and V. V. Deo, "Highly sensitive and quickly responding ultrasonically sprayed nanostructured SnO_2 thin films for hydrogen gas sensing," *Sensors and Actuators B*, vol. 143, no. 1, pp. 270–277, 2009.

[13] T. Okuno, T. Oshima, S. D. Lee, and S. Fujita, "Growth of SnO_2 crystalline thin films by mist chemical vapour deposition method," *Physica Status Solidi C*, vol. 8, no. 2, pp. 540–542, 2011.

[14] H. S. Randhawa, M. D. Matthews, and R. F. Bunshah, "SnO_2 films prepared by activated reactive evaporation," *Thin Solid Films*, vol. 83, no. 2, pp. 267–271, 1981.

[15] T. Mohanty, Y. Batra, A. Tripathi, and D. Kanjilal, "Nanocrystalline SnO_2 formation using energetic ion beam," *Journal of Nanoscience and Nanotechnology*, vol. 7, no. 6, pp. 2036–2040, 2007.

[16] T. Gui, L. Hao, J. Wang, L. Yuan, W. Jia, and X. Dong, "Structure and features of SnO_2 thin films prepared by RF reactive sputtering," *Chinese Optics Letters*, vol. 8, supplement 1, p. 134, 2010.

[17] G. Neri, A. Bonavita, G. Rizzo et al., "Towards enhanced performances in gas sensing: SnO_2 base nanocrystalline oxides application," *Sensors and Actuators B*, vol. 122, pp. 564–571, 2007.

[18] P. S. Patil, "Gas-chromism in ultrasonic spray pyrolyzed tungsten oxide thin films," *Bulletin of Materials Science*, vol. 23, no. 4, pp. 309–312, 2000.

[19] Z. Zeng, K. Wang, Z. Zhang, J. Chen, and W. Zhou, "The detection of H_2S at room temperature by using individual indium oxide nanowire transistors," *Nanotechnology*, vol. 20, no. 4, pp. 44–51, 2009.

[20] R. S. Niranjan, V. A. Chaudhary, I. S. Mulla, and K. Vijayamohanan, "A novel hydrogen sulfide room temperature sensor based on copper nanocluster functionalized tin oxide thin films," *Sensors and Actuators B*, vol. 85, no. 1-2, pp. 26–32, 2002.

[21] ASTM, card no.05-0467.

[22] G. E. Patil, D. D. Kajale, S. D. Shinde et al., "Effect of thermal annealing temperature on gas sensing performance of SnO_2 thin films prepared by spray pyrolysis," *Sensor and Transducers*, vol. 12, pp. 96–108, 2010.

[23] Ü. Kersen and L. Holappa, "H_2S-sensing properties of SnO_2 produced by ball milling and different chemical reactions," *Analytica Chimica Acta*, vol. 562, no. 1, pp. 110–114, 2006.

[24] M. Rumyantseva, M. Labeau, G. Delabouglise, L. Ryabova, I. Kutsenok, and A. Gaskov, "Copper and nickel doping effect on interaction of SnO_2 films with H_2S," *Journal of Materials Chemistry*, vol. 7, no. 9, pp. 1785–1790, 1997.

[25] G. Fang, Z. Liu, C. Liu, and K. L. Yao, "Room temperature H_2S sensing properties and mechanism of CeO_2-SnO_2 sol-gel thin films," *Sensors and Actuators B*, vol. 66, no. 1, pp. 46–48, 2000.

[26] J. Liu, S. Gong, J. Xia, L. Quan, H. Liu, and D. Zhou, "The sensor response of tin oxide thin films todifferent gas concentration and the modification of the gas diffusion theory," *Sensors and Actuators B*, vol. 138, no. 1, pp. 289–295, 2009.

[27] I. S. Hwang, J. K. Choi, S. J. Kim et al., "Enhanced H_2S sensing characteristics of SnO_2 nanowires functionalized with CuO," *Sensors and Actuators B*, vol. 142, no. 1, pp. 105–110, 2009.

[28] S. D. Sartale and C. D. Lokhande, "Preparation and characterization of nickel sulphide thin films using successive ionic layer adsorption and reaction (SILAR) method," *Materials Chemistry and Physics*, vol. 72, no. 1, pp. 101–104, 2001.

[29] L. A. Patil, A. R. Bari, M. D. Shinde, V. Deo, and M. P. Kaushik, "Detection of dimethyl methyl phosphonate—a simulant of sarin: the highly toxic chemical warfare—using platinum activated nanocrystalline ZnO thick films," *Sensors and Actuators B*, vol. 161, no. 1, pp. 372–380, 2012.

[30] L. A. Patil, A. R. Bari, M. D. Shinde, and V. Deo, "Ultrasonically prepared nanocrystalline ZnO thin films for highly sensitive LPG sensing," *Sensors and Actuators B*, vol. 149, no. 1, pp. 79–86, 2010.

[31] L. A. Patil, A. R. Bari, M. D. Shinde, and V. Deo, "Ultrasonically synthesized nanocrystalline ZnO powder-based thick film sensor for ammonia sensing," *Sensor Review*, vol. 30, no. 4, pp. 290–296, 2010.