International Journal of Pure and Applied Physics.
ISSN 0973-1776 Volume 13, Number 2 (2017), pp. 219-229
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Effect of Energy Band Gap and Substrate Temperature on Gas Sensing Properties of F and PEG-6000 Co-Doped SnO_2 Thin Films

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Abstract

Metal oxide composite SnO_2-F:PEG-6000 thin films have been prepared to analyze on Structural, electrical, optical and gas sensing properties. SnO_2-F:PEG-6000 thin films were synthesized by varying substrate temperature using chemical spray pyrolysis technique. The films were deposited at four different temperatures ranging 300^0 C to 425^0C. The precursor solution was prepared by dissolving stannous Chloride ($SnCl4.5H_2O$) in Ethanol and adding equally 4% of Ammonium Florid (NH_2F) and Polyethylene Glycol-6000($H(OH_2CH_2)_nOH$) (1:1) in Precursor solution. The deposited films were characterized by using XRD, SEM,UV-Vis-Spectrometry and current-voltage measurement. H_2S gas was used to study the gas sensing behavior.

Keywords*:* - Spray Pyrolysis, Thin Film*, XRD, H_2*S, 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 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 [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 Spray Pyrolysis method was used for fabricating SnO_2-F:PEG-6000 thin films , the purpose of this work was to investigate the effect of energy band gap of and substrate temperature ranging from 300^0C to 425^0C on sensing properties of SnO_2-F:PEG-6000 thin film.

II. MATERIALS AND METHODS

2.1. Fabrication of SnO_2-F:PEG-6000 Thin Film:

All the chemicals used for the synthesis of SnO_2-F:PEG-6000 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. Ethanol (C_2H_5OH) was used as the solvent for all the synthesis is obtained from sd-fine chemicals, India. Ammonium Florien (NH_4F) was used as dopant , it is purchased from Thomas Baker, India. Polyethylene Glycol-6000 ($H(OH_2CH_2)nOH$) used as surfactant that was purchased from Fisher Scientific, India. Commercially available laboratory glass slides of dimensions 25 mm x75 mm and thickness 1mm were used as substrate our home made chemical spray pyrolysis setup is adopted for the synthesis of SnO_2 films.

The first precursor solution was prepared by the dissolving 0.15M of Stannous chloride($SnCl_4.5H_2O$) in 25ml of ethanol and adding 4% of Boric acid (H_3BO_3) and Polyethylene Glycol-6000($H(OH_2CH_2)_nOH$) (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 SnO_2-F:PEG-6000 films were produced for different substrate temperatures ranges 300^0C to 425^0C. 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 SnO_2-F:PEG-6000 Thin Films:

The prepared SnO_2-F:PEG-6000 films were used for further characterization. X-ray diffractometer (Ultima IV Japan) with CuKα 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. Morphogical 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˚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-F:PEG-6000 thin films were deposited by the Spray Pyrolysis technique. Deposited films were transparent, electrically conducting and sensitive to H_2S gas.

3.1 Structure Analysis:

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

confirmed by the reduction in Crystallite size which will reduce grain boundary scattering of charge carriers.

XRD:

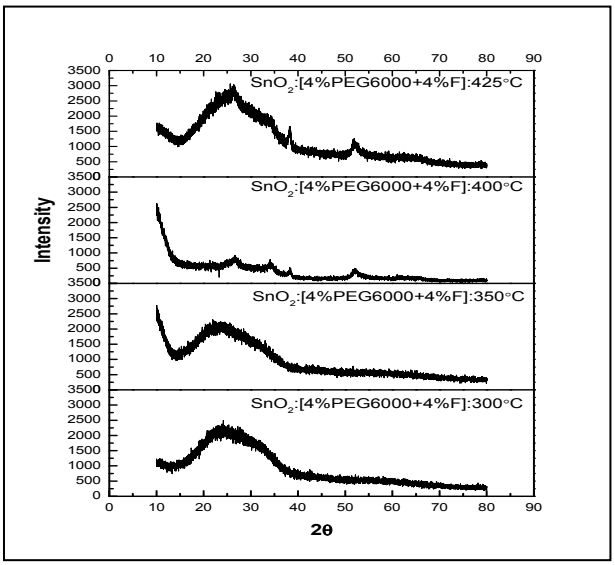

Figure 1:X-ray Diffraction Pattern of Spray Deposited SnO_2-F:PEG6000 Thin Films with Variation of Substrate Temperature. (d) SnO_2-F:PEG6000 with 425^0C.

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 SnO_2-F:PEG-6000 thin film with different temperature is estimated and is given in table -1.

T*able 1*: Particle Size Estimated for SnO_2-F:PEG-6000 Films with Different Substrate Temperature using X-ray diffraction

Sl.NO	Samples	Particle size
01	SnO_2:[4%PEG 6000+4% F]with300°C	6.99 nm
02	SnO_2:[4%PEG 6000 +4% F]with 350°C	7.18 nm
03	SnO_2: [4%PEG6000+4%F]with 400°C	6.59nm
04	SnO_2: [4%PEG6000+4%F]with 425°C	5.88 nm

3.2 Morphological Analysis:

The surface morphology of SnO_2-F:PEG-6000 thin films at different substrate temperatures was investigated from scanning electron microscopic (SEM) images and is presented in Figure (2). Grain shaped small grains with smooth surface and dense

packing are seen at Ts = 425°C [21]. No distinct shape is apparent at other Ts though the film is densely packed with grains. 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.

Morphology:

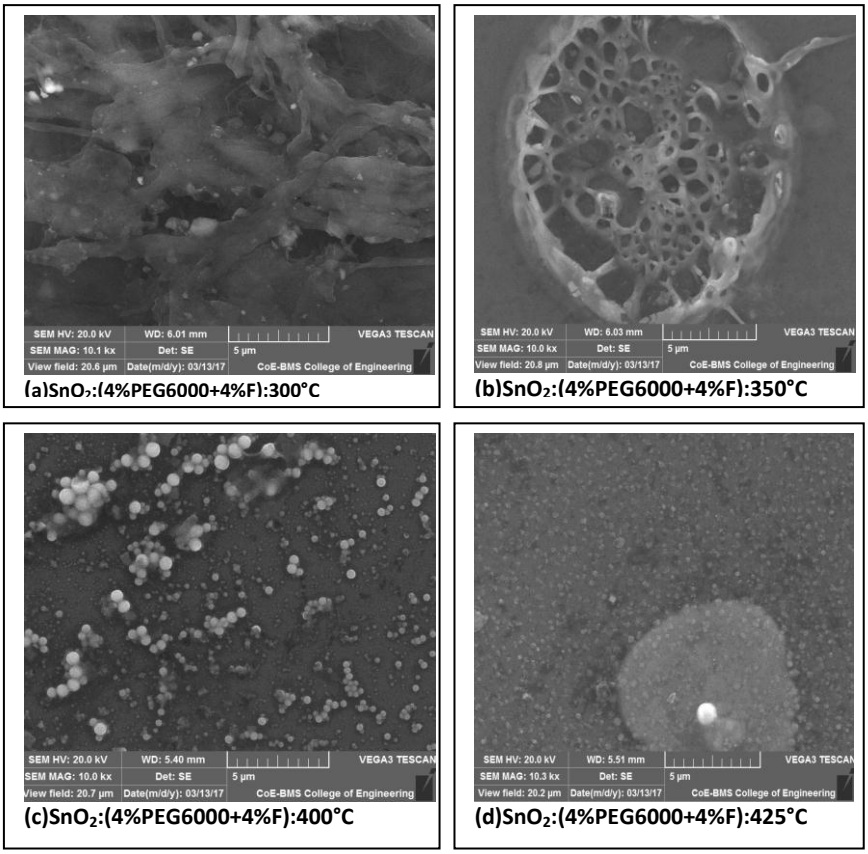

Figure2: SEM Image of SnO_2-F:PEG6000 with Different Substrate Temperature.

3.3 Optical properties

Absorption curve of SnO_2-F: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 2.8-3.5 eV. The absorbance curve of the SnO_2-F:PEG-6000 thin films with different substrate temperature Show in Figure (3). At 350°C substrate temperature thin film energy gap is 3.5 eV has exhibited maximum sensitivity to H_2S. The sensitivity decreases for higher substrate temperature. The energy gap for SnO_2-F:PEG-6000 thin film with different temperature is estimated and is given in table -2.

Table 2: Energy Gap Estimated for SnO_2-F:PEG-6000 Films with Different Substrate Temperature.

Sl.NO	Sample	Energy Gap
01	SnO_2:[4%PEG6000+4%F]with300°C	3.3 eV
02	SnO_2: [4%PEG6000+4%F]with 350°C	3.5 eV
03	SnO_2: [4%PEG6000 +4%F]with 400°C	3.0 eV
04	SnO_2: [4%PEG6000 +4%F]with 425°C	2.8 eV

Optical Properties:

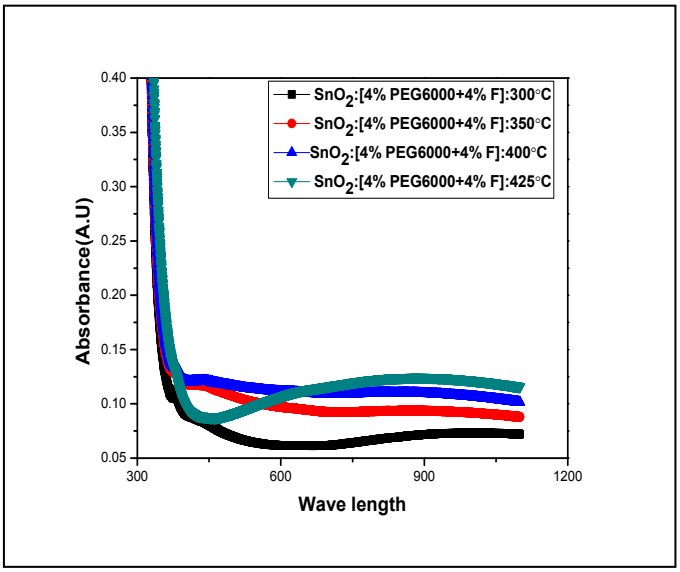

Figure3: Optical Absorption of SnO_2-F:PEG6000 Thin Films with Different Substrate Temperature.

3.4 Electrical properties:

Room temperature electrical resistivity measurements were made by Keithley source meter. The I-V characteristics curve of the SnO_2-F:PEG-6000 thin films with different substrate temperature Show in Figure (4).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 28.5 KΩ has exhibited maximum sensitivity to H_2S. The sensitivity decreases for higher

substrate temperature, The resistivity for SnO_2-F:PEG-6000 thin films with different temperature is estimated and is given in table -3.

Table 3: Resistivity Estimated for SnO_2-F:PEG-6000 Films with Different Substrate Temperature.

Sl.NO	Sample	Rasistance
01	SnO_2: [4%PEG6000+4%F]with 300°C	20.2 KΩ
02	SnO_2: [4%PEG6000+4%F]with 350°C	29.5 KΩ
03	SnO_2: [4%PEG6000+4%F]with 400°C	12.8 KΩ
04	SnO_2: [4%PEG6000+4%F]with 425°C	5.5 KΩ

Electrical Properties:

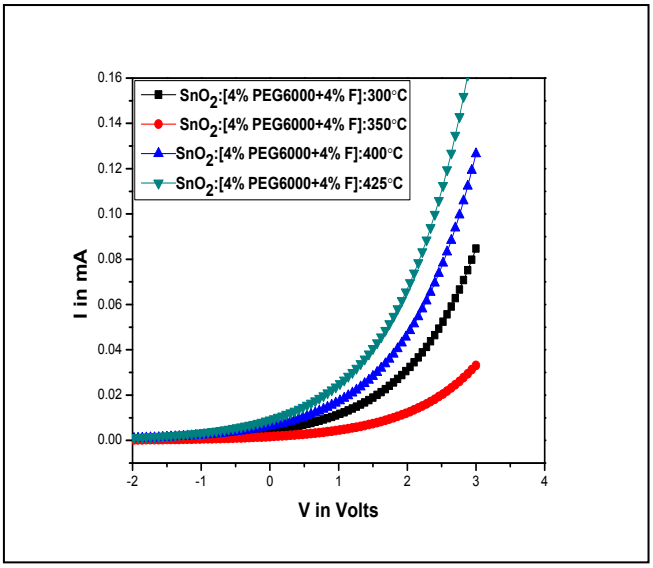

Figure 4: Current-Voltage (I-V) Characteristic Curves of SnO_2-F:PEG6000 Thin Films with Different Substrate.

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˚C, as the substrate temperature increases sensitivity thin film decreases [24]. At 350°C substrate temperature thin film shows exhibited maximum sensitivity to H_2S.The gas response characteristics are shown in

Figure (5). The sensitivity for SnO_2-F:PEG-6000 thin film with different temperature is estimated and is given in table -4.

Table 4: Sensitivity is Estimated for SnO_2-F:PEG-6000 Films with Different Substrate Temperature.

Sl.NO	Sample	Sensitivity
01	SnO_2:(4%PEG6000+4%F)with 300°C	16 %
02	SnO_2:(4%PEG6000+4%F)with 350°C	25.87 %
03	SnO_2:(4%PEG6000+4%F)with 400°C	7.60 %
04	SnO_2:(4%PEG6000+4%F)with 425°C	2.14%

Gas Sensing Characteristics:

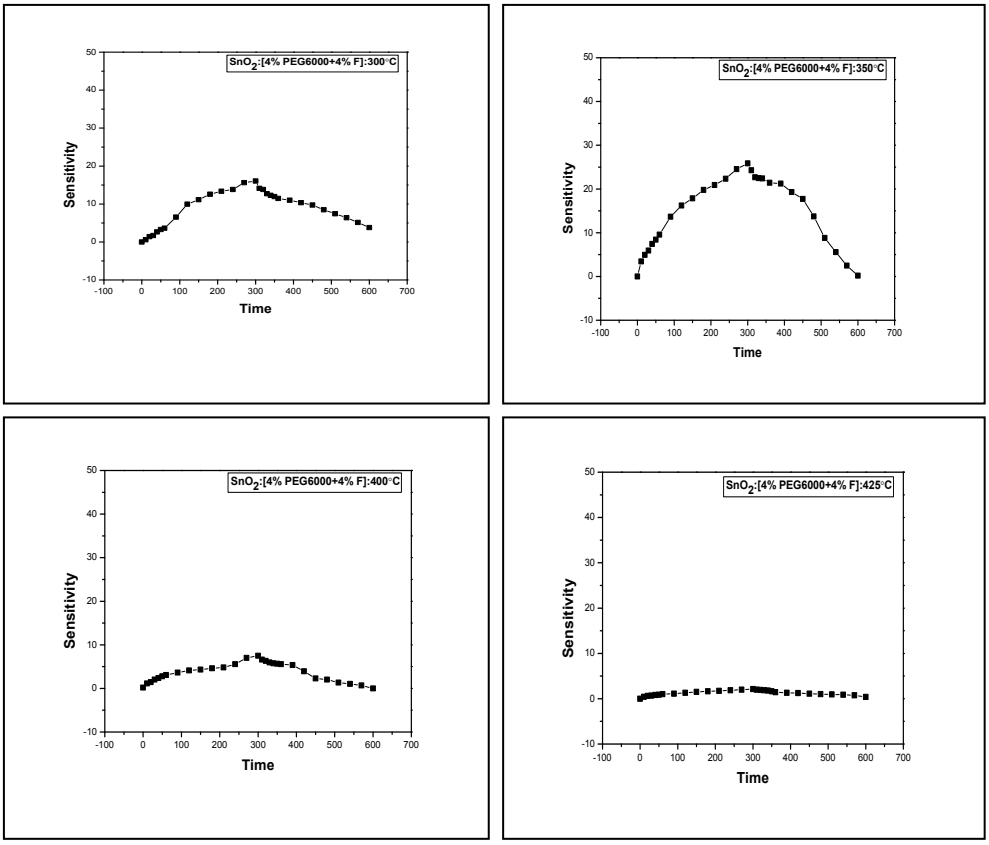

Figure *5*: Sensitivity of SnO_2-F:PEG6000 Thin Films for H_2S (a) SnO_2-F:PEG6000 with 300^0C (b) SnO_2-F:PEG6000 with 350^0C (c) SnO_2-F:PEG6000 with 400^0C

IV. CONCLUSION

In the Paper as substrate temperature while deposition of SnO_2-F: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 H_2S.

V. ACKNOWLEDGEMENT

The authors would like to acknowledge SECAB A.R.S.Inamdar College for women, Vijayapur, Karnataka, India, for providing Research center to carry on this work **.**

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