SnO_2-Surfactant Composite Films for Superior Gas Sensitivity

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Abstract

Porous Tin Oxide (SnO_2) thin films have been prepared using Chemical Spray Pyrolysis technique in conjunction with surfactant Triton X-100. The effect of surfactant on the gas sensing properties of SnO_2 have been investigated using characterization techniques, XRD, SEM, EDAX, UV-Visible spectroscopy. SnO_2-Surfactant composite films were deposited by adding Triton X-100 in step of 1%, 2%, 3%, 4%, 5%, and 6% to the precursor solution of $SnCl_4$ in Ethanol. The results reveal the successful enhancement of gas sensitivity of SnO_2-Triton X-100 composite thin films as compared with pristine SnO_2. Films of SnO_2 with 4% Triton X-100 have exhibited maximum sensitivity for H_2S gas, whereas the films with less and more than 4% Triton X-100 has shown less sensitivity. Thus, the percentage of Triton X-100 has been optimized to achieve maximum sensitivity.

Keywords — *SnO_2 –Triton X100, Gas Sensor, Spray Pyrolysis, Composite Films,*

I. INTRODUCTION

The conductometric semiconducting metal oxide gas sensors constitute one of the most investigated groups of gas sensors. These sensors have attracted much attention in the field of gas sensing due to their low cost and flexibility in production and simplicity in their use. Numerous researchers have shown that the reversible interaction of the gas with the surface of the material is a characteristic of conductometeric semiconducting metal oxide gas sensors. The interaction can be influenced by the natural properties of base material, surface area and micro structure of sensing layers, surface additives, and temperature. Although a good amount of work is done on metal oxide gas sensors [1], sensitivity has been attracting more attention and many efforts have been made to enhance the sensitivity and selectivity of gas sensors.

On the other hand, the composite Zn-SnO_2 sensors exhibit higher sensitivity than sensors constructed using tin oxide or zinc oxide separately, when tested under identical experimental conditions [2]. Sensors based on the two components mixed together are more sensitive than the individual components alone suggesting a synergistic effect between the two components. In addition to the synergistic effect, hetrojuntion interface between two or more components also contributes to the enhancement of the composite gas sensor performance [3]. Enhancement in the sensitivity of metal oxide gas sensors have also been achieved using surface modification by noble metal particles. Noble metals are highly effective oxidation catalysts and this ability has been used to enhance the reaction on gas sensor surfaces. A wide diversity of methods, including impregnation, so-gel, sputtering and thermal evaporation have been used for introducing noble metal additives into oxide semiconductors. There have been reports for enhancement of sensitivity modified by noble metals such as Pt, Au, Pd, Ag, etc. [4,5].

In recent years there are many attempts made to stabilize and regulate the size of the nanoparticles by adding surfactants to the precursor solution. For the fast diffusion of the gases porous materials are highly beneficial. Preparation of mesoporous materials for gas sensitivity enhancement is being investigated [6]. Synthesis of mesoporous SnO_2 using an anionic surfactants as synthetic template has been reported [7]. Intrigued by the above observations and in an attempt to develop new materials for gas sensors, herein we report the synthesis of SnO_2 thin films with surfactant, Triton X-100 (TX100) and the gas sensing behavior of the deposited films has been studies for H_2S gas.

II. EXPERIMENTAL TECHNIQUES

A. Materials and Methods

All the chemicals used for the synthesis of SnO_2 thin films were of analytical grade and were used without further purification. Stannous chloride ($SnCl_4.5H_2O$) used as the precursor that was obtained from Thomas Beker, India. TX-100 [$C_{14}H_{22}O(C_2H_4O)_n$] is procured from Himedia Laboratories Pvt. Ltd. Mumbai. Our home made chemical spray pyrolysis setup is adopted for the synthesis of SnO_2 films, the details of which is reported [8]. Here the spraying system consists of spray nozzle, air compressor and mechanical arrangement for one dimensional to and fro motion. And heating unit consists of a hot plate, thermocouple, temperature indicator and a dimmerstat. Spray nozzle and hot plate with glass substrate are housed in a

metallic box and the out let of the box is fitted with an exhaust fan to remove the toxic gases produced during the decomposition of spray solution. Commercially available laboratory glass slides of dimensions 25 mm x75 mm and thickness 1mm were used as substrate

B. Synthesis of SnO2 Thin Films

$SnCl_4.5H_20$ was dissolved in ethanol, stirred well for a long time and filtered using filter paper to get a clear solution. The concentration of the precursor solution of $SnCl_4.5H_20$ in ethanol was maintained to be 0.2M. Films were deposited by adding T X-100 in step of 1% (0.2ml), 2% (0.4ml), 3% (0.6ml), 4% (0.8ml), 5%(1ml) and 6%(1.2ml) to 20ml precursor solution.. The glass slides were washed with de-ionized water, rinsed in ethanol and dried and placed in laboratory oven at temperature approximately 50 ^{0}C. The prepared 20 ml solution was sprayed on a preheated glass substrate. The temperature of the substrate was maintained at a constant value of 400 ^{0}C with ±1 ^{0}C by using dimmerstat and digital temperature controller. The nozzle to substrate distance was kept constant at 35 cm. The entire solution was sprayed in about 4-5 minutes. For the uniform deposition of the solution the substrate is kept stationary while the nozzle is made to move to and fro on a line with a programmed stepper motor using microcontroller, where the program is such that one can set the speed of nozzle motion and the number of cycles to be repeated during the deposition. Once the spray is completed the heater was turned off and the SnO_2-TX100 films were allowed to attain the room temperature. To test the workability of the sensing element H_2S gas was used. It was generated using FeS and dilute HCl in a sealed container in a controlled manner; its chemical reaction is given below

$$FeS\downarrow + 2\ HCl\downarrow \rightarrow FeCl_2\downarrow + H_2S\uparrow$$

C. Characterization Techniques

The as prepared SnO_2–TX100 films were used for further characterization. X-ray diffractometer (Ultima IV Japan) with CuK_α radiation (λ=1.5405 Å) at 40 mA and 40 kV at a scanning rate of 0.02˚ per second was used to study the crystalline state of these films. Optical properties of the films were studied using UV-VIS spectrometer (Specord- 200 plus Germany) in the wavelength region 200 – 1100 nm. The surface morphology of the films was studied using Scanning Electron Microscope (SEM) (ZIESS Optical systems Germany with EHT-8KVm magnification 100KX WD 5nm) . And the elemental composition was studied using EDAX spectrum (scanned between 0-15keV) The current-voltage (I-V) characteristics of the films were studied using programmable Keithley source meter (Keithley 2636A).

D. Gas Sensing Measurements

The gas sensing behaviour of the films was studied in terms of variation in the resistance upon exposure to a gas. Our home made miniaturised setup for gas sensor [9] and bulk setup [10] for gas sensing have been used to carry out gas sensor measurements of the as deposited SnO_2-TX100 thin films. Here digital multimeter is used to measure resistance and the temperature of the micro heater by digital thermometer using alumel- chromel thermocouple [11]. H_2S is used as probing gas. In our measurements, first the temperature of the oven is set to a particular value by applying 12.5 V to the heater to produce stable temperature of 110˚C and the resistance of the sensor in air is recorded. A known amount of H_2S gas is injected into the bottle and the cap is locked tightly the fall in resistance of the sensor with respect to time is recorded. Once the minimum constant resistance value is reached the bottle is opened and the sensor is exposed to open air. Now the increase in the resistance with respect to time is recorded. Similar procedure was repeated for several times for all samples (films) under the identical conditions.

III.RESULT AND DISCUSSION

The deposited SnO_2-TX100 films using chemical spray pyrolysis were uniform and almost transparent on glass slide. The films were used for X-ray analysis, the recorded powder diffraction pattern is shown in figure (1). The peaks are observed at 2θ =26.61˚, 33.89˚, 37.95˚, 51.78˚ and 54.75˚ corresponds to the Miller indices (110), (101), (200), (211) and (220) respectively. This reveals that the observed peaks are comparable to the characteristic peaks of tetragonal phase of SnO_2 (JCPDS Card No. 41-1445). From the pattern, the average crystallite size is estimated using Debye Scherer formula $d = k\lambda / \beta \cos\theta$ (where k is shape factor which is about 0.9, λ is the X ray wave length, β is the full width half maxima (fwhm) and θ is the Bragg angle). The particle size is estimated from fwhm of broad peak is found to be less than 5 nm. In the present study the XRD peak is broad which indicate the small size of the particles. The smaller size particulate films have the advantage of having a large surface-to-volume ratio. This gives large density of surface dangling bonds on the surface of film, which is more suited for gas sensing applications that helps in obtaining the improved gas sensitivity of a material.

XRD pattern for the TX 100 with 1%, 2%, 3%. 4%, 5%, 6% and 7% are also shown in Fig 1. The particle size for films with different percentage of TX is estimated and is given in the following Table-1.

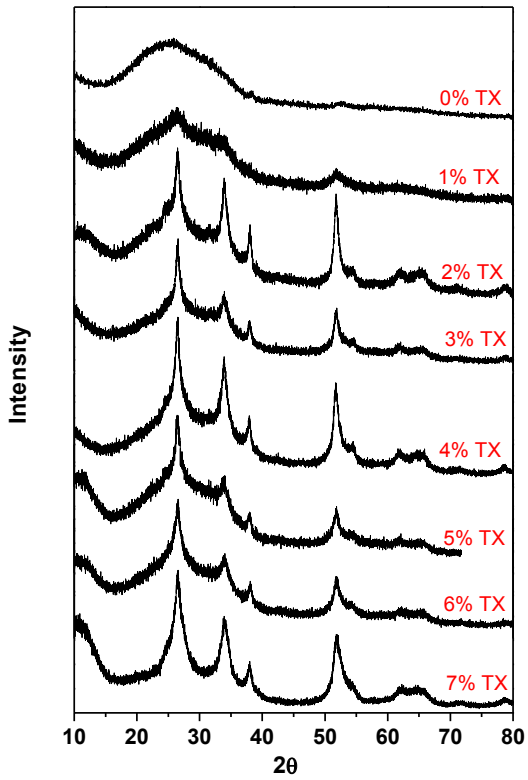

Figure 1: X-Ray Diffraction Pattern of Spray Deposited $SnO_2$with TritonX100

Table 1: Particle Size Estimated for Different Compositions Of TX100 With Sno_2 Using X-Ray Diffraction Patterns.

Sl. No	Sample	Particle size
1	SnO2 with 0% TX100	5.00 nm
2	SnO2 with 2% TX100	4.82 nm
3	SnO2 with 3% TX100	4.59 nm
4	SnO2 with 4% TX100	3.91 nm
5	SnO2 with 5% TX100	4.70 nm
6	SnO2 with 6% TX100	4.80 nm

Further, the patterns showed sharp peaks as compared to that for pristine SnO_2. It is indicative of increase particle size and increase in crystallalinty of the films. The sharpness and increase in number of peaks may also be due to agglomeration and formation of grain boundaries and polycrystalline material. However, the superior crystallinity is an essential requirement to achieve superior performance of gas sensors due to fact that the electron transport undergoes less scattering as compared to less crystalline materials.

These films were used to study the optical absorbance in the wavelength region from 200-1100 nm, a typical curves for various films are shown in Fig 2. The absorption curve shows its optical gap transition close to 350 nm which corresponds to the optical band gap (E_g) of about 3.5 eV. It is observed that the films have highest transmittance that is close to 80%. T Serin et al., have carried out optical absorption studies and reported optical band gap of SnO_2 films in the range 3.94-3.96 eV [12]. In the present work, absorption curve of intrinsic SnO_2 shows its optical gap transition close to 350 nm corresponding to the band gap (E_g) equal to 3.5 eV , similar results were reported by U Nerle et al. and it has almost flat base prior to absorption edge [13]. The absorbance curve for the as deposited SnO_2 with TX-100 films is shown in fig (2). It is observed that the absorbance peak shift towards the higher wavelength region indicating the decrease in optical band gap. The absorbance peak is observed nearer to 670 nm in addition to main absorption peak. As the percentage of TX 100 is increased the peaks become sharper. Maximum sharpness in observed for 4% doped. TX100 in SnO_2. Above this concentration the peak sharpness decreased.

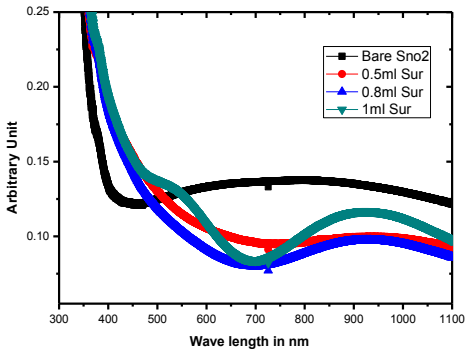

Figure 2: Optical Absorption of Sno_2 Doped with TX 100 Thin Film Recorded Between 300 Nm and 1100 Nm.

The surface morphology of SnO_2 doped with TX100 thin films were studied using scanning electron microscope (SEM). The SEM images of SnO_2 with TX100 deposited on glass substrate by spray pyrolysis technique are shown (Fig. 4a–4f). From the figures, it is clear that the SEM image of bare SnO_2 thin film exhibited a uniform and granular morphology, whereas Fig. 4b with SnO_2-TX100 (1%) exhibited formation of grains. Fig. 4c with SnO_2-TX100 (2%) showed decrease in particle size and agglomeration of particles and similar morphology is observed in Fig.4d with SnO_2-TX100 (3%). Grain boundaries are prominent and the films with 4% TX100 (Fig.4e) has exhibited maximum sensitivity to H_2S. The sensitivity decreases for higher percentage of TX.

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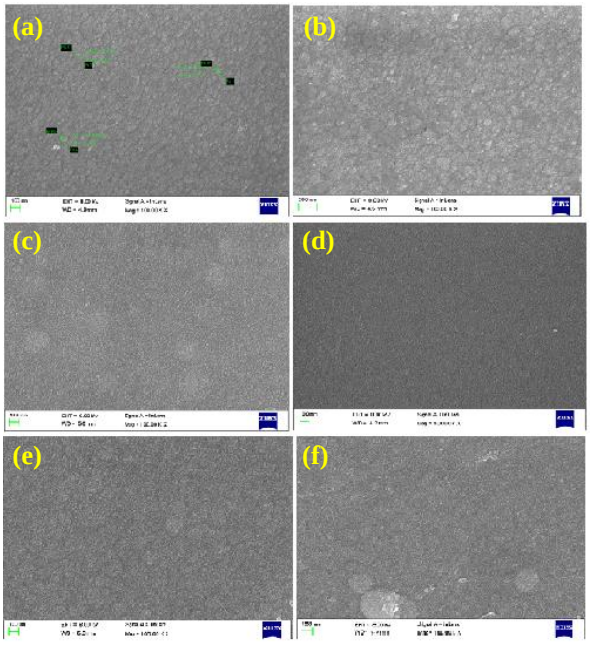

Figure 4: SEM Image of SnO_2-TX100 Thin Films (a) Pristine SnO_2 (b) SnO_2 with 1% TX100 (c) SnO_2 with 2% TX100 (d) SnO_2 with 3% TX100 Doped (e) SnO_2 with 4% (f) SnO_2 with 5% TX100

It is observed from the elemental analysis that as the percentage of surfactant, TX100 increases there are formation of Tin rich regions. The EDAX spectrum of the thin films of bare SnO_2 is shown in Fig. 5a and that of SnO_2-TX100 (4%) is shown in Fig. 5b. It is observed that as the percentage of TX is increased the wt% of Tin has increased. It has been concluded that addition of surfactant has led to the formation of tin rich regions in the films.

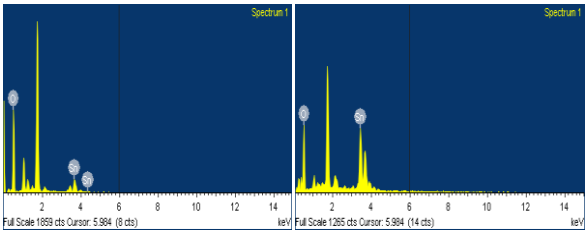

Figure 5: (a) EDAX Spectrum of Pristine SnO_2 (b) EDAX Spectrum of SnO_2 with 4% TX100

A. Gas Sensing Characteristics

Sensitivity 'S' is defined as the ratio of effective change in resistance for the test gas to the original value of the resistance in air. It is given by $S=\frac{(Ro-Rg)}{Ro}$ x100%. Where R_g is the sensor resistance in the presence of the test gas and R_o is the sensor resistance in dry air, measured at that temperature [14] Fig. (6a–6e) showed the sensing characteristics of SnO_2 with different percentage of TX100 thin film measured at 110˚ C upon exposure to a fixed amount of H_2S gas. Upon exposure to the H_2S gas the films resistance is seen to decrease. From the sensing characteristics it is found that the response time is less, where as the recovery time is slightly more. The reproducibility of these curves is very good. Comparison of gas sensing characteristics of SnO_2 based gas sensors by others[15] (nanofibres, nanocrystals, thin films, submicrotubes, etc) to H_2S for different concentration is made and established that SnO_2 thin films show maximum response to H_2S at an operating temperature of 100˚C for 80 ppm. In present study we have recorded the gas sensor response using our miniaturized setup to sense H_2S gas at 110˚C.

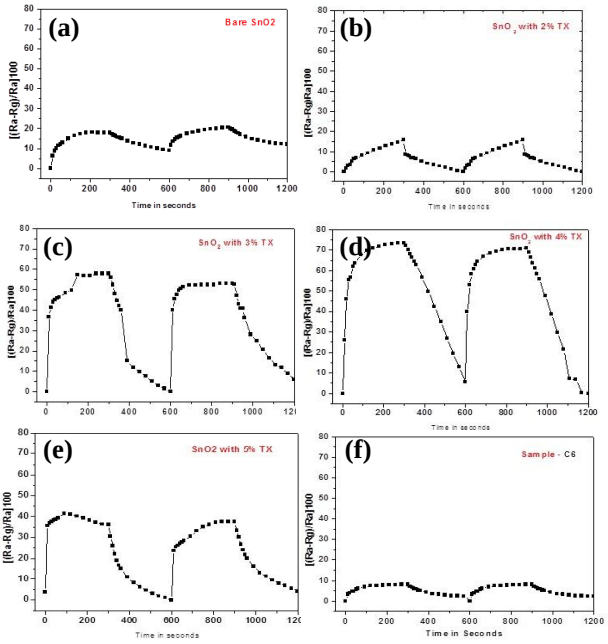

Figure 6 : Gas response of SnO_2 - TX film for H_2S (a) Princeton SnO_2 (b)SnO2 with 2% TX (c) SnO_2 with 3% TX (d)SnO2 with 4% TX (e) SnO_2 with 5% TX (f) SnO_2 with 6% TX

The gas sensing response of thin films of SnO_2 doped with TX100 in different percentage for hydrogen sulphide gas have been investigated. The gas response characteristics are shown in Fig. 6. Thin films of bare SnO_2 and with 2% TX100 have shown almost the same sensitivity. The sensitivity of these films for H_2S is about 20% shown in Fig. (6a & 6b). The gas sensitivity for the deposited SnO_2 thin films doped 3% TX100 (Fig. 6c) shown increase in the sensitivity to 60%. The SnO_2-TX100 (4%) has exhibited a tremendous increase in the sensitivity of more than 70% as shown in Fig. 6d. As the percentage of TX 100 was increased to 5% and above, a decrease in the gas sensitivity is observed (Fig. 6e). The films of SnO_2-TX100 (4%) exhibited the maximum sensitivity for H_2S.

IV. CONCLUSIONS

Porous Tin Oxide (SnO_2) thin films have been prepared using Chemical Spray Pyrolysis

technique in conjunction with surfactant TX-100. Films were deposited by adding 1% TX -100 to $SnCl_4$ and then amount of TX-100 was increased to 2%, 3%, 4%, 5% and 6%. The deposited films have been characterised by various techniques such as XRD, SEM, and EDAX to understand their physical, chemical electrical and gas sensing properties. It was observed that the grain boundaries are formed as the percentage of surfactant is increased and became prominent for the films with 4% TX. The gas sensing properties of these films are studied for H_2S gas by using our home-built cost effective and miniaturized setups at 110^0C. SnO_2-TX100 has shown maximum sensitivity of more than 70%. Again the sensitivity is found to decrease to 40% for the films with 5% TX 100. For films with 6% TX100 the sensitivity reduced to 10%. EDAX spectrum reveals the percentage of Tin in the films has increased and found be highest for the film with 4% TX as compared to the bare SnO_2 films. The doping of TX is making the film Tin rich. These factors are likely to contribute for the enhanced sensitivity.

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