CHAPTER - 2

REVIEW ON TRANSPARENT CONDUCTING TIN OXIDES (TOs)
AND POROUS SILICON (PSi) MATERIALS

2.1  INTRODUCTION

Transparent and conducting oxide thin films have figured prominently for many years in a wide variety of applications, such as heating elements on aircraft windows for deicing and defogging, antistatic coatings on instrument panels and electrical contacts in liquid crystals, electronic and electroluminescent displays. The high reflection in the infrared region, in conjunction with high transparency in the visible region, has been exploited to make heat-reflecting mirrors. The renewed research interest in these films in recent years stems from the possibility of fabricating large area, stable, and high-efficiency silicon based solar cell utilizing these films. Recently, to increase the junction area and reduce material cost, porous silicon (PSi) structures are developed and TO/PSi solar cells are under intense research.

A variety of techniques have been employed to deposit transparent conducting oxides. These include DC, RF and ion beam sputtering, ion plating, spray pyrolysis, CVD, electron beam and vacuum evaporation. PSi structures are formed by electrochemical and chemical routes. In this chapter various physical properties published by various researchers for SnO\textsubscript{2} and PSi are reviewed.

The undoped SnO\textsubscript{2} when fully stoichiometric in oxygen is non-conducting. However oxygen deficient undoped SnO\textsubscript{2} and SnO\textsubscript{2} doped with Sb or F are very interesting n-type semiconductors possessing specific combined electrical, optical and chemical properties.
2.2 TRANSPARENT CONDUCTING OXIDE MATERIALS

With the classical electromagnetic theory, the simultaneous occurrence of high visible transparency and electrical conductivity is anomalous. Because, when there are large numbers of charge carriers available, they give rise to high electrical conductivity and the incoming electromagnetic radiation is dissipated by heating the charge carriers. The typical example is a metal, the good conductor and a poor light transmitter.

It may be noted that partial transparency and reasonable electrical conductivity are obtainable in thin films of a variety of metals. This may be achieved by means of reducing the thickness of the metal films. The metals that have been used as transparent conductors include, Au, Pt, Rh, Ag, Cu, Fe and Ni and the typical thickness ranges between 5 to 10 nm, so that the sheet resistance of the metal films and often a trade off is required, while employing metal films as transparent conductors.

It is possible to view the anomaly of simultaneous occurrence of transparency and conductivity in a material with ideas of the quantum theory. Accordingly, the electrical and optical properties of a solid are governed by its electronic band structure. The band structure arguments may be enlightened by considering the typical types of solids, the metal and insulators. In metals, there is a high density of free electrons in the upper most partially occupied energy band with the energy levels of the electrodes closely spaced to give rise to a quasi-continuous. As a result, the transmission of visible and IR (exact wave length range depends upon the metal) radiation is arrested; the radiation is either reflected or absorbed (free earner absorption of low energy photons). Hence the metals are good electrical conductors, but poor visible light transmitters. In an insulator, the upper most occupied band is completely filled (valence band) and is separated from the empty ‘conduction band’ by a characteristic energy band gap. All the wavelengths corresponding to the energies less than the band gap will be transmitted through the material.
It is possible to induce electrical conduction in an insulator by introducing donor impurity levels close to the conduction band or acceptor impurity levels close to valence band. If the magnitude of such ‘doping’ is to the extent of creating a high carrier density comparable to that in a metal then the insulator is transformed into an electrical conductor. When this ‘heavy’ doping is done in an insulator whose band gap is greater than 3 eV, the material transmits most part of the visible radiation (1.66 eV to 3.21 eV) and hence is termed as ‘Transparent Conductors’.

There are oxides of many metals such as Tin, Indium, Zinc, Cadmium and their alloys, which possess the transparent conducting property. These metal oxides have a band gap greater than 3 eV and their non-stoichiometry (particularly in the thin film form) brings in the effects of heavy doping. Most of the studied transparent conducting metal oxides are anion deficient (i.e., Oxygen deficient) and hence are always n-type conductors. The transparent conducting metal oxides are also referred as oxide semiconductors.

Among the various transparent conducting oxide films, undoped Tin Oxide, Fluorine doped Tin Oxide (FTO) and Antimony doped Tin Oxide (ATO) thin films have considerable attraction due to their numerous applications in devices. These thin film devices include the following: resistors, transparent heating elements for aircraft and automobile window, antistatic coatings for instrument windows, heat reflecting mirrors for glass windows and incandescent bulbs, antireflection coatings, selective absorber components in solar heat collectors, gas sensors, electrodes for liquid crystal, electrochromic and ferroelectric photo conductor storage and display devices, productive and wear-resistant coatings for glass containers etc., In addition, the transparent conductors have found important uses in photovoltaic devices as window layer and/or antireflection coatings and also as one of the functions in heterojunction based silicon solar cells.

Though the oxide semiconductors are studied for quite some time, there has been a deficiency of detailed basic understanding of the material properties.
Empirical formulae have been used with various successes to explain the optical data, but very few attempts at quantitative theoretical models have been made. There are several reviews on transparent conductors that appear in the literature.

2.3 REVIEW ON TIN OXIDE, SnO\textsubscript{2} (TO)

As an undoped binary oxide – when fully stoichiometric in oxygen – SnO\textsubscript{2} is nonconducting, so in a perfect tin oxide lattice, all the charge carrying valence electrons are tightly bound to the tin and oxygen atoms. Since an activation energy of 3.7eV is required to lift the valence electrons upto the conduction band, the probability of spontaneously elevating one electron at room temperature is a negligibly small value of 3.85 x 10\textsuperscript{-64}. Since a typical film will have about 10\textsuperscript{22} atoms of tin per cm\textsuperscript{3}, each having an electron which could be promoted, the carrier density in a pure undoped fully stoichiometric SnO\textsubscript{2} film is 3.85 x 10\textsuperscript{-42} per cm\textsuperscript{3} which is practically zero. In order to make it appreciably conducting, the carrier density must be greater than 10\textsuperscript{17} per cm\textsuperscript{3}. However, the electrical conduction does result, in undoped SnO\textsubscript{2} films, due to the existence of point defects in native atoms which act as donors. This is achieved by oxygen vacancies in the lattice that can leave two unbound electrons on a tin atom or by a tin atom that may be located in an interstitial site with its valence electrons not particularly bound to any lattice point. The properties of SnO\textsubscript{2} are presented in Table 2.1.

2.3.1 LATTICE STRUCTURE OF SINGLE CRYSTAL SnO\textsubscript{2}

SnO\textsubscript{2} crystallizes with tetragonal rutile structure with space group D\textsubscript{4h}\textsuperscript{14} [P4\textsubscript{2}/mmn] [4]. The unit cell contains six atoms, two tin and four oxygen as shown in Fig.2.1. Each tin atom is at the centre of six oxygen atoms placed approximately at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms approximately at the corners of an equilateral triangle. Thus, it is the structure of 6:3 coordination.
Fig. 2.1 Tetragonal rutile structure of tin oxide (SnO$_2$)

Fig. 2.2 Ball model of a nearly perfect SnO$_2$ (110) surface
Table 2.1 Properties of SnO₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Colour</td>
<td>White or gray</td>
</tr>
<tr>
<td>Type</td>
<td>n-type</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>Direct, 3.7</td>
</tr>
<tr>
<td>Structure</td>
<td>Tetragonal rutile</td>
</tr>
<tr>
<td>Space group</td>
<td>D₄th₁₄(P₄2/mnn)</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>a = b</td>
</tr>
<tr>
<td></td>
<td>4.737</td>
</tr>
<tr>
<td></td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>3.185</td>
</tr>
<tr>
<td>Electron mobility μ (cm²V⁻¹s⁻¹)</td>
<td>10 - 40</td>
</tr>
<tr>
<td>Carrier concentration (cm⁻³)</td>
<td>10¹⁷ - 10¹⁹</td>
</tr>
<tr>
<td>Effective mass of electron (m₀)</td>
<td>0.17m₀</td>
</tr>
<tr>
<td>Melting point (° C)</td>
<td>1630</td>
</tr>
<tr>
<td>Boiling point (° C)</td>
<td>1900</td>
</tr>
<tr>
<td>Density (gm/cm³)</td>
<td>6.95</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>Parallel to c-axis</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>Perpendicular to c-axis</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
</tr>
<tr>
<td>Electron affinity (χ, eV)</td>
<td>4.85</td>
</tr>
<tr>
<td>Thermal expansion coefficient (° C⁻¹)</td>
<td>4.0 x 10⁻⁶</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Formal oxidation state</th>
<th>Formal electronic configuration</th>
</tr>
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<tr>
<td>O</td>
<td>21.23</td>
<td>-2</td>
<td>[He].2s².2p⁶</td>
</tr>
<tr>
<td>Sn</td>
<td>78.77</td>
<td>4</td>
<td>[Kr].4d¹⁰</td>
</tr>
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</table>
Atomic positions are determined by the c/a ratio and by the internal parameter \( u \). Experimental values of these parameters are \( u = 0.3064 \), \( a = 4.737 \text{Å} \), \( c/a = 0.6726 \). Each tin atom has two oxygens at a distance \( d_1 = 2ua \) and four at \( d_2 = \sqrt{2(1/2 - u)^2 + c/2a^2} \) (both distances are in the range \( 2.05 \text{Å} \)) and each oxygen is bonded to a tin atom in a planar trigonal configuration. Early studies on \( \text{SnO}_2 \) were directed at the evaluation of the band structure of oxides in the rutile family [1-3], whereas the more recent ones have addressed the comparison between the tin oxides, \( \text{SnO} \) and \( \text{SnO}_2 \), and silicon oxides [4, 5]. In agreement with experiments, these calculations show that \( \text{SnO}_2 \) exhibits a direct-forbidden gap. Its conduction band minimum is largely Sn s-like, while its valence band maximum is O-like and is localized on the pd states. Oxygen vacancies are the more common defects of bulk \( \text{SnO}_2 \) and produce a donor state at about 0.1 eV below the conduction band minimum [1].

2.3.2 SURFACE STRUCTURE OF \( \text{SnO}_2 \) THIN FILM

Tin oxide serves as an important base material in a variety of conductance-type gas-sensing devices. Tin oxide is an n-type, wide-band-gap (\( E_g = 3.6 \) eV) semiconductor with the rutile (\( \text{TiO}_2 \)) structure. The electrical conductivity of tin oxide results primarily from the existence of oxygen vacancies, which act as donors. The (110) surface of \( \text{SnO}_2 \) is energetically the most stable and the predominant crystal face found in polycrystalline samples [6].

Figure 2.2 is a ball model illustration of a nearly perfect (ideal) \( \text{SnO}_2 \) (110) surface based on the ionic radii of the ions. The small balls (green) represent \( \text{Sn}^{4+} \) cations, while the larger balls (blue) represent \( \text{O}^{2-} \) anions. All the visible tin cations are in the second atomic layer. Increased shading of the oxygen anions represents increased depth away from the surface. Several "bridging" oxygen anions have been removed from the terminal layer to represent oxygen vacancies and to give a clearer view of the normally six fold-coordinated tin cations in the second layer.
2.4 LITERATURE ON PREPARATION AND CHARACTERIZATION OF SnO₂

In 1937 Bauer [7] prepared first SnO₂ semiconductor films by heating a thin film deposited on quartz substrate in oxygen atmosphere. Jarzebski and Marton [8] have brought out an excellent review article summarizing the optoelectronic properties of SnO₂. Bosnell and Waghoene [9] have produced r.f sputtered tin oxide and indium tin oxide thin films. The structure have been investigated by transmission electron diffraction and suggested annealing at 450°C in air alters resistivity appreciably and did not alter the structure dramatically. Tadashi Ishida et al. [10] produced Tin oxide and Flourine doped Tin Oxide thin films using a new raw material Sn(CH₃)₄, O₂ containing 5 mol % of O₃ and HF acid. At a substrate temperature of 350°C, the films had properties such as sheet resistance of 1.6 and 4.5Ω/□, resistivities of 3.4 and 4.5×10⁻⁴Ω-cm, transmittance including substrates of 70% and 80% and 550nm. Optical and Electrical properties of SnO₂ thin films were studied in relation to their stoichiometric deviation and their crystalline structure by Manifacier et al. [11]. They followed two methods viz., spray method and vacuum evaporation.

Tetsuo Muraner and Mitsuo Furukoshi [12] produced transparent and conductive stannic oxide films at a relatively low temperature of 250°C from SnCl₄, H₂O and SnCl₄ H₂O₂ reaction systems by a CVD method. The impurity free films produced by two systems were analysed. X-ray diffraction and Mossbauer spectroscopy analysis were conducted on the quantities of β-Sn, α-SnO and SnO₂. The phases present depended on the oxygen concentration in the mixture of argon and oxygen in the DC/Sputtering chamber. Isomer shifts and quadrupole splitting also analyzed by Leja et al. [13]. Hall effect studies and carrier concentration were analysed on SnO₂ films prepared by reactive ion plating onto insulating substrates, by Howson et al. [14].
Advani et al. [15] carried out a thermodynamic analysis on the deposition of SnO$_2$ thin films from the vapour phase and the results indicate that the rate of deposition of SnO$_2$ is a strong function of the temperature and the ratio of the reactants. The crystallinity dependent on the substrate temperature was analysed by Sundaram and Bhagavat [16] by oxidation of stannous chloride. Manifacier and Fillard [17] thoroughly analysed the electrical properties of spray deposited tin oxide and indium doped tin oxide. The fundamental conflict between transparency and conductivity were analysed for identical thin layers prepared by different methods. The semiconductors that have large energy gaps and sufficiently high electrical mobilities and carrier concentrations to give good electrical conductivity have proved to be the oxides of indium, tin and cadmium and their alloys of these metals. This was analysed by Howson et al. [18] by producing these films by ion plating.

Srinivasa Murthy and Jawalekar [19] studied the effect of deposition parameters on the microstructure of chemically vapour deposited SnO$_2$ films. The tin oxide films were deposited onto pyrex glass substrates by oxidation of SnCl$_2$. It was found that the film uniformity and mean grain size increase with increasing deposition temperature and decreasing oxygen flow rate. They also analysed the structural properties of chemically vapour deposited tin oxide films by oxidation of SnCl$_2$ instead of SnCl$_4$. They characterized antimony doped tin oxide films for solar cell applications. A maximum figure of merit of 6.78 x 10$^{-3}$ $\Omega^{-1}$ was achieved for an antimony dopant of 3-mol % and nitrogen flow rate of 0.071 m$^{-1}$.

Lou et al. [20] studied physical characteristics of SnO$_x$ films deposited onto pyrex glass substrates by chemical vapour deposition. Temperature dependence indicates that the films deposited at 600$^\circ$C have good poly crystallinity. Prodan et al. [21] showed computer simulation of transmission electron diffraction patterns with structural considerations that $\beta$-SnO$_2$ is equivalent to the high-pressure form SnO$_2$-II. It crystallizes in a columbite-like structure under the influence of the substrate in the case of epitaxial oxidation of $\alpha$ SnO to SnO$_2$. 
SnO$_2$ thin film ethanol gas sensor has been fabricated by electron-gun evaporation by Fang and Lee [22] and their processing yielded a SnO$_2$ thin film with fine particles and good structure after proper annealing in ambient oxygen gas. Pyrolytically sprayed tin dioxide coatings were analysed by multiple angle of incidence ellipsometry by Haitjema and Woerlee [23]. They developed a methodology to determine non-ideal film parameters such as surface roughness, anisotropy and in homogeneity. At 623 nm SnO$_2$ behaved as transparent film with apparent surface roughness. Vasu and Subrahmanyan [24] studied the dependence of substrate temperature and substrate nozzle distance on spray coated SnO$_2$ films. Films of about $10^{-3}$ $\Omega$ cm resistivity and high visible transparency of about 90% were obtained at a substrate temperature of 400$^\circ$C and a substrate-nozzle distance of 30 cm. It is observed that distance plays an import role in the reaction kinetic of SnO$_2$ films.

The growth rate of SnO$_2$ films prepared from SnCl$_4$ $\cdot$5H$_2$O was observed to be higher and the resistivity was lower than for films prepared from unhydrous SnCl$_4$ by Vasu and Subramanyam [25]. Optically transparent and electrically conducting SnO$_2$ films doped with antimony and fluorine were deposited by CVD method, by the oxidation of SnCl$_2$, for solar cell applications by Jawalekar [26]. Heterojunction solar cells were fabricated by depositing it on single crystal silicon wafers. Bhagavat and Sundaram [27] studied SnO$_2$-Si heterojunctions, using n-type and p-type single crystals of silicon by CVD technique. SnO$_2$/n-Si solar cells fabricated by spray pyrolysis technique was analysed by Takao Nagotomo et al. [28]. They achieved a maximum conversion efficiency of 7.2%.

The optical characterization was made with a spectroscopic total integrating scattering instrument by Tomas Lindstrom et al. [29] in their investigation of surface roughness, in sputtered SnO$_2$ films.

Impedance spectroscopy has been used to investigate the properties of sol-gel derived ultrafine-grained tin oxide thin films by Oomman K. varghese and Malhotra [30]. A low frequency spur has been observed in the impedance diagram.
at medium and high humidity level and attributed the migration of absorbed ions towards the electrode sample contact region under the influence of electric field. Juanpena et al. [31] have studied the textural evolution and characterized, by $N_2$ adsorption and Hg porosimetry for the Sn$_2$O$_3$ films obtained by spray pyrolysis (300 - 900°C) and subjected to thermal treatments at 600 and 800°C. These materials were characterized by XRD, SEM and Energy dispersive spectroscopy (EDS).

Chitra Agashe et al. [32] have deposited transparent and conductive thin films of Sn$_2$O$_3$ by spray pyrolysis on corning substrates. Films were investigated by XRD and Seebeck measurements to study the structural and electrical transport properties. The films were polycrystalline and Sn$_2$O$_3$ cassiterite oxide phase was observed. The films were preferentially oriented along (200) and the trap densities along (310) and (101) have been calculated for the first time. Assigning the traps mainly to the grain boundaries, the grain boundary barrier height was calculated and compared with that obtained from the Seebeck measurements. Nam et al. [33] have sputter deposited 3000Å Sn$_2$O$_3$ thin films into which metallic Li (6000Å) was reacted were studied to develop a new negative electrode for thin film rechargeable Li batteries. The crystal structure and chemical composition of the Li reacted Sn$_2$O$_3$ films were characterized by XRD and AES.

Sn$_2$O$_3$ ultrafine particle thin films were deposited by the dc gas discharge activated reaction evaporation technique Sheng Yue Wang et al. [34] over four different substrates. Fused quartz, monocrystalline Si, micro crystalline glass and commercial glass. Changes in both the morphology and crystallinity of the films were studied by STEM and XRD as a function of different substrate and deposition conditions. It suggests that a high discharge voltage was necessary to obtain the films with rich crystallinity and special microstructure.

Abass et al. [35] have grown thin films of tin of thickness (500 to 1500Å) on clean glass plates by vacuum evaporation method. The as grown thin films were thermally oxidized in an open muffle furnace for a period of two hours at
The SnO$_2$ films formed exhibited the presence of p-SnO, SnO, SnO$_2$ and Sn$_2$O$_3$ oxides of tin as per XRD analysis. The majority of the exhibited peaks belong to SnO oxide. The band gap variation with thickness between 500 and 1500Å is found to be from 3.82 eV to 3.75 eV for direct and 3.35 eV to 2.75 eV for indirect transitions.

Conducting tin (IV) oxide thin films have been developed with a sol-gel method by Chul Lee et al. [36], which is a low cost process as electrode materials for solar cells. The precursor solution was made of tin iso-propoxide dissolved in isopropyl alcohol. The hydrolysis rate was controlled by the addition of triethanolamine. Dipping and spin coating technique were used to coat SnO$_2$ on borosilicate glass. The resistivity of the thin film was lower than 0.01 Ωcm and transmittance was higher than 90% in the visible range. Utriainen et al. [37] employed the conventional atomic layer epitaxy process for preparing pure SnO$_2$ thin films using SnCl$_4$ as precursors and N$_2$ as the carrier gas. By applying gas phase additives (n-hexane) or using oxygen as a carrier gas a reduced electrical conductivity was obtained. This phenomenon is associated with the modification in the grain structure or/and in the point defect concentration. To verify this, structural studies by XRD, AFM, AES and SIMS were performed. The results suggest that the variations in electrical resistivity (0.1 – 89 Ω cm) are predominantly due to variations in the carrier concentration.

Sebastian Kunju et al. [38] prepared good quality transparent conducting SnO$_2$ films by vacuum evaporation and its optical and electrical properties were investigated. The Uv-Vis transmittance of SnO$_2$ films annealed at different temperature revealed that the percentage of transmittance increased with the annealing temperature. Conducting films of SnO$_2$ prepared by RF sputtering by Advani and Jordan et al. [39] were studied for their stability following a heat treatment at 200°C in air. Auger spectroscopy was used to analyze the surface and bulk compositions both before and after the tests. The results indicated that the main changes in the film took place in the top first 400Å. This was viewed as
seriously limiting the efficiency of solar cells employing transparent window on the front surface.

SnO$_2$ thin films were prepared by a low temperature atmosphere pressure CVD method in air (Toslinomaruyana and Ikuta [40]). The starting material was tin (II) acetylacetonate. At a reaction temperature above 230°C polycrystalline thin films were obtained with a high deposition rate and the thickness about 1000 nm. The texture co-efficients show a dominant (002) orientation. Demiryont and Nieteing [41] have investigated the relationship between macroscopic and microscopic properties of SnO$_2$ films. Three kinds of SnO$_2$ films were evaluated: 1) Amorphous films deposited by thermal evaporation of SnO$_2$ powder. 2) Spray deposited SnO$_2$ films with low crystallinity. 3) Spray deposited SnO$_2$ films with high crystallinity XRD studies for structural morphological investigation and FTIR spectra for bond properties were also evaluated to define the micro-macro properties relationship. Kim et al. [42] obtained, using a rather simple CVD apparatus, transparent and conducting SnO$_2$ films through the decomposition of SnCl$_4$.5H$_2$O. The films showed good electrical properties but high chlorine content could be removed by annealing at 500K in hydrogen ambient. This has been established by AES and RBS spectroscopic results.

Digiulio et al. [43] have reported on the growth and characterization of tin oxide thin films prepared by reactive sputtering. The optical and electrical measurements have been carried out on these SnO$_2$ thin films at different annealing temperatures. Transmission electron microscopy observations have also been performed in order to analyze the evolution of the structure and morphology of the films with the heat treatment. The optical observation results indicate that in the range of incident photon energy between 3 and 5.5 eV both direct and indirect transitions take place in the analyzed films. The variation of the Hall mobility and conductivity with the annealing temperature can be ascribed to increase in the grain size and to decrease in the oxygen vacancies of the films after heat-treatment.
Gu Feng et al. [44] have prepared the nano SnO$_2$ particles by a simple sol-gel method. The samples were characterized by XRD, FTIR, UV-Visible absorption and photoluminescence spectroscopy. The as-prepared SnO$_2$ nanoparticles appear to be single phase with tetragonal crystal structure and the diameter is about 2.6 nm. The origin of luminescence is assigned to the recombination of electrons in single occupied oxygen vacancies with photo excited holes in the valance band.

Jcong et al. [45] has reported the photoluminescence properties of SnO$_2$ thin films grown by thermal CVD with different substrate temperatures. X-ray diffraction showed that the crystallinity of the grown thin films increased with increasing substrate temperature. Two narrow peaks and two broad peaks were observed from the photoluminescence measurements at 6K. The intensity and shape of the broad peaks changes with increasing substrate temperature. The origin of the broad peak at 2.4 eV was due to oxygen vacancies and of peak at 3.1 eV was related to structural defects.

Zhang et al. [46] has reported that the SnO$_2$ nanosphere with fine structure were prepared with SnCl$_4$.5H$_2$O as raw materials by a solvent thermal process. The x-ray diffraction pattern and selected area electron diffraction show that the as-prepared SnO$_2$ are well crystallised. Transmission electron microscope micrographs show that the prepared product contains nano-spheres with sizes of 50-80 nm. Magnified TEM image further reveals that the nano spheres display fine structure consisting of 2-6 nm ultrafine particles. This structure tend to have high specific surface area and favorable for the application in gas-sensitive detection. Nabi et al. [47] have presented self consistent calculations for the electronic and optical properties of tin dioxide (SnO$_2$) in the rutile structure. The calculations were performed within the local-d-approxn APW method (Fp-LAPW). The calculated electronic band structure as well as the density of states are in good agreement with experiments. The dielectric and absorption co-efficient values were calculated and compared with the available experimental data.

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Uen et al. [48] have reported on the preparation and characterization of some tin oxide films prepared by this technique (reactive evaporation) with a d.c. glow discharge of oxygen. The structures and composition of the films were characterized by Mossbauer spectroscopy, X-ray diffraction and scanning electron microscopy. The valency of tin atoms in the films determined by Mossbauer spectroscopy is mostly divalent in the samples prepared without discharge, but mostly tetravalent in the samples prepared with discharge. Measurements of electrical conductivity and Hall mobility were also carried out and the data were found to correlate with the concentration ratio \([\text{Sn}^{4+}]/[\text{Sn}^{2+}]\) determined from Mossbauer spectroscopy.

Amtouk et al. [49] have reported on the transport properties of polycrystalline tin oxide films. Device quality tin oxide polycrystalline layers deposited by spray pyrolysis technique have been characterized in terms of morphological, electrical and transport properties. The samples exhibit high values of mobility (ranging between 30 and 70 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). The behavior of the mobility reported as a function of the carrier concentration and of the size of the crystallites, reveals a transport governed by the processes at the grain boundaries. Furthermore, the behavior of the mobility with the temperature strongly suggests a transport mechanism determined by tunneling of the potential barrier existing between the grains, and rules out the importance of the thermionic emission process.

Ocampo et al. [50] have studied the effects of the carrier gas on properties of Sn0\(_2\) deposited by pyrolysis. The electrical, optical and structural properties of fluorine doped polycrystalline Sn0\(_2\), deposited by the pyrosol method using different types of carrier gas, have been investigated. Measurements of resistivity, optical transmittance X-ray diffraction and SEM microscopy have been done on a series of samples deposited at different temperatures and using oxygen or nitrogen alternatively as carrier. It has been found that samples deposited using oxygen present lower resistivity in the complete range of temperatures. The specular
optical transmittance does not depend too much on the carrier gas. The possible

correlation between the electro-optical properties and the structural properties has
been studied.

Srinivasamurthy and Jawalkar [51] have studied the structural properties of
the SnO$_2$ films prepared by the CVD technique. The films were polycrystalline
and majority of the films were found to be oriented in the (110) direction. A few
were oriented in the (200) and (101) directions. No definite correlation could be
obtained between the direction and degree of preferential orientation of the SnO$_2$
films and the deposition parameters. They seemed to vary at random. XRD data
did not show the presence of tin or SnO$_2$ in the films. The authors found a
diffraction peak 2$\theta$= 31.80 ($d$=2.814Å) in almost all the samples examined and
attribute it to Sn$_3$O$_4$.

Nagano [52, 53] have studied the films of SnO$_2$ obtained by chemical
vapour deposition on rutile single crystal SnO$_2$ and rutile (TiO$_2$) are isomorphous
with only a slight lattice misfit. The authors found that the single crystal rutile
substrate surfaces are more favourable for epitaxial growth of SnO$_2$ films and the
peak intensities are in the descending order of (100), (110) and (001).

Sanon et al. [54] have reported on the growth and characterization of tin
oxide films prepared by chemical vapour deposition. They have studied the effect
of deposition parameters on the sheet resistance of the films. They have found that
the films are highly transparent (about 90%) in the visible region and have a quite
low sheet resistance (25 $\Omega/\square$). X-Ray diffraction shows the structure to be
polycrystalline with a grain size of 57nm. The preferred orientation is (101) for the
films deposited at substrate temperature up to 350°C, after which the preferred
orientation changes to (200). The electrical properties of the films also exhibit a
change at this deposition temperature. Direct and indirect band gaps are calculated
to be 3.93 eV and 2.53 eV respectively. Degradation of the films with time has
also been studied. The figure of merit $\varphi = T^{10}/R_{sh}$ (9.4 $\times$ 10$^{-3}$ $\Omega^{-1}$ at 0.66$\mu$m)
obtained is the highest amongst the values reported for undoped tin oxide films.
Maruyama and Ikuto [55] have reported on the tin dioxide thin films prepared by a low – temperature atmospheric pressure chemical vapor deposition method in air from tin (II) acetylacetonate. At a reaction temperature above 230°C, polycrystalline thin films were obtained with a high deposition rate. When the thickness of the film is larger than 1000 nm, the texture coefficients show a dominant (002) orientation, which is independent of both substrate temperature and vapor pressure of source material. Advani and Jordan [56] have reported on the stability of SnO₂ thin films used for photovoltaic devices. Conducting films of SnO₂ prepared by RF sputtering, were studied for their stability following a heat treatment at 200°C in air. Auger spectroscopy was used to analyze the surface and bulk compositions both before and after the tests. The results so obtained, indicated that the main changes in the film took place in the first 400Å. This was viewed as seriously limiting the efficiency of solar cells employing transparent window on the front surface.

Minami et al. [57] have employed radio frequency (RF) magnetron sputtering under an external d.c magnetic field to prepare electrically conducting transparent SnO₂ films. The films were undoped and were formed on unheated substrates (T≤90°C). The lowest resistivity obtained was 1.9 x 10⁻³ ohm cm. Films with a sheet resistance less than 200 Ω/□ and an average transmittance >85% in the wavelength range 400 to 700 nm were obtained on glass substrate.

Stjerma et al. [58] have prepared non-stoichiometric SnO₂ thin films by magnetron sputtering of Sn in Ar + O₂ atmosphere onto unheated glass substrate. Resistivity, spectral transmittance and reflectance were studied as a function of sputtering parameters. Optimized conditions produced films with a resistivity of 3 x 10⁻³ ohm cm at a very low deposition rate and about 10⁻² ohm cm at 3 nm/s. The luminous transmittance observed was ~75%. Isidorsson and Granqvist [59] have prepared SnO₂ films by reactive rf magnetron sputtering under optimized conditions that led to both electronic and ionic conductivity. Interestingly Li⁺ intercalation produced electrochromism with coloration efficiency peaked in the
infrared region. Cobianu et al. [60] have reported on tin dioxide sol-gel derived thin films deposited on porous silicon. Undoped and Sb-doped SnO₂ sol-gel derived thin films have been prepared for the first time from tin (IV) ethoxide precursor and SbCl₃ in order to be utilized for gas sensing applications where porous silicon is used as substrate. Transparent, crack-free and adherent layers were obtained on different types of substrates (Si, SiO₂/Si). The evolution of the Sn-O chemical bonds in the SnO₂ during film consolidation treatment was monitored by infrared spectroscopy. By energy dispersive X-ray spectroscopy performed on the cross section of the porousified silicon coupled with transmission electron microscopy, the penetration of the SnO₂ sol-gel derived films in the nanometric pores of the porous silicon has been experimentally proved.

Djaoued et al. [61] have prepared indium tin oxide films by the computer controlled sol-gel dip coating method using both organic and inorganic precursors. They have reported that the optimized coatings exhibit a sheet resistance of around 100 Ω/cm² and an average visible solar transmittance of around 85%. The results indicate high potential of sol-gel prepared ITO films for application especially in large area devices.

Lee et al. [62] have reported on the fabrication of tin oxide films by sol-gel method for photovoltaic solar cell system. Transparent conducting tin (IV) oxide thin films have been developed with a sol-gel method, which is a low-cost process for the electrode materials of solar cell substrate. The precursor solution was made of tin isopropanoxide dissolved in isopropyl alcohol. The hydrolysis rate was controlled by the addition of triethanolamine. Dipping and spin-coating techniques were applied to coat tin oxide on borosilicate glass. The resistivity of the thin film was lower than 0.01 Ω.cm and the transmittance was higher than 90% in the visible range.
2.5 LATTICE OF DOPED TIN OXIDE (SnO$_2$:Sb, SnO$_2$:F) CRYSSELLINE MATERIALS

Higher conductivity can be attained by doping SnO$_2$ with antimony SnO$_2$:Sb (ATO) or Fluorine SnO$_2$:F (FTO). The contribution of free electrons for the increased conductivity is illustrated in Fig.2.3. Substitution of pentavalent antimony, Sb$^{5+}$ for tetravalent Sn$^{4+}$ leaves one unbound electron contributing one more electron to the conduction band as shown in Fig.2.3a. Substituting a monovalent anion F$^-$ for the divalent O$^{2-}$, a nearby tin atom is left with one excess electron, which goes into the conduction band as shown in Fig.2.3b.

Doped SnO$_2$ is an important TCO used both in displays and as a solar coating. In general, FTO is more conductive than the antimony doped tin oxide films. The widely attributed reason for this is the higher carrier mobility in FTO, which arises due to the reduction in grain boundary scattering. But, to achieve 10 ohms/square sheet resistance a film thickness of about 0.5 – 1.0 micron is necessary and this will lead to the problem of hazy or cloudy appearance in the film. SnO$_2$ is remarkably chemically stable. It can be etched only using nascent hydrogen produced from a zinc/hydrochloric acid reaction.

2.5.1 LITERATURE ON PREPARATION AND PROPERTIES OF SnO$_2$:F FILMS

Shanthi et al. [63] reported the deposition of transparent electrically conducting tin oxide and fluorine doped tin oxide films on alkali free corning borosilicate glass plates in the temperature range of 375-450°C by spray pyrolysis method. The visible transmittance and electrical resistivity of the films decreased with the increase in fluorine concentration. Increase in free carrier concentration results in decrease of transmission percentage slightly from undoped films.

Gordillo et al. [64] investigated on highly transparent and conducting SnO$_2$ thin films deposited by the spray pyrolysis techniques using tin chloride and SnCl$_4$ as pre-cursor solutions and NH$_4$F and HF as sources of doping impurities. A
ANTIMONY DOPED

Fig. 2.3a Sb-doped two-dimensional SnO\textsubscript{2} lattice

FLUORINE DOPED

Fig. 2.3b F-doped two-dimensional SnO\textsubscript{2} lattice
comparative study revealed that samples prepared using SnCl₂ and HF has lower values of resistivity than those obtained from SnCl₄ and NH₄F. SnO₂ films with resistivities of about $2.5 \times 10^{-4}$ Ωcm and transmittance greater than 90% were obtained. XRD measurements indicated that SnO₂ films, prepared from SnCl₄, have a preferential growth along (200) direction whereas samples from SnCl₂ has a tendency to grow preferentially along (101), (211) and (301) directions. The introduction of fluorine impurities in the SnO₂ samples gave rise to decrease of its resistivity by a factor of 20 without causing significant changes.

De Wall et al. [65] studied the electrical properties of fluorine doped SnO₂ films and showed that this type of coating behaves as a semi metal. The optical properties showed a high electron density of about $3 \times 10^{26}$ m⁻³. Above 200°C, thermal aging is observed particularly in vacuum which affects the D.C. resistivity slightly. Pommier et al. [66] studied the transmission and resistivity of large area fluorine doped tin oxide thin films prepared by spray pyrolysis method. The solution for coating is pulverized with a neutral gas (e.g: Nitrogen gas), so that it arrives at the substrate in the form of very fine drops.

Bruneaux et al. [67] investigated on the structural and electrical properties of polycrystalline sprayed SnO₂ films formed at 500°C in a wide concentration range ($7 \times 10^{17}$ cm⁻³ $< N_a < 4 \times 10^{20}$ cm⁻³). The characterization studies revealed that i) The grain size is in the 20-80 nm range ii) There are number of planar defects which are thought to reduce the bulk mobility of the crystallites iii) Fluorine doping increases the density of twins. The dependence of resistivity on the carrier concentration $N_a$ can be accounted for within the frame of the grain boundary scattering.

Agnihotri et al. [68] deposited thin layers of conducting (SnO₂:F) films of 3 ohm per square sheet resistance on borosilicate glass for potential applications in SIS solar cells. The layers exhibit 90% optical transmission at the solar maximum (0.5 μm). A direct allowed transition at 4.1 eV and an indirect allowed transition was also observed at 2.65 eV. A technique of marking ohmic contacts with SnO₂:
F is also given. Manifacier et al. [69] reported highly conductive and transparent thin films of SnO₂:F prepared using simple pyrolytic method. The prepared films were highly chemical resistant, transparent and conductive. This method is effective for the preparation of films, on an industrial scale, in solar energy conversion systems. For these purposes, the scattering observed in the properties of these layers should be of no practical importance.

Manifacier et al. [70] studied and prepared highly conductive and transparent thin films of SnO₂:F using the pyrolytic spray method. The electrical and optical properties of these layers are studied in relation to their dopant concentrations and their stoichiometric derivation. The films obtained by SnO₂:F layers have the best overall properties such as higher transparency and lower sheet resistance, resistivities ranging between 4 and 6 x 10⁻⁴ Ω cm with transparency exceeding 85% over the visible and near infra-red range of the spectrum. Chitra Agashe et al. [71] studied and deposited transparent and conducting thin films of SnO₂:F on alkali free corning 7059 glass substrates by spray pyrolysis. The films deposited with the optimized process have a sheet resistance of 4 Ω/□, an average visible transmission of 86% (0.4-0.9 μm) and a thickness of 0.165 μm. The electrical conductivity of the SnO₂:F films was approximately 10⁵ Ω⁻¹ cm⁻¹. The films were poly-crystalline and the oxide phase observed was SnO₂ in cassiterite structure. Since doping generally favours defect induced film growth, heavily doped films were randomly oriented. Rearrangement of grains in the films was apparent for thicker films.

Thick r.f. sputtered films of SnO₂ doped with Sb exhibit moderate optical transmission and high electrical conductivity Vossen et al. [72]. The preferred system for high transmission applications is SnO₂ : Sb which was found to be useful, stable and reproducible even in thickness as small as 50Å. Film transmission averaging 98% in the visible has been achieved with a sheet resistivity of 30 KΩ/□. The bulk resistivity of the films thicker than 300Å is 0.006 Ω cm. The resistivity increases to 0.05 Ω cm at a thickness of approximately
50Å°, because high resistivity surface layer becomes an appreciable fraction of the total film volume.

Asomoza et al. [73] have reported the resonant nuclear reaction technique to determine fluorine content in SnO\textsubscript{2} films prepared by spray pyrolysis. Singhet et al. [74] deposited SnO\textsubscript{2}:F on a thin SiO\textsubscript{x} layer grown in concentrated HNO\textsubscript{3} and on n-Si substrates with (100) orientation. X-Ray photo electron spectroscopy studies of the SnO\textsubscript{2}:F films revealed fluorine doping in SnO\textsubscript{2}. Bhardwaj et al. [75] have prepared SnO\textsubscript{2}:F films by spray pyrolysis of an alcoholic solution of SnCl\textsubscript{4} with NH\textsubscript{4}F as dopant on glass substrates. At a doping level of 1.2 wt% the lowest resistivity (about 5.4 x 10\textsuperscript{-4} ohm cm) and the highest figure of merit (about 10\textsuperscript{-2} ohm\textsuperscript{-1}) were obtained. A direct band gap of 4.27 eV and an indirect band gap of 2.73 eV were deduced from optical data.

Krishnakumar et al. [76] have prepared highly conducting transparent fluorine doped tin oxide films on glass substrates by employing SnCl\textsubscript{2} by spray pyrolysis from alcoholic solutions. Ma et al. [77] have presented the structural, electrical and optical properties of transparent conducting F-doped textured SnO\textsubscript{2} films prepared by atmospheric pressure chemical vapour deposition (APCVD). Polycrystalline SnO\textsubscript{2}:F films having a variable preferred orientation have been obtained with resistivity as low as 5 x 10\textsuperscript{-4} ohm cm with carrier concentration between 3.5 x 10\textsuperscript{20} and 7 x 10\textsuperscript{20} cm\textsuperscript{-3} and Hall mobilities from 15.7 to 20.1 cm\textsuperscript{2}/Vs. The average transmittance of a 655 nm film is as high as 94% in the visible spectrum and the maximum infrared reflectance is about 92%. The figure of merit 7.12 x 10\textsuperscript{-2} ohms\textsuperscript{-1} is the highest amongst the results reported on doped SnO\textsubscript{2} films.

2.5.2 LITERATURE ON PREPARATION AND MATERIALS

PROPERTIES OF SnO\textsubscript{2}:Sb FILMS

Viirola and Niinistö [78] studied deposition of ATO thin films with low resistivity and high transparency on glass substrates using SnCl\textsubscript{2} and H\textsubscript{2}O as reactants. The effect of Sb doping on growth rate, crystal structure, electrical and
optical properties was studied. XRD measurements indicated that the crystallites in the polycrystalline films had a preferred orientation which depended on the Sb doping level and film thickness. With increasing doping the reflection became gradually more intense and being dominant at highest doping level. The resistivities and electron concentrations of thick SnO$_2$ films varied with Sb doping. Most ATO thin films were highly transparent, but the transmittance decreased with increasing Sb doping, the decrease being highly pronounced at high doping levels.

Yung-Jen Lin et al. [79] have reported the properties of antimony doped tin-oxide thin films prepared by the sol-gel processing of alcoholic solutions of stannic chloride. ATO thin films were deposited by two techniques, the first from spin-coating of colloidal gel suspensions and the other from spray-coating of suspensions of sol-gel derived powder. Their investigations revealed the addition of antimony dopants affects the sol-gel processing in many ways: (i) It accelerates the gelation of the sol-gel prepared from stannic chloride in alcohol, (ii) It not only decrease the crystallinity, but also reduces the particle size of the dried gel. (iii) It decreases significantly the resistance of tin oxide powder and thin films, but the resistance does not change with the amounts of antimony in the range of 2.6-5.2 mol %. Upto 5.2 mol%, antimony exits in tin oxide structure as solid solution. The antimony dopants decreases the degree of crystallinity of the tin oxide structure. Thin films prepared both by spin-coating and spray-coating techniques exhibit similar visible light transparency (transmission >80%) and sheet resistance. However spin-coated films are smooth and free of cracks while spray coated films contain large particles, comprising agglomerates from the powder suspension.

Shanthi et al. [80] investigated the variations of electrical and optical properties of tin oxide films as a function of antimony concentration and prepared ATO films on glass substrates by spray-pyrolysis technique. The temperature dependence on electron mobility has been analyzed to establish the electron conduction mechanism. Optical properties near the plasma edge has been analyzed.
using Drude’s theory. It is found that grain boundary scattering is dominant scattering mechanism limiting the mobility of free careers at room temperature for undoped and 1.4 mol% Sb-doped films. The conduction band of tin oxide films is non-parabolic and a large Burstein shift is observed with Sb doping.

Shanthi et al. [81] presented the structural, electrical and optical properties of F and (Sb+F) doped tin oxide films prepared by spray-pyrolysis technique. The studies revealed that the thin films prepared have low resistivity (5.5 x 10^{-4} ohm cm) with high optical transmission (>80%) and high infrared reflection (~90%). Shanthi et al. [82] observed the annealing characteristics of pure and antimony doped tin-oxide films prepared by spray pyrolysis technique. The studies explained that the chemisorption and desorption of oxygen from the grain boundaries enhances (or) decreases respectively the potential barrier height at grain boundaries, thereby governing the electrical properties of the films.

Shanthi et al. [83] investigated the effects of donor impurities such as antimony, fluorine and antimony plus fluorine on the structural, electrical and optical properties of tin oxide films prepared by spray pyrolysis. The dopant concentration in the films, as determined by auger analysis is less than that in the solution. The mobility of free carriers in doped tin oxide films is found to depend on the nature and the concentration of the dopant. The difference in the mobility behavior in films doped with antimony and with fluorine can be explained on the basis of variations in the grain boundary potential. Drude theory successfully explains the optical properties near the plasma edge. A large Moss-Burstein shift was observed in the doped films.

Tsuna Shima et al. [84] studied and prepared 100 to 300 nm thick Sb-doped TO films at 600°C on glass substrate by thermal deposition of butanol solution of tin 2-ethylhexanote and antimony tributoxide. The application of solution on a substrate was made by dipping the substrate into the solution and withdrawing it. The thin films prepared showed no preferred orientation. The lowest resistivity of about 2.1 x 10^{-2} ohm-cm was attained by using substrates precoated with an SiO2
layer of 30 nm thickness, and the films had a transmittance of 80% over a wavelength range from 0.4 to 2.0 film. Electrical properties were more or less poor, compared with those of films obtained by other methods such as spraying, CVD and R.F. sputtering. However, advantages of the present process lie in the simplicity of film preparation; which will make it possible to use the films in number of electronic devices.

Shanthi et al. [85] investigated on the optical properties of undoped, fluorine doped and antimony doped tin oxide films prepared on quartz plate by spray pyrolysis technique. From transmission spectra it is observed that, 57 at % F/Sn and 9 at % Sb/Sn are the optimum concentrations for obtaining the best values of transmission. It is also observed that the % of transmission in the visible region and reflection in the IR region are higher for F doping than that of Sb doping. For undoped tin oxide the absorption edge lies at 3.65 eV and for FTO and ATO it lies in the range 3.9-4.14 eV and 3.82- 4.1 eV respectively. This shift in shorter wavelength region is advantageous for solar cell applications since it improves the short wavelength response of the cell. The effective mass of electrons in F doped tin oxide films is higher than Sb doped TO films.

James Kane et al. [86] prepared transparent conducting layers of antimony - doped tin oxide has been developed utilizing dibutyl tin diacetate, antimony pentachloride, O₂, H₂O and N₂ as carrier gas at a substrate temperature of 400°- 500°C. The antimony concentrations measured in the films that were deposited under widely varying temperature and reactant flow conditions ranged from 0.002 to 0.11 atomic ratio Sb/Sn. The optimum dopant concentrations was found to be with in the range of 0.6-2.7 atomic % (or mole percent) Sb in SnO₂:Sb. Typical samples are 1500- 3600A° thick with sheet resistance values of 50-150 ohm/square, and have a specific resistivity in the range 1.5 x 10⁻³ to 3.2 x 10⁻⁵ ohm-cm. Light transmission in the visible region of light spectrum ranges from 85 to 91%. The films are free of volatile chlorine or chlorides coatings are thermally
stable in air up to 1000°C in air for several hours. When heated in hydrogen the coatings were rapidly destroyed due to reduction of the oxide, as expected.

Sabnis et al. [87] investigated on the conductivity of d.c.-sputtered Sb-doped tin oxide films which improved at higher substrate temperatures. The conductivity is stable and is not influenced by the substrate material. Heating in open air does not deteriorate the film conductivity. The films are over 90% transparent in the visible spectrum.

Goyal et al. [88] studied the effects of antimony doping on structural and electrical properties using X-ray diffraction technique and room temperature Hall measurements. The films were preferentially oriented along (200) irrespective of the doping level. The relative invariance of the structural properties was because of the incorporation of Sb at Sn sites as revealed from the structure factor calculations. From the Flail measurements the lowest electrical resistivity, i.e., $5.2 \times 10^{-4}$ ohm cm, was observed for the films with the doping level of 2.3 at % in the solution. The career concentration has increased with doping level. The mobility behaviour showed that the electron transport at room temperature was governed by the grain boundary scattering at lower dopant levels whereas by the ionized impurities scattering at higher dopant levels.

Srinivasa Murty et al. [89] have presented the properties of transparent and electrically conducting tin oxide films which where deposited onto pyrex glass substrates by oxidation of SnCl$_2$. The deposition temperature was in the range of 400-500°C and oxygen with the flow rate of 1.35 - 2.50 ml min$^{-1}$ was used as both the carrier gas and the oxidizing agent. SEM studies of these films indicate the uniformity and mean grain size of SnO$_2$ films increases with increasing deposition temperature at a constant oxygen flow rate. The doping of SnO$_2$ films with antimony to 4 mol% has no influence on the above properties. It is concluded that in order to obtain SnO$_2$ films with good uniformity and large grain size, a high deposition temperature (about 500°C) and a low oxygen flow rate (about 1.35 ml m$^{-1}$) should be employed.
Carroll et al. [90] reported the effects of adding Sb and In to pyrolytic SnO₂ films. The large raise in resistivity for larger addition of Sb was studied using X-ray diffraction. Ten order of magnitude raise in resistivity found when Sb concentration is increased in SnO₂ films from 1 - 20 m/o is caused by loss of crystallinity. These films behave as typical amorphous semiconductors in which impurities do not serve as electron donors or acceptors. Heat treatment caused resistivity of undoped SnO₂ films to raise by 4 orders of magnitude due to film oxidation removing oxygen vacancies. Heat treatment caused resistivity of the film with 20 m/o Sb to decrease by 10 orders of magnitude because crystallinity was partially restored. The opposing effects explain why the location of the resistivity minimum sensitive to deposition conditions.

Mulla et al. [91] suggested antimony doped tin oxide films with resistivity as low as 9 x 10⁻⁴ ohm cm can be prepared by spray pyrolysis. They studied the structural, electrical and optical properties by varying the antimony concentration, film thickness and deposition temperature. About 94% average transmission in the visible region and about 87% infrared reflectance were obtained for antimony doped SnO₂ films by systematic optimizations of the preparation parameters. As the best combination, an average transmission of 88% in the visible region and an infrared reflectance of 76% was possible for doped SnO₂ films.

Chow et al. [92] investigated and prepared ATO films by simultaneous oxidation of tetra methyl tin (TMT) and tri-methyl antimony (TMA) at relatively low temperature (450-585°C). Since TMT and TMA have similar vapour pressures at room temperature (~100 mm Hg at 25°C), the TMA was diluted in a pressurized argon cylinder to accurately control the doping concentration of antimony in the tin oxide. This deposition has allowed the growth of films with excellent electrical conductivity, while retaining the high transparency of undoped tin oxide.

Takahashi et al. [93] observed that transparent, highly conducting thin Sb-doped SnO₂ films can be deposited on a glass by dip coating method using a solution of tin tetra iso-propoxide- triethanolamine-water-isopropanol. The
resistivity of the film depended slightly on film thickness. It was 0.025 ohm cm below 1000Å and decreased to a constant value of 0.005 ohm cm above 2000Å. Average transmittance of visible light was higher than 95% of undoped films and higher than 85% for Sb-doped films. Optimum conditions of heat treatment were 600 °C for 30-60 min, where the SnO₂ (4-6 mole % Sb) films with minimum resistivity of 0.005 ohm cm and transmittance higher than 80% were obtained.

Robert Sinclair et al. [94] investigated and presented reports on tin oxide films doped with antimony oxide formed by reactive sputtering of tin-antimony alloy cathodes which can be made conductive at room temperature by heating in air at elevated temperatures (710°C), if the atom percent of antimony in the cathode is between 3.0 and 14%. Annealing of the film at about 300°C is required to stabilize the temperature coefficient of resistivity for the interval 25 - 300°C.

Sabnis et al. [95] concluded that tin oxide films, prepared by DC glow - discharge sputtering using a target of compressed tin oxide powder, are conductive at room temperature by mixing Sb₂0₃ powder with tin oxide powder in varying proportions. Conductivity and optical absorption increases with increasing Sb content. Transparency as high as 85% is obtained in doped 90 nm films on glass. Maximum room temperature conductivity was observed in films deposited from a target containing about 7% Sb₂0₃. An Sb₂0₃ content of 10% and more increases the lattice disorder films, there by making them non-conducting, due to excessive impurity- induced disorders. Such films can be made conductive by heat treatment. These films are n-type and non-degenerate and the activation energy decreases with increasing antimony content.

Elliott et al. [96] has reported some electro chemical properties of poly crystalline tin oxide in the form of thin films. For a variety of antimony doped specimens, the carrier concentration has been determined from the space charge capacity.

Kulaszewicz [97] developed a new apparatus with a rotating sprayer designed for depositing thin transparent conducting films on to glass by
hydrolysis. Investigations on the effect of concentrations of the antimony dopant showed that the optimum concentration for SnO₂:Sb films with the best conductivity was in the range 0.01-0.02 (g Sb) (g Sn)⁻¹. An increase of the antimony concentration in SnO₂ slightly changed the transmission in the UV and visible regions of the spectrum. Where as it markedly reduced the transmission in IR.

Randhawa et al. [98] studied the properties of transparent conducting films of SnO₂ doped with antimony which were prepared on glass substrates by activated reactive evaporation. The sheet resistance and optical transmittance in the wave length range 0.4-0.6 pm were studied as functions of various deposition parameters such as ambient pressure of 85% Ar-15% O₂ mixture, the substrate temperature and the antimony doping concentration in Sn-Sb alloys. A 90 at % Sn-10 at % Sb alloy evaporated in 85% Ar-15% O₂ at a parial pressure of about 5 x 10⁻⁴ Torr with a substrate temperature about 350°C. These films, with a sheet resistance of 10 ohm cm had an average transmittance of 95% over the wave length range 0.4 - 0.6 pm and the film thickness was about 25 pm. Thicker films of about 0.5 pm had a sheet resistance as low as 1.5 ohm cm with an average transmittance 85%.

Lehmann et al. [99] investigated on the methods of reactive co-sputtering to determine the optimum dopant concentration for low resistivity InO₃/SnO₂ and SnO₂/Sb₂O₅ films. The optimum concentration of Sb₂O₃ in SnO₂ about 7 mole %. The resistivity increased sharply at lower concentrations but changed only slightly at higher dopant concentrations. Vaynshteyn [100] developed a technique by which the doping metal could be directly introduced into the film during cathode sputtering, thus giving conductive tin oxide films with properties completely determined by sputtering process. The conductivity of ATO films show that low doping with a donor element has almost no effect on film conductivity; as doping increases, the conductivity increases sharply.
Kaneko et al, [101] observed the physical properties of Sb doped SnO$_2$ thick films, prepared by a repeating chemical spray deposition method. 1000-14000Å thick films were deposited on fused quartz, borosilicate glass, and sodalime glass substrates at 600°C using an aqueous solution of a mixture of SnCl$_4$ and SbCl$_3$. The optical band gap of the films on fused quartz and boro silicate glass substrates is independent of the film thickness and is almost the same 3.75 eV. The hall mobility and carrier concentration of the films were also measured and are reported.

Singh and Basu [102] employed combined spray pyrolysis and CVD techniques to produce smooth, transparent and adherent SnO$_2$ films from SnCl$_4$·5H$_2$O on glass substrates. The polycrystalline films obtained were either antimony or fluorine doped. With antimony doping, a maximum figure of merit of 6.9 x 10$^3$ ohm$^{-1}$ and with fluorine doping, a figure of merit of 2.419 x 10$^2$ ohm$^{-1}$ were obtained. The SnO$_2$:Sb films were doped with more percent of SbCl$_3$ and were 2000Å thick while the SnCV-F films were doped with 1:2 weight percent on NH$_4$F and were 1900Å thick.

M. Honore et al. [103] have prepared semiconductor gas sensors with screen printing techniques and based on home made tin dioxide inks are presented. The tin dioxide ink is made from tin dioxide powder mixed with polymer solution, printable on 96% alumina substrates. The resulting sensors prepared from pure tin dioxide produced according to two different methods show appreciable differences in sensitivity, selectivity and optimum operating temperature.

Elangovan and Ramamurthy [104] have studied the optical properties of spray deposited antimony (Sb) doped thin films, prepared from SnCl$_2$ precursor, as a function of antimony doping concentration. The doping concentration was varied from 0.4 wt % of Sb. All the films were deposited on microscope glass slides at the optimized substrate temperature of 400°C. The films are polycrystalline in nature with tetragonal crystal structure. The doped films are degenerate and n-type conducting. The sheet resistance of tin oxide films was
found to decrease from 38.22 ohm/square for undoped films to 2.17 ohm/square for antimony doped films. The lowest sheet resistance was achieved for 2 wt% of Sb doping. The transmittance and reflectance spectra for the as-deposited films were recorded in the wavelength range of 300 to 2500 nm. The transmittance of the films was observed to increase from 42% to 55% (at 800 nm) on initial addition of Sb and then it is decreased for higher level of antimony doping.

Rembeza et al. [105] have reported on the influence of laser and isothermal treatments on microstructural properties of SnO$_2$ films doped with Sb (Ca 3%). The films were deposited on glass and silicon substrates by magnetron sputtering and heat-treated by laser or isothermal treatment. The films were characterized for their composition, morphology, and crystalline structure by x-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found that the tin oxide films consisted only of the SnO$_2$ tetragonal phase; they were well crystallized and no microstructural defects were observed. The average grain size of the laser treated films was approximately 6.3 - 8.9 nm, which is two times smaller than the grain size of the isothermally treated films.

Lin and Wu [106] have reported on the antimony-doped tin oxide thin films. Films prepared either using spin coating of colloidal gel suspensions or from spray coating of suspension of sol-gel derived powder. Both coating methods result in thin films with similar visible light transmission >80% and sheet resistance of $\sim 5 \times 10^7 \Omega/\square$. However, the surface of the spin coated films is much more smooth than that of spray coated films, whilst the spray coated films contain large particulates, which can form agglomerates in the powder suspension. Antimony doping of the tin oxide produces a number of effects: it accelerates the gelation, reduces the particle size and the degree of crystallinity of the gel, and decrease the resistance of the powder and films.

Bemardi et al. [107] have studied the influence of heat treatment on the optical properties of SnO$_2$:Sb thin films deposited by dip coating using aqueous solution. Antimony doped tin oxide films were deposited on glass by a route
derived from Pechini method. Particular emphasis was given to the microstructure of crystallized films. The GIXRD patterns obtained are characteristic of the SnO₂ crystallites with the tetragonal rutile structure and no evidence was shown on the presence of second phases such as antimony oxides, suggesting the formation of solid solutions. High transmittance, in the range of 80-88% were obtained for 1 mole % Sb₂O₃ doped SnO₂ films with medium thickness of 500 nm. For the films prepared at 550°C/4h in O₂ atmosphere and the film prepared at ambient condition leads to the highest refractive index, 1.8 to 1.9, close to 2.0, which is the value for monocrystalline SnO₂, as an indication of the good degree of densification achieved in the films. The optical band gap of doped and undoped SnO₂ films practically did not show differences, remaining nearer to 4.2 eV.

2.6 POROUS SILICON STRUCTURE

Although porous silicon was first discovered by Uhlir [108] in 1956, great interest in this material is very recent. The small amount of interest shown in porous silicon from the mid-1970’s and throughout the 1980’s relates almost exclusively to its use for device isolation in integrated circuits [109, 110]. The noticeable interest shown from the nineties came with the demonstration by Canham [111] of room temperature photoluminescence from this material. Since then the majority of research into porous silicon has focussed on observations and explanations for both photoluminescence from this material and its potential optoelectronic applications, especially in developing new type of silicon based solar cells. In the following sections, the materials aspect of PSi and the literature scattered over the years are presented.

2.6.1 THE FABRICATION AND STRUCTURE OF POROUS SILICON

The porous silicon described in this thesis was fabricated by the electrochemical anodisation of silicon in a hydrofluoric acid (HF) based electrolyte. This is the most common method of fabricating porous silicon though
the use of an ammonium fluoride based electrolyte has also been reported [112 - 114]. The fabrication is usually conducted in the dark to prevent photogenerated currents contributing to the formation process.

An alternative method for fabrication is by a chemical strain etch [115] that requires dipping the silicon substrate in a hydrofluoric acid : nitric acid : water solution for 3-15 minutes. The porous silicon fabricated using this method is, however, inhomogeneous in both porosity and thickness due to the fact that hydrogen gas evolved during fabrication remains on the surface of the wafer.

2.6.2 PORE FORMATION AND BANDGAP WIDENING

The electrochemical anodisation of silicon will only provide porous silicon if the supply of holes to the silicon substrate is the rate-limiting step. Figure 2.4 illustrates the chemical dissolution mechanism suggested by Lehmann et al. [116, 117].

Once exposed to an air ambient, however, this surface changes to an oxide contaminated surface, the major contaminants being mainly those elements that occur in the air in gaseous form [118, 119]. Lehmann and Gosele [116] expanded their model by suggesting that, providing the current density remains below Jps, the pore formation is self-limited by the availability of holes within the silicon branches. For p-type silicon substrates under anodic bias, the limitation of the hole supply may be caused by quantum confinement. Figure 2.5 [117], shows the proposed band structure at the silicon - porous silicon interface. It is initially assumed that the pore walls are depleted of the holes necessary for the dissolution. If a hole in the silicon substrate has sufficient energy it can penetrate into the silicon branch causing additional dissolution and a further increase in the band gap. Holes will continue to penetrate into the branches until the band gap has increased sufficiently to prevent further migration of holes into the branches, limiting the dissolution to the bulk silicon - pore interface. Increased dissolution of
1. In the absence of electron holes, a hydrogen saturated silicon surface is virtually free from attack by fluorine ions in the HF based electrolyte. The induced polarization between the hydrogen and silicon atoms is low because the electron affinity of hydrogen is about that of silicon.

2. If a hole reaches the surface, nucleophilic attack on an Si-H bond by a fluorine ion can occur and a Si-F bond is formed.

3. The Si-F bond causes a polarization effect allowing a second fluorine ion to attack and replace the remaining hydrogen bond. Two hydrogen atoms can then combine, injecting an electron into the substrate.

4. The polarization induced by the Si-F bonds reduces the electron density of the remaining Si-Si bonds making them susceptible to attack by the HF in a manner such that the remaining silicon surface atoms are bonded to the hydrogen atoms.

5. The silicon tetrafluoride molecule reacts with the HF to form the highly stable SiF$_6^{2-}$ fluorocenion.

The surface returns to its 'neutral' state until another hole is made available.

Fig.2.4 Suggested mechanism for the electrochemical dissolution of silicon
Top left - schematic diagram for the formation of porous silicon.

Top right - silicon branch isolated by two pores. Two possible ways for the hole to cross the silicon - porous silicon interface are shown (broken and dotted arrow).

Bottom - band diagram of the silicon - porous silicon interface and the two different energy barriers for the hole penetrating into the wall (broken arrow) or into the electrolyte (solid arrow).

Fig. 2.5 Band diagram of the silicon-porous silicon interfaces where the radius of a silicon branch is small enough to exhibit quantum confinement.
the branches (increased porosity) is observed as the current density is increased due to the additional energy, the increased current density gives to the hole.

2.6.3 PSI MICROSTRUCTURE AND OPTICAL NATURE

The crystal lattice of original silicon remains unchanged but it is somewhat expanded [120], and filled with grid or pores and cavities. Under visual inspection, the face of PSi is smooth and mirror-like with blue gray or golden brown colour. State of porous silicon is characterized by a parameter called 'porosity', i.e. the ratio of empty volume (volume of the pores) to the total volume of the sample porous layer, as well as the average size of the microstructure elements. The pore form, depending on crystalographic orientation of a silicon wafer, and also the type and quantity of a dopant, can be column type or represent a structure such as a coral or sponge type [121-123]. Depending on a size range of pores, the following classification of PSi layers [124] is made: microporous ($d_{por} < 2$ nm), mesoporous ($2 < d_{por} < 50$ nm) and macroporous ($d_{por} > 50$ nm) as shown in Fig. 2.6a, b and c respectively. The pores merge among themselves with the increase of porosity (Fig. 2.6c), forming columns of single-crystal silicon of diameter of the order $2 \pm 5$ nm [123], These silicon columns, which later received the name 'quantum wires' [125], consist, in turn, of spherical or other form silicon clusters of nanometric size [123, 124], The energy gap of PSi, being changed typically from 1.5 to 1.8 eV [126], is a function of the quantum wire (silicon) diameter. The silicon wire diameter depends on conditions of PSi formation processes and provides opportunity to vary band gap of this silicon. Just due to formation of quantum wires, transformation of the energy spectrum of single-crystal Si takes place and it converts from indirect bandgap semiconductor into the direct bandgap one and also enlarge the bandgap of silicon (1.1 eV) to a maximum of about 1.8 eV as shown in Fig. 2.7.
Fig. 2.6 Ideal model of porous silicon structure with different porosity.
Fig. 2.7 Schematic energy diagram of the radiative recombination process for H-PSi and D-PSi
2.6.4 PSi BAND DIAGRAM FOR PHOTOOLUMINESCENCE (PL)

It should be obvious to assume that photoluminescence (PL) intensity is proportional to the number of electrons present in the initial energy state (from which the transition takes place) and the number of vacancies of electrons (holes) in the final state to which the transition takes place. For simplicity, we also assume that the PL is observed because of the radiative recombination of confined holes in valance band with the electrons at the bottom of the conduction band, which is always filled at room temperature and in presence of the exciting light of higher energy than the band gap of silicon. That is, the origin of PL lies in the recombination of photo generated excess electrons with the confined holes (in case of p-type sample) in the valance band of a well (Fig.2.8). Now, if the state in the neighboring well of same energy (as that of hole) is filled then the electron can tunnel to the vacant state in presence of radiative recombination centres. The energy barrier faced by such an electron is \((h\nu - E_g)\), where \(h\nu\) is the energy difference between the lowest conduction band level and the energy level of the hole and \(E_g\) is the band gap energy of bulk silicon. As we have assumed that the PL intensity is proportional to the number of vacancies in the valance band, the PL intensity \(W\) in presence of electric field should be \(W_0 (1 - T)\), where \(W_0\) is the PL intensity in absence of electric field and \(T\) is the tunneling probability of such electron through a parabolic barrier [127],

2.6.5 LITERATURE REVIEW ON PSi DEVELOPMENTAL STUDIES

Yin et al. [128] have reported the result on the photoluminescence of porous silicon using organic cyano compounds. Using atomic force microscopy (AFM) and spectroscopic ellipsometry, the power spectral density, layer microstructure and quality of the films were studied. It shows that HC1/PIF-mixtures can be used to obtain samples with sharper porous silicon. Erickson et al. [129] have reported red luminescence of silicon wafers. The photoluminescence
Fig. 2.8 Schematic of proposed band diagram of porous silicon and possible transition during photoluminescence
enhancement effects was studied on porous silicon and no new luminescent compounds were formed surface during absorption of cyano compounds.

Moreno et al. [130] have reported the results on electroluminescence origin at p-type silicon layers. They had employed two technique for multilayer analysis: (i) Single-crystalline silicon and silicon carbide was characterized using Rutherford backscattering spectrometry (RBS), (ii) Electrochemically prepared porous silicon layers (PSL) were investigated by Spectroscopic Ellipsometry (SE).

Gelloz and Bsiesy [131] have reported the results on porous silicon carrier transport mechanisms using a diffusion process. A large blue shift of electroluminescence was obtained from oxidized n-type porous silicon. Structural and spectroscopic luminescence are studied by Gupta and Jain [132] on erbium-doped PSi layer. The erbium concentration in the porous layer can be controlled by varying the mobility of erbium solution [133], Kang and Jorne [134] have studied the dissolution of n-type silicon using photoelectrochemical process. They had investigated the quenching effect of porous silicon with adsorption of glycerol at high viscosity.

Moreno et al. [135] observed electroluminescence and photoluminescence in porous silicon by electro oxidation process. Oxidizing agents with positive redox potential inject holes into HF-pretreated silicon. Gong et al. [136] have reported the preparation of Holmium-Doped porous silicon by electrochemical approach and its photoluminescence. The molecular electronic structure of (ground state-singlet, and low-lying triplet-electronic states) oxyhydrides was investigated. Matsumoto et al. [137] have reported the results on the photoluminescence of Deuterium terminated porous silicon. Lee et al. [138] have proposed a mechanism for porous silicon formation. The TEM results show that the microstructure depends on the doping level and consists of silicon dots of size 3-4 nm. Mouffak et al. [139] have discussed the quantum effect of n-type porous
silicon. Baranov et al. [140] have explained the formation of porous silicon using ethanol solutions of hydrogen fluoride in water.

Gesele et al. [141] have reported the result on the thermal conductivity of porous silicon. The transient current in porous amorphous silicon was investigated after treatment in a hydrogen plasma at 200°C. They have discovered that the post hydrogenation of the material increases the dimension of the conducting channel. Unal and Bayliss [142] have reported the results on the photovoltaic effect of porous silicon. The thermal conductivity in PSi layer was formed to increase with temperature. Zheng et al. [143] have prepared Rare-Earth doped porous silicon by electrochemical method. Bhave et al. [144] have observed recrystallization and photoluminescence of porous silicon by radiation process. The cleaved cross-section of electrochemically processed porous-silicon was investigated using Atomic Force Microscope.

Theiss [145] has prepared layers of porous silicon by electrochemical etching of PSi under natural light, incandescent light and light from mercury lamp. Robert et al. [146] have studied the effect of porosity and elastic reflection of electrons in porous silicon layers and their relationship to photoluminescence. Matsumoto et al. [147] have reported the results on the coupling effect and quantum confinement of carriers in porous silicon. The electrical and optical properties of porous silicon layers are given. Choi et al. [148] have reported the result on the electrochemical doping of porous silicon using Rare-Earth element. The electronic structure of porous silicon was investigated by X-ray fluorescence spectroscopy. Aleksandrov and Novikov [149] have studied in detail the formation of porous silicon structure using heavily and lightly doped silicon by anodization process. Torchinskaya et al. [150] have reported the results on photoluminescence and EPR studies of porous silicon. The chemical bonds and electronic structure of porous silicon are studied by Auger electron spectroscopy (AES). Aliev et al. [151] have reported porous silicon sensitivity to various environmental gases.
They have reported two important features of light-emitting diodes on PSi p-n junction and their operation.

Mawhinney et al. [152] have studied the oxidation of porous silicon using FTIR spectroscopy. Matsumoto et al. [153] have reported optical and electrical properties of deuterium terminated porous silicon. The replacement of hydrogen with deuterium reduces photoluminescence and electroluminescence. Tsybeskov et al. [154] have studied the junction current drift effect in the Cu/porous silicon device (Cu/PSi). Kadar et al. [155] have observed structured tubular porous silicon by small-angle neutron scattering. Wang et al. [156] have reported the properties of porous silicon investigated using FTIR spectroscopy, SPS (Surface photovoltage spectroscopy) and PLS (photoluminescence spectroscopy) and their solar cell properties as well. Bjorklund et al. [157] recorded the colour changes in thin porous silicon film, when it was exposed to an ambient atmosphere saturated with various organic solvent vapours. Lalic and Linnros [158] have reported the electrical and optical properties of porous silicon was under pulsed condition. Salonen and Laine [159] have reported the results on the photoluminescence quenching effect in different atmospheres and in vacuum.

Bsiesy and Vial [160] have studied the PL of porous silicon by voltage-tunable method, observed voltage-tunable electroluminescence (VTEL) and voltage-induced quenching photoluminescence. Thonisson et al. [161] have fabricated optical interference filters made up of porous silicon. They have investigated the dependence of the refractive index of PSi layers on the formation of current density for different substrates. Fauchet [162] has reviewed the properties and origins of the red and blue photoluminescence bands of porous silicon. The device stability, efficiency, modulation speed-emission wavelength and compatibility are discussed.

Gardelis et al. [163] have analyzed the chemical nature of the luminescence centres in fresh and aged PSi layers. In the case of fresh PSi, Si-Si bonds were involved while in aged PSi, both Si-Si and Si-O bonds were involved in the
luminescence process. Nakamura [164] has reported the results on porous silicon resonance measurements using electron paramagnetic device. Lee et al. [165] have enumerated the oxide formation in porous silicon films by anodic-oxidation process. Wu et al. [166] studied the electrical properties of thermally oxidized porous silicon. They have observed conducton limiting mechanisms of the tunnelling type, pool-frenkel thermally activated type and an anomalous conduction type on several typical wafers.

Boswell et al. [167] have investigated the porous silicon morphologies, thickness and different substrate types and their field emission properties. Popescu et al. [168] have observed amorphous phase in oxidized porous silicon and calculated the radial distribution function on the basis of XRD. Tanino et al. [169] have measured the Raman Spectra of free-standing porous silicon at 10 K. Quantum size effect was correlated with the spectral change of the first and second order scattering. Konstantinova et al. [170] have reported the modification of spin and recombination centers in porous silicon. They have investigated the influence of molecules adsorption of porous silicon made by the chemical and photochemical routes. Dudel et al. [171] have observed the photoluminescence in the earliest stages of PSi formation by electrochemical etching of p-Si surface.

Dimovamalinovska et al. [172] have proposed a correlation between photoluminescence intensity and oxidized valence states of Si. The results show that PSi has suboxide states of Si. Peter [173] has reported the result on the luminescence tuning and quenching in porous silicon. Osaka et al. [174] have reported that the luminescence wavelength range can be changed by adjusting the saturated photocurrent density during anodization. Hill and Whaley [175] have given the details about the geometry of luminescent region in porous silicon.

Valance [176] has reported the results on the stability of silicon-electrolyte and calculated the dissolution speed and derive scaling laws for interpore spacing as a function of the doping level of Si. The photoluminescence of partially oxidized porous silicon (POPSi) are studied. Lin et al. [177] have reported the
results on the diamond growth on porous silicon by Hot-Filament vapour deposition process. The various properties were studied by scanning electron microscopy, Raman spectroscopy and X-ray diffraction analysis. Matthai et al. [178] have suggested that the different substructures might be responsible for the photoluminescence. Gardelis et al. [179] have shown that the luminescence intensity is dependent on the porosity and not on the surface area.

Joubert et al. [180] have examined the growth of porous silicon in polycrystalline films. Steiner et al., [181] deposited Indium and aluminium into the pores of porous silicon by electroplating process and the electroluminescence efficiency was highly increased. Jeske et al. [182] used the electroless and cathodic electrodeposition routes to incorporate metals into PSi. Gosele and Lehmann [183] have given an overview of PSi research, with special emphasis on the formation and the origin of the visible luminescence. Bhoraskar et al. [184] have prepared PSi with anodic current of 5 to 30 mA/cm² and characterized of PSi are using photoluminescence, grazing angle XRD, photoconductivity, thermally stimulated exoelectron emission and work function measurements. Kimura [185] proposed a new electrochemical method for the preparation of Er³⁺ doped PSi layers showing sharp and intense Er³⁺ photoluminescence at about 1.54 μm at room temperature. Takasuka and Kamei [186] found a relationship between the microstructure and photoluminescence of PSi and observed thread like structures of Si and Si crystallites in the PSi layers.

Vincent [187] has prepared PSi superlattice by electrochemical process. Which acts like a multilayer dielectric device. Banerjee [188] has studied the microstructure and related PL of PSi. Chen et al. [189] have measured the current through PSi p-n junctions as a function of voltage and temperature.

Difrancia and Salerno [190] have reported the results on the concentration of HF and the electrical charge on the formation of porous silicon. Propsk and Kohl [191] investigated the photoelectrical oxidation and dissolution of silicon in the absence of water. They found that the anodic dissolution of p-Si without H₂.
gas at 1.4 A/cm yielded a novel porous structure. Benchorin et al. [192] studied the AC conductivity of various samples of porous silicon in the frequency range 10 Hz to 100 KHz at different temperature. They have found that the conductivity increase with frequency and the density of state at the fermi level is finite. Kozlowski et al. [193] have observed that PL light is emitted from 5 /xm layer, whose dimension is < 50Å° and, the EL light is emitted from 1-2 fim wide layer. The luminescence mechanism was explained by excitonic recombination in quantum structures. Searson et al. [194] have found out that porous layers in n-type silicon exhibit low porosity and large pore dimensions. Teschke et al. [195] studied on the nanosize structure in porous silicon and its relation to photoluminescence efficiency. Noguchi and Suemune [196] engaged photosynthesis to make porous silicon by visible light irradiation in a hydrofluoric acid solution.

Bomchil et al. [197] have presented in details about the pore size, crystallographic structure and microstructure of porous silicon. The optical absorption coefficients of porous layers are discussed. Jain et al. [198] reported the first operation of light emitting p-n junction diode in porous silicon by diffusion. Bresler and Yassicvieh [199] have reported the results on the physical properties and photoluminescence of porous silicon. Beltran et al. [200] have calculated the dielectric function of PSi by observing the interband optical transition. Kortkus and kcakiro [201] have reported the efficiency improvement of multicrystalline solar cells by porous silicon coating. They have demonstrated more than 25% improvement in short circuit current and photovoltaic energy conversion efficiency.

Lisa Kore and Gijs Bosnian [202] have reported the result on the feasibility of porous silicon as a primary material in solar cell. The relationship between photoluminescence peak emission wavelength and the parameters of each etch condition are determined. The results obtained from I-V curves showed non-linear behaviour. Photovoltaic behaviour was seen with $I_{sc}$ of about 0.02 mA, $V_{oc}$ of
about 0.1 V and a calculated fill factor of about 0.2. Nayfeb and kcakiro [203] have explored micro size regions, where photoluminescence has a highly non-linear threshold. The result, in terms of stimulated emission, was discussed from quantum confinement engineered intrinsic Si-Si radiative traps. Liu et al. [204] have reported the optical properties and picosecond response of PSi wafer. The porosity, final structure and optical properties of PSi are studied.
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