New insights on temperature dependent electrical properties of samarium doped tin oxide thin films

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Abstract. Samarium doped tin oxide (SmDTO) nano particles were synthesized and deposited in the form of thin film by RF sputtering and was characterized using XRD and SEM. XRD images revealed the crystalline nature of tin oxide and reduced peak intensities in doped samples. SEM micrographs showed fine granular nature of tin oxide, mostly spherical and well isolated grains and slight agglomerations in doped sample. The current – voltage behavior of samarium doped tin oxide thin film was investigated using Electrochemical Impedance Spectroscopy (EIS). Temperature dependent EIS was performed on 0.5% SmDTO thin films to analyze the effect of doping on its charge transfer resistance. Due to doping, the charge carrier concentration improved surface conduction in SnO2 thin films which was reflected as a steady and gradual decrease in the charge transfer resistance.

Keywords: Electrochemical Impedance; Tin oxide; Samarium; electrical conductivity; I-V profile; thin films.

1. Introduction

Metal oxide semiconductors possess extensive range of applications such as transparent conducting oxides (TCO), electrodes in solar cells & lithium ion batteries, gas sensors and catalysts [1-3]. Electrical conductivity of metal oxide semiconductors improve as a result of free electric charge per unit volume of the bulk material and surface charge concentration which is bound to vary with temperature [4]. Tin oxide, a direct band-gap n-type semiconductor, is generally preferred in optoelectronics applications due to its optical transparency in the visible region [5]. The annealing temperature and oxygen vacancies play a vital role in enhancing the sensitivity and conductivity of tin oxide thin films [6]. The conductivity and sensitivity of tin oxide thin films improve upon doping with suitable element. The selection of samarium is considered owing to its unique physical and gas sensing properties [7, 8]. Increase in optical band gap between undoped and samarium doped samples of tin oxide thin films have been reported earlier [9]. Effect of post treatment annealing in pure and samarium doped thin films was also investigated [10]. As the ionic radius of Sm is greater than that of SnO2, experimental reports showed improved magnetic moment, electrical properties and occupancy of oxygen vacancies upon doping with samarium in traces or in very low concentration. Thus in the present investigation 0.5% concentration of samarium has been considered for SmDTO.

Electrochemical stability is of great importance as they indirectly affect the stability of the implicated systems. The electrochemical perturbations and the effect of cathodic polarization in ITO
(Indium Tin Oxide) thin films had been reported in the literature \cite{11}. Electrical properties of copper doped tin oxide were studied and the variations in electrical conductivity were extensively analyzed from its variation in surface state densities \cite{12}. Parameters affecting response of modified electrodes were optimized by comparing with unmodified electrodes. Improvement in conductivity around $10^8$ times with increase in Iridium concentration in iridium doped tin oxide thin films is also known \cite{13}.

Thus in the present work the electrochemical analysis of SmDTO thin film is carried out to analyze (i) the effect of temperature on electrical conductivity, (ii) changes in charge transfer resistance and (iii) variations in I-V profile at different load conditions. In contrast to the literature on electrochemical studies of SmDTO thin films, in this work, we depict the variations in mass transfer coefficient due to samarium addition in tin oxide at variable temperature and electrical loads.

### 2. Methods And Materials

In order to make pellets, weighing about 20gms, 19.24 gms of pure tin oxide nano powders were added to 0.5\% samarium concentration, weighing 0.752 gms. Nano particles were mixed homogenously using mortar and pestle and were pressed using HERBST Hydraulic press and sintered in a furnace to achieve 2 inch diameter pellets for sputter targets. The sputter targets were used to coat silicon substrate by RF magnetron DC sputtering to achieve a uniform thickness of 100nm supplied by Hind HIVAC systems. In order to perform temperature dependent electrochemical studies on SmDTO thin films, conventional two contacts technique was adopted. A small glass plate was kept on the hot plate to hold the substrate in position and the two electrodes of IVIUM Potentiostat were connected to either side of the thin film coated with 99.9\% silver paste. Wide frequency measurements were carried out in the impedance range of 10 mHz to 10 kHz and the experiment was repeated for temperature from 40° to 90°C at an interval of 10°C. All electrochemical measurements were conducted in dark conditions at potentiostatic mode. Nyquist plots of the thin film is analysed by fitting the equivalent circuit using ZMAN software.

### 3. Results And Discussion

The structural, morphological, compositional, optical and electrochemical studies of 0.5\% SmDTO thin film is discussed in the subsequent sections.

#### 3.1 Structural characterization

X-ray diffraction studies of SmDTO thin films revealed their crystalline nature. As shown in Fig. 1, the peaks observed at $27.9^\circ$, $34.3^\circ$ and $52.4^\circ$ corresponds to the (110), (101) and (211) planes of polycrystalline rutile/tetragonal structure of tin oxide which coincides with JCPDS21-1250\cite{17}. It is observed that the crystalline nature of SnO$_2$ reduces with incorporation of Sm. This may be ascribed to the inclusion of large ionic radius (1.08 Å) Sm$^{3+}$ ions into the SnO$_2$ lattice, which intrudes and reduces the crystalline nature of the material\cite{17}.

![Figure 1: XRD of pure and doped thin films](image_url)
3.2 Morphological analysis

Nanostructured SnO$_2$ thin films samples were characterized for their morphology using high resolution Quanta 200 FEG Field Emi Scanning Electron Microscope (FESEM). High resolution SEM images ascertain the fine granular nature of tin oxide, mostly spherical and well isolated grains and slight agglomerations in SmDTO samples as shown in Figs 2 a & b. This may be accredited to the changes in crystallographic properties due to Sm doping.

![Figure 2a: SEM image of Pure tin oxide](image)

![Figure 2b: SEM image of SmDTO](image)

TEM image and the corresponding EDAX spectrum of 0.5% SmDTO sample are as shown below in Figs 2 c & d respectively. TEM analysis of the doped sample was done using JEM 200 PLUS HR-TEM. It reveals the crystalline nature of the doped sample and the spherical shape of particles of size in the range of 50 nm which is in conformity with the XRD data. As can be seen from the elemental analysis, peaks corresponding to Sn, O, Sm are found which confirms the doping of samarium in tin oxide lattice.

![Figure 2c: TEM Image of SmDTO](image)

![Figure 2d: EDAX of SmDTO](image)

3.3 Optical studies

The UV- vis absorption spectroscopy of the thin films were performed to study the variations in absorbance spectra using Agilent UV-vis Spectrometer. It is clearly noticeable from Fig 3 that the optical absorption of SnO$_2$ thin films (in 290 to 790 nm range) decrease with Sm doping. Absorption of light causes free electrons to move to the valence band thereby increasing the conductivity$^{[18]}$. 

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18. Reference to support the statement about conductivity increase.
Figure 3: UV-vis spectra of pure tin oxide and SmDTO films

The optical band gap variation from Tauc’s plot was calculated by using absorbance values and extend the linear portion of the curve \((\alpha h\gamma)^2\) versus \((1/\lambda)\) to intersect the photon energy axis as shown in Fig 4. \(\alpha\) indicates absorption coefficient, \(h\gamma\) is the photon energy, \(B\) is a constant relative to the material, \(\lambda\) refers absorption wavelength. The calculated optical band gaps of pure and 0.5% SmDTO were 2.5eV and 3.1eV respectively. The difference in band gap between pure and SmDTO samples may be ascribed to the intrinsic stresses and structural modification in tin oxide due to samarium doping[9].

Figure 4: Tauc’s plot of SnO\(_2\) and SmDTO

3.4 Raman Spectra

Fig 5 reveals the Raman spectra of SnO\(_2\) and SmDTO thin films. The main scattering peaks were observed in the range of 485, 633 and 786 cm\(^{-1}\) which correspond to three elemental modes of vibrations of SnO\(_2\). Similar peaks were also observed in SmDTO nanoparticles calcined at 400°C[8]. Weak scattering bands have been observed at 343 cm\(^{-1}\) in the case of SmDTO which indicate the lattice mismatch due to Sm doping in SnO\(_2\). Massive shift in peak intensities were also observed in SmDTO which is an indication of oxygen vacancies getting occupied by Sm. As the ionic radii of Sm\(^{3+}\) ions is much smaller than oxide anion (1.08 Å and 1.40Å\(^{\circ}\)), due to distortion in the SnO\(_2\) lattice, Sm\(^{3+}\) can occupy oxygen vacancy sites easily.
3.5 Electrochemical studies

3.5.1 I-V Characteristics of SmDTO
I-V profiles of the thin film at different loads and temperature range are shown in Fig 6. As the temperature varied from 40°C to 90°C, there was a steady increase in current value from 4.62 μA to 19.22 μA corresponding to open circuit voltage of 0.22 V. In addition, the dependence of current on load resistance is prominent till 60°C and then becomes negligible up to 90°C. This phenomenon is indicative of the improvement in semiconductor performance of doped films with temperature.

Figure 5: Raman spectra of SnO₂ and SmDTO
Figure 6 (a)-(f): I-V profile of SmDTO thin films at different temperatures

3.5.2 EIS analysis

The impedance variations were found to exhibit a diffusion profile at lower temperature and semicircular charge transfer shift at higher temperatures. The semicircular arc becoming more prominent with increase in temperature indicating complete charge transfer as seen from Fig 7. Due to doping, the charge carrier concentration improved surface conduction in SnO₂ thin films and thereby lead to uniform reduction in $R_{ct}$ with temperature. The variations in charge transfer resistance as temperature increased from 40° to 90°C were tabulated. $R_s$ represents the series resistance comprising of (i) resistance between particles of SmDTO thin film and (ii) resistance between SmDTO particles and current collector. $R_{ct}$ represents the charge transfer resistance associated with the thin film. $R_{ct}$ varied from 308kΩ to 72.11kΩ as temperature increased from 40° to 90°C.

Figure 7: Nyquist plot of SmDTO thin film at different temperatures
4. Summary:
The electrochemical studies of SmDTO thin film were analyzed. Impedance characteristics shifted from diffusion to charge transfer profile as temperature increased. I-V plots as a function of load resistance indicated negligible dependence on loads at higher temperatures. Hence 0.5% SmDTO thin films exhibited improved performance in the temperature range of 60° - 90°C.

5. Acknowledgements:
The authors wish to acknowledge the Nanotechnology Research Centre (NRC), SRMIST for SEM results, Micro Raman facility at SRMIST for Raman spectroscopy and HRTEM facility at SRMIST set up with support from MNRE (Project No. 31/03/2014-15/PVSE-R&D), Government of India for TEM and EDAX results.

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