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Synthesis and Characterization of Pure and Fluorine Doped Tin-Oxide Nano-Particles by Sol-Gel Methods

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Abstracts: ***Thin films of tin oxide (SnO_2) and fluorine doped tin oxide (SnO_2:F) (FTO) were prepared by sol-gel dip-coating (SGDC route) method by using easily available low cost materials as we use $SnCl_2$, $2H_2O$ and HF. X-ray diffraction (XRD) spectrum showed all the peaks of the crystalline SnO_2 . The amount of strain was obtained 1.2 x 10^{-2} and the particle size as ~ 28 nm, indicating the nano-structural nature of the films. FTIR spectroscopy showed strong Sn-O and Sn-O-Sn bonding. UV-Visible spectrophotometric measurement showed high transparency of the films in the visible region and the direct band gap was calculated to be 3.35 eV. Current-voltage (I-V) characteristics of the films were non-linear in nature, which can be explained by the Poole-Frenkel model of thermionic emission.***

Keywords: Transparent Conducting Oxides, Sol-Gel dip-coating (SGDC) method

1. Introduction

Transparent Conducting Oxides (TCO) are extensive research element during the last four decades. Among these materials Indium tin oxide (ITO) and Zinc oxide (ZnO) etc. are most important semiconductors because of their special electrical and optical properties. Tin oxide (SnO_2) is an n-type wide band gap semi-conducting transparent material which has tremendous interesting applications in opto-electrical device technology [1-5] such as window layer of solar cells, flat panel display, substrate materials in electrolysis, electrode for electro-chromic devices, gas sensors[6] etc.

In order to improve its optical and electrical properties tin oxide films were doped with Mo, Cd, F, Sb [7-10] etc. Among various dopants fluorine doped SnO_2 (FTO) films have more higher transparency and good conductivity. It is very important to study the electron-transport phenomena in these films for the application of gas sensors[6] . Several methods have been used for deposition of the films which are chemical vapor deposition (CVD), sputtering, chemical thermal evaporation, spray pyrolysis and sol-gel dip coating techniques (SGDC). Among these, SGDC method has more advantages over the other methods such as, low-cost, simple process, easier doping layer control on the substrate, possibility of using higher purity starting materials and coating on large and complex shaped substrate etc.

According to the literature survey, there exists very few publications on fluorine doped SnO_2 films. All are very costly procedure to prepare the required film. Most of them had used organic complex (NH_4F)[11-12] as fluorine source. In this present study FTO films were prepared by a easier method which is SGDC route by using easily available low cost starting materials as we use $SnCl_2$, $2H_2O$ and HF as starting materials because of easier availability, low cost and for greater degree of incorporation of fluorine atoms in SnO_2 matrix. The films were characterized by different techniques such as XRD, FTIR, UV-VIS-NIR Spectroscopy etc. Electrical properties are studied, as this property is very important to use SnO_2 films in gas sensing applications.

2. Experimental

2.1 Cleaning of Substrate

To prepare high quality thin film made of good type cleaning procedure of substrates glass is more essential. The step by step cleaning procedure is given below.

1. Clean with dilute HCl (1-5)% and rinse in water.
2. Rub the substrate with brush and a mild detergent.
3. Wash in double distilled de-ionized water several times.
4. Place in an ultrasonic cleaner with the glass slide immersed in water.
5. Boiled them in an electric heater.
6. Degrease in vapour of Isopropyl alcohol in a degreasing chamber fitted to a condenser system.

2.2 Procedure of Film Preparation

$SnCl_2$, $2H_2O$ (99.9%), HF (40%) and isopropyl alcohol (99.8%) were taken as starting materials. Several solutions were made by varying the concentration of HF taken in the starting materials. The resulting solutions were stirred for 1 hour at a temperature of 75^0 C and then cooled for 2 hours at room temperature. Cleaned glass slides and silicon substrates were dipped into the solution and then withdrawn vertically from the solution very slowly for 12 to 15 times. Between two successive dipping the substrates along with the solution were dried at 80~100^0C to form gel. After dipping and withdrawing procedure the films were annealed at 300-350^0C in air for half an hour.

Steps:

1. Powdered Stannous Chloride ($SnCl_2.2H_2O$) [purity ~ 99.9%] + Water (H_2O) + Isopropyl Alcohol.
2. The solution stirred in an ambient of 75^0C for 1 Hour.

3. A homogeneous solution was prepared.
4. The solution was cooled for 4 hours to room temperature.
5. Cleaned glass slides were dipped into the solution and withdrawn vertically from the solution very slowly for 12-15 times.
6. Between two successive dipping the substrates along with the solution were dried at 80-100^{0}C to form gel.
7. The films were annealed at 300-350^{0}C in air for half an hour.
8. It was ready for the required SnO_2 film.

2.3 For F doped SnO_2 Film preparation

Powdered Stannous Chloride ($SnCl_2.2H_2O$) [purity ~ 99.9%], Hydrofluoric Acid [HF] (40%), Water (H_2O) and Isopropyl Alcohol (99.8%) were taken as starting materials.

2.3 Deposition Mechanism

The deposited films were studied by X-ray diffraction (XRD, Philips PW 1730/10) using the Cu $K_{\alpha 1}$ radiation operating at 30 kV, 20 mA. The spectra were recorded at room temperature. Also Bruker, Advance D8 X-ray diffractometer was used to record the XRD spectra. FTIR (Shimadzu FTIR-8400S spectrometer) and UV-VIS-NIR spectroscopy (Shimadzu UV-3101 PC spectrophotometer) analyzed to examine the film morphology, structural and also optical transmittance properties. The electrical properties of the films were studied by standard four probe method and obtained data were used for analysis.

3. Results and Discussions

3.1 Structural Properties

Fig. 1 shows the X-ray Diffraction pattern of a typical sol-gel dip coated SnO_2 thin film on a3.5 x 2.5 cm^2 glass substrate. The peaks are identified to originate from (110), (101), (200), (211), (220) and (002) reflections of tetragonal SnO_2 crystal structure. Crystallites[13] with crystallographic (110) and (200) planes parallel to substrate are predominant in the films. The relative amounts of crystallites with a (110) and (200) orientation[14] depend on film thickness and deposition mode. No peaks of starting materials (e.g. $SnCl_2$ or HF) have been found, which conclusively indicates that reactants were completely mixed to form the proper phase of tin dioxide.

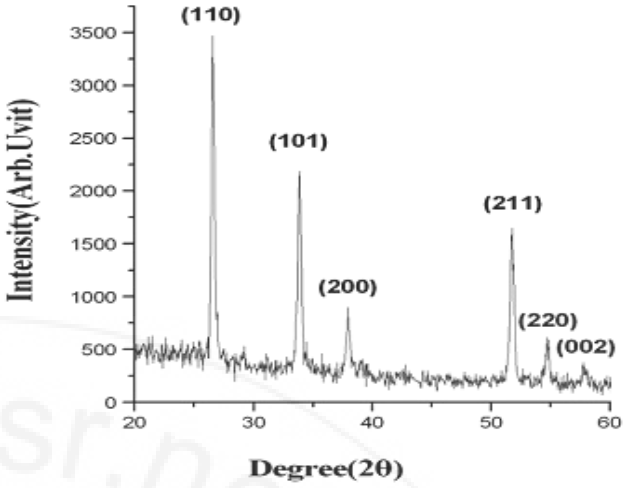

Figure 1 : XRD patterns of the SnO_2 films on glass substrate

The results on strain and the particle size is obtained from the full-widths at half- maximum (FWHM) of the diffraction peaks. The FWHM (β) can be expressed as a linear combinations of the contributions of the strain (ε) and particle size (L) through the following relation[15] :

$\beta \cos \theta/\lambda = 1/L + \varepsilon \sin \theta/\lambda$ (1)

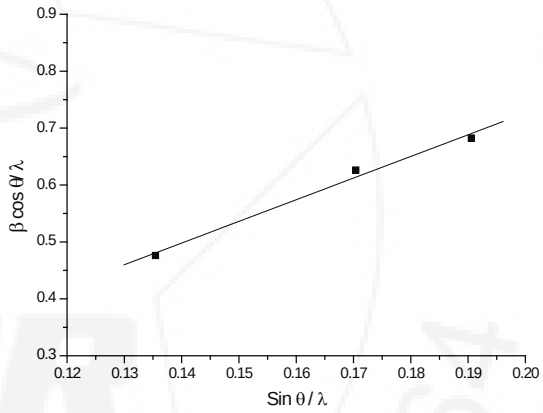

Figure 2: Plot to determine strain and particle size of SnO_2 thin film on glass substrate. Data obtained from XRD pattern.

Fig.2 represents the plot of *β cos θ/λ vs. sin θ/λ*. From the slope of the line the amount of strain is obtained 1.2 x 10^{-2} and from the intercept on the *β cos θ/λ* axis it is obtained the particle size as ~ 28 nm, indicating the nano-structural nature of the films.

FTIR spectrum of the SnO_2 film deposited on Si substrate is shown in **Fig. 3** . The spectrum shows several absorption peaks which confirm the formation of the material. Peaks between 400-700 cm^{-1} assigned to Sn-O and Sn-O-Sn vibration[16] . Small peaks between 600 – 1900 cm^{-1} are due to Sn-OH vibration. Broad peak 3000- 3500 cm^{-1} is due to O-H stretching vibration. Peak at 1081 cm^{-1} occurs due to Si-O vibration due to substrate.

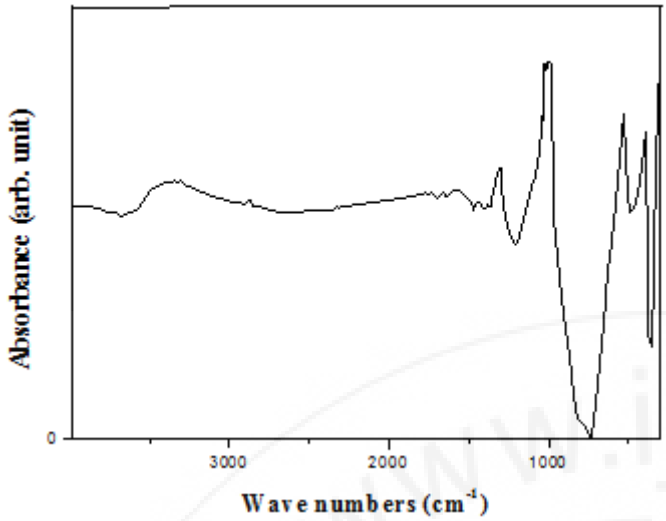

Figure 3: FTIR spectra of SnO_2 :F film on Si substrates indicating different Sn-O bonds

3.2 Optical and Electrical Properties

The optical transmission spectra shown in **Fig. 4** represents that the film is highly transparent in the visible region. From transmittance data absorption coefficients (α) were calculated by using Manifacier Model[17] in the strong absorption region. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap.

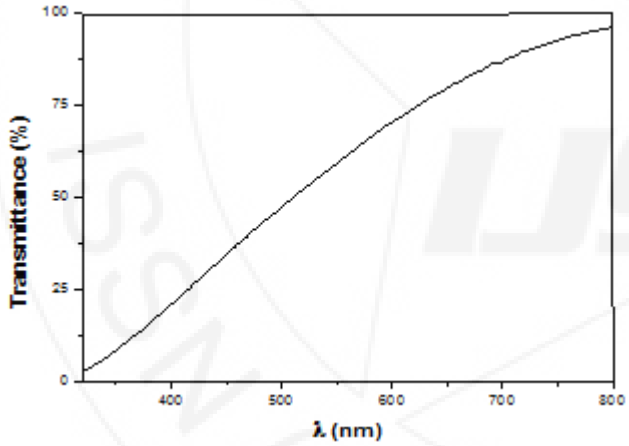

Figure 4: Optical transmission of FTO film deposited on glass substrates.

Due to crystalline in nature of the film the relation between the absorption coefficients (α) and incident photon energy (hν) can be written as[18]

$(\alpha h\nu)^2 = A(h\nu - E_g)$ (2)

Where A is a constant and E_g is the band gap of the materials. The $(\alpha h\nu)^2$ vs. $h\nu$ plot is shown in the **Fig.5**.

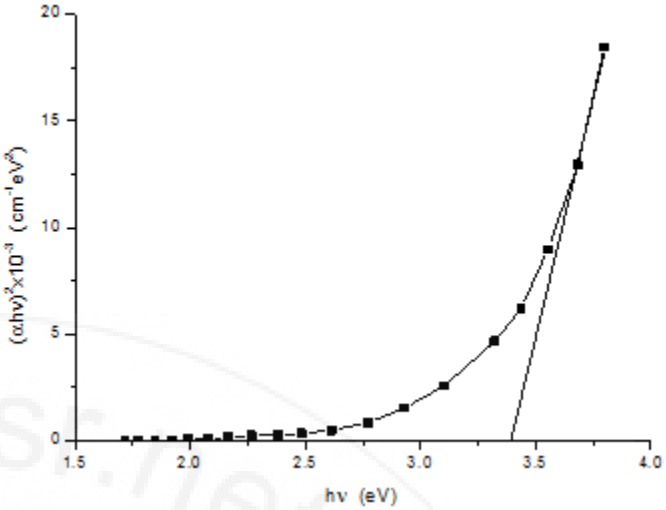

Figure 5: The $(\alpha h\nu)^2$ vs. $h\nu$ plot for direct band gap calculation.

Extrapolating the linear portion of the graph to the $h\nu$ axis, the obtained direct band gap from the intercept is equal to 3.35 eV which is comparable to others[16] . The reported[19] band gap values for SnO_2 films are between 3.3 and 4.0 eV.

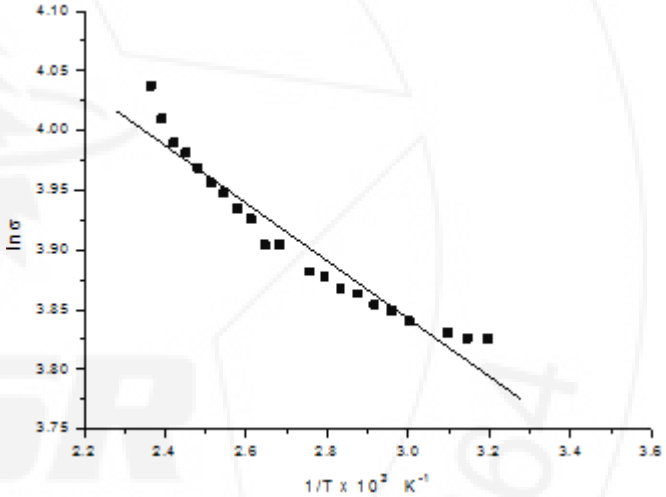

Figure 6: Plot of *lnσ vs. 1/T* of a FTO film.

Electrical conductivity was studied by standard four-probe method. **Fig.6** shows the plot of *lnσ vs. 1/T* of a FTO film. The straight line nature of the Arrhenius plot indicates the thermally activated conduction as often found in doped semiconductors. From the slope of the line the value of activation energy (E_a) which corresponds to the minimum energy required to transfer electrons from donorlevel to the conduction band and the value of E_a comes out to be 16 meV.

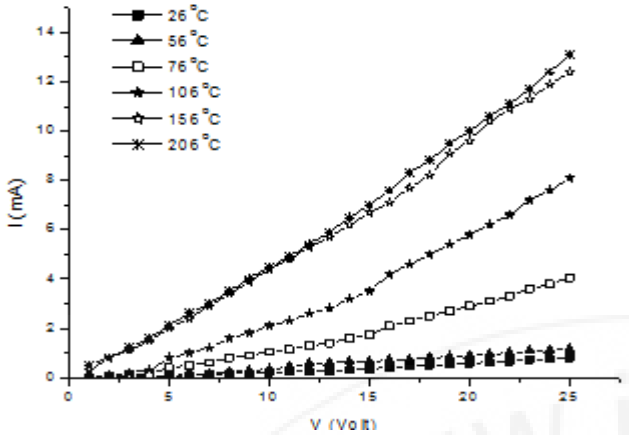

Figure 7: Current – Voltage (I-V) characteristics of the FTO film at different temperatures.

The I-V characteristics of the FTO film is shown in **Fig.7** at different temperatures. The curves are non-linear in nature. Non-linearity is significant above 20V. This is due to presence of an electron depleted layer at the grain boundary and the formation of a potential barrier. The shape of I-V curve is typical of thermionic emission over the barrier which can be explained by the Poole-Frenkel model of thermionic emission[20] . With an increase in temperature, the non-linearity becomes more and more prominent. The presence of absorbed oxygen and fluorine atoms at grain boundaries is assumed to be the cause of this effect. These atoms produce defect levels, which trap electrons and create a potential barrier across the grain boundaries. Therefore the SnO_2 and F doped SnO_2 materials are used for the preparation of a gas sensor.

4. Conclusions

In this present work FTO films were prepared by a easier method which is SGDC route by using easily available low cost materials as we use $SnCl_2$, $2H_2O$ and HF as starting materials because of easier availability, low cost and for greater degree of incorporation of fluorine atoms in SnO_2 matrix. X-ray diffraction (XRD) spectrum showed all the peaks of the crystalline SnO_2 . The amount of strain was obtained 1.2 x 10^{-2} and from the intercept on the $\beta \cos \theta/\lambda$ axis it is obtained the particle size as ~ 28 nm, indicating the nano-structural nature of the films.

Peaks in FTIR Spectrum between 400-700 cm^{-1} assigned to Sn-O and Sn-O-Sn vibration. Small peaks between 600 – 1900 cm^{-1} are due to Sn-OH vibration. Broad peak 3000-3500 cm^{-1} is due to O-H stretching vibration. Peak at 1081 cm^{-1} occurs due to Si-O vibration due to substrate.

UV-Visible spectrophotometric measurement showed high transparency of the films in the visible region and the direct band gap was calculated to be 3.35 eV. It was observed that the current-voltage (I-V) characteristics of the films were non-linear in nature, which can be explained by the Poole-Frenkel model of thermionic emission. With an increase in temperature, the non-linearity becomes more and more prominent. The presence of absorbed oxygen and fluorine atoms at grain boundaries is assumed to be the cause of this effect. These atoms produce defect levels, which trap electrons and create a potential barrier across the grain boundaries. Therefore the SnO_2 and F doped SnO_2 materials are used for the preparation of a gas sensor.

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