Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO₂ thin films from SnCl₂ precursor

B. Thangaraju*

Department of Physics, Bharathidasan University, Trichy 620 024, Tamil Nadu, India

Received 18 August 2000; received in revised form 10 May 2001; accepted 21 September 2001

Abstract

Tin oxide thin films doped with fluorine, antimony and both have been prepared by spray pyrolysis from SnCl₂ precursor. The respective deposition temperatures of SnO₂:F, SnO₂:Sb and SnO₂:(F+Sb) are 400 °C, 350 °C and 375 °C. The as-prepared films are polycrystalline with a tetragonal crystal structure. The lattice parameter values are not changed by the addition of dopants. The films are preferentially oriented along the (200) direction. The grain sizes vary between 200 and 650 Å. The films have moderate optical transmission (up to 70% at 800 nm) and the calculated reflectivity in the infra-red region is in the range of 88–95%. The figure of merit (f) values of SnO₂:F and SnO₂:Sb samples are 2.5 × 10⁻³ (Ω⁻¹) and 1.4 × 10⁻⁴ (Ω⁻¹), respectively. The films are heavily doped, degenerate and exhibit n-type electrical conductivity. The lowest sheet resistance (Rₛₑ) of 5.65 V/□ obtained for a SnO₂:F sample, is even lower than the values reported for the spray deposited tin oxide thin films prepared from SnCl₂ precursor. The resistivity (ρ) and mobility (μ) are in the range of 10⁻⁴–10⁻³ Ω·cm and 7–17.2 cm² V⁻¹ s⁻¹. The electron density lies between 1.3 × 10²⁰ and 13.2 × 10²⁰ cm⁻³. A thorough electrical investigation reveals that the film's conductivity depends only on carrier concentration. It is found that ionised impurity scattering is the dominant mechanism, which limits the mobility of the carriers. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrical properties and measurements; Pyrolysis; Tin oxide; X-Ray diffraction

1. Introduction

An important application of thin film technology from the point of view of global energy crunch is solar cell, which converts the energy of the solar radiation into useful electrical energy. In recent years there has been a growing interest in the use of transparent conducting oxide thin films as conducting solar window materials in thin film solar cells [1], heat reflectors for advanced glazing in solar applications [2,3] and as various gas sensors [4–7]. Tin oxide is the first transparent conductor to have received significant commercialisation [8]. Among the different transparent conductive oxides, SnO₂ films doped with fluorine or antimony seem to be the most appropriate for use in solar cells, owing to its low electrical resistivity and high optical transmittance. SnO₂ is chemically inert, mechanically hard and can resist high temperature. Many excellent reviews of transparent conductive oxides are available [9–14]. SnO₂ either doped or undoped can be synthesised by numerous techniques such as thermal evaporation [4], sputtering [4,15–22] chemical vapour deposition [23,24], metallo-organic chemical vapour deposition (MOCVD) [5], sol–gel dip coating [25], painting [26], spray pyrolysis [2,9,27–45], hydrothermal method [46] and pyrosol deposition [47,48]. Among the various deposition techniques the spray pyrolysis is the well suited for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping material, reproducibility, high growth rate and mass production...
Stoichiometric SnO$_2$ is a perfect insulator but the material becomes semi-metallic when fabricated by the spraying method [27]. Spray pyrolysis basically comes under the category of a chemical solution deposition technique [49]. The fine mist of very small droplets of the aqueous solution containing the desired species is sprayed onto a preheated substrate. The thermal decomposition takes place on the hot substrate surface giving rise to a continuous film. The tin oxide films prepared by the spray pyrolysis using SnCl$_2$ based solution as the source of tin is common [2,9,35–47] though other precursors are also reported [12,13]. Very few reports are available using SnCl$_2$ as a precursor of tin for tin oxide thin film [25,28,42,47,50]. The author has already reported the preparation and characterisation of PbSnS$_2$, SnS and SnS$_2$ thin films by the spray pyrolysis using SnCl$_2$ as a source material for tin [51,52]. The advantages of the SnCl$_2$ are that is cheaper than SnCl$_4$ and can be produced easily in a laboratory [42]. The prime aim of this work is to produce highly conducting F and Sb doped tin oxide thin films from SnCl$_2$ precursor solution and to investigate their structural and electrical properties.

2. Experimental details

A laboratory built double nozzle glass sprayer is used to prepare the thin film samples of the present study. The schematic diagram of the experimental set-up and other details have been reported elsewhere [53,54]. A mixture of 15 g of SnCl$_2$·2H$_2$O salt and 5 ml of HCl is heated slightly. This mixture is diluted by adding methanol and the diluted solution is made up to 50 ml by adding triply distilled water. This forms the basic solution of the spray liquid. Ammonium fluoride diluted with water is added to this solution in proper proportions to effect fluorine doping. Antimony doping is done with SnCl$_2$ dissolved in methanol.

Filtered compressed air is used as carrier gas and the flow rate is 7 l/min at a pressure of 7.59×10$^4$ N m$^{-2}$. The solution flux is kept at 4 ml min$^{-1}$. The normalised distance between the spray nozzle and the substrate is 35 cm. Optical microslide glass plates with an effective area of 7.5×2.5 cm are used as substrates. The substrates are cleaned with organic solvents and rinsed with triply distilled water before spraying. The spray liquid, prepared from the basic solution with different concentrations of NH$_4$F or SbCl$_3$ or both, is then sprayed onto the hot substrates where pyrolysis and film deposition occurs. The normalised deposition temperatures are 400 °C, 350 °C and 375 °C for fluorine, antimony and (F + Sb) doped films, respectively. At a temperature lower than these optimum values a yellowish coloration of the sample appears due to the unconverted precursor and for higher temperatures a white fog is found due to the excess of tin.

The spray time is maintained at 1 s. To avoid excess cooling of the substrates a 2-min waiting time is allowed between successive spraying applications. Uniform coating is achieved by rotating the substrate through a predetermined angle in its plane after each application. The F, Sb and (F + Sb) dopant ratio are varied over a wide range and all other experimental parameters are fixed at their optimum values. The [NH$_4$F]/[SnCl$_2$] ratio by weight percentage in the spray liquid is kept at values of 4, 6, 8, 10 and 15, the [SbCl$_3$]/[SnCl$_2$] ratio at 0.2, 0.4, 0.6, 1 and 2 and the [NH$_4$F+SbCl$_3$]/[SnCl$_2$] ratio at 7.5+1, 8+1, 12+1, 10+0.2, 10+0.5 and 15+0.5. Reproducibility is achieved by controlling the deposition parameters. In all, more than 50 films were deposited for each concentration, fixing the thickness at a constant value. The as-prepared films were structurally, electrically and electro-optically characterised. All the measurements were carried out on 1-μm-thick films. The thickness of the film was measured by a conventional mass method [38,52–55].

The structural properties of the films were studied by computer controlled RIGAKU, X-ray diffractometer using CuK$_\alpha$ (1.5418 Å) radiation. The scanning angle 2θ was varied from 10 to 90° in step of 0.02° and the scanning speed was fixed at 2° min$^{-1}$.

The electrical resistivity and Hall mobility were measured using the standard van der Pauw four probe method [56]. Colloidal silver paint was used as the ohmic contact. The variation of resistivity with temperature was measured from 30 to 200 °C. The n-type electrical conductivity of the films was confirmed by the Hall measurement. The Hall probe experimental arrangement and the measurement details can be found in Thangaraju [57]. Optical transmittance measurements were carried out using a Hitachi model 3400 UV-VIS-NIR, double beam spectrophotometer.

3. Results and discussion

3.1. Structural analysis

Since changes in the structural properties of SnO$_2$ films can be correlated with the variations of the electrical and optical properties, XRD measurements were made to determine the phase, crystallographic structure and the grain size of the crystallites. Typical X-ray diffraction spectra recorded on SnO$_2$:F ([NH$_4$F]/[SnCl$_2$] = 10 wt.%), SnO$_2$:Sb ([SbCl$_3$]/[SnCl$_2$] = 0.4 wt.%) and SnO$_2$:(F+Sb) ([NH$_4$F+SbCl$_3$]/[SnCl$_2$] = 10+0.5 wt.%) films are shown in Fig. 1. All the diffractograms contain the characteristic SnO$_2$ peaks only. Other phases (SnO, Sn$_2$O$_3$ or SnF$_2$), as reported to occur in SnO$_2$ films [23,58,59] are not observed in the deposited layers. The (200) peak is the strongest
peak observed for all the films. Other peaks observed are (110), (211), (220), (310), (301) and (400). The addition of dopants does not affect the preferred (200) orientational growth of the films. One significant difference is the intensity of this peak. Antimony doping leads to the peak intensity higher than the other dopants.

The most striking feature from the XRD results is that the films prepared for the present study are highly oriented with the (200) plane parallel to the substrate. It was, however, reported by Grodillo et al. [42] that doped and undoped SnO films prepared by spray pyrolysis from SnCl₂ precursor present a preferential growth along the (110) direction. The precursor chemistry and growth rate have been analysed by them for the deposition of SnO films from SnCl₄ and SnCl₂. The exact reasons for this difference may be sought in the differences in the preparation of starting solutions. Smith et al. [47] have analysed the preparation of SnO₂ films, with and without addition of HCl in SnCl₂·2H₂O solution. It is found that without addition of HCl in the starting solution, the films preferred orientation is (110), whereas the HCl (≥0.2 mol l⁻¹) added with the starting solution, the films are highly oriented in (200) direction. This can be attributed to the different formation of the molecules in the starting solution. In SnCl₂·2H₂O solution, tin based polymer molecule is formed. SnCl₄ dissolved in alcohol forms complexes like SnCl₄·2CH₃OH [60], which decompose at the pyrolysis temperature to form hydrated SnO₂ on the substrate. The hydrated SnO₂ molecule is formed by yet another way, from SnCl₂·2H₂O + HCl solution. SnCl₂·2H₂O reacts with HCl to form HSnCl₃; this neutral HSnCl₃ molecule is unstable and highly reactive [61]. At the pyrolysis temperature, HSnCl₃ is thermally decomposed to form the hydrated SnO₂ molecule.

It has been reported from the SEM micrograph analysis that the film morphology of SnCl₂·2H₂O with HCl precursor is similar to that obtained with SnCl₄ [47]. It is well established now, that SnO₂ films deposited from SnCl₄ precursor at temperatures of approximately 400 °C always grow in the (200) direction [35,37,39,41–43]. It is therefore not surprising that in the present investigation the films are highly oriented in the (200) direction since they are prepared from the SnCl₂·2H₂O + HCl starting solution.

Fig. 1. X-Ray diffraction spectra of (a) SnO₂:F ([NH₄F]/[SnCl₄] = 10 wt.%); (b) SnO₂:Sb ([SbCl₃]/[SnCl₄] = 0.4 wt.%); and (c) SnO₂:(F+Sb)[NH₄F]/[SnCl₄] + [SbCl₃]/[SnCl₄] = [10] + [0.5] wt.% thin films.

Table 1

<table>
<thead>
<tr>
<th>Standard*</th>
<th>Observed (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>(hkl)</td>
</tr>
<tr>
<td>3.351</td>
<td>110</td>
</tr>
<tr>
<td>2.369</td>
<td>200</td>
</tr>
<tr>
<td>1.765</td>
<td>211</td>
</tr>
<tr>
<td>1.675</td>
<td>220</td>
</tr>
<tr>
<td>1.498</td>
<td>310</td>
</tr>
<tr>
<td>1.415</td>
<td>301</td>
</tr>
<tr>
<td>1.184</td>
<td>400</td>
</tr>
</tbody>
</table>

The spray solution dopant wt. ratios correspond to [NH₄F]/[SnCl₄] = 10 wt.%, [SbCl₃]/[SnCl₄] = 0.4 wt.% and [NH₄F]/[SnCl₄] + [SbCl₃]/[SnCl₄] = [10] + [0.5] wt.%.

* JCPDS card no: 21-1252.

Table 2

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>Standard*</th>
<th>F</th>
<th>Sb</th>
<th>(F+Sb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>4.737</td>
<td>4.761</td>
<td>4.768</td>
<td>4.765</td>
</tr>
<tr>
<td>c (Å)</td>
<td>3.187</td>
<td>3.225</td>
<td>3.210</td>
<td>3.194</td>
</tr>
</tbody>
</table>

* JCPDS card no: 21-1252.
smaller in size. Antimony doping increases the size of the 
grains and the combined (F + Sb) doping increases 
the grain size further.

3.2. Electro-optical studies

Sheet resistance \( R_{\text{sh}} \) is a useful parameter in 
comparing thin films, particularly those of the same material 
deposited under similar conditions. The plots of sheet 
resistance vs. dopant concentration in the spray solution 
for SnO\(_2\):F (FTO) and SnO\(_2\):Sb (ATO) films are shown 
in Figs. 2 and 3, respectively. \( R_{\text{sh}} \) decreases with 
concentration initially reaches a minimum and increases 
beyond this particular concentration.

In the fluorine doped tin oxide films, the F\(^-\) anion 
substitutes for an O\(^{2-}\) anion in the lattice, creates more 
free electrons and decreases the value of \( R_{\text{sh}} \). The 
minimum value is obtained at \([\text{NH}_4\text{F}] / [\text{SnCl}_2] = 10 \) 
wt.%. Increasing the value of \( R_{\text{sh}} \) after a specific level 
of F content probably represents a solubility limit of F 
in the tin oxide lattice. The excess F atoms do not 
occupy the proper lattice positions to contribute to the 
free carrier concentration and at the same time the 
increasing disorder leads to the increase of the sheet 
resistance.

When Sb is added to SnO\(_2\), Sb is incorporated into 
the Sn\(^{4+}\) sites of the SnO\(_2\) lattice substitutionally. In 
ATO samples, Sb is in two different oxidation states 
namely, Sb\(^{5+}\) and Sb\(^{3+}\). During the initial addition of 
Sb in tin oxide film, the Sb\(^{5+}\) substituted on the Sn\(^{4+}\) 
site act as donors and create excess electrons. So the 
free carrier concentration is higher and consequently the 
sheet resistance decreases with the addition of Sb up to 
a certain level. At \([\text{SbCl}_3] / [\text{SnCl}_2] = 0.6 \) wt.%, the film 
reaches the minimum value of sheet resistance. Further 
addition of Sb introduces the Sb\(^{3+}\) sites, which act as 
acceptors. The Sb\(^{3+}\) species would compensate the 
donor levels, which were created by the Sb\(^{5+}\) species, 
leaving to an increase in the \( R_{\text{sh}} \).

The minimum value of sheet resistance is 5.65 and 
8.1 \( \Omega / \square \) for FTO and ATO films, respectively. These 
sheet resistance values agree with the reported films 
deposited by SnCl\(_4\) [28,30–32,36–38,40–
42,44,45,47,55]. The \( R_{\text{sh}} \) of 5.65 \( \Omega / \square \) is the lowest 
value among the reported SnO\(_2\) films, prepared from 
SnCl\(_2\) starting solution [28,42,47].

Transparency \( T \) and conductivity are strongly inter-
related and the nature of this interdependence is dictated 
by the influence of various deposition parameters on the 
electro-optical properties of the films. For films depos-
ited under optimum conditions, \( R_{\text{sh}} \) and \( T \) depend 
significantly on the film thickness. In the present study the 
thickness of the films are approximately 1 \( \mu \)m, which 
is higher compared to the reported film thickness 
[28,42,47]; this higher thickness affects the optical 
transmission. All the films show only moderate trans-
mission. The highest transmittances obtained (at 800 
nm) are in FTO samples at \([\text{NH}_4\text{F}] / [\text{SnCl}_2] = 6 \) wt.\% 
and in ATO samples at \([\text{SbCl}_3] / [\text{SnCl}_2] = 0.2 \) wt.\% are 
70\% and 55\% respectively. A good criterion to define 
the quality of highly transparent and conductive thin 
film is through the introduction of a figure of merit 
calculated using Haacke’s equation \( \phi = T^{10}/R_{\text{sh}} \) [62].

The figure of merit of FTO and ATO samples are 
2.5 \( \times \) \( 10^{-3} \) (\( \Omega \) \(^{-1}\)) and 1.4 \( \times \) \( 10^{-4} \) (\( \Omega \) \(^{-1}\)), respectively.
The FTO film figure of merit is one order higher than 
the figure of merit of the ATO film. This is quite 
expected because antimony doping leads to higher \( R_{\text{sh}} \) 
values and the appearance of bluish coloration due to 
the addition of doping leads to the poor transmission 
[41]. A comparison of electro-optical properties of 
SnO\(_2\) films prepared by various techniques can be found 
reference [33]. The transmittance spectra of the films 
and the optical investigations will be published 
elsewhere.

The reflectivity \( R \) of the samples is calculated using 
the relation [33]

\[
R = (1 + 2 \varepsilon_0 C_0 R_{\text{sh}})^{-2}
\]

with \( 1/\varepsilon_0 C_0 = 376 \) \( \Omega \) (the free space impedance), which 
is valid over a wide range in the IR region. The
calculated $R$ values are lying in the range of 88–95%. The high $R$ values of the samples, along with high $T$ values, make them suitable for photothermal conversion of solar energy.

3.3. Electrical studies

The variation of Hall mobility, carrier density and resistivity at room temperature against the doping concentration is shown in Figs. 4 and 5. The values of $\mu$, $n$ and $\rho$ are obtained from the combined measurements of resistivity and Hall coefficient. These values are comparable with the values found in literature \cite{29,30,34}. The electrical resistivity is almost constant throughout the temperature range from 30 to 200 °C. All the samples are heavily doped and are degenerate. Film degeneracy is established by evaluating the Fermi energy by the expression

$$E_F = \left( \frac{h^2}{8am^*} \right) \left( \frac{3n}{\pi} \right)^{1/3}$$  \hspace{1cm} (2)

where $h$ is the Planck’s constant, $n$ is the concentration of free carrier and $m^*$ is the reduced effective mass. In all the calculations a mean value of $m^* = 0.3m$ \cite{63}, where $m$ is the electron rest mass, is used. The evaluated $E_F$ values are very high compared to $kT$ (~0.03 eV) at room temperature. The observed variation of $\mu$ and $\rho$ is small in the composition ranges investigated. For both the dopants, the carrier density initially increases with increasing concentration and then decreases. The respective peak concentrations occur at the weight ratios of $[\text{NH}_4\text{F}]/[\text{SnCl}_2] = 10$ wt.% and $[\text{SbCl}_3]/[\text{SnCl}_2] = 0.6$ wt.%. 

A semiconducting system may return to equilibrium after the application of an external field as a result of scattering. Free carriers may interact with a variety of scattering centres. These centres may be impurity atoms (ionised or neutral), thermal vibrations (acoustical and optical) of the lattice atoms, structural defects (dislocations, vacancies) and other obstacles. In polycrystalline thin film semiconductors, apart from the above scattering centres, the influence of the grain boundary has also to be taken into account. The interaction between the carriers and the scattering centres determines the actual value of the mobility of the carriers in these materials.

In the interpretation of the results obtained for a given transport phenomenon, one has to deal with the problem of mixed scattering of carriers. To solve this problem, one has to identify the main scattering mechanisms and then determine their contributions. The scattering also varies with the temperature and with the impurity concentration.

In analysing the mobility data of the samples, the relaxation times characteristic of the various scattering mechanisms can be added together reciprocally to give an effective relaxation time \cite{64}, if the mechanisms can be regarded as independent. The mobility $\mu$ is obtained as

$$\mu = \frac{e}{m^*(\tau)}$$  \hspace{1cm} (3)

With $\langle \tau \rangle$ a suitable average over the energy-dependent relaxation times. The angle brackets are omitted in the following discussion.

For the scattering by neutral impurities we have approximately \cite{65}

$$\tau_n = \frac{(\pi m^* e)^2}{10\varepsilon h^2 N_n}$$  \hspace{1cm} (4)

where $N_n$ the concentration of neutral impurities and $\varepsilon$ the absolute dielectric permittivity; the other symbols have their usual meanings. For the heavy doping case, this form of scattering is unimportant because, right down to low temperatures (~77 K), impurities in heavily doped semiconductors are fully ionised.

All the doped SnO$_2$ films prepared here are polycrystalline. They are composed of crystallites joined together by grain boundaries, which are transitional regions between different orientations of neighbouring crystallites. These boundaries between grains play a significant role and influence the properties of the film. The electrical properties of the films are significantly affected by the grain boundaries. These boundaries are expected to act as scattering centres for the carriers.

In Fig. 4, the variation of Hall mobility $(\mu)$, carrier density $(n)$ and resistivity $(\rho)$ with dopant weight ratio for SnO$_2$:F thin films is shown. The high $\mu$ values of the samples, along with high $T$ values, make them suitable for photothermal conversion of solar energy.

In Fig. 5, the variation of Hall mobility $(\mu)$, carrier density $(n)$ and resistivity $(\rho)$ with dopant weight ratio for SnO$_2$:Sb thin films is shown. The high $\mu$ values of the samples, along with high $T$ values, make them suitable for photothermal conversion of solar energy.
role in the scattering of charge carriers in polycrystalline thin coatings. To analyse the effects of grain boundaries on electrical properties of thin film materials two models have been employed. The first is a charge trapping model [66,67] where it is assumed that grain boundaries contain trapping states induced by lattice defects. These states compensate a fraction of the charge carriers of the ionised uniformly distributed dopants. This process creates a potential barrier across the depletion region, impeding the carrier motion from one crystallite to another. The influence of the grain size becomes very important when the depletion layer width becomes comparable with the grain size of the crystallite. The second model is a dopant segregation model. In this case the grain boundaries are assumed to act as sinks for the preferential segregation of the dopants. Therefore they become inactive in the boundary layers [68,69].

The first model has been employed to analyse the experimentally measured mobility values of the charge carriers in doped and undoped SnO2 films [29,49]. In this model the conduction mechanism is based on thermionic emission over the potential barrier. This, of course, requires a barrier energy larger than kT. The barrier energy calculation is done by fitting the measured mobility to some functional form derived on the basis of thermionic emission over intergrain barriers. As for the degenerate samples, since the mobility shows feeble variation with temperature, this model is not suitable because the activation energy is smaller than kT. This is true in the present study also, since the resistivity remains nearly constant throughout the temperature range of 30–200 °C for all the samples.

Another condition is that the mean free path l of the free carriers should be comparable to the size of the grains in the films. For the degenerate samples l can be estimated with the expression [70]

$$l = \frac{\hbar}{2e} \left( \frac{3n}{\pi} \right)^{\frac{1}{3}} \mu$$

where n is the carrier concentration and μ is the measured mobility. The mean free path values calculated for the sample lie in the range of 14–20 Å. These l values are considerable shorter than crystallite dimensions calculated using X-ray data. Based on the above discussion it is concluded that grain boundary scattering is not the dominant mechanism. The resistivity and carrier concentration of fluorine doped SnO2 films determined by Hall measurements at room temperature have been analysed by Bruenaux et al. [40] within the frame of the grain boundary model. The conclusion arrived at is that at large carrier densities, the influence of grain boundaries becomes negligible. Similar conclusions have been arrived by Haitijema et al. [39] in the case of fluorine doped layers with high electron concentrations. The explanation given in arriving at this conclusion is that the Fermi energy, which is proportional to $n^{2/3}$ is much higher for the doped samples. So, the free electrons in the doped samples have a much higher energy and will move easily across the inter-grain energy barriers.

Another scattering mechanism prevalent in doped semiconductors is the ionised impurity scattering. According to the Brooks–Herring formula [71], the relaxation time for coupling to ionised impurities is, in the degenerate case, given by

$$\tau_i = \frac{(2m^*)^{1/2} e^2 E_v^{1/2}}{\pi \epsilon^4 N_i f(x)}$$

with $N_i$ the carrier concentration of ionised impurities and f(x) given by

$$f(x) = \ln(1 + x) - \frac{x}{1 + x}$$

with

$$x = \frac{8m^* E_v R_s^2}{\hbar^2}$$

The screening radius $R_s$ is given by

$$R_s = \frac{\hbar}{2e} \left( \frac{e}{m^*} \right)^{1/2} \left( \frac{\pi}{3N_i} \right)^{1/6}$$

where $\epsilon$ is the absolute dielectric permittivity and $m^*$ is the effective mass of the carriers.

Substitution of the $\tau_i$ expression [Eq. (6)] in Eq. (3) yields the expression for mobility due to ionised impurities as

$$\mu_i = \frac{2}{m^*} \left( \frac{e^2}{\pi \epsilon^4 f(x) N_i} \right)^{1/2}$$

Since all the dopant atoms will be fully ionised at room temperature, impurity ion concentration will be equal to the free carrier concentration. Thus taking $N_i = n$ and calculating $E_v$ with the expression given in Eq. (2), mobility values are calculated using the expression in Eq. (10).

The calculated mobility values are tabulated in Table 3 along with mean free path, carrier concentration and measured mobility values for different dopants. The calculated mobility values are comparable to the measured values. This clearly indicates that the main damping mechanism limiting the mobility in doped SnO2 samples is the ionised impurity scattering. In addition, scattering by impurity ions predicts an increasing mobility with decreasing concentration, which is also evident from Table 3. This further supports the above conclusion.

From the foregoing discussion, it is concluded that ionised impurity scattering is the dominant mechanism in the films. Similar conclusions have been reported by other workers [2,9,27,39,43]. This conclusion means
Table 3
Comparison of observed and calculated mobility ($\mu$) data along with carrier concentration ($n$) and mean free path (l) values of different dopant ratios of SnO$_2$ thin films

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Wt. ratio</th>
<th>$n$ ($\times 10^{20}$ cm$^{-3}$)</th>
<th>l (Å)</th>
<th>$\mu_{\text{obs}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_{\text{cal}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>4</td>
<td>5.701</td>
<td>14</td>
<td>9.6</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.800</td>
<td>16</td>
<td>9.0</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>8.333</td>
<td>18</td>
<td>8.5</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>10.420</td>
<td>15</td>
<td>7.5</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>13.160</td>
<td>16</td>
<td>7.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Sb</td>
<td>2</td>
<td>1.671</td>
<td>19</td>
<td>16.7</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.102</td>
<td>17</td>
<td>12.6</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>5.162</td>
<td>13</td>
<td>10.1</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>5.950</td>
<td>17</td>
<td>9.6</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>9.523</td>
<td>20</td>
<td>8.1</td>
<td>7.2</td>
</tr>
<tr>
<td>(F+Sb)</td>
<td>10+0.5</td>
<td>1.333</td>
<td>18</td>
<td>17.2</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>15+0.5</td>
<td>1.553</td>
<td>18</td>
<td>16.1</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>10+0.2</td>
<td>2.645</td>
<td>17</td>
<td>13.0</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>12+1</td>
<td>4.055</td>
<td>18</td>
<td>11.6</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>7.5+1</td>
<td>4.257</td>
<td>17</td>
<td>11.2</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>8+1</td>
<td>5.061</td>
<td>16</td>
<td>10.0</td>
<td>9.3</td>
</tr>
</tbody>
</table>

that the conductivity $\sigma$ is mainly determined by the free carrier concentration in these films, because mobility and carrier concentrations are no longer independent of each other.

Further effort is under progress to decrease the film thickness and increase the optical transmission without increasing the sheet resistance. This combination is needed for the usage of transparent conducting window material in thin film solar cells.

4. Conclusion

Transparent conducting doped SnO$_2$ layers have been prepared by spray pyrolysis from SnCl$_2$ precursor solution. Structural and electrical properties of the films have been analysed for three cases of doping: fluorine, antimony, and (F+Sb). Structural investigations using XRD reveal that the layers are composed of SnO$_2$ only. No other phases are detected. The lattice parameter values are not affected by the doping. The preferred orientation is in (200) direction and the grain sizes are independent of the dopant. The average grain size is approximately 300 Å. The lowest sheet resistance of 5.65 $\Omega$/□ is obtained for the SnO$_2$:F film. Better transparency is achieved with fluorine doping. Moderately high figure-of-merit values are obtained for ~1-μm-thick fluorine doped samples. All the films are degenerate with carrier concentrations in the range of $1.3\times10^{20}$-$1.3\times10^{21}$ cm$^{-3}$. The resistivities of the samples are of the order of $10^{-3}$-$10^{-4}$ $\Omega$-cm. Fluorine doped samples are having lower mobility than the antimony and (F+Sb) doped samples. From the electrical investigations it is concluded that the ionised impurity scattering is the dominant mechanism limiting the mobility of the samples. The carrier concentration determines the resistivity of the films.

Acknowledgements

The author is gratefully acknowledged to Prof. E.S.R. Gopal and Dr. K.S. Sanguuni, Department of Physics, Indian Institute of Science; Prof. M. Laxmanan and Dr. K. Ramamurthi, Department of Physics, Prof. C. Thangamuthu, Department of Economics, Bharathidasan University and Prof. A. Srinivasan, Department of Physics, Indian Institute of Technology, Guwahati, for their help, moral support and encouragement, when I had difficulties during the course of this work. The author sincerely thanks to the referee’s valuable suggestions to improve the quality and clarity of the manuscript. The Department of Physics, Sri Venkateswara University, Tirupathi, and the Inter University Consortium, Indore, are acknowledged sincerely for the usage of Hall set-up and for recording the XRD spectra, respectively. The author would like to thank Dr. R. Arvinda Narayanan and S. Jaisankar, for their critical reading of the manuscript.

References


