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Abstract
Tin oxide (SnO$_2$) thin films were deposited on quartz substrates using sol-gel dip coating technique. X-ray diffraction (XRD) pattern indicated that the film annealed in air at 350°C was amorphous in nature, whereas, the films annealed in oxygen atmosphere at 350°C showed crystalline phase. The films were further annealed in oxygen atmosphere at 450°C and 550°C. All the diffraction peaks can be indexed to the tetragonal phase of SnO$_2$. The surface morphology (SEM) showed that surface of all films were continuous and without micro cracks. The Energy dispersive X-ray spectroscopy (EDXS) spectra indicated an increase in the concentration of oxygen content with increase in annealing temperature. The energy band gap value for the film annealed in air was 3.88 eV. The optical band gap increased to 4.05 eV when annealed in O$_2$ atmosphere. The photoluminescence (PL) spectra showed the presence of emission peaks in UV region and visible region of the electromagnetic spectra. Transparent oxide semiconductor SnO$_2$ film finds potential application as an active channel layer for transparent thin film transistor.

1. Introduction
SnO$_2$ is a wide direct band gap n-type semiconductor possessing much importance in various fields of science and technology. In the form of thin films, SnO$_2$ posses interesting applications in opto-electronic devices, gas sensors, flat panel displays[1-2 ]. There are very few reports on the synthesis and systematic study on the films prepared by sol–gel dip coating technique and annealing in oxygen-rich environment. Sol gel process posses several advantages like lower processing temperature, better homogeneity, controlled stoichiometry and flexibility of forming thin films or nanoparticles. The environment in which the films are prepared plays an important role in controlling defects like oxygen vacancies, which consequently determine the physical properties of the films. In this study, we report the preparation and characterisation of nanocrystalline transparent tin oxide thin films by sol-gel dip coating technique.

2. Experimental details
The SnO$_2$ solution was prepared and were deposited onto well cleaned quartz substrates by sol–gel dip coating technique[5].The dip coated films were pre-fired at 250°C for 15 minutes in air and O$_2$ atmosphere respectively. The film pre-fired in air was annealed only at 350°C. The films pre-fired in O$_2$ were annealed at different temperatures 350°C, 450°C and 550°C respectively. All the samples were annealed at the rate 4°/minute, and held at respective temperature for 15 minutes each during the course of annealing. The process of dipping, pre-firing and annealing were repeated seven times.

The phase analysis of the SnO$_2$ films were characterized by XRD using X-ray diffractometer (Model-PW 1710 PHILIPS). The surface morphology of the annealed films was investigated by using SEM (Model - JSM 5600LV JEOL). Elemental analysis of the films was done by EDXS (JEOL JSM 6390LA). Optical transmittance was studied using a spectrophotometer.
(Model – JASCO-V550). PL spectra were recorded by using a Perkin-Elmer Fluorescence spectrometer (Model-LS55) with a 40 W Xenon Lamp as the excitation source.

3.1 Structural studies

3.1.1 X ray diffraction Studies: The XRD patterns of SnO₂ films annealed at 350°C in air and at different temperatures in O₂ atmosphere are shown in the Figure 1. The films annealed in air at 350°C were amorphous in nature (Figure 1a). When the films were annealed in O₂ atmosphere at 350°C, low intensity XRD peaks (110) and (211) were visible, indicating that the crystallisation of the SnO₂ particles have started. At lower annealing temperatures, the SnO₂ particles are in the initial phase of structural formation preventing full crystallization of the films. Since low intensity peaks appeared at 350°C when annealed in O₂ atmosphere, the higher temperature annealing were performed in O₂ atmosphere. When the temperature increased to 450°C and 550°C, the XRD patterns indicated that the intensity of peaks (110) and (211) increased, along with the appearance of (101) phase. All the diffraction peaks can be indexed to the tetragonal phase of SnO₂. Annealing in O₂ atmosphere at higher temperatures causes improvement in crystallinity as well as O₂ chemisorption at the inter grain boundaries [6]. The grain size of the films were calculated using Scherrer’s equation (Table 1). The increase in crystallite size is mainly due to an increase in the thermal energy for crystallization and growth of grains in the films.

| Annealing Temperature(°C) | Crystallite size(nm) | Band gap(eV) |
|---------------------------|----------------------|--------------|
| 350                       | 8.6                  | 4.05         |
| 450                       | 15.7                 | 4.0          |
| 550                       | 23.5                 | 3.96         |

Table 1: Crystallite size and Band gap of films annealed in O₂ atmosphere

3.1.2. Scanning electron micrographs: The micrographs of films annealed at 350°C in air and at different temperatures in O₂ atmosphere are shown in the Figure 2. It is evident from the micrographs that all the films display a homogenous crack-free appearance. The micrograph of the film annealed in air at 350°C, shows agglomeration of particles (Figure 2a), whereas, the micrographs of the films annealed in O₂ atmosphere showed the presence of few tiny grains confirming the partial crystalline nature. At 450°C and 550°C, some spherical shaped grains have started forming on the surface. It is obvious from the micrographs that by increasing the annealing temperature, grains gradually grown up and the surface of the films became slightly rough in nature. The origin of rough surface can be speculated to be due to the increase of total volume during the transformation from a metallic tin film to a tin oxide film. The roughness of the thin films plays a vital role for developing optical coatings especially in the ultraviolet region for applications such as lithographic uses [8,9].

Figure2: SEM micrographs of SnO₂ films annealed in air at a) 350 °C and in O₂ at b) 350°C c) 450°C d) 550°C
The EDXS (Figure 3) indicates that films were composed of elements Sn and O. It is evident from EDXS, that as the annealing temperature increased, the concentration of O\textsubscript{2} is found to increase for O\textsubscript{2} annealed samples.

![Figure 3: EDX Spectra of SnO\textsubscript{2} films annealed in air at a) 350°C and in O\textsubscript{2} at b) 350°C c)450°C d)550°C](image)

### 3.2 Optical Studies

The transmission spectra of SnO\textsubscript{2} films annealed in air at 350°C and in O\textsubscript{2} atmosphere at different temperatures are shown in Figure 4. It was seen from the spectra, that the transmission of the films were approximately 80%. This may be attributed to the formation of the Fermi level in the conduction band\cite{10}. The plots of (α\textsubscript{h}ν)\textsuperscript{2} as a function of energy (inset figure 4) shows that the investigated films have a direct optical band gap (E\textsubscript{g}). The calculated E\textsubscript{g} \cite{11} is given in Table 1. The estimated E\textsubscript{g} of film annealed in air is found to be 3.88eV which is lower than for the films deposited in O\textsubscript{2} environment. The E\textsubscript{g} values are sensitive to O\textsubscript{2} content during the annealing process. Hence, O\textsubscript{2} vacancies play an important role in determining the optical properties of thin films. The observed decrease in the energy gap of films, upon increasing the annealing temperature, may be due to the increase in the crystalline size. The decrease in E\textsubscript{g} shows that annealing the film causes a strong red shift in the optical spectra, due to the agglomeration of the nanocrystallites into larger crystallites. This change has been attributed to grain size dependent properties of the energy bandgap.

#### 3.2.1. Photoluminescence studies

The room temperature PL spectra of the SnO\textsubscript{2} films annealed in air at 350°C and in O\textsubscript{2} atmosphere at different temperatures are shown in Figure 5. At 350°C in air, PL spectrum (Figure 5a) of the films exhibited a exciton related UV emission peak at 385 nm (3.22eV). The excitonic emissions are sensitive to imperfections and particle size in a crystal. XRD patterns of the films showed amorphous nature (Figure 1a). Also, it is evident from EDXS profiles (Figure 3a) that the concentration of O\textsubscript{2} is less in films annealed in air. This can trap the electrons from the valence band and can act as luminescent centres. Hence, PL peak may be related to the crystalline defects induced during growth of the film. When the films were annealed in O\textsubscript{2} atmosphere at 350°C, the peak shifted to 382nm (Figure 5b). The XRD pattern (Figure 1b) of the film indicates partially crystalline nature. This verifies the fact that O\textsubscript{2} atoms flowed from the O\textsubscript{2} atmosphere into the film during the annealing process, leading to decrease of O\textsubscript{2} vacancies in the film. The lower intensity after annealing in O\textsubscript{2} indicates a reduction in the number of defect states. As the annealing temperature increased to 450°C and 550°C, UV peak shifted to 376nm (3.29eV). The weak emission peaks at 456 nm and 480 nm at 450°C lies in the visible region. The visible light emission of SnO\textsubscript{2} is known to be related to defect levels within the band gap of SnO\textsubscript{2} associated with Sn interstitials. At 550°C, the peak at 456 nm shifted to 441nm and peak at 480 nm disappeared. The intensity of the PL peaks decreased with increase in annealing temperatures at 450°C and 550°C. As the temperature increased, the grain size of nanocrystals became larger, in turn, favours a decrease in the concentration of non-radiative defects. This can lead to the
decrease in number of the luminescence centers due to reductions on both the ratio of surface area and concentration of O₂ vacancies. Hence, SnO₂ nanoparticles annealed in O₂ atmosphere posses unique property of luminescence characteristics, whose specific emission wavelengths mainly depend on the nature of the semiconductors and the chemical environments, bringing on great application potentialities in the fields of light-emitting devices.

4. Conclusion
This study systematically discussed the effect of annealing atmosphere and temperature on the structural and optical properties of nanocrystalline SnO₂ thin film. The intensity of the XRD peaks increased with annealing temperature leading single structure formation. The surface morphology of the films was found to be strongly dependent on the annealing atmosphere and temperature. The intensity of PL emission peak decreased with increase in annealing temperature. Nanocrystalline SnO₂ films with wide band gap and short wavelength luminescence emission can serve as a better luminescent material for photonic applications.

Figure 4: Transmittance spectra of SnO₂ films annealed in air at a)350°C and annealed in Oxygen at b)350°C c)450°C d)550°C

Figure 5: PL spectra of SnO₂ films annealed in air at a)350°C and annealed in Oxygen at b)350°C c)450°C d)550°C

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