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Synthesis of the SnO_2 Thin Film by Spray Pyrolysis for H_2S Gas Sensing

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Abstract

In this work, SnO_2 thin films were deposited onto microspores glass substrate at 250°C by spray pyrolysis technique. The films were studied after annealing in air at temperatures 200°C, 250°C and 300°C for 15 min. These films were tested in H_2S gas at different operating temperatures ranging from 50-300°C. The film showed maximum sensitivity to H_2S gas. The effect of annealing temperature on the optical and gas sensing properties of the films were studied and discussed. It was found that the annealing temperature significantly affects the sensitivity of the SnO_2 to the H_2S. The sensitivity was found to be maximum for the film annealed at temperature 250°C. The quick response and fast recovery are the main features of this film.

Keywords: Annealing, spray pyrolysis technique, sensing, sensitivity.

Introduction

Since the last decade there has been a great deal of interest in the preparation of inexpensive thin films of SnO_2. This is because tin dioxide based thin films with large band gap (Eg>3eV) n-type semiconductors are attractive from the scientific and technological point of view [1].It has been widely used for various catalytic applications such as a transparent conductive electrode for solar cells [2], a gas sensing material for gas sensors devices [3], transparent conducting electrodes [4], photochemical and photoconductive devices in liquid crystal display [5], gas discharge display, lithium-ion batteries, etc. Their properties depend on their microstructure, the quantity of doped impurities and the size effects of their particles. A variety of techniques have been used to deposit tin oxide (SnO_2) thin films. These include spray pyrolysis [6], ultrasonic spray pyrolysis [7], chemical vapour deposition [8], activated reactive evaporation [9], ion-beam assisted deposition, sputtering [10], and sol-gel [11] methods. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive, as well as suitable for large area application. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coating make them useful for industrial as well as solar cell applications. In addition, spray pyrolysis opens up the possibility to control the film morphology

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and particle size in the nm range. Spray pyrolysis is a versatile technique for deposition of metal oxides. Till now, many researchers have prepared SnO_2 using chemical spray pyrolysis. For example, they have grown tin dioxide films by spray pyrolysis on microspores glass substrate. However, metal oxides which have been used for nearly four decades for gas sensing ability was first discovered by Seiyama who reported that ZnO thin films exhibit changes in their electrical conductivity with small amount of reducing gases and the same year by Taguchi who reported that partially sintered SnO_2 pellets respond similarly[12, 13]. These were the beginning of a rapid gas sensor development phase. Also some recent studies on the sensing properties of pure nanocrystalline SnO_2 thin films toward H_2S and H_2 seems to contradict the general trend that higher sensitivity is to be expected for smaller crystals, and it was, therefore, concluded that small size of crystals was an essential but not sufficient condition for the achievement of maximum gas sensitivity and fast response [14, 15].

Therefore, our objective in this work was to prepare SnO_2 thin films by the spray pyrolysis method and to investigate the influence of various exposure times of H_2S gas and corresponding flow of current in the sample. Also this paper demonstrates the H_2S sensing properties of SnO_2 thin films. The results of these studies are presented here.

Experimental

Materials and Method

Materials used were $SnCl_4.5H_2O$, HCl, H_2O_2, and H_2S gas. Double distilled (DD) water was used in all the experiments.

SnO_2 Thin Film Preparation

Cleaning of Glass Slide: For thin film deposition we used microspores glass slide as a substrate. Cleaning solution is $3HCl{:}1H_2O_2$and the glass slides were dipped into the cleaning solution for overnight. Then wash the glass by DD water and put it under sunlight for an hour.

Weighing of Glass: After cleaning glass slide measure the weight of glass slide in which we want to deposit the film.

Details of Spray Pyrolysis System

The schematic experimental set up of the spray pyrolysis system built in our lab is shown in figure 1. It consists of substrate heater, variac, compressor, pressure, regulator, motor with controller and power supply. Due to air pressure s, a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts. The spray funnel is fixed at an appropriate distance from the substrate. The precursor solution was sprayed on to the substrate in air as small drops and around a high temperature zone where thermal decomposition and possible reaction between solutions occur, through compressed air. The flow rate was controlled through air compressor regulator.

Deposition of SnO_2 Thin Film

First of all $SnCl_2$ was taken as starting material; the clean glass slide was heated for an hour to increase the temperature of the glass slide to 300°C. Now put the material in the canonical flask in which there are two pipes connecter. The first pipe connector is connected with the pump and the other, connected with nozzle (By) for spray the vapour on the slide. After heating the glass slide upto 250 °C put the canonical flask on another heater. The spray is done for 10 min. only. After ten more minutes when the temperature of the slide is reduced, the slide was removed from the heater. We can see that there is deposition of film on the slide. Check its conductivity by using the avometer. After making the film again take the weight of glass slide.

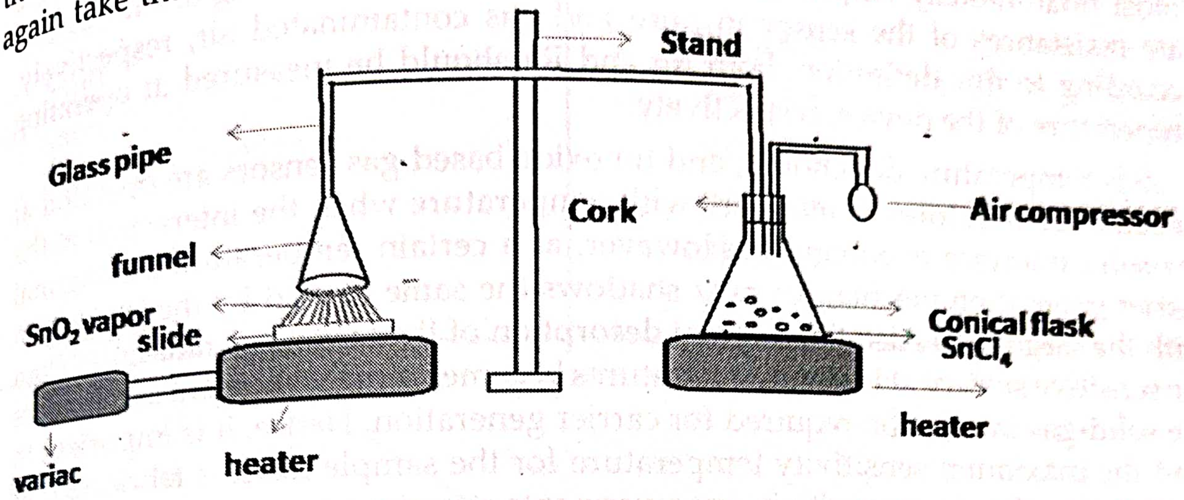

Fig. 1: Apparatus Arrangement of Spray Pyrolysis Method

Result and Discussion

Thickness Measurement: For determining the thickness of different films first we have to measure the mass of glass substrate and deposited film substrate respectively. Now measure the difference between the mass of deposited film and non-deposited glass substrate. We know that density of the given material any using the formula.

$$Density\,\rho = \frac{mass\ of\ deposite\ thinfilm - mass\ of\ glass\ slide}{volume}$$

$$\rho = \frac{Mf - Mb}{A.t} \qquad \text{............. (1)}$$

When film is deposited by using spray pyrolysis method nanoparticle are deposited by layer and layer on the glass substrate. The thickness of layer can be calculated by eq. (1). When we deposited thin layer on the glass substrate of SnO_2 the conductivity vary with temperature. The thickness of prepared SnO_2 thin film is 82.4nm.

Annealing: Annealing, in metallurgy and materials science, is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable. It involves heating a material to above its recrystallization temperature, maintaining a suitable temperature, and then cooling. In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to the change in ductility and hardness.

Sensitivity v/s Temperature: To measure the efficiency of gas sensor. The graph has been plotted between sensitivity and temperature. Figure 2 shows that with the increase of temperature, sensitivity also increases linearly and reaches its saturation limit. With further increase of temperature the sensitivity decreases. It shows that sensitivity of the sensor is variable and is good only at a maximum temperature.

However most recently, the authors of the related technical papers have almost unanimously employed S = Ra/Rg, in which Ra and Rg are the steady state resistances of the sensor in pure and gas contaminated air, respectively. According to this definition, both Rg and Ra should be measured at operating temperature of the device, respectively.

S is temperature dependent, and tin oxide based gas sensors are operated at elevated temperatures. S increases with temperature when the interaction at the gas-solid interface is enhanced. However, at a certain temperature the thermal carrier generation mechanism over shadows the same caused by the interaction with the target gas. Also the thermal desorption of the target gas molecules from the sensitive surface at higher temperatures becomes more significant and hinders the solid-gas interaction required for carrier generation. Hence, it is important to find the maximum sensitivity temperature for the sample devices fabricated. In Fig.2 the results of our sensitivity measurements at various operating temperatures is presented.

Table 1: Sensitivity Measurements at Various Operating Temperatures

Voltage	Temp (°C)	Ra(resistances of the sensor in air) (ohm)	Rg(resistances of the sensor in gas) (ohm)	Sensitivity S= Ra/Rg
10V	100	1.18	7.5	0.157
10V	150	1.50	9.5	0.157
10V	200	1.66	10.5	0.158
10V	250	2.94	9.5	0.309
10V	300	1.28	8.5	0.151

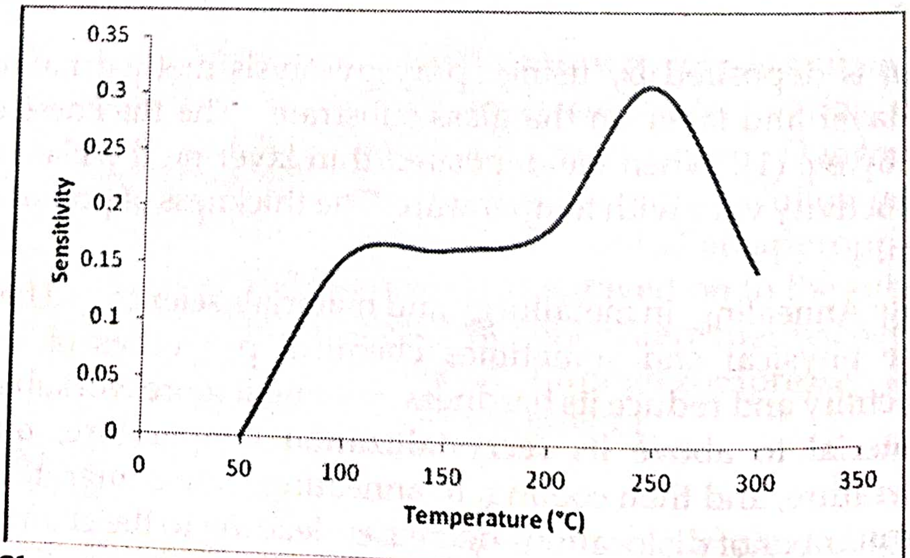

Fig. 2: Graph Showing Sensitivity Measurement at Various Operating Temperatures

Table 2: Various Exposure Time of H_2S Gas and Corresponding Flow of Current in the Sample

Time	Current
1min	10μAm
2min	9.9 μAm
3min	9.7 μAm
4min	9.5 μAm
5min	9.2 μAm
6min	9.1 μAm
7min	9.0 μAm
8min	8.9 μAm
9min	8.9 μAm
10min	8.9 μAm

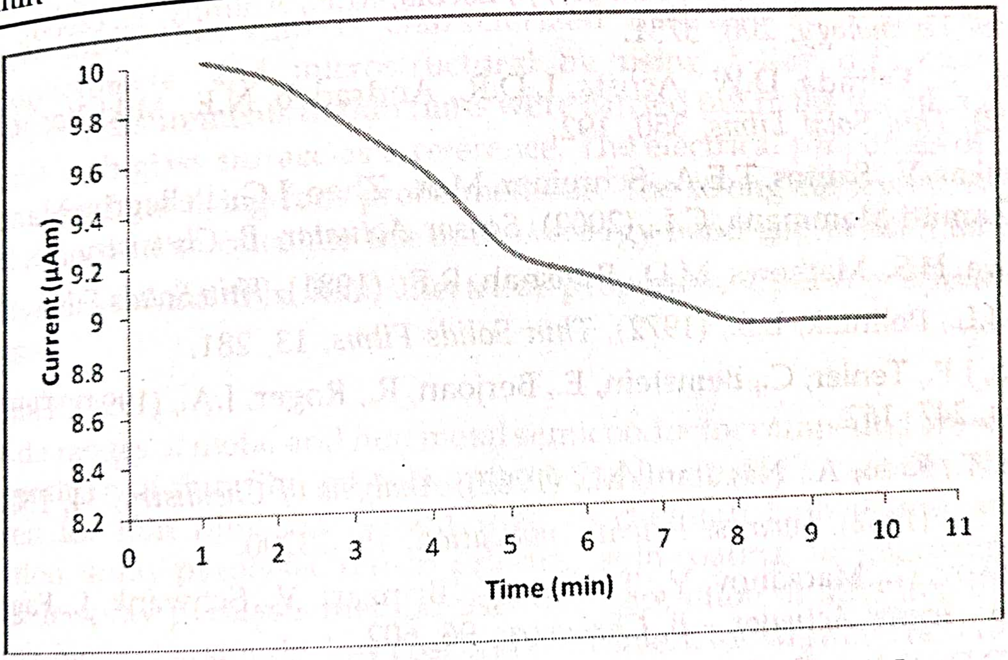

Fig. 3: Graph Showing the Exponential Decay of Current with Increase in Exposure Time of H_2S Gas

Fig.2 shows that the exposure time of H_2S gas and variation of current. To measure the sensitivity of the sensor for H_2S gas the graph has been plotted between exposure time and current which shows that in the early minutes of exposure of gas the current were found to be high and as the exposure time of gas increases the value of current start decreasing exponentially and reaches to its saturation value.

This happens because in the early minute of exposure the gas molecules occupied the free space of the specimen slide and current is found to be maximum. With the further exposure of gas more and more molecule of gas occupies the free space and when all the free space of specimen slide is being occupied, the current value decreases and reaches to its saturation value.

Conclusion

We have prepared tin oxide thin films by a simple and convenient method. We have successfully prepared SnO_2 films by spray-pyrolysis method using $SnCl_2 \cdot 5H_2O$.The sensor exhibited excellent sensitivity and rapid response to the presence of H_2S gas at low temperature. The maximum sensitivity was obtained at an operating temperature of 250°C for the exposure of H_2S. The results of the H_2S sensing studies reveal that the SnO_2 film prepared by spray pyrolysis method is a suitable material for the fabrication of the H_2S sensor.

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