Ultrasonically sprayed nanostructured SnO_2 thin films for highly sensitive hydrogen sensing

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ABSTRACT

Nanostructured SnO_2 thin films were prepared by ultrasonic spray pyrolysis technique. Aqueous solution (0.05M) of $SnCl_4{\cdot}5H_2O$ in double distilled water was chosen as the starting solution for the preparation of the films. The stock solution was delivered to nozzle with constant and uniform flow rate of 70 ml/h by Syringe pump SK5001. Sono-tek spray nozzle, driven by ultrasonic frequency of 120 kHz, converts the solution into fine spray. The aerosol produced by nozzle was sprayed on glass substrate heated at 150^oC. The sensing performance of the films was tested for various gases such as LPG, hydrogen, ethanol, carbon dioxide and ammonia. The sensor (30 min) showed high gas response (S = 3040 at 350 ◦C) on exposure of 1000ppm of hydrogen and high selectivity against other gases. Its response time was short (2 s) and recovery was also fast (12 s). To understand reasons behind this uncommon gas-sensing performance of the films, their structural, microstructural, and optical properties were studied using X-ray diffraction, electron microscopy (SEM and TEM), and UV–vis spectroscopy, respectively. The results are interpreted.

Keywords: Ultrasonic spray pyrolysis technique, Nanostructured SnO_2 thin films, Hydrogen sensing, Gas response, Selectivity Response time, Recovery time

1. INTRODUCTION

There has been considerable interest in recent years in nanostructured gas-sensing materials in thin film form [1-13]. In comparison with conventional sintered bulk gas sensors, nanostructured thin film materials have good response, optimum operating temperature and selectivity. In addition, sensors based on thin film gas-sensing materials are essential to the development and fabrication of integrated gas sensors. For industrial applications, a low cost method is vital; hence, an ultrasonic spray pyrolysis technique is often preferred. The ultrasonic spray method(uses nebulizer) ensures generation of ultra fine droplets of narrow size distribution in the range of a few micrometers, whereas an ordinary spray method (uses spray gun) gives rise to droplets of varied sizes ranging from micrometers to a few tenths of a millimeter. Hence, the ultrasonic spray method, in present article, may be the best approach to obtain highly uniform spot-free films. Nanostructured SnO2 based hydrogen sensors prepared by ultrasonic spray pyrolysis technique are reported in present article. The most important features of the present investigation are that the sensors show high hydrogen response, selectivity, fast response and quick recovery.

2. EXPERIMENTAL

2.1. Experimental set up to prepare nanostructured thin films

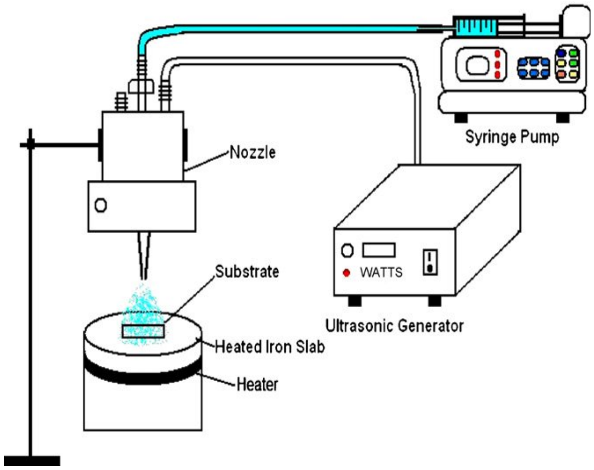


Fig. 1: Ultrasonic spray pyrolysis set up

Fig. 1 shows an ultrasonic spray pyrolysis set up to prepare nanostructured thin films. High frequency (120 kHz) from ultrasonic generator (120 kHz) is applied to piezoelectric transducer associated in nozzle which converts the precursor solution into the smoke or spray. This spray was used to prepare nanostructured thin films. The stock solution (0.05M) of $SnCl_4{\cdot}5H_2O$ in double distilled was delivered to nozzle with constant and uniform flow rate of 70 ml/h by Syringe pump SK5001. The aerosol produced by nozzle was sprayed onto the glass substrate heated at 150^OC. A pyrolytic reaction takes place and nanocrystalline metal oxide was produced. The films were prepared by spraying for different spraying time intervals (5 min, 10 min, 20 min and 30 min) onto a glass substrate. Different spraying time intervals would give films of different thicknesses. As prepared thin films were fired at 500^OC for 30 min. Gas-sensing properties of the films were tested.

2.2. Material characterizations

2.2.1 Structural properties: X-ray diffraction studies

Crystallite sizes of the samples with spraying time of 5min and 30 min were calculated (From fig 2) using Scherer formula which was found to be 14nm and 16.66

nm, respectively, indicating their nanocrystalline nature. XRD corresponding to 30 min film has sharper peaks as compared to 5min film. Crystallite size has a direct dependence on spraying time interval and thickness of the film.

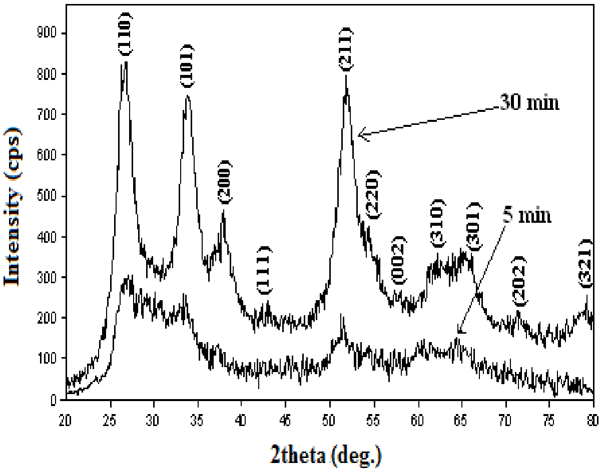


Figure 2. XRDs of SnO_2 thin films

2.2.2 Transmission electron microscopy (TEM).

Fig. 3 shows the TEM [CM 200 Philips (200kV HT)] of SnO_2 powder obtained by scratching the thin film (30 min). It is clear from TEM image that the grains are nanocrystalline in nature which are smaller than 7 nm with narrow size distribution. Surface to volume ratio of such nanoparticles is very high. Therefore, these particles are highly reactive to exposed gases. The interaction between the gases and the sensitive layer is limited to the surface itself [5]. This is one of the reasons that nanostructured films give high gas response.

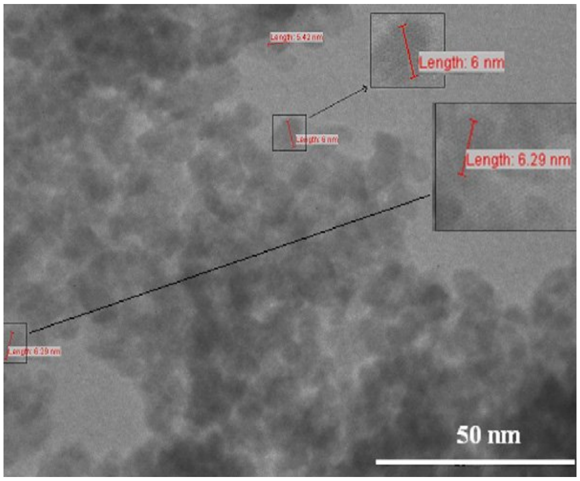


Fig. 3. TEM SnO_2 (30 min) thin film.

2.2.3 Absorption spectra

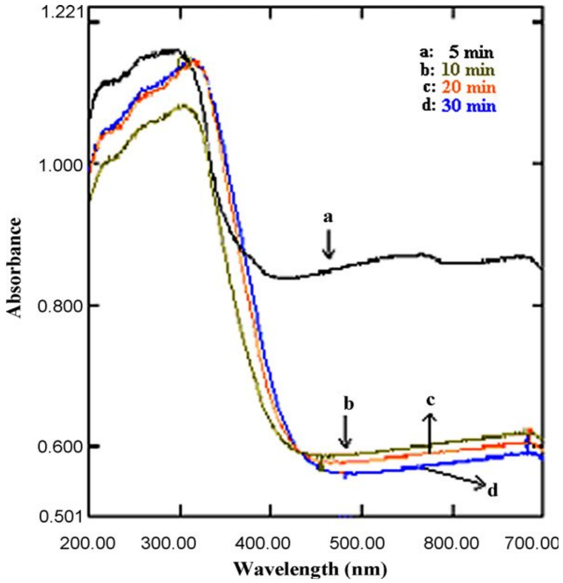


Fig.4. Absorption spectra SnO_2 thin films.

2.3 Gas sensing performance
2.3.1Gas response and Selectivity

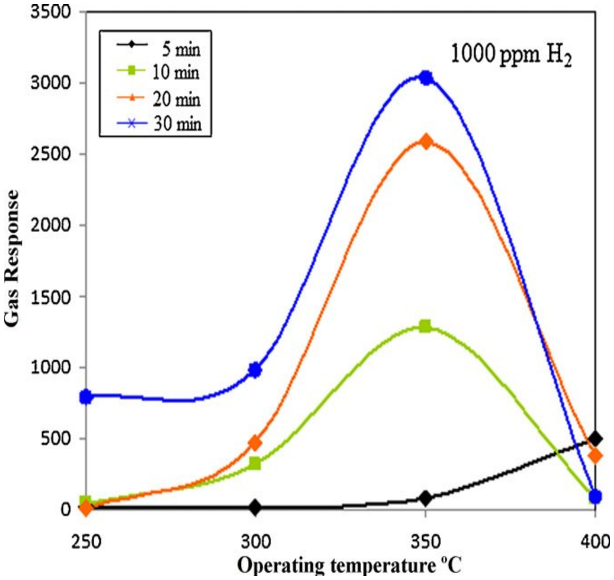
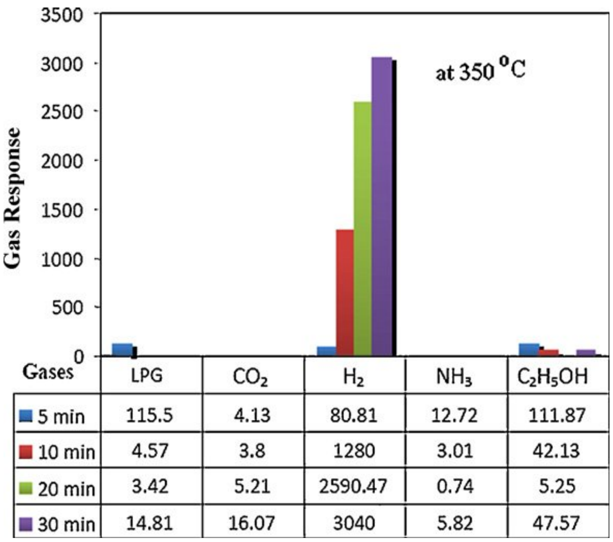


Fig. 5. H_2 response-temp. profile.

Hydrogen sensing performance of nanostructured SnO_2 thin film sensors was measured by using static gas sensing system [8]. It is clear from the Fig. 5 that the gas response increases with operating temperature, reaches to maximum (S=3040) at 350°C and falls with further increase in operating temperature.

2.3.2 Selectivity



Gases	LPG	CO_2	H_2	NH_3	C_2H_5OH
🟦 5 min	115.5	4.13	80.81	12.72	111.87
🟥 10 min	4.57	3.8	1280	3.01	42.13
🟩 20 min	3.42	5.21	2590.47	0.74	5.25
🟪 30 min	14.81	16.07	3040	5.82	47.57

Fig. 6. Hydrogen selectivity

Fig. 6 shows selectivity of nanostructured SnO_2 thin films to H_2 against CO_2, LPG, NH_3 and ethanol gases at 350 ^{0}C.

2.3.3 Response and recovery of the sensor

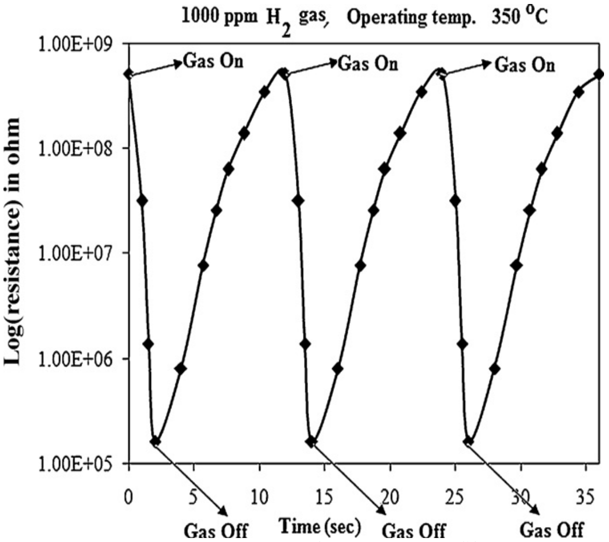


Fig. 7. Response and recovery profile.

Response and recovery of pure-SnO2 based thin film (30 min) was studied on exposure of 1000ppm hydrogen. Variation of resistance (of this film) with time was measured by using Agilent data acquisition/switch unit (Model 34970A). Typical hydrogen on-off cycle was used to monitor the flow of hydrogen on the film surface. After every new cycle, the chamber was refreshed with air. Fig. 11 represents response and recovery profile of the sensor. The sensor responded quickly (~2 s) and the recovered back fastly (~12 s). The negligible quantity of the surface reaction products and their high volatility explain the quick response to H2 and fast recovery to its initial chemical status.

2.4 References

[1] J. Hotovy, D. Bue, S. Hascik, O. Nennewitz, Characterization of NiO thin films deposited by reactive sputtering, Vacuum 50 (1998) 41–44.
[2] C.C. Chai, J. Peng, B.P. Yan, Characterization of _-Fe2O3 thin films deposited by atmospheric pressure CVD onto alumina substrates, Sens. Actuators, B 34 (1996) 412–416.
[3] M. de la, L. Olvera, R. Asomoza, SnO2 and SnO2:Pt thin films used as gas sensors, Sens. Actuators, B 45 (1997) 49–53.
[4] L.A. Patil*, M.D. Shinde, A.R. Bari, V.V. Deo, Highly sensitive ethanol sensors based on nanocrystalline SnO2 thin films, Current Applied Physics, (2010) 1-6
[5] I. Simon, N. Barson, Micromachined metal oxide gas sensors: opportunities to improve sensor performance, Sens. Actuators, B 73 (2001) 1–26.
[6] L.A. Patil ∗, M.D. Shinde, A.R. Bari, V.V. Deo, Novel trapping system for size wise sorting of SnO2 nanoparticles synthesized from pyrolysis of ultrasonically atomized spray for gas sensing, Sensors and Actuators B 143 (2009) 316–324
[7] D.R. Patil, L.A. Patil, Cr2O3-modified ZnO thick film resistors as LPG sensors, Talanta 77 (2009) 1409–1414
[8] L.A. Patil ∗, M.D. Shinde, A.R. Bari, V.V. Deo, Highly sensitive and quickly responding ultrasonically sprayed nanostructured SnO2 thin films for hydrogen gas sensing, Sens. Actuators, B 143 (2009) 270–277
[9] Y.H. Choi, S.H. Hong, H2 sensing properties in highly oriented SnO2 thin films, Sens. Actuators, B 125 (2007) 504–509.
[10] R.S. Niranjan, Y.K. Hwang, D.K. Kim, S.H. Jhung, J.S. Chang, I.S. Mulla, Nanostructured tin oxide: synthesis and gas-sensing properties, Mater. Chem. Phys. 92 (2005) 384–388.
[11] V.A. Chaudhary, I.S. Mulla, K. Vijayamohanan, Selective hydrogen sensing properties of surface functionalized tin oxide, Sens. Actuators, B 55 (1999) 154–160.
[12] K.S. Yoo, S.H. Park, J.H. Kang, Nano-grained thin film indium tin oxide gas sensor for H2 detection, Sens. Actuators, B 108 (2005) 159–164.
[13] H.R. Kim, K.I. Choi, J.H. Lee, S.A. Akbar, Highly sensitive and ultra-fast responding gas sensors using self-assembled hierarchical SnO2 sphere, Sens. Actuators, B 136 (2009) 138–143.