

Effect of Substrate Temperature on Porosity and Gas Sensing Properties of B and PEG-6000 Co-Doped SnO₂ Thin Films

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Abstract

Porous SnO₂-B:PEG-6000 thin films have been prepared to analyze on Structural, electrical, optical and gas sensing properties. SnO₂-B:PEG-6000 thin films were synthesized by varying substrate temperature using chemical spray pyrolysis technique. The films were deposited at four different temperatures ranging 300⁰ C to 425⁰C. The precursor solution was prepared by dissolving stannous Chloride (SnCl₄.5H₂O) in Ethanol and adding equally 4% of Boric acid (H₃BO₃) and Polyethylene Glycol-6000(H(OH₂CH₂)_nOH) (1:1). The deposited films were characterized by using XRD, SEM,UV-Vis-Spectrometry and current-voltage measurement. H₂S gas was used to study the gas sensing behavior.

Keywords: - Spray Pyrolysis, Thin Film, XRD, H₂S, PEG-6000, and Gas Sensor.

I INTRODUCTION

In the recent year, semiconducting metal oxide thin films have received intensive attention due to their very important role in optoelectronics devices such solar cells, heat reflectors and sensors. Stannic chloride is a semiconductor which has been used in making heterojunction thin films, it is preferred because it is a wide band gap semiconductor having good thermal stability & can be used as light dependent resistors sensitive to visible & near infrared light. It is found that substrate temperature influences the structural, optical, electrical properties of thin film [1-4].

Sensitivity has been attracting more attention and many efforts have been made to enhance the sensitivity and selectivity of gas sensors.

We prepared thin films by Chemical spray pyrolysis technique (CSP), because of its simplicity and inexpensiveness has found to be better chemical method for the preparation of thin films with larger area. In the chemical spray pyrolysis technique; various parameters like air pressure, rate of deposition, substrate temperature, distance between nozzle to substrate, cooling rate after deposition affect the physical, electrical and optical properties of the thin films [5-6].

The conduct metric 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 conductometric 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 [7-9], sensitivity has been attracting more attention and many efforts have been made to enhance the sensitivity and selectivity of gas sensors.

In this paper $\text{SnO}_2\text{-B:PEG-6000}$ material are used for fabricating thin films by Spray Pyrolysis method, the purpose of this work was to investigate the effect on structural, optical, electrical and sensing properties of $\text{SnO}_2\text{-B:PEG-6000}$ thin film for various Substrate temperatures from 300-425°C.

II. MATERIALS AND METHODS

2.1. Fabrication of $\text{SnO}_2\text{-B:PEG-6000}$ Thin Film:

The first precursor solution was prepared by the dissolving 0.15M of Stannous chloride $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 25ml of ethanol and adding 4% of Boric acid (H_3BO_3) and Polyethylene Glycol-6000($\text{H}(\text{OH}_2\text{CH}_2)_n\text{OH}$) (1:1). The nozzle was kept at a distance of 35cm from the substrate during deposition and the solution flow rate was held constant at 5ml/min. When aerosol droplets came close to the substrates, a pyrolysis process occurred and highly adherent $\text{SnO}_2\text{-B:PEG-6000}$ films were produced for different substrate temperatures ranges 300°C to 425°C. Once the spray is completed the heater was turned off and the films were allowed to attain the room temperature [10-12]. The thin films are deposited on surgical microscopic glass plates.

2.2. Characterization of $\text{SnO}_2\text{-B:PEG}$ Thin Films:

The prepared $\text{SnO}_2\text{-B:PEG-6000}$ films were used for further characterization. X-ray diffractometer (Ultima IV Japan) with $\text{CuK}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) 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. Morphological properties of the films were studied using scanning electron

microscopic (SEM) [13]. Optical properties of the films were studied using UV-VIS spectrometer (Specord- 200 plus Germany) in the wavelength region 200 – 1100 nm. The current-voltage (I-V) characteristics of the films were studied using programmable Keithley source meter (Keithley 2636A)[14].

2.3. Gas Sensing Measurements:

Gas Sensing measurements were carried out using a Gas sensor unit [15]. In which a digital multimeter is used to measure resistance and the temperature of the micro heater by digital thermometer using alumel- chromel thermocouple. 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 $150^\circ C$ and the resistance of the sensor in air is recorded. A known amount of H_2S gas is injected into the chamber, 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 condition [16-18].

III. RESULTS AND DISCUSSION

SnO_2 -B:PEG-6000 thin films were deposited by the Spray Pyrolysis technique. Deposited films were transparent and electrically conducting.

3.1 Structure Analysis:

The structure of SnO_2 -B:PEG-6000 thin films at different substrate temperatures was investigated from XRD Pattern and is presented in Figure (1).

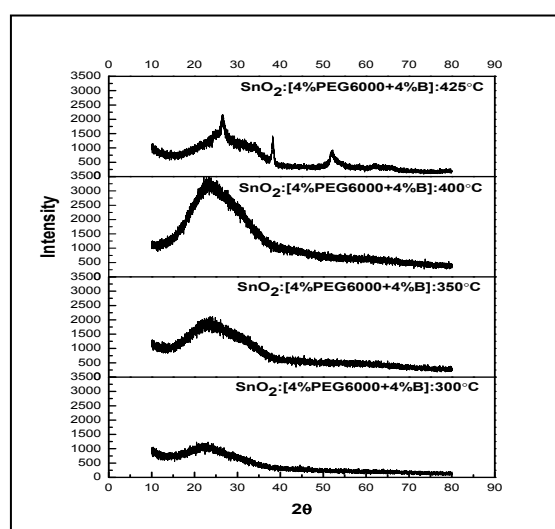


Figure 1: X-ray Diffraction Pattern of Spray Deposited SnO_2 -B:PEG-6000 Thin Films with Variation of Substrate Temperature.

From the XRD pattern, the average crystallite size is estimated using Debye Scherer formula. The XRD pattern for the temperature 425°C is with less noise and the major peak is more intense than those obtained at lower temperatures. This confirms the improvement of crystalline nature at higher Ts. As temperature of the substrate is increased the crystallite density increases and also the peaks become thinner and refined as confirmed by the reduction in Crystallite size which will reduce grain boundary scattering of charge carriers.

The increase in dislocation density with increase in substrate temperature is due to the rise in vacancy concentration which promotes electron transfer. The lattice constants show a decrease in dimension as temperature increases which agrees with the reduction in crystal size [19-20]. The practical size for SnO₂-B:PEG-6000 thin film with different temperature is estimated and is given in table -1.

Table 1: Particle Size Estimated for SnO₂-B:PEG-6000 Films with Different Substrate Temperature using X-ray diffraction

Sl.NO	Samples	Particle size
01	SnO ₂ :[4%PEG 6000+4% B]with300°C	6.20 nm
02	SnO ₂ :[4%PEG 6000 +4% B]with 350°C	9.05 nm
03	SnO ₂ : [4%PEG6000+4%B]with 400°C	6.09 nm
04	SnO ₂ : [4%PEG6000+4%B]with 425°C	5.81 nm

3.2 Morphological Analysis:

The surface morphology of SnO₂-B:PEG-6000 thin films at different substrate temperatures was investigated from scanning electron microscopic (SEM) images and is presented in Figure (2).

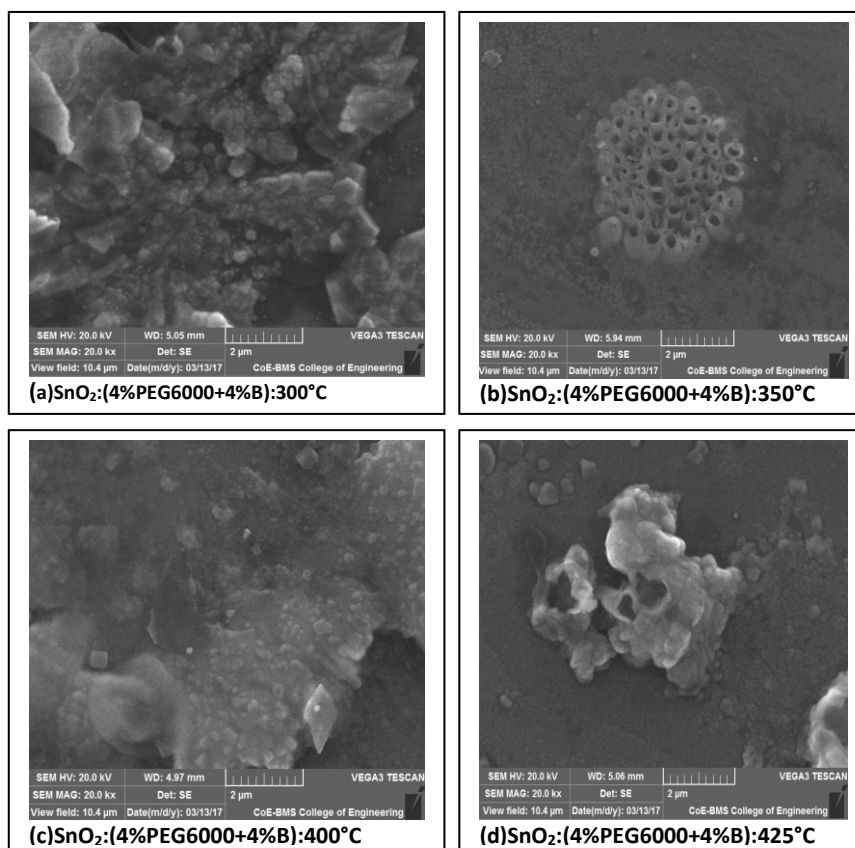


Figure2: SEM Image of $\text{SnO}_2\text{-B:PEG-6000}$ with Different Substrate Temperature.

Grain shaped small grains with smooth surface and dense packing are seen at $T_s = 425^\circ\text{C}$ [21]. No distinct shape is apparent at other T_s though the film is densely packed with grains. At 300°C large shaped grain are seen, due to the incomplete dissociation of the precursor solution. At 350°C substrate temperature thin film grain boundaries are prominent and porosity has exhibited maximum sensitivity to H_2S . The sensitivity decreases for higher substrate temperature.

3.3 Optical properties

Absorption curve of $\text{SnO}_2\text{-B:PEG-6000}$ film with different Substrate temperature, observed that as substrate temperature increases the absorbance peak shift towards the higher wavelength region indicating the decrease in optical band gap[22]. The band gap of these films estimated to be in the range of 3.1-3.4 eV. The absorbance curve of the $\text{SnO}_2\text{-B:PEG-6000}$ thin films with different substrate temperature Show in Figure (3).

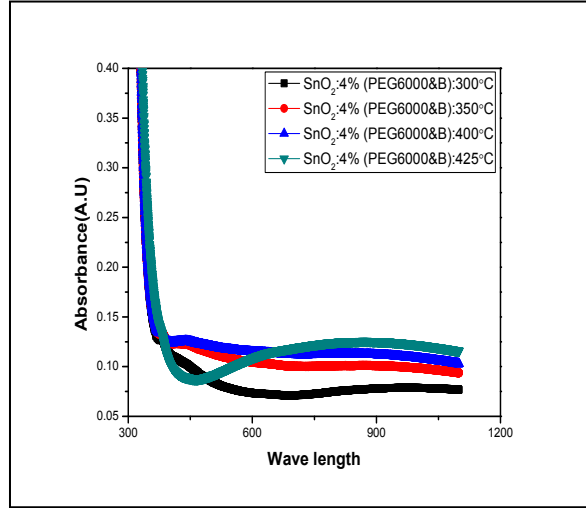


Figure3: Optical Absorption of SnO₂-B:PEG-6000 Thin Films with Different Substrate Temperature.

At 350°C substrate temperature thin film energy gap is 3.5 eV has exhibited maximum sensitivity to H₂S. The sensitivity decreases for higher substrate temperature. The energy gap for SnO₂-B:PEG-6000 thin film with different temperature is estimated and is given in table -2.

Table 2: Energy Gap Estimated for SnO₂-B:PEG-6000 Films with Different Substrate Temperature.

Sl.NO	Sample	Energy Gap
01	SnO ₂ : [4%PEG6000+4%B]with300°C	3.4 eV
02	SnO ₂ : [4%PEG6000+4%B]with 350°C	3.5 eV
03	SnO ₂ : [4%PEG6000 +4%B]with 400°C	3.3 eV
04	SnO ₂ : [4%PEG6000 +4%B]with 425°C	3.1 eV

3.4 Electrical properties:

Room temperature electrical resistivity measurements were made by Keithley source meter. The I-V characteristics curve of the SnO₂-B:PEG-6000 thin films with different substrate temperature Show in Figure (4).

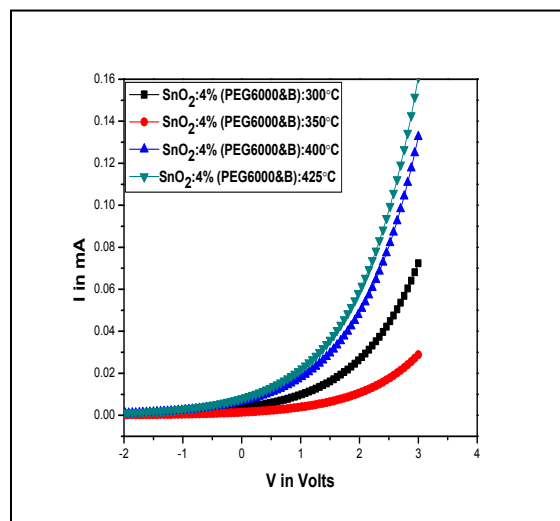


Figure 4: Current-Voltage (I-V) Characteristic Curves of SnO₂-B:PEG-6000 Thin Films with Different Substrate.

The electrical resistivity of the film is found to decrease with increase in substrate temperature. This may be due to the improvement in crystallinity of the film which in turn improves the mobility of the charge carriers. Inter granular effects play a major role in the transport of charge carriers in polycrystalline thin films. With increase in substrate temperature the crystal size is observed to decrease indicating the Grain shaped growth of the crystal and the number of crystallites/unit volume is also found to increase which reduces the grain boundary potential[23]. At 350°C substrate temperature thin film resistivity is 23.5 K Ω has exhibited maximum sensitivity to H₂S. The sensitivity decreases for higher substrate temperature, The resistivity for SnO₂-B:PEG-6000 thin films with different temperature is estimated and is given in table -3.

Table 3: Resistivity Estimated for SnO₂-B:PEG-6000 Films with Different Substrate Temperature.

Sl.NO	Sample	Rasistance
01	SnO ₂ : [4%PEG6000+4%B]with 300°C	19.2 K Ω
02	SnO ₂ : [4%PEG6000+4%B]with 350°C	23.5 K Ω
03	SnO ₂ : [4%PEG6000+4%B]with 400°C	11.8 K Ω
04	SnO ₂ : [4%PEG6000+4%B]with 425°C	6.5 K Ω

3.5 Gas Sensing Characteristics:

In present study we have recorded the gas sensor response using Laboratory gas sensor setup to sense H_2S gas at $150^\circ C$, as the substrate temperature increases sensitivity thin film decreases [24]. At $350^\circ C$ substrate temperature thin film shows exhibited maximum sensitivity to H_2S . The gas response characteristics are shown in Figure (5).

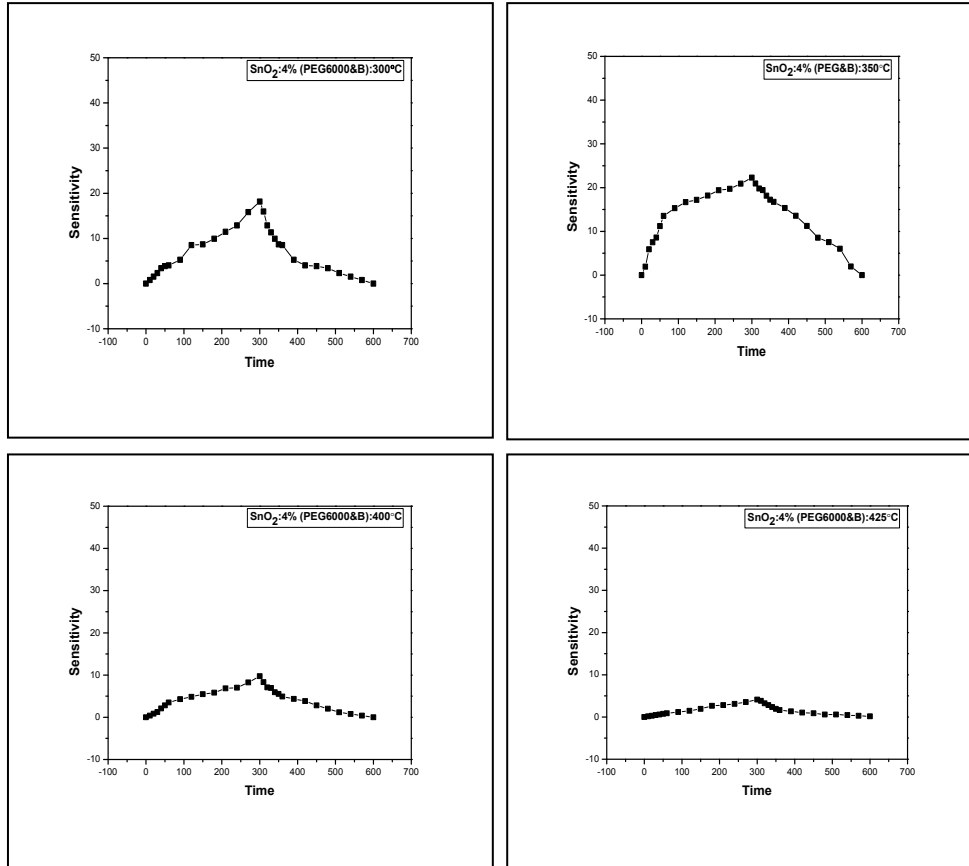


Figure 5: Sensitivity of SnO_2 -B:PEG-6000 Thin Films for H_2S (a) SnO_2 -B:PEG6000 with $300^\circ C$ (b) SnO_2 -B:PEG6000 with $350^\circ C$ (c) SnO_2 -B:PEG6000 with $400^\circ C$ (d) SnO_2 -B:PEG6000 with $425^\circ C$.

The sensitivity for SnO_2 -B:PEG-6000 thin film with different temperature is estimated and is given in table -4.

Table 4: Sensitivity is Estimated for SnO₂-B:PEG-6000 Films with Different Substrate Temperature.

Sl.NO	Sample	Sensitivity
01	SnO ₂ :(4%PEG6000+4%B)with 300°C	18.13 %
02	SnO ₂ :(4%PEG6000+4%B)with 350°C	22.11 %
03	SnO ₂ :(4%PEG6000+4%B)with 400°C	9.72 %
04	SnO ₂ :(4%PEG6000+4%B)with 425°C	4.45%

IV. CONCLUSION

In the Paper as substrate temperature while deposition of SnO₂-B:PEG-6000 thin film the XRD peaks become sharper indicating the decrees in particles size and improved crystalline. In morphological analysis the particle size decrees. In UV-VIS Spectrum analysis the absorption edge shifted towards higher wave length indicting the decrease in energy gap. From I-V characteristics it is found that resistance decreases with substrate temperature and the gas sensitivity decreases with substrate temperature. For substrate temperature 350°C were observed that fine porous, high energy gap, more resistance and thin films are exhibited maximum sensitivity to H₂S.

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BIOGRAPHICAL SKETCH:

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