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Low temperature NO₂ sensing performance of nanostructured SnO₂ thin films

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ABSTRACT

 SnO_2 thin films were prepared by spray pyrolysis technique. Aqueous solution (0.05M) of $SnCl_2 \cdot 2H_2O$ in deionized water was chosen as the starting solution for the preparation of thin films. The aerosol produced by nozzle was sprayed on glass substrate heated at 250 °C. The sensing performance of the films was tested for various gases such as LPG, hydrogen, ethanol, carbon dioxide, ammonia, nitrogen dioxide, nitrogen monoxide and sulphurdioxide. The sensor (30 min) showed high gas response (S = 1165 at 150 °C) on exposure of 100 ppm of NO₂ and high selectivity against other gases. Its response time was short (4 s) and recovery was also fast (9 s). To understand reasons behind this uncommon gas-sensing performance of the films, their structural and microstructural properties were studied using X-ray diffraction, electron microscopy (FE-SEM and TEM) respectively. Elemental composition was studied using energy dispersive of X-rays (EDAX). The results are discussed and interpreted.

Keywords: Spray Pyrolysis, Nanocrystalline SnO₂, NO₂ gas sensing, X-ray diffraction, Surface morphology.

INTRODUCTION

SnO₂ is an n-type semiconductor, which has attracted considerable attention due its unique electrical, optical and catalytic properties useful for variety of applications. For example, stannic oxide is used in transparent heaters for windshield defrosting, in anti-reflection coating for solar cells, as a transparent electrode for electro chromic devices, as a sensing material for combustible gas sensors and as a electro catalysts for organic oxidation reaction [1]. SnO₂ posses excellent capability of exchange of oxygen from the atmosphere due to natural non- stoichiometry, that makes it the most suitable material for gas sensing application. The adsorption/desorption of oxygen on the surface of SnO_2 is the key parameter for change in conductance. The adsorbed oxygen on the surface (or grain boundaries) of SnO_2 captures the free electrons and becomes O^{-2} . It is important to point out that chemisorption of oxygen is crucial for gas sensing mechanism. Gas sensing applications demand materials at a quick responserecovery time and high response for trace level detection of various gases. Semi-conducting tin oxide is found useful for various gas sensing applications and improve 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, lithium-ion batteries, etc. There has been intensive research on improving the gas response and selectivity by controlling the particle size [6], nanostructures [7], sensing temperature [8, 9], surface structure [10] and catalysts [11].

The sensors based on SnO_2 nanostructures demand higher operating temperatures. On the other hand, the practical on field gas sensors demand room temperatures operating sensors with enhanced response characteristics for trace

level detection of harmful gases. NO_2 is the major cause of formation of ground-level ozone in the stratosphere, acid rains, and an active ingredient to global warming [12]. Exposure to high concentrations of NO_2 can make living organisms more susceptible to bacterial infections and lung cancer. Just like other pollutants, nitrogen dioxide affects people with existing medical conditions more severely than healthy people.

Nanostructure thin films of SnO_2 have been prepared by various techniques such as spray pyrolysis [13], ultrasonic spray pyrolysis [14], chemical vapour deposition [15], activated reactive evaporation [16], ion-beam assisted deposition [17] and sol–gel [18] 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 them 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 [19] spray pyrolysis is a versatile technique for deposition of metal oxides.

In the present investigations, nanostructured SnO₂ 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. Elemental composition was studied using EDAX. Microstructure was studied using FESEM and TEM. These nanocrystalline SnO₂ thin films were tested for sensing different gases and were observed to be most sensitive to NO₂ at 150 °C.

MATERIALS AND METHODS

2.1. Preparation of nanostructured SnO₂ 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.



Fig.1. Schematic diagram of spray pyrolysis system for the preparation of nanostructured SnO₂ thin films.

Nanostructured SnO_2 thin films were prepared using the above set up. Aqueous solution (0.05M) Tin (II) chloride dehydrate ($SnCl_2.2H_2O$), Purified Merck) 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 compressed air. 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 referred to as S1, S2, S3 and S4 respectively. The aerosol produced by nozzle was sprayed on the glass substrate heated at 250° C. It is well known that when the aqueous Tin (II) chloride dehydrate solution is sprayed on a heated substrate, a pyrolytic reaction takes place and nanocrystalline metal oxide is produced. The as prepared nanocrystalline SnO₂ thin film samples S1, S2, S3 and S4 were annealed in air at 500° C for 1 h.

The usual expressions for this reaction are presented in Eq. (1) $SnCl_2$. $2H_2O \rightarrow SnO_2 + 2H_2 \uparrow + Cl_2 \uparrow$ ------ (1)

2.2. Sensing system to test the gases



Fig. 2. Block diagram of gas sensing system

Figure 2 shows block diagram of gas sensing system. The gas sensing studies were carried out using a static gas chamber to sense NO_2 gas in air ambient. The nanocrystalline SnO_2 thin films were used as the sensing elements. Cr-Al thermocouple is mounted to measure the temperature. The output of thermocouple is connected to temperature indicator. Gas inlet valve fitted at one of the ports of the base plate. Gas concentration (100 ppm) inside the static system is achieved by injecting a known volume of test gas in gas injecting syringe. Constant voltage (5V) is applied to the sensor and current can be measured by picoammeter.

3. MATERIAL CHARACTERIZATIONS

The nanostructured SnO₂ thin film were characterized by X-ray diffraction (Miniflex Model, Rigaku, Japan) using CuK α radiation with a wavelength, $\lambda = 1.5418$ Å. The microstructure and elemental composition of the films was analyzed using field emission scanning electron microscope coupled with energy dispersive spectrophotometer ((FE-SEM, JEOL. JED 6300) And Transmission electron microscopy (TEM) [CM 200 Philips (200 kV HT)]. Electrical conductivity and gas sensing properties were measured using a static gas sensing system. The sensor performance on exposure of LPG, CO₂, H₂, NH₃, C₂H₅OH, Cl₂ NO₂, NO and SO₂ was examined.



Fig. 3. X-ray diffractogram of nanostructured SnO₂ thin films samples: (a) S1, (b) S2, (c) S3 and (d) S4.

RESULTS AND DISCUSSION

4.1. X-ray diffraction analysis

Figure 3 shows the X-ray diffractogram of thin film samples S1, S2, S3 and S4. The peaks in the XRD pattern match well with the reported ASTM data of pure SnO_2 (ASTM data Card no.05-0467) [20]. It is revealed from X-ray diffractogram that the material is crystalline in nature with tetragonal phase. The average crystallite size of tin oxide thin film samples were calculated by using the Scherrer formula

 $D = 0.9\lambda/\beta\cos\theta \dots (2)$

Where, D = Average crystallite size; $\lambda = X$ -ray wavelength (1.5418 Å); $\beta = FWHM$ of the peak; $\theta = Diffraction$ peak position.

The calculated crystallite sizes were presented in Table 2

4.2. Surface Morphology

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

Figure 4(a)-(d) shows the FESEM images, showing surface topography of S1, S2, S3 and S4 thin film samples respectively. The morphology of the grains was roughly spherical in shape. Thus the grain size goes on increasing with the increase in spraying time of the solution. In Fig. 4 (a), (b) and (c) grains are uniformly distributed and Fig.4 (d) show agglomeration of grains. It may be due to collapse of larger grains into smaller with the increase of spraying time of the solution. The observed grain sizes were presented in Table 2.



Fig.4. FESEM images: (a) S1, (b) S2, (c) S3 and (d) S4.

4.3. Microstructured property using TEM



Fig.5. TEM images of most sensitive nanostructured SnO₂ thin film sample (S3)

Figure 5 shows the TEM of nanocrystalline SnO_2 thin film was obtained by scratching the thin film. The powder was dispersed in ethanol. Copper grid was used to hold the powder. It is clear from TEM image that the grains are nanocrystalline in nature. Observed average grain size was 10 nm.

4.4. Quantitative elemental analysis (EDAX)

The quantative elemental composition of the nanostructured SnO_2 thin film (sample S3) was analyzed using an energy dispersive spectrometer shown in Figure 6.



Fig. 6. Elemental analysis of nanostructured SnO₂ thin film sample (S3)

Table 1. Quantative elemental analysis as prepared nanostructured SnO₂thin film

Element	mass%	at %
0	25.03	71.24
Sn	74.97	28.26
Total	100	100

Stoichiometrically expected at % of Sn and O is 33.30 and 66.70, respectively, observed at% Of Sn and O (Table 2) was: 28.26 and 71.24, respectively. It is clear from Table 1. that as prepared nanocrystalline SnO_2 thin films was observed to nonstoichiometric in nature.

4.5. Determination of film thickness

Film thickness was measured by using a micro gravimetrical method [21] (considering the density of the bulk tin oxide). The films were deposited on clean glass slides whom mass was previously determined. After the deposition the substrate was again weighted, determining the quantity of deposited SnO_2 . Measuring the surface area of the deposited film, taking account of SnO_2 specific weight of the film, thickness was determined using the relation:

 $T = M_{SnO2} / A^* \rho * 10^4 - \dots (3)$

Where A = Surface area of the film $[cm^{2}]$; M_{SnO2} = Quantity of the deposited tin oxide ; ρ = Specific weight of SnO₂

5. ELECTRICAL PROPERTIES

5.1. I–V characteristics



Fig. 7. I–V characteristics of nanostructured SnO₂ thin film sensors.

The contacts were made by silver paste on thin film surface. The configuration was $1.5 \text{ cm} \times 1 \text{ cm}$. Figure 7 shows I–V characteristics of nanocrystalline SnO₂ thin films for the samples sprayed for 10 min, 20 min, 30 min. and 40 min. The graph is symmetrical, but not in a completely ohmic behavior. It may be due to the semiconducting nature of the films. The graphs are observed to be symmetrical in nature indicating ohmic contact. Confirmation of ohmic contacts would ensure that the change in resistance could only be due to the influence of gas exposure.

5.2. Electrical conductivity



Fig. 8. Variation of log (σ) with operating temperature (°C).

Figure 8 shows the variation of log (σ) with operating temperature. The conductivity of each sample is observed to be increasing with an increase in temperature range between 100 °C and 200 °C in steps of 25 °C. The increase in conductivity with increase in temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of nanocrystalline SnO₂. It clearly indicates that the nanostructured SnO₂ thin films were semiconducting in nature.

Sample No.	Spray time	Thickness (nm)	Crystalline size from XRD	Grain size from	Activation energy (CE)	
	(min)	(nm)	FE-SEM (nm)	50 °C	200 ^o C	
S1	10	205	19	17	0.57 eV	0.49 eV
S2	20	241	26	23	0.51 eV	0.46eV
S 3	30	302	30	27	0.43 eV	0.35eV
S 4	40	329	33	30	0.31 eV	0.28eV

rable 2. Measurement of spray time, film thickness, crystallite size, grain size and activation energ

It is clear from Table 2 that as the spraying time of the solution increases, thickness of the film goes on increasing with an increase in crystalline and grain size while activation energy decreasing. Crystallinity of the material is direct dependence on the film thickness. Crystallinity has been observed to improve with an increase of the film thickness [22]. Moreover, the increase of crystallite size could be attributed to the improvement of the crystallinity and an increase in the cluster formation leading to agglomeration of small crystallites. These agglomerated crystallites coalesce together resulted in the formation of larger crystallites with better crystallinity.

It is reported [23, 24] as the thickness of the film increases activation energy goes on decreasing. Electrical conductivity was calculated using the relation:

$$\sigma = \sigma_0 \exp\left(-\Delta E/kT\right) - \dots$$
 (4)

Where, $\sigma =$ conductivity; $\sigma_o =$ conductivity constant; k = Boltzmann constant; T = Temperature

In Table 2 the activation energy is calculated from slopes of line for sample S1, S2, S3 and S4 thin films. It is clear from Table 2 that, as film thickness of the sample goes on increasing; the activation energy goes on decreasing. The decrease in activation energy with increasing film thickness may be due to the change in structural parameters, improvement in crystalline and grain size [25].

6. GAS SENSING PERFORMANCE OF THE SENSORS

6.1. Measurement of response

Gas response (S) of the sensor is defined as the ratio of change in conductance to the conductance of the sensor on exposure of target (at same operating conditions).

 $S = G_g - G_a / G_a - \dots$ (5)

where $G_a =$ the conductance of the sensor in air

 G_g = the conductance on exposure of a target gas.

6.2. Gas response

Figure 9 shows the variation in response with the operating temperature to 100 ppm of NO₂ for S1, S2, S3, and S4 samples. For all the samples the response increases with increase in operating temperature and reach maximum (S=1165 for sample S3) at 150°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 [26, 27]. 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.



Fig. 9. Gas response of nanocrystalline SnO_2 thin films with operating temperature.

Thus, in the present case the optimum operating temperature for nanocrystalline SnO_2 films was 150°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.

6.3. Selectivity



Fig. 10. Selectivity of nanocrystalline SnO₂ thin films for different gases.

Selectivity or specificity is defined as the ability of the sensor to respond to certain gas in the presence of the other gases. Selectivity of nanocrystalline SnO_2 thin film sensors is measured at an operating temperature of 150 °C. Figure 10 depicts the bar diagram to indicate NO_2 selective ability of the sensor. It is clear from the figure that the responses of all samples to LPG, CO_2 , H_2 , NH_3 , C_2H_5OH , CH_3OH , Cl_2 , NO and SO_2 gases are lower as compared to their response to NO_2 .

6.4. Response and recovery of the sensor with concentration of gas (ppm)

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 most sensitive thin film S3 sensor on exposure of 100 ppm of NO₂ at 150°C are represented in Figure 11.



Fig. 11. Response and recovery of the sensor (most sensitive sample= S3).

It is observed that the response increases linearly as the NO₂ concentration increases from 25 to 200 ppm and then remains nearly constant with further increase in the NO₂ concentration. The linear relationship between the response and the NO₂ concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the NO₂. 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 NO₂ and fast recovery.

DISCUSSION

7.1. Gas sensing mechanism

The gas response of any metal oxide semiconductor to a particular gas increases with the decrease in the size of nanocrystallites [26, 27] due to an increase in surface to volume ratio and therefore the reactivity.



Fig. 12. Sensing mechanism of thin film consisting of nanograins:

(a) in absense of NO_2 gas and (b) in presence of NO_2 gas.

Grain sizes and microstructures of the sensor affect the gas sensing 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 enhances largely. Nanostructured material would be expected to show much better gas sensing performance as compared with the sensor fabricated from bulk materials [26 - 29]. The resistance of the nanostructured SnO₂ thin films decreases as gas flows into the test chamber and adsorbed on the surface of the nanostructured SnO₂. However, as shown in Figure 12(a), when nanocrystalline SnO₂ thin film consisting of

nanograins in absence of NO_2 , 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 NO₂ gas environment (see Figure 12(b)), the depleted layer would shrink quickly as it obtains conduction electrons due to reaction between NO₂ adsorbed oxygen, and the resistance of the nanostructured SnO_2 would experience a large change.

CONCLUSION

Nanostructured SnO_2 thin films could be prepared by simple and inexpensive spray pyrolysis technique. Surface morphology having nanostructured grains are found to be important for obtaining enhanced response characteristics. Thickness of the films was observed to increase from 205 to 329 nm with increase in spray time of solution. Crystallite and grains size was increases with increase in film thickness. SnO_2 thin film thin film based sensor structure have been designed for the trace level (500 ppm) detection of NO₂ gas at low operating temperatures (<150 °C) and exhibit the response of S= 1165. The sensor has good selectivity to NO₂ 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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