Chapter 7

Synthesis and characterization of nanostructured tin oxide films- Successive ionic layer adsorption and reaction technique

7.1 Introduction

Literature reveals that a good number of the DSSC utilize nanoporous electrodes made from titanium dioxide (TiO$_2$) [1-7] or ZnO [8-15]. However, some applications require that the conduction band potential of the nanoporous electrode of DSSC is more positive than that of TiO$_2$ [16-20]. SnO$_2$ is a chemically stable oxide and is one of the few wide band gap semiconductors that possess this property. Its conduction band potential is approximately 0.5V more positive than that of TiO$_2$ (anatase) [21, 22]. It can therefore be used as electrodes in DSSCs in combination with dyes with low-lying lowest unoccupied molecular orbital (LUMO) potential that inject poorly into TiO$_2$ [22].

Wet chemical synthesis of SnO$_2$ films at low temperature (<373K) is seldom reported and it is a challenging task to prepare quality films with high crystallinity. In this chapter, synthesis of nanostructured SnO$_2$ films at room temperature and at temperature, less than 373K was demonstrated using the environmentally benign wet chemical method SILAR.

In the present study, SnO$_2$ film electrodes were synthesized on soda lime glass substrates by SILAR technique using stannic chloride (i) with and without triethanolamine at room temperature (ii) with glacial acetic acid at room temperature (iii) with ethanol solution at 353K (iv) with monoethanolamine at 353K (v) with triethanolamine and ammonium chloride at 353K.

Another set of films were prepared by using tin chloride with triethanolamine at 353K temperature and tin sulfate with triethanolamine at 353K temperature separately. Films were also synthesized by using tin chloride and triethanolamine at 353K temperature on paper substrates. To investigate the effect of annealing on the properties, the films were annealed in air. Structural, morphological, optical, textural, and electrical properties of the as-synthesized and annealed SnO$_2$ films were studied and compared.
7.2 Synthesis of tin oxide films using stannic chloride

7.2.1 With and without triethanolamine at room temperature

7.2.1a Experimental

The chemicals used are analytic grade and used as received. The wet solution synthesis method SILAR has been extensively described in detail elsewhere [23-28]. Experimental set up of SILAR technique is shown in Fig. 2.1. In the present work, immersion time in cationic and anionic solutions was optimized to 4 s. The optimized immersion time for rinsing the substrates was 8 s. First set of SnO₂ thin films were fabricated from cationic precursors prepared by dissolving 300 mg tin (II) chloride (SnCl₂.2H₂O) in 1 ml hydrochloric acid (35%) mixed distilled water. 1ml Hydrogen peroxide (30%) mixed distilled water served as anionic precursor. Both cationic and anionic precursors were kept at room temperature. Second set of films were grown by adding 1 ml triethanolamine (7.4 M) in the cationic precursor prepared in the first case while the anionic precursor being the same.

SnO₂ films were synthesized by choosing 150 SILAR cycles in both cases of experiments. After the film deposition, the substrates were washed in distilled water and dried in hot air before characterization. To study the effect of temperature on the properties, SnO₂ films were annealed gradually in air at 773K for 2 hours in a muffle furnace.

The as-grown and annealed films prepared without triethanolamine were named as STO-A and STO-AA respectively. Films prepared with triethanolamine were named as STO-B and STO-BA respectively.

7.2.1b Results and discussion

Highly adherent off-white SnO₂ films prepared were patch free and uniform. Several sets of films were synthesized and their structural, morphological, electrical and optical qualities were found to be highly reproducible.

(i) Structural and morphological characterization

Figs. 7.1(a, b) and 7.2(a, b) show XRD patterns of the as-grown and annealed SnO₂ thin films synthesized without and with TEA respectively. Films prepared without TEA show poor crystallinity with a broad hump extending from 2θ value
20° to 30°. However, on annealing, this disappears and small peaks corresponding to the SnO$_2$ phase were appeared.

Fig. 7.1 XRD patterns of the (a) as-synthesized and (b) annealed SnO$_2$ thin films prepared without TEA

Fig. 7.2(a), the XRD patterns for film STO-B, show (110) as the dominant peak along with other peaks corresponding to reflections from (101) and (211) planes. These patterns confirm that SnO$_2$ films synthesized with TEA were polycrystalline with crystallites of tetragonal rutile structure. (JCPDS File No. 41-1445). No characteristic peaks of impurity were observed in the XRD patterns. The intensity and width of the SnO$_2$ diffraction peaks were found to be increased and decreased respectively on annealing at 773K for 2 hour in air. This suggests an improvement in crystallinity and increase in the crystallite sizes of SnO$_2$ films.

The mean crystallite sizes of SnO$_2$ films STO-B and STO-BA were determined using the full width half maximum (FWHM) of the (110) and (101) peaks using the Debye-Scherrer’s equation given in Eq. (2.3).

The grain size of as-grown films is 4.25 nm and that of annealed films is 7.55 nm. This is in good agreement with the other experimental results in the literature that the size of grains even after annealing at 1073K did not exceed 6–8 nm. [29]. It has been reported that the most stable structure of rutile-type SnO$_2$ has c/a ratio
equal to 0.674 [30]. In the present work, for all SnO$_2$ films fabricated using SILAR technique, the c/a ratio obtained is in good agreement with this.

The FWHM of XRD patterns is affected by factors such as grain size, inhomogeneous stress distribution and crystal quality of the films [30]. The low FWHM and the increase in grain size of the annealed film STO-BA indicates that the small grain size contributed much to the observed broadening of FWHM of as-grown SnO$_2$ films. There are reports indicating that the non-uniform stress distribution will induce FWHM broadening [30].

Compared with standard data, the XRD peak positions shift towards high 2$\theta$ values, which confirm the existence of a compressive stress in the films, especially in the as-grown films. The films deposited at our experimental conditions may have higher stress and hence a large FWHM can be expected. The widening of diffraction peak may be also due to the presence of defects and imperfections in the grains developed due to the scarcity of oxygen [31]. The reduction in broadening of FWHM observed for the annealed SnO$_2$ films may be resulted due to the chemisorbed oxygen while annealed in air. From Fig. 7.2(b) it is clear that annealing of the as-grown films has tremendous effect on reducing the broadening of the diffraction peaks and hence fetches increase in grain size and improves the crystalline quality of SnO$_2$ films. The lattice parameters of the samples were calculated using the...
observed values of 2θ and d-values for the tetragonal structure using Eq. (2.9). The primitive cell volume (Vc) was calculated using the Eq. (2.18).

Fig. 7.3 shows the variation in primitive cell volume of STO-B and STO-BA films. As shown in Fig. 7.3, the cell volume of as-grown films was slightly reduced from than that of the ideal one. The cell volume of the annealed film was further reduced. The compressive stress may be responsible for the reduction in cell volume in the case of both as-grown and annealed films. Table 7.1 provides the lattice parameters of the films. The cell parameters are close to the standard values (JCPDS File No. 41-1445).

<table>
<thead>
<tr>
<th>Sample*</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>0.4737</td>
<td>0.3185</td>
<td>0.6724</td>
</tr>
<tr>
<td>STO-B</td>
<td>0.4710</td>
<td>0.3135</td>
<td>0.6656</td>
</tr>
<tr>
<td>STO-BA</td>
<td>0.4658</td>
<td>0.3159</td>
<td>0.6782</td>
</tr>
</tbody>
</table>

*Prepared with TEA

Fig. 7.4 Texture coefficient variations of SnO₂ films grown with TEA
The texture coefficient \( (T_c) \) for different crystallite orientations of the films was estimated using the Eq. (2.20) [32]. The texture coefficient variations of STO-B and STO-BA films are shown in Fig. 7.4. For the as-grown films the preferential orientation is in the (110) plane with texture coefficient 1.83. The (101) and (211) planes have texture coefficients less than one. For the annealed films, the preferential orientation was retained along (110) with highest texture coefficient 1.31. Texture coefficient of (101) of annealed films increased from 0.62 to 1.3. This indicates that on annealing orientation was improved along the (101) plane while the orientations along the other two planes were moderately reduced. Hence, both the as-grown and annealed films exhibit random orientation.

Fig. 7.5 SEM images of as-grown and annealed SnO\textsubscript{2} films synthesized without (a, b) and with TEA (c, d)

Fig. 7.5(a-d) shows SEM images of the surface morphology of SnO\textsubscript{2} films grown without and with TEA and the corresponding annealed films. All the films consist of snow like granulates. A dense closely structured film can be observed for films synthesized with TEA compared to the films formed without using TEA. Films were formed by the agglomeration of granulates. Films synthesized using TEA is comprised of agglomerates of size in the 50-800 nm range. Thus a porous aggregate structure is originated, which is distributed evenly on the substrate. It is evident from the high intensity XRD peaks that these agglomerates are polycrystalline and not fine-dispersed formations.
The peculiar morphology obtained yields large specific surface area together with high ruggedness. Since these SnO$_2$ films are invariably porous largely, the surface is accessible to modification and treatment by liquids and gases.

**(ii) Thickness of the films**

Thickness of the films was determined by gravimetric method. The film thickness ($t$) was computed using Eq. (2.21). The bulk density of the material is assumed as 6.99x10$^3$ kg/m$^3$. The thickness of the films prepared with and without TEA obtained was 2450 nm and 1400 nm respectively.

**(iii) Optical Properties**

The absorption spectra of as-synthesized and annealed samples are shown in Fig. 7.6. The spectra reveal a low absorbance in the case of films STO-B and STO-BA in the entire visible region and slight increase in the infrared region. However, for films STO-A and STO-AA, absorbance is low and steady in the entire visible region and gradually decreasing in the infrared region. All films have a steep absorption edge in 300-400 nm range. For annealed samples, the absorption edge was blue shifted and the spectra of these films shows no considerable change in absorbance. The observed blue shift reveals the improved crystallinity of films.

![Absorption spectra of as-grown and annealed SnO$_2$ films](image)

*Fig. 7.6 Absorption spectra of as-grown and annealed SnO$_2$ films*

The optical band gap energy, $E_g$, was evaluated using Eq. (2.22) for the allowed direct interband transition in a crystal [33]. In Fig. 7.7, $(\alpha h\nu)^2$ versus $h\nu$ plots of the films were shown.
The band gap ($E_g$) was determined by extrapolating the linear region of $(\alpha h\nu)^2$ vs $h\nu$ plots. The value of $E_g$ of the films prepared without and with TEA are 3.13 eV and 3.75 eV respectively. For the corresponding annealed films, it is 3.64 eV and 4.30 eV respectively. The low value of $E_g$ for the films STO-A and STO-AA films prepared without TEA as compared with the crystalline films STO-B and STO-BA obtained using TEA can be attributed to band tailing caused by disorderedness in the films [34]. Increase in $E_g$ values on annealing at 773K temperature may be due to improved crystalline structure and/or better quantum confinement [35]. This can be further attributed to the widening of the band gap with increasing carrier densities on annealing [36]. There are reports in the literature, which establish the dependency of the band gap energy on the carrier concentration. The band gap energy varies linearly with the variation in carrier concentration to the power \(\frac{2}{3}\) [37-39]. Hence, the high band gap of 4.3 eV obtained for the annealed films STO-BA indicates the presence of higher carrier concentration in the samples. The $E_g$ values obtained were in agreement with the reports that SnO$_2$ usually exhibits band gap energy in the range of 3.4 - 4.6 eV [37, 38]. The permeated band gap energy of SnO$_2$ films may be resulted from the varied extent of non-stoichiometry of the deposited layers.
Fig. 7.8 Transmittance spectra of the as-grown and annealed SnO$_2$ films

Fig. 7.8 depicts the variation of transmittance of the as-deposited and annealed SnO$_2$ films as a function of wavelength. SnO$_2$ films prepared without and with TEA have exhibit steady value of transmittance 58% and 70% respectively in the entire visible region of the spectrum. Both films exhibit transmission above 50% in the entire near-infrared region. Note that the absorption edge of the transmittance shifted slightly towards smaller wavelength on annealing in case of all films. Annealing has not affected the transmittance of the films and this indicates the absence of defects in the films.

Fig. 7.9 Reflectance spectra of the as-grown and annealed SnO$_2$ films
Fig. 7.9 shows reflectance spectra of the as-grown and annealed films as a function of wavelength. SnO$_2$ films prepared without and with TEA show different trends in a wide range of wavelength extending from visible to near-infrared region. For films STO-A and STO-AA synthesized without TEA, reflectance is decreasing from 20% to 15%, while for films STO-B and STO-BA prepared with TEA, reflectance is increasing from 14% to 20%. Refractive index, n, of the films was determined from the extinction coefficient ‘k’ and the reflectance ‘R’ using Eqns. (2.25) and (2.26) [40, 41].

![Fig. 7.10 Plot of extinction coefficient of as-grown and annealed SnO$_2$ films](image)

Fig. 7.10 depicts the variation in extinction coefficient as a function of wavelength. ‘k’ of the films increases with increase in wavelength. For STO-A and STO-AA films, ‘k’ has a sharp linear increase compared to the films prepared with TEA. The plot of refractive index as a function of wavelength of the as-grown and annealed films is shown in Fig. 7.11. The values of ‘n’ obtained for all films were in the range 2.1-2.6 in the visible and near-IR regions (450-1900 nm). Fig. 7.11 shows a gradual decrease in refractive index with an oscillatory behavior for films STO-B and STO-BA in the visible and near-IR regions. However, films STO-A and STO-AA exhibit a gradual increase in refractive index in the visible region, shows a steady value in the 900-1200 nm range and then it gradually decreases in the near-infrared region. As in the case of films prepared without TEA, its nature is not oscillatory in
the respective regions of the spectrum. Annealing has no considerable affect on the refractive index of the films. The values of refractive index obtained agree to the reported values [42].

![Graph showing variation of refractive index](image)

Fig. 7.11 Variation of refractive index of as-grown and annealed SnO₂ films

(iv) Electrical characterization

The electrical behavior of SnO₂ thin films was examined through the electrical resistivity. Measurements were carried out by dc two-point probe method using silver electrode contacts. The electrical behavior of polycrystalline films depends on crystallite size, growth orientation and the effect of ambient oxygen [43, 44]. The resistivity is inversely proportional to the carrier mobility (m), carrier concentration (N) and electronic charge (e) given by the Eq. (2.33).

\[
\rho = \frac{1}{mN \mu}
\]

Resistivity of STO-B films prepared with TEA is of the order of \(10^2\ \Omega\text{cm}\) and that of the annealed films is \(10^1\ \Omega\text{cm}\), which is one order of magnitude lower than that of the as-deposited films. Increase in grain size decreases the grain boundaries density and accordingly the carrier diffusion by the grain boundaries is reduced [45]. Hence, the improved crystallinity and the slight increase in grain size of the annealed films contribute to an increase in mobility. According to Eq. (2.33), this results in a decrease in resistivity. Measured value of resistivity of annealed films was in agreement with this concept. Simultaneously, a decrease in carrier concentration takes place due to the chemisorbed oxygen on air annealing.
Chemisorbed oxygen acts as a strong trap to free carriers resulting in large decrease in carrier concentration [45]. As per Eq. (2.33), this leads to increase in resistivity. Due to the simultaneous multiple effects leading to the increase and decrease of resistivity of the films, much decrease in resistivity was not achieved on air annealing. On the other hand, films prepared without TEA showed high resistivity of the order of $10^4 \, \Omega \text{cm}$. For these films, annealing has made no effect on resistivity.

High resistivity of these films may be due to the very small crystallite size and the chemisorbed oxygen during synthesis. SEM images exposed that the sample synthesized without TEA has sparse surface morphology and no well-defined crystallites can be seen, which renders higher electrical resistivity in it. Whereas sample prepared with TEA has uniform dense surface morphology than the other, which is probably responsible for their lower value of electrical resistivity. The higher crystallinity of these films as evidenced by XRD results may also be contributed to this lower value.

### 7.2.1c Conclusion

Using the low cost simple method, SILAR, polycrystalline SnO$_2$ thin films were synthesized at room temperature with and without TEA having nanocrystallites <8 nm in size on glass substrates. The present method is easily scalable for any large-area SnO$_2$ thin-film deposition and could be used to fabricate films on other low temperature enduring substrates. As-synthesized SnO$_2$ films prepared with TEA were single phase and polycrystalline with (110), (101) and (211) oriented crystallites of tetragonal rutile structure. The XRD data showed the formation of SnO$_2$ nanocrystallites and on annealing, the nanocrystallite size was found to increase from 4 nm to 8 nm. SEM images of all the films confirmed the uniformly distributed assembly of nanocrystallites. SnO$_2$ films were invariably porous and yield large specific surface area together with high ruggedness. Post-air-annealing of the films at 500°C enhanced the crystalline properties with optical blue shifting. Films have good transmittance in the visible and near-infrared regions and possess high refractive index. Due to quantum confinement effects band gap energy of the films was found to be increased on annealing. The room temperature
electrical resistivity of the as-prepared and annealed films with TEA lies in the range $10^1$-$10^2$ $\Omega$cm. Films prepared without TEA showed high resistivity of the order of $10^4$ $\Omega$cm. These films can find applications as an oxidation catalyst, a solid-state gas sensing material and as a semiconducting dye carrier in dye sensitized solar cells.

7.2.2 With glacial acetic acid at room temperature

7.2.2a Experimental

SnO$_2$ thin films were fabricated from cationic precursor prepared by dissolving 2.25 g of SnCl$_2$.2H$_2$O in 10 ml glacial acetic acid (35%) followed by the addition of 70 ml distilled water. Anionic precursor was prepared by mixing 2ml Hydrogen peroxide (30%) in 80 ml distilled water. Cationic and anionic precursors and distilled water for rinsing the substrate were kept at room temperature. SnO$_2$ films were synthesized by optimizing to 250 SILAR cycles keeping the immersion time as 4 s and 8 s in precursors and water respectively.

After the film deposition, the substrates were washed in distilled water and dried in hot air before characterization. Films were annealed gradually in air at 773K for 2 hours in a muffle furnace to study the effect of temperature on the properties. The as-grown and annealed films prepared were named as STO-C and STO-CA respectively.

7.2.2b Results and discussion

(i) Structural and morphological characterization

XRD profiles of the highly adherent, off-white as-grown SnO$_2$ films are shown in Fig. 7.12(a, b). The patterns for as-grown SnO$_2$ films show (110) as the dominant peak along with other peaks corresponding to reflections from (101), (211) and (301) planes. Absence of characteristic peaks of impurities in the XRD patterns indicates the purity of the films. XRD patterns in Fig. 7.12(a) are that of pure polycrystalline SnO$_2$ phase having tetragonal rutile structure, which are closely in agreement with the JCPDS data (JCPDS File No. 71-0652).
The crystal quality of tin oxide films can be improved by eliminating the lattice disorders by gradual annealing. Annealing temperatures larger than 400°C is necessary to get better crystal quality [46]. Hence, SnO$_2$ films were gradually annealed in air at 500°C for 2 hours. Fig. 7.12(b) shows the XRD patterns of the annealed SnO$_2$ films. Peak corresponding to the plane (110) is the dominant peak as in the case of as-grown films. Along with other peaks corresponding to reflections from (101), (211) and (301) planes, peaks of reflections from the planes (200), (220) and (112) are newly emerged for the annealed films. The intensity and width of the SnO$_2$ film diffraction peaks shown in Fig. 12(b) were found to increase and decrease respectively. This confirms the improvement in crystallinity and increase in the crystallite sizes of the films and/or a decrease in the strain on air annealing [47].

The mean crystallite sizes of SnO$_2$ films were determined using the full width half maximum (FWHM) of the (110) and (101) peaks using the Debye-Scherrer’s Eq. (2.3). The grain size of as-grown SnO$_2$ films was 4 nm and that for the annealed films was 6 nm. This is in good agreement with other experimental results reported in the literature that the size of grains even after annealing at 1073 K did not exceed 6–8 nm [29]. The lattice parameters of the samples were calculated using the
observed values of $2\theta$ and $d$-values for the tetragonal structure using Eq. (2.9). The primitive cell volume ($V_c$) was calculated using the Eq. (2.18). The lattice parameters of SnO$_2$ films are close to the standard values (JCPDS File No. 71-0652). The $c/a$ ratio and cell volume of the films are presented in Table 7.2. As depicted in Table 7.2, the cell volume of as-grown and annealed films was slightly reduced from than that of the ideal one due to the compressive stress. It has been reported that the most stable structure of rutile-type SnO$_2$ has $c/a$ ratio equal to 0.674 [30]. The $c/a$ ratio obtained for all the SnO$_2$ films synthesized in this work is in good agreement with this.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>$c/a$</th>
<th>$V_c$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>0.4737</td>
<td>0.3185</td>
<td>0.6724</td>
<td>0.07146</td>
</tr>
<tr>
<td>STO-C</td>
<td>0.4724</td>
<td>0.3153</td>
<td>0.6674</td>
<td>0.07040</td>
</tr>
<tr>
<td>STO-CA</td>
<td>0.4731</td>
<td>0.3160</td>
<td>0.6678</td>
<td>0.07076</td>
</tr>
</tbody>
</table>

Microstrain in the nanocrystals of SnO$_2$ films in the direction normal to the diffracting plane was computed by using Eq. (2.17) [48]. Variation of microstrain in (110) plane oriented nanocrystals of SnO$_2$ films is shown in Fig. 7.13.

Fig. 7.13 Microstrain of SnO$_2$ films in (110) plane
The strain developed in the films was negative and very small. Moreover annealing decreased the magnitude of the strain. This microstrain may be developed in the polycrystalline SnO$_2$ thin films due to the predominant recrystallization process. The microstrain associated in the material is uniform since it causes the unit cell to expand or contract in an isotropic manner [49, 50] and a shift of the peaks.

Fig. 7.14 SEM images of STO-C films

Fig. 7.14 shows the low and high-magnified SEM images of the as-grown SnO$_2$ films. SEM images of annealed films show similar morphology. It is clear that the films exhibit a coarse and porous surface morphology. This kind of cauliflower like morphology is capable of affording a large inherent adsorptive surface area.

The surface of the film becomes rougher as the particle size increases [51]. XRD studies revealed that the particle size of the annealed films has slightly increased, which implied that the films surface might have become rougher than the as-grown films. With the increase in particle size and film surface roughness, optical scattering loss also increases, which is discussed in Section 7.2.2b(iii).

The porosity of the SnO$_2$ thin film can be assessed indirectly using the refractive indices of the films. As-grown films are more porous than that of the annealed films, which is discussed detailed in Section 7.2.2b(iii). No significant signals from other elements except Sn and O were detected and hence the compositional purity of all the SnO$_2$ films has been confirmed by EDAX analyses.
(ii) Thickness of the films

Thickness of the films was determined by gravimetric method. The film thickness \( t \) was computed using Eq. (2.21). The thickness of the as-grown film was 1200 nm. Annealed films showed no considerable change in thickness.

(iii) Optical properties

The optical band gap energy, \( E_g \), was evaluated using Eq. (2.22) for the allowed direct interband transition in a crystal [33]. In Fig. 7.15, \((\alpha h\nu)^2\) vs \( h\nu \) plots of the films is shown. The band gap \( (E_g) \) was determined by extrapolating the linear region of \((\alpha h\nu)^2\) vs \( h\nu \) plots. The optical band gap evaluated was 3.75 eV and 3.25 eV for the as-grown and the annealed films respectively.

![Fig. 7.15 Plot of \((\alpha h\nu)^2\) versus \( h\nu \) and variation of absorbance with wavelength (inset) of SnO₂ films](image)

Inset plot in Fig. 7.15 shows the variation of absorbance of both as-grown and annealed films. The absorbance of SnO₂ films was increased on annealing and the band edge is optically red shifted. The abrupt edge in the absorbance spectra of both as-grown and annealed films indicates the good structural quality of the film [52]. The variation of optical band gap with particle size is shown graphically in Fig. 7.16. The particle size variation on annealing was discussed in section 7.2.2a(i).
The surface topography of both the substrate and the film determines the quality of optical transmission of the film [51]. The surface scattering due to the peculiar surface morphology of the films can reduce the transmitted intensity. Optical transmission through a rough surface is much affected by scattering of light having wavelengths near to the magnitude of the film surface features [53-56]. Fig. 7.17 shows the variation of transmittance of the as-grown and annealed SnO₂ films with wavelength. Due to the rough surface of the SnO₂ films as discussed in Section 7.2.2.a(i), it can be noticed that the as-grown films possess only 80% transmission in the visible region.

Reduction in the transmittance of the annealed films to 65% in the visible region indicates that its surface roughness has increased corresponding to the increase in particle size on annealing. Annealed films show a decrease in transmittance throughout the Vis-NIR region. Inset plot in Fig 7.17 indicates that the transmittance of both the films has a steady value in the entire visible region.
Refractive index, $n$, of the films was determined from the extinction coefficient ‘$k$’ and the reflectance ‘$R$’ using Eqns. (2.25) and (2.26) [40, 41]. The porosity of the films was determined from the refractive index of the film and the refractive index ($ns$) of SnO$_2$ ($ns \sim 2.006$) using the Eq. (2.31) [57].

As shown in Fig. 7.18, the refractive of the as-grown films has a lower value than that of the annealed films throughout the Vis-NIR region of the spectrum. Both
the films show lower values of refractive index in the visible region. The higher transmission in the visible region shown by the as-grown films may be due to the low refractive index possessed by it. Annealed films show particular peak values of refractive index at 900 nm and 1500 nm. It has been reported that the refractive index of thin films decreases as the porosity increases [58-60]. As depicted in the inset of Fig. 7.18, the as-grown SnO$_2$ films possess higher porosity and lower refractive index than that of the annealed films. This lowering of refractive index may be due to the trapping of air (refractive index of air is unity) from the ambient atmosphere by the porous centers in the as-grown films [53]. Slight increase of particle size from 4 nm to 6 nm on annealing might have reduced the void spaces in the film and as a result annealed films are relatively less porous and exhibits higher refractive index.

(iv) Electrical properties

The electrical resistivity of the films was examined to study the electrical behavior of SnO$_2$ thin films. Measurements were carried out by dc two-point probe method using silver electrode contacts. As-grown films has $10^{-2}\ \Omega \text{cm}$ and annealed films has $10^{-1}\ \Omega \text{cm}$ resistivity. This indicates that resistivity of the annealed films was one order less than that of as-grown films. The reduction in resistivity or improvement in conductivity implies that on annealing the slight increase in the particle size reduces the voids in the films discussed in section 3.3 and might have improved the continuity and uniformity of the films.

7.2.2c Conclusion

A novel photo-anode was developed by synthesizing SnO$_2$ films using SILAR technique. Comprehensive characterizations of the films were carried out. Films with cauliflower like morphology exhibited a large inherent adsorptive surface area. As-grown and annealed films have a steady transmittance of 80% and 60% respectively and resistivity in the range of $10^{-2}$-$10^{-1}\ \Omega \text{cm}$. As-grown SnO$_2$ films have higher porosity and lower refractive index than that of the annealed films.
7.2.3 With ethanol solution at 353K temperature

7.2.3a Experimental

In this work, immersion time in cationic and anionic solution was optimized to 4 s. The optimized immersion time for rinsing the substrates was 8 s. SnO$_2$ thin films were fabricated from the cationic precursor prepared by dissolving 700 mg of SnCl$_2$.2H$_2$O in aqueous/ethanolic solution and followed by the addition of 2 ml hydrochloric acid (35%). The cationic precursor solution was kept at room temperature. 1 ml hydrogen peroxide (30%) mixed distilled water kept at 353 K served as anionic precursor. Magnetic stirring was performed for thorough mixing while each of the chemical reagents were added to prepare the precursor solutions. Distilled water and ethanol was used to prepare the solvent. The volume ratios of water to ethanol (V$_W$/V$_E$) employed in the experiment were 1/0, 4/1, 3/2 and 1/1 to explore the solvent effect on the film deposition. Anionic precursor and other experimental conditions were unchanged for preparing all the SnO$_2$ films in this work.

Films were synthesized by choosing 150 deposition cycles to get highly adherent films. Accordingly, the deposition time was almost around 45 minute. After deposition, the samples were rinsed in distilled water for several times and dried under hot air flow prior to characterization. The samples were also post-annealed at 773K in air for 2 hour in a muffled furnace to investigate the effect of annealing on the properties. The films prepared with volume ratios of 1/0 and 1/1 were named as STO-D and STO-E. The as-grown films prepared with volume ratios of 4/1 and 3/2 were named as STO-F and STO-G and the corresponding annealed films as STO-FA and STO-GA respectively.

7.2.3b Results and discussion

(i) Effect of ethanol on film formation

Ethanol content in the cationic precursor solution has significant effect on the adsorption process in SILAR and hence in the film morphology and the corresponding crystallinity. In SILAR, film formation is due to the successive adsorptions and reactions [26, 28, 61]. Adsorption is the beginning of the process.
involved in SILAR and is a surface phenomenon between ions in the cationic precursor solution and the surface of substrate. The forces like cohesive/Van-der Waals/chemical attractive forces are responsible for this adsorption process [61]. The factors like pH, temperature, surface tension, solvent viscosity and solvent polarity of cationic precursor solution and the nature of the substrate etc affect the adsorption process [61, 62]. Ethanol is a neutral molecule and the pH of a solution of ethanol in water is nearly 7. The addition of even a few percent of ethanol to water sharply reduces the surface tension of water from 71.97 mN/m to 29.63 mN/m at 298 K. [63]. It has higher solvent viscosity and lower solvent polarity compared with water [64, 65]. The presence of ethanol content would reduce the interaction between molecules of solvent and the tin precursor, which would make the surface tension of the water-ethanol solvent to decrease [62]. Due to the decrease in surface tension of the solvent, the attractive force between ions in the solution and surface of the substrate will be more effective in presence of ethanol. The higher solvent viscosity and the lower solvent polarity may also help the tin ions to interact with the immersed substrate surface easily. Hence, ethanol addition in water will be highly enhancing the adsorption of tin ions on the substrate.

(ii) Structural and morphological analysis

Fig. 7.19(a, b) depicts the X-ray diffraction (XRD) patterns of the films STO-D and STO-E. XRD patterns illustrate the poor crystallinity of such films. Distinct peaks are not there in the patterns to match with the standard data. These results suggest that poorly crystalline or almost amorphous films will be formed when the solution is purely aqueous (V_W/V_E =1/0) or when there is equal amount of water and ethanol (V_W/V_E =1/1) in the solution. Moreover, under direct physical observation, these films were with patches and were less adhered to the substrates. SEM images shown in Fig. 7.20(a, b) reveals the non-uniformity of these films. Therefore, these low quality films were not used for further studies. It is to be noted that, there was no film formed when the solution is purely ethanolic. i.e. when the ratio V_W/V_E is 0/1.
Fig. 7.19 XRD patterns of the films prepared at $V_W/V_E$ ratios of (a) 1/0 and (b) 1/1

Fig. 7.20 SEM images of SnO$_2$ films (a) STO-D and (b) STO-E

Fig. 7.21(a-d) illustrates the XRD patterns of films STO-F, STO-G and that of the respective annealed films STO-FA and STO-GA. The strongest reflections for the films are observed from planes (110), (101) and (211). Low intensity peaks corresponding to the reflections from the planes (200) for films prepared at $V_W/V_E$ ratios of 4/1 and 3/2 and the reflections from (301) for the films prepared at $V_W/V_E$ of 4/1 can be observed in the XRD patterns.
Fig. 7.21 XRD patterns of as-grown and annealed SnO$_2$ films prepared with different $V_W/V_E$ ratio

With the introduction of ethanol in the solution ($V_W/V_E = 4/1$), the crystallinity of the SnO$_2$ films (Fig. 7.21(a)) improved significantly. However, when the ethanol content is increased in the solution ($V_W/V_E = 3/2$), the peak intensity of the XRD patterns are found decreasing (Fig. 7.21(c)). This can be attributed to the decrease in the crystallinity of the films. These patterns confirm that SnO$_2$ films were polycrystalline with crystallites of tetragonal structure (JCPDS File No. 71-0652). No characteristic peaks of impurity were observed in the XRD patterns.

Figs. 7.21(b) and 7.21(d) depict the XRD patterns of the films annealed in air at 773 K for 2 hour. The high intensity peaks reveals that crystallinity of both the annealed films is highly improved with respect to the as-grown crystalline films. The strongest reflections for the annealed films STO-FA and ST0-GA remains the same as that of the respective as-grown films, which is observed from planes (110), (101) and (211). Reflections from planes (200) and (301) are now more distinct and the peaks from planes (220) and (112) are newly evolved. Preferred orientation is still dominated in the (110) plane as in the case of as-grown films.
The crystallite sizes of SnO$_2$ films were determined using the full width half maximum (FWHM) of the (110) and (101) peaks using the Debye-Scherrer’s Eq. (2.3). Fig. 7.22 provides the average grain sizes of the tin oxide films. The grain size of as-grown and that of annealed films was in the 4-7 nm range. It was found that there is a small increase in the grain size on annealing. This is in good agreement with other experimental results reported in the literature [29]. The gas-sensing properties of SnO$_2$ increases when the crystallite size is below 10 nm [29].

![Fig. 7.22 The grain size of various SnO$_2$ films](image)

Hence, it can be confirmed that the volume ratio of water to ethanol is crucial for the formation of crystalline SnO$_2$ films. In fact, no films, with patch free, uniform and crystalline can be deposited in case a single solvent (either water or ethanol) is used to prepare the films.

SEM images shown in Figs. 7.23(a, b) and 7.24(a, b) illustrates the morphology of the as-grown STO-F and STO-G films and that of the respective annealed SnO$_2$ films STO-FA and STO-GA. These images expose the uniform distribution of crystallites on the surface of the substrate. As shown in Fig. 7.23(a), STO-F films are comprised of grains with cauliflower like morphology. The films have a porous microstructure with very fine pores distributed nearly uniformly on the substrate surface.
Fig. 7.23 SEM images of (a) as-grown and (b) annealed SnO$_2$ films prepared with $V_w/V_e$ ratio 4/1

Fig. 7.24 SEM images of (a) as-grown and (b) annealed SnO$_2$ films prepared with $V_w/V_e$ ratio 3/2
The rough and porous surface morphology will ensure a large solid-to-gas interface due to the high surface-to-volume ratio. Annealing had reduced the pores considerably while keeping the roughness of the films as depicted in the SEM images shown in Fig. 7.23(b). On the other hand, Fig. 7.24(a) illustrates that the STO-G films possess grains of definite shapes with certain boundaries. Accordingly, the roughness and porous nature of the films are not as much as that of the films STO-F. Film morphology of the annealed films shown in Fig. 7.24(b) indicates an increased roughness. In appearance, the porosity of these films is less than that of the films prepared with the V$_W$/V$_E$ ratio 4/1. Porosity determined from the optical data, which is discussed in Section 7.2.3a(iv), confirmed these inferences made about the as-grown and annealed films prepared with the different volume ratios. Morphological studies corroborated that uniform and dense films could be prepared from the solution by employing a mixed solvent like water and ethanol. The chemical composition of the samples was analyzed by EDAX, which indicated the formation of pure tin oxide.

(iii) Thickness of the films

Film thickness was determined by gravimetric method. The film thickness was computed using Eq. (2.21). The thickness obtained for the films STO-F and STO-G was respectively 1800 nm and 1650 nm. It can noted that for a given deposition time, the film thickness is decreased with increasing ethanol content.

(iv) Optical properties

Fig. 7.25(a) illustrates the optical absorbance spectra of the SnO$_2$ films deposited at various V$_W$/V$_E$ ratios. All the films possess a sharp absorbance edge. A red shift of the absorption edge is observed with increasing ethanol content in the solution. The red shift of absorption edge may be due to the decrease of carrier concentrations [66]. The spectra in Fig. 7.25(a) reveal that the as-grown and annealed films STO-G and STO-GA have high absorbance than that of the films STO-F and STO-FA. Annealing has increased the absorbance of both the films.

From the measured optical absorbance data, the values of optical absorption coefficient, ‘$\alpha$’ was determined by using the Beer–Lambert law [67]. The optical
band gap \( (E_g) \) of the films were determined by plotting \((\alpha h \nu)^2\) against photon energy \((h \nu)\) as shown in Fig. 7.25(b). As can be seen \((\alpha h \nu)^2\) varies linearly with \(h \nu\) above the optical band gap energy of the SnO\(_2\) films. Accordingly, the energy band gap is obtained by extrapolating the straight-line portion of the curve to the \(h \nu\)-axis. The values of band gap energies \((E_g)\) are plotted in Fig. 7.26 against the grain size of respective films.

![Fig. 7.25 (a) Optical absorbance spectra and (b) plot of \((\alpha h \nu)^2\) vs. \(h \nu\) of SnO\(_2\) deposited for various \(V_W/V_E\) ratios](image)

With respect to the small increase in grain size due to change in ethanol content or annealing, there is a decrease in the optical band gap values except that of the annealed films STO-FA. Films prepared with \(V_W/V_E\) ratio 4/1 possess high optical band gap of 3.75 eV and that of the films prepared with \(V_W/V_E\) ratio 3/2 possess 3.50 eV. This clearly indicates that the amount of ethanol in water determines the value of the optical band gap of SnO\(_2\) films. This result substantiates that by merely changing the solvent ratio using ethanol, optical band gap
engineering is possible in the SnO$_2$ films. Annealing has slightly decreased the band gap values of the films as shown in Fig. 7.26. It can be noted that on annealing, red shift of the band gap value is negligibly small in films STO-F and STO-FA. So improvement in crystalline quality of such films can be easily achieved by air-annealing without any variation in the band gap. This also points out that the minimum use of ethanol is good in keeping the optical quality of the films stable against the temperature variation even up to 773 K.

The optical transmittance and reflectance spectra of the samples are shown in Fig. 7.27(a, b). Nearly 70-75% transmittance in the visible region is obtained for the as-grown SnO$_2$ films. Transmittance of the films is decreasing with increase in wavelength in the near-infrared (NIR) region of the spectrum. A decrease in transmittance of the films is observed in the visible-NIR region of the spectrum with increasing ethanol content in the solution. The decreased optical transmittance of the SnO$_2$ films may be due to the scattering at the grain boundaries [68, 69] and hence due to the corresponding greater absorbance and reflectance. The different morphology created by the increase in ethanol content (with V$_W$/V$_E$ ratio 3/2) discussed in Section 7.2.3a(ii) substantiate this fact. The reflectance spectra shown
in Fig. 7.27(b) clearly show the increase in the reflectance of the SnO₂ films in the NIR region. Annealing has decreased the transmittance and increased the reflectance of both type of the films. This may be due to the increased roughness created on annealing and the corresponding scattering of light from these rough surfaces. Optical transmission through a rough surface is much affected by scattering of light having wavelengths near to the magnitude of the film surface features [53, 54].

![Graph](image)

**Fig. 7.27** (a) Optical transmittance and (b) the reflectance spectra of the SnO₂ films deposited at various V₆/V₅ ratios

Refractive index, n, of the films was determined from the extinction coefficient ‘k’ and the reflectance ‘R’ using Eqns. (2.25) and (2.26) [40, 41]. Refractive index of the material influences the film optical characteristics such as transmission spectrum, reflection spectrum etc. Fig. 7.28(a) illustrates the variation of refractive index of films with wavelength. The values of ‘n’ obtained for all films were between 1.9-2.27 in the 400-2000 nm wavelength range. Variation of
refractive index shows a wavy nature in the case of films STO-G and STO-GA. STO-F and STO-FA films possess relatively small value of refractive index than that of the films STO-G and STO-GA. The higher transmission in the visible region shown by the as-grown films may be due to the low refractive index possessed by it. The values of refractive index obtained are in agreement with the reported values [42, 70]. Gradual increase in refractive index can be noticed with respect to the increase in wavelength in the visible and NIR region of the spectrum. Annealing has made a uniform increase in the refractive index of the all the SnO₂ films. Refractive index of SnO₂ films gradually increases in the visible region and attains a steady value in the NIR region of the spectrum.

![Graph](image)

Fig. 7.28 (a) Variation of refractive index and (b) extinction coefficient of films with wavelength of SnO₂ films deposited at various Vₑ/Vₑ ratios

Fig. 7.28(b) depicts the variation in extinction coefficient as a function of wavelength. ‘k’ of the films shows a gradual linear increase with increase in
wavelength in the visible region and lower part of the NIR region of the spectrum. However, it shows almost a sharp increase in the far end of the NIR spectrum. Through annealing 'k' values of the films were increased. STO-F and STO-FA films possess relatively small value of 'k' than that of the films STO-G and STO-GA. Hence, to synthesize SnO₂ films with low value of refractive index and extinction coefficient, it is better to minimize the volume of ethanol in the solution.

Fig. 7.29 Porosity of as-grown and annealed SnO₂ films deposited at various V₆/V₇ ratios

Porous film contains air in the pores in addition to the material of the film. The porous structure of the films helps in reducing the effective refractive index of the film material and air [71]. It has been reported that the refractive index of thin films decreases as the porosity increases [58, 59]. The porosity of the films was determined from the refractive index of the film and the refractive index (nₛ) of SnO₂ (nₛ ~2.006) using the Eq. (2.31) [57].

As depicted in Fig. 7.29, the as-grown SnO₂ films STO-F possess higher porosity than that of the STO-G films. Hence, decrease in the ethanol content in the solution creates highly porous SnO₂ films. As discussed, these films possess lower values of refractive index than that of the annealed films. This low refractive index may be due to the trapping of air from the ambient atmosphere by the porous
centers in the as-grown films [53]. Slight increase of particle size on annealing might have reduced the void spaces in the film and as a result, annealed films are relatively less porous as depicted in Fig. 9 and exhibits higher refractive index.

(v) Electrical properties

The electrical behavior of the SnO$_2$ films was studied by determining the electrical resistivity ($\rho$). Measurements were carried out by dc two-point probe method using silver electrode contacts. As-grown STO-F films exhibit a resistivity in the order of 10$^0$ $\Omega$cm and the corresponding annealed films have 10$^{-1}$ $\Omega$cm resistivity. As-grown STO-G films show a resistivity in the order of 10$^{-1}\Omega$cm and annealed films exhibit 10$^{-2}\Omega$cm resistivity. It is clear that the resistivity of the annealed films is one order less than that of as-grown films. For comparison, the plot of log ($\rho$) of the films is shown in Fig. 7.30. The reduction in resistivity implies that on annealing, the slight increase in the particle size, which was discussed in Section 7.2.3b(ii), reduces the voids in the films and might have improved the continuity and uniformity of the films. This indicates that with increase in ethanol content the resistivity of the films are decreasing. This is further substantiated by the decrease in porosity of such films, which was discussed in Section 7.2.3b(iv).

![Fig. 7.30 Variation of resistivity of as-grown and annealed SnO$_2$ films](image-url)
7.2.3c Conclusion

SnO$_2$ films were fabricated and the solvent effect on the properties of the films was investigated by an aqueous-ethanol solvent based SILAR technique using the cost effective precursor SnCl$_2$.2H$_2$O. Ethanol content in the cationic precursor solution has significant effect on the adsorption process in SILAR. High crystallinity and various morphologies together with good optical and electrical properties of the films have been realized by varying the volume ratio of water to ethanol ($V_W/V_E$). SnO$_2$ films synthesized at $V_W/V_E$ ratios 4/1 and 3/2 and the respective annealed films are highly crystalline and the crystallite size of the films lie in the 4-7 nm range. The film deposition rate is decreased with increasing ethanol content in the solution. Rough and porous surface morphology of the films ensures large solid-to-gas interface due to the high surface-to-volume ratio. Annealing had reduced the pores considerably while keeping the roughness of the films. A red shift of the absorption edge was observed with increasing ethanol content in the solution. The as-grown SnO$_2$ films have nearly 70-75% transmittance in the visible region. In the 400-2000 nm wavelength range, refractive index of all the films lies between 1.9 and 2.27. Films prepared with $V_W/V_E$ ratio 4/1 and 3/2 possess high optical band gap of 3.75 eV and 3.50 eV respectively. The minimum use of ethanol was found good in keeping the optical band gap of the films stable against the annealing temperature 773 K in air. SnO$_2$ films prepared with $V_W/V_E$ ratio 4/1 possess higher porosity than that of the films prepared with $V_W/V_E$ ratio 3/2. SnO$_2$ films prepared with $V_W/V_E$ ratios 4/1 and 3/2 have resistivity in the order of $10^0$ $\Omega$cm and $10^{-1}$ $\Omega$cm and the corresponding annealed films have $10^{-1}$ $\Omega$cm and $10^{-2}$ $\Omega$cm respectively. We have demonstrated that using aqueous-ethanol solvent in SILAR technique can provide high quality SnO$_2$ films, which are beneficial in applications like gas sensors, dye-sensitized solar cells etc.

7.2.4 With monoethanolamine at 353K temperature
7.2.4a Experimental

SnO$_2$ thin films were synthesized from the cationic precursor prepared by dissolving 1mg of SnCl$_2$.2H$_2$O in distilled water, followed by the addition of 3 ml
hydrochloric acid (35%) and 2 ml MEA. The cationic precursor solution was kept at room temperature. 2 ml hydrogen peroxide (30%) mixed distilled water kept at 353 K served as anionic precursor. Magnetic stirring was performed for thorough mixing while each of the chemical reagents were added to prepare the precursor solutions. Films were synthesized by choosing 175 deposition cycles keeping the immersion and rinsing time 4 s and 8 s respectively to get highly adherent films. Accordingly, the deposition time was almost around 65 minute. After deposition, the samples were rinsed in distilled water and dried under hot air flow prior to characterization. Films were named as STO-H.

### 7.2.4b Results and discussion

#### (i) Effect of MEA and film formation mechanism

SnCl\textsubscript{2}.2H\textsubscript{2}O used was dissolved in distilled water and followed by the addition of HCl acid solution and thereby adequate amount of Sn\textsuperscript{2+} ions were made available in the solution. Like triethanolamine, when MEA was added, it complexes with Sn\textsuperscript{2+} to form a chelate compound [Sn(MEA)\textsubscript{k}]\textsuperscript{2+} [72]. MEA wraps around the Sn\textsuperscript{2+} ions and averts the ions from further chemical changes or early release into the solution.

During the first SILAR process, on immersing the substrate in the cationic solution the [Sn(MEA)\textsubscript{k}]\textsuperscript{2+} complex was adsorbed on it. On the second process, i.e. when rinsing the substrate in distilled water kept at room temperature, [Sn(MEA)\textsubscript{k}]\textsuperscript{2+} on the substrate reacts with H\textsubscript{2}O and forms tin hydroxide (Sn(OH)\textsubscript{2}). Excess and loosely held species on the substrate were removed during this process. In the third process, the strong oxidizer H\textsubscript{2}O\textsubscript{2} present in the distilled water kept at 353 K was oxidizing (Sn(OH)\textsubscript{2}) into SnO\textsubscript{2} and the excess H\textsubscript{2}O\textsubscript{2} was simultaneously removed at this temperature on exposure to air. In the last immersion process, loosely held chemical species were removed from the film surface. Rapid deposition of SnO\textsubscript{2} films was achieved within 1 hour, which is a noticeable property of the unique MEA bath used here. The rapid deposition of ZnO films from chemical bath containing MEA have been reported by Michael Kokotov et al. [73]. SnO\textsubscript{2} film formation reaction may be as follows:
\[
\text{SnCl}_2 + k(\text{MEA}) \Leftrightarrow [\text{Sn(MEA)}_k]^{2+} + \text{Cl}^- \quad (7.1)
\]

\[
[\text{Sn(MEA)}_k]^{2+} + 2\text{OH}^- \Rightarrow \text{Sn(OH)}_2 + k(\text{MEA}) \quad (7.2)
\]

\[
\text{Sn(OH)}_2 + \text{H}_2\text{O}_2 \Rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \quad (7.3)
\]

(ii) Structural and morphological analysis

The XRD profile of the STO-H films is depicted in Fig. 7.31. These films were not treated after deposition. High intensity XRD peaks corresponding to the planes (110), (101), (200), (211) and (301) indicate that the films are polycrystalline. All the peaks can be indexed to tetragonal structured SnO\(_2\), which are in good agreement with JCPDS data file (File No. 71-0652). The XRD analysis detected no other impurity peaks. For estimation of the crystallite size ‘D’ of the films, Scherrer formula given in Eq. (2.3) was used. The grain size estimated from the main peak (110) is 4.5 nm.

![XRD patterns of the STO-H films](image)

**Fig. 7.31** XRD patterns of the STO-H films

The lattice parameters of the samples were calculated using the observed values of \(2\theta\) and \(d\)-values for the tetragonal structure using Eq. (2.9). The primitive cell volume \(V_c\) of SnO\(_2\) films was calculated using the equation Eq. (2.18).
Table 7.3 Lattice parameters, c/a ratio, cell volume and dislocation density of the SnO$_2$ films

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$c/a$</th>
<th>$V_c$ (nm$^3$)</th>
<th>Dislocation density (10$^{16}$ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Using D from Scherrer formula</td>
</tr>
<tr>
<td>Ideal</td>
<td>0.4738</td>
<td>0.3186</td>
<td>0.6724</td>
<td>0.0715</td>
<td>-</td>
</tr>
<tr>
<td>STO-H</td>
<td>0.4683</td>
<td>0.3124</td>
<td>0.6669</td>
<td>0.0685</td>
<td>4.9</td>
</tr>
</tbody>
</table>

The crystallite-size and strain developed in the SnO$_2$ films were further determined by the technique developed by the Williamson and Hall (W-H plot) [74]. The W-H equation is given in Eq. (2.15). W-H plot for the films was constructed by plotting ‘$\beta \cos \theta$’ vs ‘4$\sin \theta$’ and is shown in Fig. 7.32. The crystallite size and strain were determined from the intercept at the ‘$\beta \cos \theta$’-axis and the slope of the W-H plot respectively according to Eq. (2.15). The microstrain extracted from W-H analysis is the non-uniform strain resulting from the systematic shifts of atoms from their ideal positions. This shift may be originating from defects like point defects, site-disorder, vacancies and due to plastic deformation [49]. Microstrain associated with the films was further determined using the Eq. (2.16) directly.

![Fig. 7.32 W-H plot and the microstrain (inset) of the STO-H films](image)

The microstrain obtained from the W-H plot and Eq. (2.16) is plotted for comparison and is illustrated in the inset of Fig. 7.32. The value of strain obtained is small and compressive (negative slope of W-H plot) in nature. Grain size obtained
from W-H plot is slightly less than that determined using Scherrer’s formula. Fig. 7.33 shows the grain size obtained from both the techniques.

![Graph](image)

**Fig. 7.33 Grain size of the STO-H films using Scherrer formula and W-H plot**

The defects in the STO-H films was quantified by computing the dislocation density ($\delta$) using Williamson Smallman relation [75]. Dislocation density of the films was determined using the grain size obtained from both Scherrer’s formula and the W-H plot. The values obtained are depicted in Table 7.3. The values obtained from both techniques show no much difference. The smaller value of dislocation densities may be an indication of the crystalline nature of the SnO$_2$ films.

![SEM images](image)

**Fig. 7.34 SEM images of the STO-H films**

Fig. 7.34 illustrates the SEM images of the SnO$_2$ films. Some aggregated structures with undefined morphologies were observed. However, the films have a coarse and porous surface morphology with very fine pores distributed nearly uniformly on the film surface. This kind of dense morphology is capable of affording
a large inherent adsorptive surface area. The compositional purity of the SnO$_2$ films has been confirmed by EDAX analyses.

(iii) Thickness of the films

Film thickness was determined by gravimetric method. Knowing the dimensions of the substrates used, the film thickness was computed using Eq. (2.21). The thickness obtained for the STO-H films was 1350 nm.

(iv) Optical properties

The optical transmittance and reflectance spectra of the sample are shown in Fig. 7.35(a). The SnO$_2$ films exhibit nearly 70% transmittance in the visible region. Transmittance of the films is decreasing with increase in wavelength in the near-infrared (NIR) region of the spectrum. Optical transmission through a rough surface is much affected by scattering of light having wavelengths near to the magnitude of the film surface features [53, 54, 68, 69]. The reflectance spectra of the STO-H films in Fig. 7.35(a) shows the reflectance below 20% and exhibit a slight increase with increase in wavelength in the NIR region.

![Fig. 7.35 (a) Transmittance, reflectance spectra and (b) plot of $(a\nu)^2$ versus $\nu$ of STO-H films](image-url)
According to inter-band absorption theory, the relation between absorption coefficient near the threshold and the incident photon energy for allowed direct transitions [76] is given by Eq. (2.22). In Fig. 7.35(b), \((ahv)^2\) versus \(hv\) plots of the films is shown. The value of optical band-gap energy \('E_g'\) was determined by extrapolating the linear region of \((ahv)^2\) vs \(hv\) plots. The \('E_g'\) value of the SnO₂ films obtained is 3.65 eV. The \('E_g'\) values obtained were in agreement with the reports that SnO₂ usually exhibits band gap energy in the range of 3.4 - 4.6 eV [37, 38, 77].

![Graph showing extinction coefficient, refractive index, and porosity of SnO₂ films](image)

**Fig. 7.36 Plot of extinction coefficient, refractive index and porosity (inset) of the SnO₂ films**

Refractive index of the material influences the film optical characteristics such as transmission spectrum, reflection spectrum etc. Refractive index, \(n\), of the films was determined from the extinction coefficient ‘\(k\)’ and the reflectance ‘\(R\)’ using Eqns. (2.25) and (2.26) [40, 41].

Fig. 7.36 shows the variation of refractive index of the SnO₂ films as function of wavelength. The values of ‘\(n\)’ obtained for the films vary from 2.05 to 2.30 in the 450-1900 nm wavelength range. A small gradual increase ‘\(n\)’ can be noted with increase in wavelength in the visible-NIR region and attains a steady value in the NIR region of the spectrum. The higher transmission in the visible region shown by the films may be due to the low refractive index possessed by it. The values of refractive index obtained are in agreement with the reported values [42, 70]. Extinction coefficient of the films shows a gradual linear increase with increase in wavelength in the visible-NIR region of the spectrum. The porosity of the films was
determined from the refractive index of the film and the refractive index ($n_s$) of SnO$_2$ ($n_s \sim 2.006$) using the Eq. (2.31) [57]. As depicted in the inset of Fig. 7.36, SnO$_2$ films possess porosity of more than 25%. Hence, these films with porous morphology ensures large solid-to-gas interface due to the high surface-to-volume ratio.

(v) Electrical properties

The electrical behavior of the SnO$_2$ films was examined by determining the electrical resistivity of the films. Experimental measurements were carried out by dc two-point probe method using silver electrode contacts. SnO$_2$ films exhibit a resistivity in the order of $10^{-1}$ $\Omega$cm. SEM images discussed in Section 7.2.4b(ii) exposed that the films have sparse surface morphology with pores, which renders comparatively higher electrical resistivity in it than the reported values of $10^{-3}$-$10^{-4}$ $\Omega$cm [78-82].

7.2.4c Conclusion

Polycrystalline SnO$_2$ thin films having thickness in the range 1000-1500 nm with crystallite size less than 5 nm were synthesized without the need of post-annealing. Rapid synthesis of SnO$_2$ thin films were carried out by SILAR technique on glass substrates using thecomplexing agent MEA. High intensity XRD peaks corresponding to the reflections from the planes (110), (101), (200), (211) and (301) were indexed. Lattice parameters, $c/a$ ratio, cell volume and dislocation density of the SnO$_2$ films were tabulated. Films have a coarse and porous surface morphology with very fine pores distributed nearly uniformly on the film surface. The crystallite size and strain developed in the SnO$_2$ films were computed by the Williamson-Hall technique. Microstrain in the films is of the order of $10^{-3}$. Transmittance is relatively high in the visible region and is nearly 70%. The optical band gap of the SnO$_2$ films is 3.65 eV. The refractive index of the films varies from 2.05 to 2.30 in the 450-1900 nm wavelength range. Extinction coefficient of the films shows a gradual linear increase in the entire visible-NIR region of the spectrum. The SnO$_2$ films exhibit a resistivity in the order of $10^{-1}$ $\Omega$cm. This interesting surface, optical and electrical characteristics make the material suitable for various applications such as in gas sensors and dye-sensitized solar cells.
7.2.5 With triethanolamine and ammonium chloride at 353K temperature

7.2.5a Experimental

In this work, the immersion time in cationic and anionic solution was optimized to 4 s. The optimized immersion time for rinsing the substrates was 8 s. First set of SnO\textsubscript{2} thin films were fabricated from cationic precursors prepared by dissolving 900 mg of SnCl\textsubscript{2}.2H\textsubscript{2}O in 3 ml HCl (35\%) mixed distilled water, followed by the sequential addition of 1 ml TEA (7.4 M) and 5 ml NH\textsubscript{4}Cl (0.05 M) solution. The cationic solution was kept at room temperature. 1 ml hydrogen peroxide (30\%) mixed distilled water kept at 353 K served as anionic precursor. Second set of films were fabricated without using NH\textsubscript{4}Cl solution in the cationic precursor while the anionic precursor and all experimental conditions being the same.

SnO\textsubscript{2} films were fabricated choosing 75 cycles to get highly adherent films. To study the effect of annealing a set of SnO\textsubscript{2} films from both the baths were annealed gradually in air at 773K for 2 hours in a muffle furnace. As-grown films synthesized with and without NH\textsubscript{4}Cl solution were named STO-I and STO-J and the corresponding annealed films were respectively named as STO-IA and STO-JA.

(i) Film formation mechanism

Basic tin chloride (Sn(OH)Cl) and beta-stannic acid (SnO\textsubscript{2}.xH\textsubscript{2}O) will not dissolve in distilled water and these impurities will give a cloudy solution if present in the precursor SnCl\textsubscript{2}.2H\textsubscript{2}O. Impurity free SnCl\textsubscript{2}.2H\textsubscript{2}O used was dissolved in HCl acid solution and thereby adequate amount of Sn\textsuperscript{2+} ions were made available in the solution. When TEA was added, it complexes with Sn\textsuperscript{2+} to form a chelate compound [Sn(TEA)\textsubscript{k}]\textsuperscript{2+} [72]. TEA wraps around the Sn\textsuperscript{2+} ions and averts the ions from further chemical changes or early release into the solution. The schematic model of complex formation of Sn\textsuperscript{2+} ions is shown in Fig. 7.37. Further the [Sn(TEA)\textsubscript{k}]\textsuperscript{2+} complex would be more stable with higher amounts of TEA [83]. Therefore, a moderate amount of TEA was used to complex the Sn\textsuperscript{2+} ions in order to assure the formation of relatively less stable complex in the cationic solution.
During the first process, on immersing the substrate in the cationic solution the $[\text{Sn(TEA)}_k]^{2+}$ complex was adsorbed on it. On the second process, i.e. when rinsing the substrate in distilled water at room temperature, $[\text{Sn(TEA)}_k]^{2+}$ on the substrate reacts with H$_2$O and forms tin hydroxide (Sn(OH)$_2$). Excess and loosely held species were removed during this rinsing. In the third process, the strong oxidizer H$_2$O$_2$ present in the distilled water kept at 353 K was oxidizing (Sn(OH)$_2$) into SnO$_2$ and the excess H$_2$O$_2$ was simultaneously removed at this temperature on exposure to air. In the last process, loosely held chemical species were removed on rinsing.

When NH$_4$Cl solution was used in the cationic precursor, along with the tin ion complex, some ammonium and chlorine ions would also be adsorbed on the substrate. In the third process, this would contribute some alkalinity when reacting with H$_2$O$_2$ mixed distilled water kept at 353 K, thus scavenges the OH$^-$, and hence lead to the formation of hydroxide free SnO$_2$ films. SnO$_2$ film formation reaction with and without NH$_4$Cl may be as follows:

\[
\text{SnCl}_2 + k(\text{TEA}) \Leftrightarrow [\text{Sn(TEA)}_k]^{2+} \quad (7.4)
\]
\[
[\text{Sn(TEA)}_k]^{2+} + 2\text{OH}^- \Rightarrow \text{Sn(OH)}_2 + k(\text{TEA}) \quad (7.5)
\]

With NH$_4$Cl solution, the possible reaction may be as follows:

\[
\text{Sn(OH)}_2 + \text{NH}_4\text{Cl} + \text{H}_2\text{O}_2 \Rightarrow \text{SnO}_2 + \text{H}_2\text{O} + \text{NH}_4\text{OH} + \text{HCl} \quad (7.6)
\]
Hydroxide free SnO$_2$ films can be prepared directly without annealing when NH$_4$Cl was used in the cationic solution. Without NH$_4$Cl solution, hydrous SnO$_2$ films with SnO phase were formed and the possible reactions may be as follows:

\[ \text{Sn(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{SnO}_2\cdot\text{nH}_2\text{O} + (2-n) \text{H}_2\text{O} \quad (7.7) \]

\[ \text{Sn(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{SnO} + 2\text{H}_2\text{O} \quad (7.8) \]

Finally, all SnO$_2$ films prepared were annealed in air at 773 K for 2 hour. Hydroxide content and the SnO phase in the SnO$_2$ films prepared without NH$_4$Cl solution was thus removed. Fig. 7.38 shows the schematic illustration of the deposition of SnO$_2$ film.

**7.2.5b Results and discussion**

Highly adherent white SnO$_2$ films were patch free and uniform. Several sets of films were synthesized and their structural, morphological, electrical and optical qualities were found to be highly reproducible.

**(i) Structural characterization**

Fig. 7.39(a, b) and 7.40(a, b) show the XRD patterns of the as-synthesized and annealed SnO$_2$ thin films prepared with and without NH$_4$Cl solution. Fig. 7.39(a) shows that the XRD pattern for the as-grown STO-I film has (110) as the dominant peak along with other peaks corresponding to reflections from (101), (211) and (301) planes. These patterns confirm that SnO$_2$ films were polycrystalline with
crystallites of tetragonal rutile structure (JCPDS File No. 71-0652). Characteristic peaks from impurity or other phases were found absent in the XRD patterns. This indicates the purity of the film.

Fig. 7.39(b) depicts the XRD patterns for the STO-IA films annealed in air at 773K for 2 hour. It has not shown much significant variation from than that of the as-grown films, except that of a small increase in intensity variation of the peaks and a very small change in FWHM values. This may be due to the slight enhancement of grain size and the corresponding improvement in crystallinity due to annealing. Peaks corresponding to reflections from (200), (220) and (112) planes were newly evolved.

The XRD patterns for as-grown STO-I films show (110) as the dominant peak along with other peaks corresponding to reflections from (101), (211), (220), (112) and (301) planes. These patterns confirm that SnO₂ films were polycrystalline with crystallites of tetragonal rutile structure (JCPDS File No. 71-0652). No characteristic peaks of impurity were observed in the XRD patterns. XRD patterns in Fig. 7.40(a) indicate the pure polycrystalline SnO₂ phase, which are closely in agreement with the JCPDS data. However, the broad peaks or the partial coalition of the peaks
corresponding to the planes (110), (101) and (200) centered around $\theta = 30^0$ and that of (112) and (301) centered around $\theta = 65^0$ is visible in the case of as-grown SnO$_2$ thin films.

The XRD patterns for STO-JA films annealed at 773K for 2 hour in air show high intensity sharp peaks. This indicates that film crystallinity improved largely on annealing. In addition, peak corresponding to reflections from plane (220) of SnO$_2$ was newly evolved. This confirmed the formation of single-phase SnO$_2$ films on annealing which is evident from the Fig. 7.40(b).

The grain size of the films was increased on annealing as shown in Table 7.4. It can be seen that grain size is now equal to that of the films prepared using NH$_4$Cl. Therefore, 773K air annealing was required in the case of SnO$_2$ films prepared without using NH$_4$Cl to meet the properties of films that prepared with NH$_4$Cl.

The lattice parameters ($a$, $c$) of the samples were calculated using the observed values of $2\theta$ and d-values for the tetragonal structure using Eq. (2.9). The structure of a unit cell is depicted schematically in Fig. 7.41. The primitive cell volume ($V_c$) was calculated using the Eq. (2.18).

Fig. 7.40 XRD patterns of (a) as-grown and (b) annealed SnO$_2$ films synthesized without NH$_4$Cl
The lattice parameters of both as-grown and annealed SnO\textsubscript{2} films as depicted in Table 7.4 are close to the standard values (JCPDS File No. 71-0652). The cell volume and tetragonality ratio of all the samples are presented in Table 7.4. The cell volume of as-grown films synthesized using with and without NH\textsubscript{4}Cl was slightly compressed from than that of the ideal one due to the compressive stress. It has been reported that the most stable structure of rutile-type SnO\textsubscript{2} has c/a ratio equal to 0.674 [30]. For all SnO\textsubscript{2} films fabricated in this work, the c/a ratio obtained is in good agreement with this.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>Tetragonality ratio c/a</th>
<th>V\textsubscript{C} (nm\textsuperscript{3})</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>0.4738</td>
<td>0.3186</td>
<td>0.6724</td>
<td>0.07152</td>
<td>-</td>
</tr>
<tr>
<td>STO-I</td>
<td>0.4718</td>
<td>0.3140</td>
<td>0.6655</td>
<td>0.06989</td>
<td>6.82</td>
</tr>
<tr>
<td>STO-IA</td>
<td>0.4678</td>
<td>0.3150</td>
<td>0.6733</td>
<td>0.06894</td>
<td>7.41</td>
</tr>
<tr>
<td>STO-J</td>
<td>0.4675</td>
<td>0.3149</td>
<td>0.6736</td>
<td>0.06885</td>
<td>5.60</td>
</tr>
<tr>
<td>STO-JA</td>
<td>0.4710</td>
<td>0.3166</td>
<td>0.6722</td>
<td>0.07025</td>
<td>6.95</td>
</tr>
</tbody>
</table>

It has been understood that strain contribution to the XRD peak broadening is negligible compared to that arising from finite particle size effect [84]. Keeping this in mind the mean crystallite sizes of SnO\textsubscript{2} films were determined using the full width half maximum (FWHM) of the (110) and (101) peaks using the Debye-Scherrer’s Eq. (2.3). Table 7.4 provides the average grain sizes of the tin oxide films.
The grain size of as-grown and that of annealed films was in the 5-7 nm range. This is in good agreement with other experimental results reported in the literature [29].

The texture coefficients \((T_c)\) for different crystallite orientations [32] of the films were estimated from the Eq. (2.20). The texture coefficient variation of both as-grown and annealed \(\text{SnO}_2\) films is shown in Fig. 7.42. The crystallite orientations are dominant both in the (110) and (101) plane with texture coefficient more than one for the as-grown STO-I films and for (211), it is less than one. For the as-grown films STO-J, dominant crystallite orientations are in the (110), (101) and (211) planes with texture coefficient greater than one.

On annealing, crystallite orientation was redistributed with the emergence of orientation in new planes but still dominant in (110), (101) and (211) planes with texture coefficients greater than one.

Generally, both of the size and strain broadening effects produce a symmetric broadening. In addition, when the residual stress in a material produces a distribution of both tensile and compressive forces, the observed diffraction profiles will be found to broaden about the original position [85, 86]. The large broadening in XRD patterns of STO-J films may be due to these simultaneous effects. This broad peak may be also due to the presence of an amorphous \(\text{SnO}\) phase which corresponds to its intense reflection at \(2\theta = 29.86^0\) [JCPDS File No. 72-1012], in

![Fig. 7.42 Texture coefficient variation of as-grown and annealed \(\text{SnO}_2\) films](image)
agreement with the XRD patterns shown in Fig. 7.40(a). This fact is well supported by the existing literature on pulsed laser deposited (PLD) SnO\(_2\) thin films, in which films grown under vacuum always consist both poly-SnO\(_2\) and amorphous SnO phases [87-90].

Table 7.5 Line shift in SnO\(_2\) films

<table>
<thead>
<tr>
<th>Plane</th>
<th>Line shift (\theta) (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample</td>
</tr>
<tr>
<td>110</td>
<td>0.159</td>
</tr>
<tr>
<td>101</td>
<td>0.425</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>211</td>
<td>0.048</td>
</tr>
<tr>
<td>220</td>
<td>-</td>
</tr>
<tr>
<td>301</td>
<td>-</td>
</tr>
</tbody>
</table>

The strain in a material produces two types of effects on diffraction patterns namely line broadening and line shifting [91]. The strain developed in the crystallites of SnO\(_2\) films during synthesis and due to annealing manifest as change in lattice planes. This was perceivable from the line shifting of observed XRD patterns from that of the standards patterns. The line shift determined corresponding to each plane of SnO\(_2\) films is given in Table 7.5.

Table 7.6 ‘d’ values of SnO\(_2\) films

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{110})</th>
<th>(d_{101})</th>
<th>(d_{200})</th>
<th>(d_{211})</th>
<th>(d_{220})</th>
<th>(d_{301})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>3.350</td>
<td>2.644</td>
<td>2.369</td>
<td>1.764</td>
<td>1.675</td>
<td>1.415</td>
</tr>
<tr>
<td>STO-I</td>
<td>3.335</td>
<td>2.613</td>
<td>-</td>
<td>1.755</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>STO-IA</td>
<td>3.308</td>
<td>2.613</td>
<td>2.356</td>
<td>1.754</td>
<td>1.670</td>
<td>1.416</td>
</tr>
<tr>
<td>STO-J</td>
<td>3.305</td>
<td>2.612</td>
<td>-</td>
<td>1.749</td>
<td>-</td>
<td>1.423</td>
</tr>
<tr>
<td>STO-JA</td>
<td>3.330</td>
<td>2.627</td>
<td>2.364</td>
<td>1.759</td>
<td>1.670</td>
<td>1.417</td>
</tr>
</tbody>
</table>

The observed and standard ‘\(d_{hkl}\)’ values corresponding to different planes are depicted in Table 7.6. It can be seen that ‘\(d_{hkl}\)’ values in all cases are slightly less than the standard values except that of \(d_{301}\) of as-grown and annealed samples prepared without NH\(_4\)Cl. Here, the decrease in \(d_{hkl}\)’ values and the observed shift in the location of the diffraction peaks also indicate the generated residual compressive stress in the surface of the crystallites. All the SnO\(_2\) films display no
tensile stress. This was corroborated by the small reduction in cell volume of all the samples as depicted in Table 7.4.

![Microstrain in (110), (101) and (211) oriented nanocrystals of SnO₂ films](image)

**Fig. 7.43 Microstrain in (110), (101) and (211) oriented nanocrystals of SnO₂ films**

Microstrain in the nanocrystals of SnO₂ films in the direction normal to the diffracting plane [48] was computed by using Eq. (2.17). Variation of microstrain in (110), (101) and (211) plane oriented nanocrystals of SnO₂ films is shown in Fig. 7.43. This microstrain may be developed in the polycrystalline SnO₂ thin films due to the predominant recrystallization process. The strain formed may also be correlated to the lattice misfit, which in turn depends upon the deposition conditions [79].

**(ii) Morphological characterization**

Figs. 7.44 and 7.45 show low and medium magnified SEM images showing the surface morphology of SnO₂ films. STO-I and STO-J films exhibit similar morphology except that of a close and compact arrangement of grains in the former film.

![SEM images (low and high magnified) of SnO₂ films synthesized with NH₄Cl](image)
Fig. 7.45 SEM images (low and high magnified) of SnO₂ films synthesized without NH₄Cl

The films consist of snow like agglomerates of size lies in the 100-500 nm range. This has originated a porous structure, which is distributed evenly on the substrate. The peculiar morphology will yield large specific surface area together with high ruggedness. High intensity XRD peaks beyond doubt prove that these agglomerates are polycrystalline and not fine-dispersed formation. Annealed films exhibit a similar morphology (not given) and size of agglomerates were not affected on annealing.

The compositional purity of all the SnO₂ films has been confirmed by EDAX analyses (not shown here), which indicate that the films contain mainly Sn and O, no significant signal from other elements being detected.

(iii) Thickness of the films

Thickness of the films was determined by gravimetric method and computed using Eq. (2.21). The thickness of the films STO-I and STO-J was 2600 nm and 2750 nm respectively.

(iv) Optical properties

Figs. 7.46 and 7.47 show the optical absorption and transmission versus wavelength curves of as-synthesized and annealed SnO₂ films. All the films show a low and steady absorbance in the entire visible and infrared regions. Films have a steep absorption edge in 300-400 nm range. For annealed samples, the absorption edge was slightly red shifted and these films show a slight increase in absorbance. The observed red shift reveals the improved crystallinity of films. This may be due
to removal of defect levels, which is observed in films prepared using wet chemical methods [92].

![Figure 7.46 Absorption spectra of as-grown and annealed SnO\textsubscript{2} films](image)

Optical transmission is above 50% in the entire visible and near-infrared regions for all the films. It is seen that the optical transmission is reduced when NH\textsubscript{4}Cl was used in the synthesize process. It can be noticed from Fig. 7.47 that transmission is slightly reduced on annealing. This behavior can be attributed to increase in porosity and hence the creation of a high surface roughness in SnO\textsubscript{2} films as evidenced by the SEM images [93- 95]. Thus, the use of NH\textsubscript{4}Cl solution during the preparation not only promotes the crystallinity of the as-grown films but also improves the surface roughness as achieved in the case of films annealed at 773K.

![Figure 7.47 Transmission spectra of as-grown and annealed SnO\textsubscript{2} films](image)
Fig. 7.48 Reflectance spectra of as-grown and annealed SnO$_2$ films

Fig. 7.48 shows reflectance spectra of the as-grown and annealed films as a function of wavelength. All SnO$_2$ films prepared without and with NH$_4$Cl solution show similar behavior in a wide range of wavelength extending from visible to near-infrared region. Spectra have a wavy nature and the value of reflectance lies in 15% - 20% throughout the region.

The optical band gap energy ($E_g$) was evaluated using Eq. (2.22) for the allowed direct transition in a crystal [33]. In Fig. 7.49, $(\alpha h \nu)^2$ versus $h \nu$ plots of the films are shown. $E_g$ was determined by extrapolating the linear region of $(\alpha h \nu)^2$ vs $h \nu$ plots. The value of $E_g$ of the films prepared with and without NH$_4$Cl are 4.11 eV and 4.29 eV respectively.

Quantum confinement varies the optical properties of the materials. It was reported that quantum confinement effects in semi-conducting nanomaterials increase the band gap energy relative to bulk materials [96]. For films associated with larger nanoparticles, the electron excitation across the band gap depends only on the energy difference between the valence and conduction band. The quantum confinement effect begins to influence the excitation energy across the band gap especially when the size is of the order of Bohr radius (2.7 nm) of the material [97-99]. When the crystallite size is smaller than 8 nm the confinement effects begin to influence the optical properties of SnO$_2$ films [96]. As depicted in Table 7.4, the grain size of both the as-synthesized and annealed films obtained in this work is less
than 8 nm. For the film with lowest grain size, the band gap is high and vice versa. Therefore, the increasingly blue-shifted value of band gap (>4 eV) of these SnO$_2$ films prepared by SILAR technique confirmed the quantum confinement effect of the grains. The band gap is red shifted on annealing as shown in Fig. 7.49.

![Graph](image)

**Fig. 7.49** $(\alpha h\nu)^2$ versus $h\nu$ of SnO$_2$ films

For the corresponding annealed films, the band gap is 3.65 eV and 3.80 eV respectively. Decrease in $E_g$ values or the observed red-shift on annealing at 773K temperature may be due to the improved crystalline structure with increase in crystallite size [35]. The $E_g$ values obtained were in agreement with the reports that SnO$_2$ usually exhibits band gap energy in the range of 3.4 - 4.6 eV [37, 38].

Structural and optical studies together established the effects of the crystallite size of the SnO$_2$ films in tuning the band gap with the use of NH$_4$Cl solution and air-annealing. Fig. 7.50 depicts the variation in band gap values with change in grain size.
Refractive index, $n$, of the films was determined [40, 41] from the extinction coefficient ‘$k$’ and the reflectance ‘$R$’ using Eqns. (2.25) and (2.26). Fig. 7.51 depicts the variation in extinction coefficient as a function of wavelength. ‘$k$’ of the films with and without NH$_4$Cl increases with increase in wavelength. ‘$k$’ of all films exhibits a linear increase.
The plot of refractive index as a function of wavelength of the as-grown and annealed films is shown in Fig. 7.52. The values of ‘n’ obtained for all films were in the range 2.1-2.3 in the visible and near-IR regions (400-2000 nm).

Fig. 7.52 Refractive index of as-grown and annealed SnO$_2$ films

Fig. 7.52 shows a gradual decrease in refractive index with an oscillatory behavior for films prepared with and without NH$_4$Cl in the visible and near-IR regions. Annealing has made a minor increase in the refractive index of the films. The values of refractive index obtained are slightly higher than the reported values [99].

**(v) Electrical properties**

Measurements were performed by dc two-point probe method using silver electrode contacts. The presence of metal interstitials and oxygen deficiency in SnO$_2$ film’s lattices generally leads to high n-type conductivity. Using the hot probe method, the films were found to be n-type conducting. STO-I films having excellent crystallinity and compactly packed grains as evidenced by XRD profiles and SEM images among other samples exhibit relatively lower resistivity of the order of $10^0$ $\Omega$cm. The corresponding annealed film has a resistivity of $10^{-1}$ $\Omega$cm. Resistivity of STO-J films is of the order of $10^2$ $\Omega$cm and that of the annealed films is $10^1$ $\Omega$cm.

The electrical behavior of polycrystalline films depends on crystallite size [43, 44]. Increase in grain size decreases the grain boundaries density and
accordingly the carrier diffusion by the grain boundaries is reduced [45]. Since the
as-grown and annealed film grain sizes were less than 7 nm, the grain boundary
density will be more and there is chance of much carrier diffusion. This might have
blocked the lowering of resistivity of the SnO$_2$ films. Normally annealed films show
improvement in conductivity than the as-grown films due to decrement in grain
boundary concentration, which enhances mobility of the charge carriers [100]. As
discussed in Section 7.2.4b(ii), annealing has no much effect on enhancing the
crystallite size and hence small variation in size of the grains in these SnO$_2$ films
plays negligible role on resistivity variation.

The annealed film STO-JA has resistivity one order of magnitude higher than
that of the STO-I films. Non-stoichiometric SnO$_2$ films are highly transparent and
conducting than the stoichiometric films [101]. In the case of air-annealed films,
while the ordering of the structure leads to a less resistant film, the oxidation draws
the film near to its stoichiometric oxide. These two mechanisms compete for the
variation of resistivity differently and have eventually led to a slight decrease in
resistivity from than that of the as-prepared films. Another reason for the high film
resistance or resistivity may be due to diminishing or removal of its defects on air-
annealing, which are responsible for the conductivity. Using NH$_4$Cl solution in the
synthesis process, the resistivity of the films was able to reduce to two orders of
magnitude from than that of the other as-grown films.

7.2.5c Conclusion

Quantum confined nanostructured transparent SnO$_2$ thin films were
synthesized at 353 K on soda-lime glass substrates by means of synthesis in
aqueous acidic medium using SILAR technique. Films were prepared with and
without using NH$_4$Cl. The present synthetic approach has advantages such as low
cost, low temperature (<100°C) and green friendly. The structural, morphological,
optical and electrical properties of SnO$_2$ films fabricated were investigated and
compared. Polycrystalline films with snow like crystallite morphology were
comprised of grains of size in the 5-8 nm range. Structural and optical studies
together established the effects of the crystallite size of the SnO$_2$ films in tuning the
band gap with the use of NH₄Cl solution and air-annealing. The optical band gap of the films prepared with and without NH₄Cl was 4.11 eV and 4.29 eV and for the corresponding annealed films 3.65 eV and 3.80 eV respectively. The increasingly blue-shifted value of band gap (>4 eV) of the as-synthesized SnO₂ films confirmed the quantum confinement effect of the grains. Refractive index for all films was in the 2.1-2.3 range in the 400-2000 nm wavelength region. As-grown and annealed SnO₂ films prepared with NH₄Cl exhibit relatively lower resistivity of the order of 10⁰ Ωcm and 10⁻¹ Ωcm respectively. The relatively low temperature synthesis demonstrated would provide a possibility to fabricate SnO₂ films onto many low-temperature enduring substrates and to enable the incorporation of quantum-based devices in a variety of industries. Large surface-volume ratio and high crystallinity of the SnO₂ films make it a potential candidate in DSSC applications.

7.3 Synthesis of tin oxide films using tin chloride and tin sulfate with triethanolamine at 353K temperature

7.3.1 Experimental

A set of SnO₂ thin films were fabricated from the cationic precursor prepared by dissolving 600 mg SnCl₂·2H₂O in 2 ml hydrochloric acid (35%) mixed distilled water followed by the addition of 1 ml triethanolamine (7.4 M). The cationic precursor solution was kept at room temperature. 1 ml hydrogen peroxide (30%) mixed distilled water kept at 353 K served as anionic precursor. Magnetic stirring was performed for thorough mixing while each of the chemical reagents were added to prepare the precursor solutions. Another set of films were prepared from the cationic precursor prepared by dissolving 600 mg SnSO₄ in 2 ml sulfuric acid (35%) mixed distilled water followed by the addition of 1 ml triethanolamine (7.4 M). Anionic precursor and other experimental conditions were unchanged for preparing these films.

Immersion time in cationic and anionic solution was optimized to 4 s. The optimized immersion time for rinsing the substrates was 8 s. Films were synthesized by choosing 100 deposition cycles to get highly adherent films. Film coated substrates were then washed in distilled water and dried by blowing hot air
before characterization. A set of films from both the baths were annealed gradually in air at 773K for 2 hours in a muffle furnace in order to study the effect of temperature on the properties of the films. Film prepared using \( \text{SnCl}_2 \cdot 2\text{H}_2\text{O} \) was named as STO-K and that film synthesized using \( \text{SnSO}_4 \) was named as STO-L. The corresponding annealed films were named as STO-KA and STO-LA respectively.

7.3.2 Results and discussion

Highly adherent off-white \( \text{SnO}_2 \) films obtained from both the baths were patch free and uniform. Several sets of films were synthesized and their structural, morphological, electrical and optical properties discussed in the following sections were found to be highly reproducible.

(i) Structural analysis

XRD patterns of the as-grown and annealed \( \text{SnO}_2 \) thin films are shown in Figs. 7.53(a, b) and 7.54(a, b). The patterns for both the STO-K and STO-KA films show (110) as the dominant peak along with other peaks corresponding to reflections from (101), (200) and (211) planes. These patterns confirm that both the STO-K films were polycrystalline with crystallites of tetragonal rutile structure (JCPDS File No. 72-1147). No characteristic peaks of impurity were observed in the XRD patterns. XRD patterns in Fig. 7.53(a) are that of polycrystalline \( \text{SnO}_2 \) phase, which are closely in agreement with the JCPDS data. However, the broad peak or the partial coalition of the peaks corresponding to the planes (110) and (101) nearby or centered around \( 2\theta = 30^0 \) is visible in the case of as-grown \( \text{SnO}_2 \) thin films. This broad peak may be due to the presence of an amorphous SnO phase which corresponds to its intense reflection at \( 2\theta = 29.86^0 \) [JCPDS File No. 72-1012], in agreement with the XRD patterns shown in Fig. 7.53(a). This fact is well supported by the existing literature on pulsed laser deposited (PLD) \( \text{SnO}_2 \) thin films, in which films grown under vacuum always consist both poly-\( \text{SnO}_2 \) and amorphous SnO phases [87-90].

XRD patterns in Fig. 7.54(a) shows the poor crystal quality of the as-grown STO-L films. The low intensity peaks corresponding to the reflections from the planes (110), (101), (211) and (301) were matching with tetragonal rutile structure
There are some unidentifiable low intensity peaks in the patterns, which challenge the purity of the films.

The crystal quality of tin oxide films or nanoparticles improves gradually as the annealing temperature increases. Low temperature annealing could not eliminate the lattice disorders though it can provide some relaxation at the interface. Annealing temperatures larger than 400°C is necessary to get better crystal quality [46]. Hence, SnO₂ films were annealed in ambient air at 500°C using a gradual thermal annealing technique for a time interval of 2 hours. The intensity and width of the STO-KA film diffraction peaks shown in Fig. 7.53(b) were found to increase and decrease respectively on annealing in air, which suggests an improvement in crystallinity and increase in the crystallite sizes of the films and/or a decrease in the strain [47].

![XRD patterns of SnO₂ films](image)

Fig. 7.53 XRD patterns of SnO₂ films (a) as-grown and (b) annealed at 773 k

On annealing the amorphous SnO phase was completely removed which is evident in the XRD patterns shown in Fig. 7.53(b). Absence of characteristic peaks of other phases in the XRD patterns confirmed the formation of single-phase SnO₂ films. Fig. 7.54(b) shows the XRD patterns of annealed STO-LA films. The patterns reveal that annealing improved the crystallinity of the films. Peaks corresponding to the reflections from the planes (110), (101) and (211) are now distinct. Peaks corresponding to the impurity phases are absent in the patterns. From the XRD analysis, it can be asserted that the better precursor of tin for preparing the SnO₂
thin films by SILAR is SnCl₂.2H₂O than SnSO₄. Also stannous chloride (SnCl₂.2H₂O) is a cost effective precursor for synthesizing low-cost tin oxide thin films of quality as good as to those prepared by SnCl₄ [102-104].

![Fig. 7.54 XRD patterns of SnO₂ films (a) as-grown and (b) annealed at 773 K](image)

The lattice parameters of the samples were calculated using the observed values of 2θ and d-values for the tetragonal structure using Eq. (2.9). The primitive cell volume (Vc) was calculated using the Eq. (2.18).

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>c/a</th>
<th>Vc (nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>0.4737</td>
<td>0.3185</td>
<td>0.6724</td>
<td>0.0714</td>
</tr>
<tr>
<td>STO-K</td>
<td>0.4721</td>
<td>0.3118</td>
<td>0.6604</td>
<td>0.0695</td>
</tr>
<tr>
<td>STO-KA</td>
<td>0.4700</td>
<td>0.3170</td>
<td>0.6743</td>
<td>0.0700</td>
</tr>
<tr>
<td>STO-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-LA</td>
<td>0.4707</td>
<td>0.3166</td>
<td>0.6724</td>
<td>0.0702</td>
</tr>
</tbody>
</table>

*Not determined due to amorphous nature*

Table 7.7 provides the lattice parameters, primitive cell volume and c/a ratio of both as-grown and annealed SnO₂ films. The cell parameters are close to the standard values (JCPDS File No. 72-1147). As listed in Table 7.7, the cell volume of as-grown films was slightly compressed from than that of the ideal one, whereas the cell volume of the annealed SnO₂ films was approximately equal to that of the ideal one. It has been reported that the most stable structure of rutile-type SnO₂ has c/a
ratio equal to 0.674 [30]. In this work, the as-grown STO-K film has c/a ratio nearer to this value and all the annealed SnO$_2$ films have c/a ratio in excellent agreement with the reported as well as the ideal values.

Finite crystallite size and strain at the atomic level are indication of deviations from ideal crystallinity, which lead to broadening of the diffraction lines. By analyzing this broadening, information about the microstructure of a material can be extracted. The mean crystallite sizes of SnO$_2$ films were determined using the full width half maximum (FWHM) of the (110) and (101) peaks without considering the line broadening due to strain using the Debye-Scherrer’s Eq. (2.3). The grain size of as-grown STO-L was not determined due to its amorphous nature. The grain size of the films obtained is depicted in Fig. 7.55. For the annealed films, the grain size was not increased as much and is still less than 8 nm. This is in good agreement with other experimental results reported in the literature that the size of grains even after annealing at 1073 K did not exceed 6–8 nm [29].

![Grain size of SnO$_2$ films (from Scherrer’s formula and W-H plot)](image)

**Fig. 7.55 Grain size of SnO$_2$ films (from Scherrer’s formula and W-H plot)**

Uniform and non-uniform strains are the two types of strains usually associated with crystalline nanomaterials and nanostructured thin films. Uniform strain developed in a material causes the unit cell to expand or contract in an isotropic manner [49, 50, 105, 106]. This may lead to an alteration in the unit cell parameters and shift of the peaks. Presence of uniform strain was noticed in the
case of all SnO$_2$ films prepared and Table 7.7 depicts the changes in lattice parameters and unit cell volume. No broadening at FWHM of XRD profile is associated with uniform strain [107, 108]. However, non-uniform strain brings in the systematic shifts of atoms from their ideal positions and to peak broadening. This non-uniform strain arises from sources like point defects, plastic deformation and poor crystallinity [49]. The line broadening in the XRD patterns indicate the existence of non-uniform strain in the SnO$_2$ films.

To distinguish the effect of crystallite-size and strain induced broadening of the XRD profile of the SnO$_2$ films, technique developed by the Williamson and Hall (W-H plot) was utilized [74]. The W-H equation is given in Eq. (2.15). W-H plot for the films was constructed by plotting ‘$\beta\cos\theta$’ vs ‘$4\sin\theta$’ and is shown in Fig. 7.56. The crystallite size and strain were determined from the intercept at the ‘$\beta\cos\theta$’-axis and the slope of the W-H plot respectively according to Eq. (2.15).

The grain size and strain obtained from the W-H plot is shown in Fig. 7.55 and Fig. 7.57 respectively. The values of strain obtained from the W-H plot are small and compressive (negative slope) in nature. In addition, grain size obtained from W-H plot is slightly less than that determined using Scherrer’s formula without considering the line broadening effect. This decrease in grain size obtained from W-H plot can be attributed to the compressive nature of the strain according to Eq.
The marginal change in grain size gives evidence to state that strain related effect on broadening is not much significant in all the SnO\textsubscript{2} films. Therefore, as per W-H plot shown in Fig. 7.56, it can be concluded that major contribution to line broadening was from the particle size. Annealed STO-KA films are showing reduced strain from than that of the as-grown STO-K films. Through annealing, surface energy of the films, increases and a state of equilibrium may be arrived with a reduction in strain. As a result, the strained SnO\textsubscript{2} films will be relaxed [109].

Microstrain developed in the films was also determined [48] in terms of the interplanar spacing ‘d’ by using Eq. (2.17). Average value of microstrain in (110), (101) and (211) plane oriented nanocrystals of each SnO\textsubscript{2} films were computed and compared with that obtained from the W-H plot and is shown in Fig. 7.57. The values of strain obtained using Eq. (2.17), more or less equals the value obtained from W-H plot.

![Fig. 7.57 Microstrain of SnO\textsubscript{2} films](image)

The defects in the SnO\textsubscript{2} films was quantified by computing the dislocation density (\(\delta\)) using Williamson Smallman relation [75] given in Eq. (2.19). Dislocation density of the films was determined using the grain size obtained from both Scherrer’s formula and the W-H plot. The smaller value of dislocation densities may be an indication of the better crystallization of the annealed STO-KA and STO-LA
films as shown in Table 7.8. Annealed STO-KA films have better crystallization with a reduced amount of dislocation density than the annealed STO-LA films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dislocation density $(10^{16} \text{m}^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Using ‘D’ from Scherrer formula</td>
</tr>
<tr>
<td>STO-K</td>
<td>3.82</td>
</tr>
<tr>
<td>STO-KL</td>
<td>1.82</td>
</tr>
<tr>
<td>STO-L</td>
<td>f</td>
</tr>
<tr>
<td>STO-LA</td>
<td>1.95</td>
</tr>
</tbody>
</table>

*Not determined due to amorphous nature*

The texture coefficients $(T_c)$ for different crystallite orientations of the films were estimated from the following relation [32]. The texture coefficient variations of both as-grown and annealed SnO$_2$ films except that of as-grown STO-L films are shown in Fig. 7.58.

For the as-grown STO-K films the preferential orientation is both in the (110) and (101) plane with texture coefficient 1.12 and 1.14 respectively. The (200) and (211) planes has the texture coefficient values less than 1. On annealing, orientation was further improved along the (110) and (101) planes while the orientations along the other two planes were moderately suppressed. For the as-grown STO-L films, there were no distinct peaks to determine the texture coefficients. In the case of
annealed STO-LA films crystallite orientations were almost similar to the annealed STO-KA films except that of (200) and (211) planes.

(ii) Morphological characterization

Figs. 7.59(a, b) and 7.60(a, b) show the surface morphology of as-grown and annealed SnO$_2$ films. STO-K and STO-KA films consist of snow like granulates and are assembled to form the films. These crystallites may be a collection of less number of unit cells due to the limitation of their dimensions. Thus a surface with intermediate porosity and roughness is originated with all these grains bound together to form a single mass, which has been distributed evenly on the substrate.

![Fig. 7.59 SEM images of SnO$_2$ films (a) as-grown and (b) annealed at 773 K](image)

![Fig. 7.60 SEM images of SnO$_2$ films (a) as-grown and (b) annealed at 773 K](image)

High intensity XRD peaks proved that these granulate is polycrystalline and not fine-dispersed formation except that of as-grown STO-L films. Agglomerates without certain boundaries are observed in the SEM images of the STO-K films. Powdery appearance was predominant in the case of as-grown STO-L films due to
its amorphous nature, which was evident from the XRD studies. Big granules with definite shape can be observed in the images of annealed STO-LA films.

The peculiar morphology of all the films would yield large specific surface area together with high roughness. It can be noted that the porous nature of the annealed films is more or less similar to the as-grown STO-K films. Therefore, crystallinity improvement without the loss of porous morphology was achieved by air-annealing of these films. Whereas annealed STO-LA film morphology is different from that of the as-synthesized films. Porosity of these films was somewhat affected on annealing. XRD studies exposed that the grain size of all films has not much increased by annealing. Thus, it is clear that film growth is not because of increase in size of grains but due to the formation of new grains with each deposition cycle. Therefore, thickness of the film could be increased to a desired value by merely increasing the number of deposition cycles keeping the grain size of the films unaltered. EDAX analyses confirmed the compositional purity of all the SnO$_2$ films.

(iii) Thickness of the films

Film thickness was determined by using gravimetric method and was computed using Eq. (2.21). The thickness of STO-K and STO-L films was respectively 2800 nm and 2700 nm.

(iv) Optical properties

Fig. 7.61(a, b) show the absorption spectra and plot of $(\alpha h\nu)^2$ versus $h\nu$ of as-grown and annealed SnO$_2$ films. STO-K and STO-KA films show a low and steady absorbance in the entire visible and infrared regions. For STO-L and STO-LA films, absorbance is low in the visible region and gradually increases with wavelength in the infrared region. All films show a steep absorption edge in the 300-400 nm range as shown in Fig. 7.61(a). For both the annealed samples, the absorption edge was slightly red shifted and the films show a slight increase in absorbance. The absorption of annealed STO-L films was relatively increased to a high value. The red shift of the absorption edge of the films gives evidence for the improved crystallinity of films. This may be due to removal of defect levels, which is observed in films, prepared using wet chemical methods [90] and the reduction in strain on annealing.
which was discussed in section 7.3.2. As shown in Fig. 7.61(b), the band gap (E₉) of the SnO₂ films was determined by fitting a straight line to the (αhv)² vs hv curve, where 'α' is the absorption coefficient and 'hv' is the photon energy. The E₉ of the films is depicted in Table 7.9. As-grown films exhibit large value of band gap energy relative to bulk SnO₂ material. It is an indication of low structural disorders in the material [70]. The quantum confinement effects begin to influence the optical properties of SnO₂ films when the crystallite size is smaller than 8 nm [96]. Therefore, the increasingly blue-shifted value of band gap can be attributed to the small grain size of the as-synthesized films, which is less than 8 nm as given in Fig. 7.55.

Both the annealed films have band gap energy in agreement with the reported values [37, 38]. Significant variation of the optical band gap energies of undoped SnO₂ thin films was reported in the literature and the values given lie between 2.25 and 4.45 eV [70, 110]. Conduction band tailing is known to occur in disordered semiconductors, which results in a reduction in the band gap energy [111]. The decrease in the band gap energy of the annealed films can be attributed to the creation of disorders and new localized states on annealing.

![Graphs showing absorption spectra and (αhv)² vs hv](image)

Fig. 7.61 (a) Absorption spectra and (b) plot of (αhv)² versus hv of as-grown and annealed SnO₂ films
Table 7.9 Optical band gap of SnO$_2$ films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-K</td>
<td>3.79</td>
</tr>
<tr>
<td>STO-KA</td>
<td>3.24</td>
</tr>
<tr>
<td>STO-L</td>
<td>4.07</td>
</tr>
<tr>
<td>STO-LA</td>
<td>3.46</td>
</tr>
</tbody>
</table>

Transmittance and reflectance spectra of all the films are depicted in Fig. 7.62(a, b). Films, except that of the annealed STO-LA film, show transmittance of more than 55% in the visible and infrared regions. Usually smooth surfaced films show interference fringes in the transmission spectra [112]. The absence of such fringes is a clear evidence for the rough or porous surface of the films. It was reported that an increase of the average roughness creates a decrease in transmittance of the films [113]. Hence, the variation of transmittance of both annealed films may be essentially due to the increased roughness of the films and the increased concentration of particles, which causes a higher light scattering.

Fig. 7.62 (a) Transmission and (b) reflectance spectra of as-grown and annealed SnO$_2$ films
Reflectance of the STO-K films is 17-20 % in the entire Vis-NIR region and the reflectance spectra have a wavy nature. For the as-grown STO-L film, reflectance is low in the visible region, but gradually increases and became steady in the infrared region. Annealed STO-L film is showing a steady value of 20% reflectance throughout the spectral regions as depicted in Fig. 7.62(b).

Refractive index, n, of the films was determined [40, 41] from the extinction coefficient ‘k’ and the reflectance ‘R’ using Eqns. (2.25) and (2.26).

Fig. 7.63 Variation of (a) refractive index and (b) extinction coefficient of as-grown and annealed SnO₂ films

The variation of refractive index of films with wavelength is shown in Fig. 7.63(a). The values of ‘n’ obtained for all films were between 2.10-2.32 in the 400-2000 nm wavelength range. The values of refractive index obtained are in agreement with the reported values [70, 42]. Gradual decrease in refractive index having a wavy nature can be noticed in the case of STO-K films. Annealing has made a small uniform increase in the refractive index of the STO-KA films. Refractive
index of STO-L films gradually increases in the visible region and attains a steady value of 2.30 in the infrared region. Annealed STO-LA films show somewhat constant value of 2.30 throughout the spectral regions. Fig. 7.63(b) exhibits the variation in extinction coefficient as a function of wavelength. ‘k’ of the films show a linear increase with increase in wavelength. Through annealing ‘k’ values of the films were increased. Extinction coefficient of STO-LA films was more affected than that of STO-KA films. The porosity of the films was determined [57] from the refractive index of the film and the refractive index ($n_s$) of SnO$_2$ ($n_s \sim 2.006$) using Eq. (2.13).

![Figure 7.64 Average porosity of the SnO$_2$ films (wavelength range 400 -800 nm)](image)

The average porosity of the films in the wavelength range 400 -800 nm is shown in Fig. 7.64. Porosity of as-grown films was less than that of the annealed films. Annealing in air had increased the porosity of the films. The value of transmittance at a certain wavelength is highly correlated to the porosity of each film. The dependence of transmittance and porosity can be seen in Fig. 7.65 for four wavelengths in the visible region taken as examples. It can be seen that porosity and transmittance of all the SnO$_2$ films are related inversely. The non-uniformly distributed irregular pores as seen in the SEM images may be creating increased roughness, hence promoting increased light scattering and lowering of transmittance. These highly porous films yield high specific surface area.
Fig. 7.65 Dependence of transmittance with porosity of as-grown and annealed SnO\textsubscript{2} films at wavelengths of (a) 500 nm (b) 600 nm (c) 700 nm and (d) 800 nm

(v) Electrical properties

Electrical measurements were performed by dc two-point probe method using silver electrode contacts. Using the hot probe method, the films were found to be n-type conducting. Resistivity ($\rho$) of as-grown STO-K films evaluated is of the order of $10^2\ \Omega$cm and that for the STO-L films is $10^3\ \Omega$cm. Air-annealed STO-KA films having excellent crystallinity as evidenced by XRD profiles exhibit relatively lower resistivity of the order of $10^1\ \Omega$cm. Annealed STO-L films have a resistivity of the order of $10^2\ \Omega$cm. For comparison, the plot of log ($\rho$) of the films is shown in Fig. 7.66.

The electrical behavior of polycrystalline films depends on crystallite size [43, 44]. Since the as-grown grain sizes were approximately 6 nm, the grain boundary density will be more and there is chance of much carrier diffusion. This might have the reason for not achieving a low resistivity as that obtained in the case
of other deposition techniques especially spray deposition [114]. Normally annealed films show improvement in conductivity than the as-grown films due to decrement in grain boundary concentration, which enhances mobility of the charge carriers [101, 102]. As discussed in Section 7.3.2(i), annealing has no much effect on enhancing the crystallite size and hence size of the grains in these SnO$_2$ films plays negligible role on resistivity variation. Another reason for the decrease in film resistance or resistivity may be due to diminishing or removal of its defects on air annealing, which are responsible for the conductivity.

![Fig. 7.66 Variation of resistivity of as-grown and annealed SnO$_2$ films](image)

On the other hand, non-stoichiometric SnO$_2$ films are highly transparent and conducting than the stoichiometric films [115]. In the case of air-annealed films, while the ordering of the structure leads to a less resistant film, the oxidation draws the film near to its stoichiometric oxide. These two mechanisms compete for the variation of resistivity differently and have eventually led to a slight decrease in resistivity from than that of the as-prepared films.

### 7.3.3 Conclusion

Cost effective and simple wet chemical technique SILAR was used to synthesize nanostructured SnO$_2$ thin films from two different precursors of tin (SnCl$_2$.2H$_2$O and SnSO$_4$) at 353 K on glass substrates. Polycrystalline tetragonal
structured films were obtained. Films with 4-8 nm sized grains show different morphology depending on the precursor of tin used. Williamson and Hall technique was utilized to study the effect of crystallite-size and strain induced broadening of the XRD profile of the SnO\textsubscript{2} films. Lattice parameters, c/a ratio, cell volume, texture coefficient and dislocation density of the SnO\textsubscript{2} films were studied and discussed. Microstrain obtained from the W-H plot was compared with that determined from the interplanar spacing. Films showed more than 55% transmittance and a reflectance of <20 % in the entire Vis-NIR regions. As-grown films exhibit blue-shifted value of band gap (>3.75). Refractive index, extinction coefficient and the porosity of the films were computed from the optical data. Porosity and transmittance of all the SnO\textsubscript{2} films were inversely related. Electrical resistivity of the films lies in the 10\textsuperscript{1}-10\textsuperscript{3} \(\Omega\)cm range. All the characteristic properties of the films were improved on annealing especially the crystallinity, resistivity and porosity. Optical band gap of the films reduced on annealing. The better precursor of tin for preparing the SnO\textsubscript{2} thin films by SILAR is SnCl\textsubscript{2}.2H\textsubscript{2}O than SnSO\textsubscript{4}. Nanostructured SnO\textsubscript{2} films developed with the promising properties make them good candidates in applications like solid-state gas sensing material and as semiconducting dye carrier in dye-sensitized solar cells, which especially demands films with high specific surface area.
References


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