CHAPTER 3
PREPARATION, CHARACTERIZATION AND OPTIMIZATION OF TIN OXIDE (SNO₂) AND ANTIMONY DOPED TIN OXIDE (ATO) THIN FILMS

3.1 PREPARATION, CHARACTERIZATION AND OPTIMIZATION OF TIN OXIDE (SNO₂) THIN FILMS

3.1.1 Introduction

The potential applications of optical gadgets such as Photovoltaic, optoelectronic and other related energy device applications demand highly transparent conducting oxide (TCO) films with high transmission, low sheet resistance, high uniformity and larger substrate area. To accomplish these requisites the search for materials are explored and among them tin oxide (SnO₂), a direct band gap semiconductor with n-type conduction, is found to be promising in material research. In addition, due to the existence of intrinsic defects, it has been widely used in many applications as photo catalysis, transparent conducting electrodes for plat panel displays and solar cells, gas sensors and as oxidation catalyst [1-4]. The use of polycrystalline SnO₂ film, as transparent electrodes and solid state gas sensor, is gaining much interest owing to its electrical properties intricacies with crystalline size. Thus the wide window of applications of SnO₂ are explored by many researchers by employing different physico-chemical methods by keeping in mind the relevance of its end use for device applications. In this regard a few excerpts of reviews are presented.

Digiulio et al. [5] investigated on the growth and characterization of tin oxide thin films prepared by reactive sputtering. The optical observation results of their studies at different annealing temperatures indicate that the incident photon energy
range is lying between 3 and 5.5 eV for both direct and indirect transitions. The results on the variation of the Hall mobility and conductivity with the annealing temperature is studied by them and revealing increase in the grain size, and the decrease in the oxygen vacancies after heat-treatment.

Gorley et al.[6] carried out the tin dioxide (SnO₂) thin films deposited by reactive magnetron sputtering technique and found that the pre-heating of the substrate to \( T = 473 \text{K} \) before the deposition of SnO₂ films decreases the material defect level, and together with further annealing in the air at \( T_a > 700 \text{K} \) leads to significant decrease of specific resistivity of the film down to the values of \( 1.5 \times 10^{-3} \) to \( 6 \times 10^{-4} \ \Omega \text{cm} \), while increasing optical transmission of the film up to 90–95%.

The spray pyrolysis via deposited tin oxide films from inorganic precursors by Amma et al. [7] reported that the Structural, electrical and optical studies as a function of substrate temperature and the precursors. Their findings indentify that improved electrical and optical properties are achieved while changing the precursor SnCl₂·5H₂O in the place of SnCl₂·2H₂O.

Sanon et al.[8] studies on the tin oxide films prepared by chemical vapour deposition and could observed that the preferred orientation [101] has not changed until to the substrate temperature reached 350⁰C, but change in orientation to [200] beyond 350⁰C.

Guorui Dai et al.[9] have studied the tin oxide thin films deposited on si wafer by ArF excimer laser assisted chemical vapor deposition. The results remark that the films deposited at room temperature are found to be amorphous and the larger grain size of the films after annealing is also noted by them. The optical studies on the SnO₂ thin film with 90% transmittance show that the absorption edge at 355 nm and the calculated energy gap of 3.49 eV asserts its presence.
Yadav et al.[10] have studied the tin oxide thin film prepared by chemical reactive evaporation method for various substrate temperatures and also for post deposition heating for 30 min. The post deposition heated films showed decrease in transmittance and increase in band gap, refractive index and sheet resistance.

The photoluminescence properties of SnO$_2$ thin films grown by thermal chemical vapor deposition have been investigated by Jeong et al.[11] for different substrate temperatures. The authors inferred that the crystallinity of the grown thin films increased with increasing substrate temperature. The PL studies at 6K observes two broad peaks related to oxygen vacancies and structural defects.

Varghese et al.[12] reported that the SnO$_2$ films deposited from inorganic precursors via sol–gel dip coating method have been found to be highly sensitive to ethanol vapor. The researchers found that the films showed fast response and recovery times. The dependence of grain size of the films on the nature of the substrate and the associated effect on sensitivity has been noted.

Chung et al.[13] reported the optical and electrical characteristic properties of dual ion beam sputtered SnO$_2$ thin films. The findings on conductivity reveal that the as-deposited films depend strongly on target material and bombardment energy. It is also observed that the resistivity shows very good step change in optical band gap and after the heat treatment above 400°C.

Chen et al. [14] studied the tin oxide thin films deposited on Si (100) substrates at room temperature using pulsed laser deposition techniques with a sintered cassiterite SnO$_2$ target and subsequently heat-treated. X-ray diffraction and scanning electron microscopy results demonstrated that the as-prepared thin films consisted of an amorphous matrix as well as plume-like features, which are shown
many micropores. The group also reported that the thin films that are heat treated for 2 h at 150 °C has tetragonal rutile nanocrystalline SnO2 structures.

Minami et al. [15] have investigated the SnO2 thin films by radio frequency (RF) magnetron sputtering under an external D.C magnetic field. When the films are on the unheated substrates (T≤90°C), the noted that lowest Resistivity is 1.9 x10⁻³ ohm cm the sheet resistance observed is less than 200 Ω/ . The average transmittance less than 85% in the wavelength range (400-700 nm) on the glass substrate is noted.

Having gone through the various techniques and the mode of preparation and optimization of SnO2 films by the number of investigators, the researcher identifies that only a few works by employing the electron beam evaporation technique have been attempted for their end use in device applications. Further, the researcher remarks that even the versatile electron beam evaporation technique also gives forth some deficiencies that (i) the tin oxide molecules decompose in the gaseous state when evaporated in vacuum and depositing as the amorphous or polycrystalline suboxide structure depending on the substrate temperature and the time of deposition. (ii) In addition, the electron beam evaporation technique wherein the coating chamber is kept in high vacuum so that there is insufficient oxygen available to produce SnO2 films. These draw backs could not give the expected transparency and conductivity. To improve these draw backs the systems should be subjected to annealing process. Hitherto in the present investigation, impact of annealing temperature on SnO2 film prepared by electron beam evaporation technique has been attempted with the view to obtain perfect TCO films by way of understanding their structural, optical and electrical properties.
3.1.2 Experimental details

3.1.2.1 A quick view on Electron beam evaporation technique.

Thin film deposition of metallic, insulating, conductive and dielectric materials plays an important role in a large number of manufacturing, production and research applications. Resistance heating, sputtering and electron beam are the processes most widely used for the deposition of thin film. Techniques employed to perform these processes differ in degree of sophistication and quality of film produced. A resistance-heated evaporation source is relatively simple and inexpensive, but the material capacity is very small. Sputter deposition can be used to coat large areas and complex surfaces in production coating environments utilizing time and power for rate control. Electron beam evaporation is the most versatile means of vacuum evaporation and deposition. This technique allows the production of thin film coatings from pure elements, including most metals, as well as numerous alloys and compounds.

3.1.2.2 Working mechanism with schematic representation

The coating process begins under a vacuum of 1CT$^5$ torr or less. A tungsten filament inside the electron beam gun is heated. The gun assembly is located outside the evaporation zone to avoid becoming contaminated by evaporant. When the filament becomes hot enough, it begins to emit electrons. The electrons from the beam which are deflected and accelerated toward and then focused on the material to be evaporated by means of magnetic or electric fields. When the electron beam strikes vaporizes the target material. The energy level achieved in this manner is quite high-often more than several million watts per square inch. Due to the intensity of the electron beam, the evaporant holder must be water cooled to prevent it from melting.
This versatile electron beam evaporation technique has been employed for the preparation of TCO films.

![Schematic diagram of Electron beam evaporation](image)

**Figure 3.1.1 Schematic diagram of Electron beam evaporation**

The tin oxide thin films were prepared by aforesaid EBE method. The co-precipitated powder was calcinated at 500°C for 1 hour, then palletized and used as source material for evaporation. The vacuum chamber was evacuated to a base pressure of 5x10⁻⁵ mbar. The glass slides were used as substrates. The substrates were cleaned using liquid detergent. Further it was agitated ultrasonically in acetone after cleaning with distilled water. The substrates were heated and the temperature was measured using a thermocouple which was in contact with the substrate holder and the substrate temperature was kept at 250°C during the film coating processes. The film thickness was measured using stylus profilometer. The structural properties of
the as-deposited and annealed films have been studied by X-ray diffractometer
(PANalytical-X’pert pro, Cu Kα radiation at λ=0.15418 nm) in the 2θ range 10-80°.
Morphological features have been analyzed through PicoSPM Picoscan 2100 atomic
force microscope (AFM). The photoluminescence (PL) was recorded using a Carry
Eclipse fluorescence spectrometer (VARIAN) employing PbS-Photo detector and a
150 W Xe arc discharge lamp as the excitation light source. Optical transmission in
the wavelength range of 250-2500 nm relative to air of all films was determined using
a UV-VIS-NIR double beam spectrophotometer (Carry 500- VARIAN). The sheet
resistance of the films was measured by a four probe method.

3.1.3 Results and Discussion

3.1.3.1 Structural studies

Fig. 3.1.2 illustrates the XRD pattern of deposited and annealed in air with
different temperatures. The XRD patterns of as-deposited and annealed films at 350°C
only show broadening feature, indicating that they are in amorphous nature. The films
annealed at and above 400°C reveal that films are polycrystalline in nature. Tin oxide

![Figure 3.1.2 X-Ray diffraction pattern for the as deposited and annealed SnO₂ films.](image)

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nucleation started at 400°C and attained SnO₂ structure could also be seen very clearly with the X-ray diffraction pattern. In sample c and d, randomly oriented Tin oxide crystallite formation initiates that plans corresponding to (110), (101) and (211) appear with very weak intensities. The presence of broad and weak peaks refer that SnO₂ has a very small crystalline size. In other words SnO₂ particles are semicrystalline in nature [16]. At the higher annealing temperature, the angular positions of Bragg reflections (110),(101),(200),and (211) (Fig.3.1.2(d, e and f)) correspond well to the standard XRD pattern of tetragonal SnO₂ are observed, but the (101) is the strongest among the plans. Consequently the number and the intensity of peaks increase with annealing temperature. The presence of a large number of vacant lattice sites and local lattice disorders might have led to the obvious reduction or even the disappearance in intensities of XRD peaks to lattice planes such as (220), (310), (112) and (301). The disappearance and reduction in intensities of XRD peaks of some lattice planes ascribing the presence of vacant lattice sites, destroying regular periodicities in some crystal planes and local lattice disorders [17].The microstructural parameters of tin oxide thin films as deposited and annealed are presented in table 3.1.1

<table>
<thead>
<tr>
<th>Annealing temperature(°C)</th>
<th>Lattice parameters</th>
<th>Crystallite size(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(Å)</td>
<td>c(Å)</td>
</tr>
<tr>
<td>As-Deposited</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>400</td>
<td>4.695</td>
<td>3.228</td>
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<tr>
<td>450</td>
<td>4.779</td>
<td>3.191</td>
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<tr>
<td>500</td>
<td>4.777</td>
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</tr>
<tr>
<td>550</td>
<td>4.746</td>
<td>3.193</td>
</tr>
<tr>
<td>JCPDS(41-1445)</td>
<td>4.738</td>
<td>3.187</td>
</tr>
</tbody>
</table>

Table 3.1.1 Microstructural parameters of SnO₂ films by electron beam evaporation.
Figure 3.1.3(a) and (b) show AFM deflection images of SnO$_2$ films as deposited and annealed at 550°C for 1 h in air atmosphere. The images illustrate that the sizes of the nodules increase from 35 to 60 nm which observed at the surface with annealing temperature. The area of the this surface decreases yielding the grain sizes increase as the result of increase in annealing temperature which is reflected in the size variation of nodules also. Further an important observation, rather characteristic of the studied sample is concerned that the observed grain sizes are found to be much higher than those grain sizes observed by XRD. Since XRD offers the grain thickness normal to the films whereas AFM gives the image of the film surface, it may be considered that the grains are not spherical, or they are spherical but they are larger at the surface of the film.

3.1.3.2 Photoluminescence studies

The room temperature excitation and emission spectra for the SnO$_2$ thin films prepared on glass substrates with thickness 340 nm as-deposited and annealed at
different temperatures are shown in fig 3.1.4. In fig. 3.1.4 insert shows the excitation spectrum of SnO₂ thin films under an emission of 398 nm. There exist two emission bands from the emission spectrum, with strong peak at 398 and a weak peak near 430 nm. Earlier reports have indicated that SnO₂ thin films exhibit a broad dominant peak near 396 nm (about 3.14 eV), which has been assigned to all the luminescent centers, such as nanocrystals and defects in the film [18]. However, in the present case, the observed weak violet emission peak near 430 nm can be ascribed to the luminescence centers formed by such tin interstitials or dangling in the present SnO₂ thin films [19]. The emission at 398 nm can be attributed to electron transition mediated by defects levels in the band. The observed variations in PL emission intensity with the change of annealing temperatures are shown in fig. 3.1.5. As the annealing temperature increases from 350 to 550°C, the particle size of SnO₂ films becomes larger (3.6 to 12 nm). The decrease in PL intensity in the luminescence spectra at 398 nm resulting from the reduction of both the ratio of surface area and the concentration of oxygen
vacancies found (shown in fig. 3.1.5). Reduction of concentration of oxygen vacancies is owing to in-diffused oxygen recombining with oxygen vacancies [20].

![Graph showing temperature dependence of relative luminescence intensity at 398 nm.](image)

**Figure 3.1.5** Temperature dependence of relative luminescence intensity at 398 nm.

3.1.3.3 Optical studies

The information concerning the optical transmittance is found to be very important for evaluating the optical performance of conducting oxide films. A high transparency for the SnO$_2$ thin film in the visible region as a transparent electrode is required for optoelectronic devices.

Fig. 3.1.6 show the wavelength dependence of optical transmittance spectra of SnO$_2$ thin films deposited on glass substrates. The films show good adhesion with poor transmittance of about 35% in the visible region. These films have become more transparent after annealing at different temperatures and show standard fringes. The increase in the transparency is likely due to the reestablishment of the stoichiometric of SnO$_2$ through the incorporation of oxygen. The high temperature annealing leads to the films with a steeper optical absorption curve, which indicates a better crystallinity.
Figure 3.1.6 Transmission spectra of tin oxide films with different annealing temperatures.

of the films and lower defect density near the band edge. The increase in optical transmittance with temperature can be attributed to the increase of structural homogeneity and crystallinity [21]. Furthermore, there is a shift in the absorption edge to shorter wavelength with increasing of annealing temperature, which is due to the Burstein-Moss shift [22]. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, is used to determine the nature and value of the optical band gap. The relation between the absorption coefficients ($\alpha$) and the incident photon energy ($h\nu$) are related by the relation [23].

\[
\frac{1}{(\alpha h\nu)^n} = A[h\nu - E_g]
\]

(3.1)

where $A$ is a constant and $E_g$ is the band gap of the material and the exponent $n$ depends on the type of transition. For direct allowed transitions $n = 1/2$, for indirectly
Figure 3.1.7 Variation of $(a\nu v)^2$ with photon energy for tin oxide films with different annealing temperatures.

allowed transitions $n = 2$, and for directly forbidden transitions $n = 3/2$. To determine the possible transitions, $(a\nu v)^{1/n}$ versus $\nu$ are plotted and the corresponding band gaps are obtained from extrapolating the straight portion of the graph on $\nu$ axis at $a = 0$ (shown in fig. 3.1.7). The calculated direct optical band gap energy as a function of

<table>
<thead>
<tr>
<th>Annealing temperature(°C)</th>
<th>Band gap (eV)</th>
<th>Transmittance At 550 nm(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited film</td>
<td>3.64</td>
<td>35</td>
</tr>
<tr>
<td>350</td>
<td>3.74</td>
<td>82</td>
</tr>
<tr>
<td>400</td>
<td>3.77</td>
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<tr>
<td>500</td>
<td>3.83</td>
<td>85</td>
</tr>
<tr>
<td>550</td>
<td>3.89</td>
<td>88</td>
</tr>
</tbody>
</table>

Table 3.1.2 Optical band gap energy ($E_g$) and Transmittance (%) at 550 nm for as-deposited and annealed SnO2 thin films.

the annealing temperature of the SnO2 films are listed in table 3.1.2. It is noted that $E_g$ increases with increasing annealing temperature and its maximum value of 3.91 eV is
found at the temperature of 550°C. The increase in optical band gap energy is due to
the increase in film transparency, which is related to the improvement of homogeneity
and crystallinity of the SnO₂ film [24, 25].

3.1.3.4 Electrical studies

The electrical resistivity (ρ) of SnO₂ is found to be decreasing with the growth of the
annealing temperature (350-500°C) in the present study elucidates the formation of
more number of grains which improves the periodicity of the planes. It is well seen
that the growth of strong intensity of peaks can be smelt from 450 and 550°C (in fig.
3.1.8) in the annealing XRD spectra may be due to the improvement of crystallinity
of the SnO₂ film leading to increase in carrier concentration resulting in better
conductivities are observed in this study. In other words lower annealing temperature

![Graph showing variation of resistivity with annealing temperature](image)

**Figure 3.1.8 Variation of electrical resistivity (ρ) with different annealing
temperature of SnO₂ thin films**

in our case below 400°C is obviously seen in the XRD profile that is amorphous
(lower thermal energy) whereas above 400°C the fine grain are increased and formed
in the preferred orientation as it is seen due to the growth of (200) planes. It is reasoned that the increase in mobility of the charge carriers are due to the increase in the crystallinity of the film. The decrease in the magnitude of the conductivity at the lower annealing profile is due to the schottky barriers at the grain boundary resulting in lower conductivity. On the other hand the reduction of schottky barrier at higher annealing temperatures provides higher mobility for charge carriers and this paves the way for the increase in conductivity.

Devices using transparent conductors require high electrical conductivity and optical transmission. Thus, Scropp [26] suggested a figure of merit \((F)\), which is a

![Figure 3.1.9 Variation of figure of merit \((F)\) with different annealing temperatures](image)

properly chosen combination of conductivity and transmission. It has been observed that the performance of such devices has improved as higher values have been obtained for \(F\), defined as follows:
\[ F = -\frac{1}{(\rho \ln T)} \]  

(3.2)

where, \( T \) is the transmittance and \( \rho \), the electrical resistivity. In fig. 3.1.9 shows the highest value of figure of merit \( 6.1 \times 10^2 \, \Omega^{-1} \, \text{cm}^{-1} \) is obtained for the film annealed at \( 550^\circ \text{C} \) for 60 mins in air.

### 3.1.4 Conclusion

Transparent and conducting nanocrystalline SnO\(_2\) thin films (340 nm thickness) have been prepared by electron beam evaporation method. The structural, morphological and optical properties of the films are studied as a function of annealing temperature. The XRD and AFM results show that the crystallinity of SnO\(_2\) thin films is improved with annealing temperature. The room-temperature PL spectra of SnO\(_2\) films show that the relative intensity of emission decreases with increasing annealing temperature. This is due to the decrease of the defects of the film, such as oxygen vacancies and Sn interstitials in the films. The optical band gap energy of SnO\(_2\) thin films are shifted from the bulk value is related to the improvement of homogeneity and crystallinity of the SnO\(_2\) film. The results also show that by increasing annealing temperature, the sheet resistance of SnO\(_2\) thin films is decreased which related to the increase of the mobility and carrier density. The highest value of figure of merit \( 6.1 \times 10^2 \, \Omega^{-1} \, \text{cm}^{-1} \) is obtained for the film annealed at \( 550^\circ \text{C} \). Thus annealing temperature for the system adopted plays a major role for optimizing the structural, electrical and optical properties of the SnO\(_2\) films has been realized.

The some optimized films are selected for Ethanol sensor applications

(i) 350\(^\circ\text{C}\) annealed film (ii) 500\(^\circ\text{C}\) annealed film

The content of the work published in "*Journal of material science and materials in electronics*".
3.2 PREPARATION, CHARACTERIZATION AND OPTIMIZATION OF ANTIMONY DOPED TIN OXIDE (ATO) THIN FILMS

3.2.1 Introduction

The search for new innovative materials for applications has created a platform for electrically conducting highly transparent thin films which have great promise for use in optoelectronic devices. Tin oxide (SnO₂) is an interesting semiconductor having a wide band gap (3.6 eV) and the highest carrier mobility among the oxide materials [27]. Owing to the inherent wide band gap the material has its absorption edge beyond the VIS spectral region [28]. SnO₂ is stable within a broad spectrum of high temperatures and shows excellent resistance to strong acids and bases. Its mechanical integrity is exemplified by good adhesion to many types of substrates [29]. The desirable properties of SnO₂ has led many researchers to study the pure and doped films and to evaluate its use as electrodes in thin-film photovoltaic solar cells [30]. Thus the wide window of applications of antimony doped-SnO₂ films are attempted to achieve high conducting and high transmittance by using different preparation techniques by many researchers by employing different physico-chemical methods by keeping in mind the relevance of its end use for device applications. A few excerpts of some selected reviews are presented.

E.S. Rembeza et al[31] reported the SnO₂ thin films doped with Sb (ca. 3%) are deposited on glass and silicon substrates by magnetron sputtering and heat-treated by laser or isothermal treatment. It is found that the tin oxide films consisted only of the SnO₂ tetragonal phase; and are well crystallized and no microstructural defects are observed.

Lee and Park [32] have studied the antimony-doped tin oxide (SnO₂:Sb) thin films are fabricated by an ultrasonic spray pyrolysis method. The SnO₂ thin film has a
preferred (211) orientation, but as the Sb-doping concentration increased, a preferred (200) orientation is observed. The grain size decreased with the Sb-doping concentration, and the lowest resistivity (about 8.4×10−4 Ω cm) is obtained for the 3 at.% Sb-doped films. The transmittance level in the near infrared region is lowered with the Sb-doping concentration.

Wanget et al.[33] investigated the antimony-doped tin oxide (SnO$_2$:Sb) films have been prepared on glass substrates by RF magnetron sputtering method. The prepared samples are polycrystalline films with rutile structure of pure SnO$_2$ and have preferred orientation of (110) direction. An intensive UV-violet luminescence peak near 392nm is observed at room temperature. The photoluminescence (PL) properties influenced by sputtering power and annealing for the SnO$_2$:Sb films are investigated in detail and corresponding PL mechanism is discussed.

Leite et al.[34] have studied the doped and undoped SnO$_2$ thin films by dip coating method. The addition of Sb ion is found to control the grain size and electrical conductivity of the SnO$_2$ thin film, resulting in a nanostructured material. The nanostructured Sb-doped SnO$_2$ thin films present the high electrical conductivity, even in the presence of high porosity, supporting the hypothesis that nanostructured material must possess strong electrical conductivity.

Outemzabet et al.[35] studied and reported the antimony doped tin oxide thin films fabricated by chemical vapour deposition. The films exhibit the usual cassiterite diffraction pattern with high crystalline structure. The surface morphology is found to be independent on the nature of the substrate. The microstructure of the films, the grain growth topics depend strongly on deposition conditions and doping concentration are observed. The observed variations of both the resistivity $\rho$ and
transmittance $T$ are correlated to antimony atoms concentration which induced variation in the microstructure and in the size of SnO$_2$ nanograins.

Liu et al. [36] have carried out the tin oxide (SnO$_2$) thin films, deposited by plasma-enhanced chemical vapor deposition (PECVD). The results show that the films are porous and the crystalline structure transforms from crystalline to amorphous phase as the deposition temperature changes from 500$^\circ$C to 200$^\circ$C, and the chemical component is non-stoichiometric. Sheet resistance of the thin films decreases with increasing of deposition temperature. Tin oxide doped with antimony (SnO$_2$:Sb) thin films prepared by same method have a better selectivity to alcohol than to carbon monoxide; the maximum sensitivity is about 220%. The gas-sensing mechanism of SnO$_2$ thin films is commentated.

Elangovan and Ramamurthy [37] have studied the optical properties of spray deposited antimony (Sb) doped tin oxide thin films, as a function of antimony doping concentration. The films are polycrystalline in nature with tetragonal crystal structure. The doped films are degenerate and n-type conducting. The lowest sheet resistance is achieved for 2 wt % of Sb doping. The transmittance of the films is observed to increase from 42% to 55% (at 800nm) on initial addition of Sb and then it is decreased for higher level of antimony doping.

Zhang et al. [38] investigated the undoped and antimony-doped tin oxide (ATO) thin films prepared by sol–gel process in the solution of metal salts of tin (II) chloride dehydrate and antimony tri-chloride. The findings reveal that the heat-treatment temperature and doping level have strong influences on the microstructure and composition of Sb:SnO$_2$ films. The SnO$_2$ crystals existed mainly as the tetragonal rutile structure in the present work. The optimum heat-treatment temperature was about 450–500$^\circ$C, and the film is composed with nano-crystals and nano-pores.
Comparing with undoped tin oxide, doped antimony tin oxide films coated glass substrate found to have homogeneous in composition and morphology after being sintered at different temperatures.

Shokr et al.[39] have studied the undoped and Sb-doped SnO$_2$ films deposited by electron beam evaporation from bulk samples prepared using sintering technique. The investigator observes that the increasing Sb content, the resistivity slightly decreases and then increases with further addition of Sb, rather acts as either donor and/or acceptor impurity atom in the SnO$_2$ lattice. The doping of Sb inside the SnO$_2$ lattice is associated with the increase in the film transmission at solar maximum wavelength and the width of optical band gap; which were interpreted in terms of the interaction between the two oxidation states of antimony, Sb$^{3+}$ and Sb$^{5+}$ and the increase of atomic bond energy, respectively.

Ma et al. [40] reported that the antimony-doped tin oxide (SnO$_2$:Sb) films prepared radio frequency magnetron-sputtering technique at low substrate temperature (30–220$^\circ$C). The polycrystalline SnO$_2$:Sb films having the rutile structure is deposited with resistivity as low as 3.7x10$^{-3}$ $\Omega$ cm on the polyimide substrate and 2 10$^{-3}$ $\Omega$ cm on the glass substrate. The average transmittance exceeded 70.6 and 85.5% in the visible spectrum for 285 and 315 nm thick films deposited on polyimide and glass substrate, respectively are noted.

These reviews complement the importance of techniques to be employed and also the furnishing various factors influencing the preparation and characterization of ATO film. With the basic glancing outlook, the preparation, characterization and optimization of antimony doped tin oxide films has been investigated.
3.2.2 Experimental details

Antimony (1 at. %)-doped tin oxide thin films were prepared by the electron beam evaporation method. A co-precipitated powder was calcinated at 500°C for 5 h, and then palletized and used as source material for evaporation. The vacuum chamber was evacuated to a base pressure of 5 x 10^{-5} mbar. Glass slides were used as substrates. The substrates were cleaned using a liquid detergent, was and then agitated ultrasonically in acetone before rinsing with distilled water. The substrates were heated and the temperature measured using a thermocouple which was in contact with the substrate holder and the substrate temperature was kept at 250°C during the film coating processes. The film thickness was measured using stylus profilometer. The structural properties of the as-deposited films have been studied by X-ray diffractometer (PANalytical-X’pert pro, Cu Kα radiation at λ=0.15418 nm) in the 2θ range 10-80°. The morphological features have been analyzed through PicoSPM Picoscan 2100 atomic force microscope (AFM). The chemical state of the elements in the ATO thin films were analyzed by XPS spectra using a Multilab 2000 X-ray Photoelectron spectroscope. The photoluminescence (PL) was recorded using a Carry Eclipse fluorescence spectrometer (VARIAN) employing PbS-Photo detector and a 150 W Xe arc discharge lamp as the excitation light source. The optical transmission in the wavelength range of 300-1000 nm relative to air of all films was determined using a UV-VIS-NIR double beam spectrophotometer (Carry 500- VARIAN).

3.2.3 Results and discussion

3.2.3.1 Structural studies

The XRD patterns of the ATO thin films as deposited and annealed at different temperatures 400, 450, 500, and 550°C for 90 min, recorded in air, are shown in Fig. 3.2.1(a). The XRD patterns associated to 400°C show formation of
predominant amorphous structure, and those formed at 450°C whereas the reflections observed through tetragonal crystallographic phase of the ATO are clearly found. These reflections are progressively intense and sharper at higher annealing temperatures. All these peaks positions are well agreed with the standard ATO tetragonal structure [JCPDS card no. 88-2348]. No phase ascribed to the antimony compounds is detected in the XRD spectra suggesting that all the antimony ions might have been accommodated into the lattice of the tin oxide as a substitute for tin ions [41]. The intensity distributions of these reflections reveal that the films are having the largest preferred crystallographic orientation along the (110) diffraction plane. This preferred orientation along the (110) plane are observed by researchers for ATO films prepared by RF sputtering [42] and plasma-enhanced chemical vapour deposition [29]. The lattice parameters (‘a’ and ‘c’), grain size (D), dislocation density (\(\delta\)), cell volume (v), and strain (\(\varepsilon\)) [43] are calculated for the (110) prominent reflection plane and presented in Table 3.2.1. The lattice constants ‘a’ and ‘c’, are found to well agree with the bulk (a=4.73 and c=3.18) values. The grain sizes of the
films are found to increase with the increase in annealing temperature is mainly due to the increase in the thermal energy for crystallization, recrystallization and growth of grains in the films. The structural parameters, such as dislocation density (δ) and micro-strain (ε)

Table 3.2.1 Structural parameters of ATO thin films annealed at different temperatures (T_A).

<table>
<thead>
<tr>
<th>T_A (°C)</th>
<th>d (Å)</th>
<th>[hkl]</th>
<th>(Å)</th>
<th>D</th>
<th>V</th>
<th>δ x 10^15</th>
<th>ε x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>450</td>
<td>26.56</td>
<td>3.3533</td>
<td>110</td>
<td>4.74</td>
<td>3.19</td>
<td>146</td>
<td>71.88</td>
</tr>
<tr>
<td>500</td>
<td>26.57</td>
<td>3.3510</td>
<td>110</td>
<td>4.74</td>
<td>3.19</td>
<td>208</td>
<td>71.83</td>
</tr>
<tr>
<td>550</td>
<td>26.56</td>
<td>3.3530</td>
<td>110</td>
<td>4.73</td>
<td>3.18</td>
<td>256</td>
<td>71.63</td>
</tr>
</tbody>
</table>

are found to show a decreasing trend with increase in the annealing temperature might be resulting due to the reduction in lattice imperfections.

The preferential orientation of the films is studied by calculating the texture coefficient TC (h k l) for all the planes using the equation [44].

\[
TC(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{N} \sum(I(hkl)/I_0(hkl))}
\]  

(3.3)
where $TC(h \ k \ l)$ is the texture coefficient of the $(h \ k \ l)$ plane, $I$ the measured intensity, $I_0$ the JCPDS standard intensity of the corresponding powder and $N$ is the number of reflections observed in the X-ray diffraction pattern. The variations in

![Image](image.png)

**Figure 3.2.2(b) Variation of texture co-efficient with annealing temperature**

texture coefficient are calculated for all the diffraction peaks of ATO films, i.e. (110), (100), (200) and (211) planes (Fig. 3.2.2 (b)). It is observed that the (110) plane is having high texture coefficient of 1.59 when annealed to 550°C whereas it is low and tends to decrease linearly for (211) plane which suggests that the maximum preferred orientation of the films along the (110) diffraction plane is associated with the increased number of grains along that plane.

Fig. 3.2.3 (a) and (b), represent AFM images of ATO films, doped with 1 at.% of antimony as deposited and annealed at 550°C for 90 min. It is found that as deposited films show smooth whereas rougher surfaces with better grains are observed at 550°C. This reveals that the increase in annealing temperature improves the crystallinity of films. The average roughness of the films is found to be 14.7nm
and 17.2nm respectively for images (a) and (b). The observed grain sizes are found to be much higher than that of those measured by XRD. The XRD and AFM studies

![AFM images](image)

**Figure 3.2.3** AFM image of ATO thin films (a) as-deposited (b) annealed at 550°C.

reasonably justify that the grains are not spherical, or are spherical but they are larger at the surface of the film.

### 3.2.3.2 X-ray photoelectron spectroscopy (XPS) studies

Fig. 3.2.4 (a) shows the XPS survey scan spectra of the ATO films annealed at 550°C. It is noted that the binding energies of Sn3d_{5/2}, Sn3d_{3/2} and O1s respectively to 486.15, 494.6 and 530 eV, are consistent with the reported results [45]. The binding energy 8.4 eV obtained between the Sn3d_{5/2} and Sn3d_{3/2} doublet levels is assigned to Sn in SnO_2, SnO (or) Sn. Due to the low doping concentration of Sb, no trace of peak is observed for Sb 3d_{3/2} in the survey spectra. The Sb 3d_{5/2} peak is found in the region of O1s peak because of its binding energy (530.3 eV) lying close to the binding energy of O1s which is deduced from Gaussian fit. The image (b) illustrates the binding energy of Sb 3d_{5/2} 531.07eV which indicates the presence of Sb^{+5} state in Sb_2O_5.
Figure 3.2.4 XPS survey scan spectra of antimony doped tin oxide films annealed at 550°C ;(a) for the whole spectra;(b) for O1s+Sb 3d5/2 XPS.

3.2.3.3 Photoluminescence studies

Fig. 3.2.5 shows the photoluminescence spectra of the ATO thin films. It is observed that blue/violet peak at 420 nm is observed for as grown and all annealed samples. This peak intensity increases gradually while increasing the annealing temperature. The blue-violet peaks found at 400 and 430 nm for undoped SnO2 are also reported by several researchers [46, 47]. Chang et al. [48] observed a blue/violet luminescence peak at 2.95 eV from undoped tin oxide powder and suggested that the origin of blue/violet luminescence peak of undoped SnO2 is due to oxygen vacancies, tin interstitial or dangling bond and structural defects. In general in polycrystalline oxide thin films/powders, oxygen vacancies are known to be the most common defects and form the donor level [49]. In this present study Sb ion doping alters the characteristic property of the host atoms by creating the acceptor and donor Sb4+ and Sb5+ which are resulting from the electron transition between the levels of these dopant ions, which might be the reason for the appearance of blue/violet peak. The
increase in peak intensity is shown in fig. 3.2.5. This may due to the annealing of the sample in atmosphere decreasing the defects and improving crystal orientation

![Figure 3.2.5 Room temperature photoluminescence spectrum of ATO thin films annealed at different temperatures.](image)

resulting in the non-radiative recombination decrease is leading to increase in the intensity of the blue/violet peak. Consequently the increase in oxidation process enhances the Sb\(^{5+}\) ions population which is led to the enhancement of blue/violet emission as shown in fig. 3.2.4.

### 3.2.3.4 Optical studies

The transmittance spectra of ATO films as deposited and annealed at temperatures 400, 450, 500 and 550°C in the air atmospheric condition are recorded. From the Fig. 3.2.6 the transmission spectra of as deposited and all annealed films are highly transparent over the visible and Near Infrared regions. The optical transmission falls very sharply near the UV region due to the onset of fundamental absorption. The spectra show the high transmission for films annealed at 550°C which is attributed to the less scattering effect, structural homogeneity and better crystallinity [50].

66
spectral shift towards the UV region may be attributed to the improved crystallinity and higher concentration of carriers [51]. Further the fundamental absorption edge is shifted towards shorter wavelength side with the increase of annealing temperature.

![Figure 3.2.6 Transmittance spectra of ATO thin films with different annealing temperatures](image)

Figure 3.2.6 Transmittance spectra of ATO thin films with different annealing temperatures

suggesting the widening of energy band gap in the films which may be due to Moss-Burstein shift [52].

Fig. 3.2.7(b) and (c) show the plot of refractive index and extinction coefficient as a function of wavelength $\lambda$ for 1 at. % antimony doped SnO$_2$ films. The transmission performance is related to the refractive index and the extinction coefficient. The refractive index $(n)$ is evaluated from the measured transmittance versus wavelength [53].

$$n^2(\lambda) = H + \sqrt{H^2 - n_0^2(\lambda)n^2_s(\lambda)}$$

$$H = \frac{1}{2}(n_0^2(\lambda) + n^2_s(\lambda)) + 2n_0n_s\left[\frac{T_{max} - T_{min}}{T_{max}T_{min}}\right]$$
Here, 'S' is the refractive index of the glass substrate (S=1.5).

The extinction coefficient (k) values are calculated using the equation:

\[ k = \frac{\alpha \lambda}{4\pi} \]  

Annealing effects on the refractive index (n) and the extinction coefficient (k) of ATO films are shown in fig. 3.2.7(a) and (b). The refractive index increased from 1.87 to 2.0 while increasing the annealing temperature 400 to 550°C may be attributed to the increase in packing density and the crystallinity of the film. The variation of absorption co-efficient with photon energy for direct band to band transition is given by the relation \( \alpha \nu = A (\nu - E_g)^n \) where \( \nu \) is the photon energy \( E_g \) is the difference between conduction and valance bands at the same electromagnetic wave length. 'n' is \( \frac{1}{2} \) for allowed transitions and \( \frac{3}{2} \) for forbidden transitions. Fig. 3.2.8 represents,
Figure 3.2.8 Variation of optical band gap with different annealing temperatures \((\alpha \text{thu})^2\) versus photon energy values for antimony doped tin oxide films. Allowed direct transitions are determined by extra plotting linear portion of the curves to zero absorption and are tabulated (Table. 3.2.2). The increase of band gap from 3.59 to

Table 3.2.2 Structural parameters of ATO thin films annealed at different temperatures (TA).

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Optical band gap(eV)</th>
<th>Refractive index(n)</th>
<th>Extinction coefficient(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited film</td>
<td>3.59</td>
<td>1.89</td>
<td>0.362</td>
</tr>
<tr>
<td>400</td>
<td>3.64</td>
<td>1.87</td>
<td>0.413</td>
</tr>
<tr>
<td>450</td>
<td>3.67</td>
<td>1.92</td>
<td>0.300</td>
</tr>
<tr>
<td>500</td>
<td>3.71</td>
<td>1.98</td>
<td>0.311</td>
</tr>
<tr>
<td>550</td>
<td>3.76</td>
<td>2.00</td>
<td>0.268</td>
</tr>
</tbody>
</table>

3.76 eV with the increase of annealing temperature is observed. The \(E_g\) values are close to that of 3.1–4.1 eV reported values [54-56]. Huang et al. reported a similar
type of variation of optical band gap with annealing temperature in RF sputtered ATO thin films. The variation of optical band gap is attributed to the improved crystallinity and higher concentrations of carriers which is leading to rise of Fermi level within the conduction in degenerate semiconductors [50, 51].

3.2.3.5 Electrical studies

The electrical resistivity of ATO films as a function of annealing temperature is shown in Fig 3.2.9(a). It is observed that electrical resistivity decreases with increase in annealing temperature. This might be due to increase in carrier concentration. At lower annealing temperature, the fine grains are formed because of a relatively lower thermal energy. However, at higher annealing temperature, the surface mobility of constituent elements increases and the growth of face grains are preferred. Hence, the increase in mobility may be due to increase in crystallinity of the films, which increases with the increase in annealing temperature is observed in the present study.

The schottky barriers at the grain boundary causes the grain boundary to show a lower

![Graphs showing variation of electrical resistivity and figure of merit with annealing temperature.](image)

Figure 3.2.9(a) Variation of electrical resistivity with different annealing temperatures and (b) variation of figure of merit with different annealing temperatures of ATO thin films.
conductivity than that found inside the grain. In other words as the annealing temperature increases which affects the schottky barriers at grain boundary causing higher mobility of charge carriers, resulting in higher concentration of carriers yielding decrease in electrical resistivity.

Devices using transparent conductors require high electrical conductivity and optical transmission. Scropp et al. [26] suggested a figure of merit \((F)\) for conductivity and optical transmission which are inversely proportional to each other. It is reported that the performance of such device is solely depend upon the improved higher values of \(F\), which is defined as eq 3.1. The figure of merit (fig. 3.2.9(b)) of the ATO films is found to increases from \(3.3 \times 10^2 \, \Omega^{-1} \, \text{cm}^{-1}\) to \(1.46 \times 10^3 \, \Omega^{-1} \, \text{cm}^{-1}\) while increasing the annealing temperature is due to the decrease in the electrical resistivity. The highest value of figure of merit \(1.465 \times 10^3 \, \Omega^{-1} \, \text{cm}^{-1}\) is noted for the film annealed at 550°C in air.

3.2.4 Conclusion

Highly transparent and nanostructured ATO thin films are prepared by electron beam evaporation technique. The structural and optical properties of these films are studied as a function of annealing temperature. The grain size increased with the enhancement of annealing temperature while cell volume \((v)\), dislocation density \((\delta)\), and strain \((\varepsilon)\) are decreased. The optical band gap energy of evaporated and annealed films obtained in the range 3.59-3.76 eV. The widening of energy band gap in the films is due to Moss-Burstein shift. The optical constants of refractive index and extinction coefficient at 550 nm decreased with the annealing temperature from 2.0 - 1.89 and 0.362 - 0.268, respectively. The results also show that by increasing annealing temperature, the electrical resistivity of In\(_2\)O\(_3\)thin films are decreased which is related to the increase of the mobility and carrier density. The highest value of figure of merit
$1.46 \times 10^3 \ \Omega^{-1} \ \text{cm}^{-1}$ is obtained for the film annealed at 550°C. Hence, it might be concluded that the effect of annealing temperature plays a pivotal role in controlling the structural, electrical and optical properties of the ATO thin films is realized in this study.

The some optimized films are selected for Ethanol sensor applications

(i) 400°C annealed film (ii) 550°C annealed film
REFERENCE


