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OPTOELECTRONIC PROPERTIES OF SPRAY DEPOSITED SnO_2:F THIN FILMS FOR WINDOW MATERIALS IN SOLAR CELLS

E. Elangovan[*], K. Ramamurthi

Department of Physics, Bharathidasan University, Tiruchirappalli – 620 024, India

Spray pyrolysis technique has been employed to prepare ~1.2 µm thick pure and fluorine doped tin oxide films from $SnCl_2$ precursor. The electrical and optical studies on the as prepared films were carried out. The sheet resistance was found to decrease with increasing doping concentration to a minimum of 1.75 Ω/□ for 15 wt. % of NH_4F, but increased thereafter. The minimum sheet resistance observed in the present study is the lowest among the reported values for SnO_2:F films prepared from $SnCl_2$ precursor. The transmittance was found to increase with the increase in fluorine concentration. The highest optical transmittance obtained is 85 % (at 800 nm). The calculated reflectivity in the infrared region is in the range of 94 - 98 % (for 5-30 wt% NH_4F). On fluorine doping, the figure of merit values of the tin oxide films were found to increase to a maximum of 5.67×10^{-2} (15 wt. % of NH_4F) from 4.73×10^{-6} (at 800 nm) for undoped ones. The obtained values of figure of merit and reflectivity are discussed in the context of the suitability of this material for transparent and conducting window materials in heterojunction thin film solar cells.

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Keywords: Spray pyrolysis, Tin oxide thin films, $SnCl_2$ precursor, Optoelectronic properties

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. The main requirement for thin film solar cells is the window material, which allows the visible region of solar spectrum to pass through but reflect the IR radiation. This can be achieved by the development of transparent and conducting oxide (TCO) coatings such as tin oxide (SnO_2), cadmium oxide (CdO), zinc oxide (ZnO), cadmium stannate (Cd_2SnO_4), cadmium indate ($CdIn_2O_4$), and indium oxide (In_2O_3). Studies on these highly conducting semiconductors have attracted the interest of many researchers because of their wide applications in both industry and research [1-7]. These films are very efficient in reflecting broadband infrared heat radiation in a manner similar to highly conducting metal-like materials and in transmitting the light in the visible region as if they are insulators. Such spectrally selective coatings have wide applications in solar thermal energy conversion, solar photovoltaic conversion, solar heating, window insulation, and thermal insulation in lamps [3].

Among the available TCOs, SnO_2 seems to be more appropriate because they are quite stable toward atmospheric conditions, chemically inert, mechanically hard and can resist high temperature. The increasing need for these films called for the employment of various deposition techniques such as magnetron sputtering [8-10], rf sputtering [11-13], chemical vapour deposition [14-16], metal-organic chemical vapour deposition [17-19], spray pyrolysis [20-22], sol-gel dip coating [23,24], evaporation [25,26], pyrosol method [27], hydrothermal method [28], photo-chemical vapour deposition [29], pulsed laser deposition [30], immersion method [31], and painting [32]. Among these techniques, the spray pyrolysis is well suited for the preparation of pure and doped tin oxide thin films. This technique has the advantage of simple and inexpensive experimental arrangement, ease of

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[*] Corresponding author: elankam29@yahoo.com

adding doping material, reproducibility, high growth rate, and mass production capability for uniform large area coatings, which are desirable for industrial and solar cell applications.

SnO_2 is a perfect insulator in its bulk form. When these materials are prepared from spraying method [33], deviation from the stoichiometry occurs and hence the material becomes semi-metallic. The challenge is to produce coatings of this non-stoichiometric oxide, which are highly transparent and conducting. To conquer this problem, variants of the standard deposition techniques and precursors are being tried out. $SnCl_4$ has been used as the very common source of tin in spray pyrolysis technique [34-36] and in few cases, organic tin compounds [37-39] and tin (II) fluoride [40] have also been used. There are very few reports available on the preparation of these materials from $SnCl_2$ precursor [1,41-50]. Thin films of other tin compounds such as $PbSnS_2$, SnS and SnS_2 have also been prepared using $SnCl_2$ precursor [51,52]. $SnCl_2$ being cheaper than $SnCl_4$ can prove to be a cost-effective precursor for preparing low-cost tin oxide thin films of quality comparable to those prepared by $SnCl_4$.

In the present work, highly transparent and conducting, fluorine doped tin oxide thin films have been prepared from $SnCl_2$ precursor and their electrical and optical properties have been investigated. A good criterion to define the quality of the window material for thin film solar cells is the figure of merit, which is a function of sheet resistance and visible transmittance. Hence, in the present paper, more light has been thrown on the optical studies of the fluorine doped tin oxide films along with the estimation of their sheet resistance values.

2. Experimental details

A schematic diagram of an in-built experimental setup for spray pyrolysis is shown in Fig. 1. The spray gun is a coaxial assembly of a corning glass tube and a capillary. One end of the glass tube is fused with the outer surface of the capillary and the other end is tapered to form the spray nozzle. The solution and the carrier gas (filtered compressed air) are passed through the inlets provided in the capillary and glass tube. The substrate heater, basically a resistively heated Kanthal wire, is covered with a stainless steel plate on which the substrates are placed. The temperature is measured using a Chromel-Alumel thermocouple and controlled by a digital PID temperature controller with an accuracy of ±5° C.

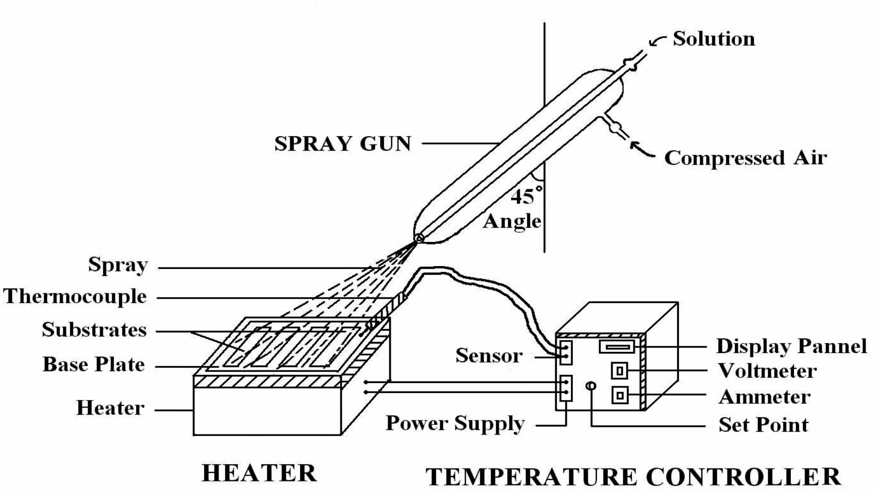

Fig. 1. Schematic diagram of the experimental setup for spray pyrolysis.

High purity stannous chloride ($SnCl_2 \cdot 5\ H_2O$ – Qualigens make) was used as the source for tin. The fluorine doping was achieved using ammonium fluoride (NH_4F – Rankem chemicals). The doping concentration was varied from 0 to 30 wt. %. Microscopic glass slides ($75 \times 25 \times 1.4$ mm^3) were used as substrates. The substrates were cleaned using distilled water and various organic solvents. The substrate temperature was fixed at 400 °C. Films of ~1.2 μm thick were grown. The thickness was optimized from our previous studies (to be published elsewhere) based on the effect of thickness on the properties of fluorine doped tin oxide films.

$SnCl_2 \cdot 5H_2O$ (11g) was dissolved in 5 ml of concentrated hydrochloric (HCl) acid by heating at 90° C for 10 minutes. The resultant transparent solution was then diluted with methanol formed the starting solution. For fluorine doping, NH_4F dissolved in doubly distilled water was added to the starting solution. The amount of NH_4F was varied to achieve different [F]/[Sn] wt. ratio. The deposition time was 40 minutes for all the depositions. The carrier gas flow rate was maintained at 6 l/min at a pressure of 6.50×10^4 N m^{-2}. The normalized distance between the spray nozzle and the substrate is 35 cm. The spray time was maintained at < 1 s and the spray interval at ~3 min. For each concentration, several sets of films were prepared and their structural, electrical and optical quality were found to be highly reproducible.

The XRD patterns recorded on the samples, using Philiphs X' Pert PRO X-ray diffraction system, confirmed that the films are polycrystalline in nature with tetragonal crystal structure. The electrical studies were carried out by Hall measurements in van der Pauw configuration. The transmission and reflection spectra of films were recorded using the Hitachi U-3400 UV-VIS-NIR double beam spectrophotometer in the wavelength ranging from 300 to 2500 nm.

3. Results and discussion

3.1. Electrical properties

The Hall mobility (μ), carrier concentration (n), sheet resistance (R_{sh}) and resistivity (ρ) as the function of fluorine doping were obtained from the Hall measurement. The values are consistent with those found in literature. From the negative sign of Hall coefficient, the films were found to be n-type conducting. For resistivity measurements, two different resistance values (R_1 and R_2) were measured at different points of the samples. The sheet resistance can be calculated using,

$$R_{sh} = f\left(\frac{\pi}{ln\ 2}\right)\left(\frac{R_1 + R_2}{2}\right) \tag{3.1}$$

where the van der Pauw correction factor (f) is given by,

$$f = 1 - \left(\frac{ln\ 2}{2}\right)\left(\frac{R_1 - R_2}{R_1 + R_2}\right)^2 \tag{3.2}$$

Sheet resistance (R_{sh}) is an useful parameter in comparing thin films, particularly those of the same material deposited under different conditions. The variation of sheet resistance as a function of fluorine doping is plotted in Fig. 2. It is found that the sheet resistance of the pure tin oxide thin films (38 Ω/□ –not shown in figure) decreases with increasing fluorine concentration initially and reaches a minimum value of 1.75 Ω/□ (at 15 wt. %) but then increases for further doping. The minimum value of sheet resistance achieved in the present study is lower than those reported earlier for films prepared from $SnCl_2$ precursor. The reported values of the sheet resistance of SnO_2:F films prepared by spray pyrolysis from $SnCl_2$ precursor are given in Table 1 for comparison.

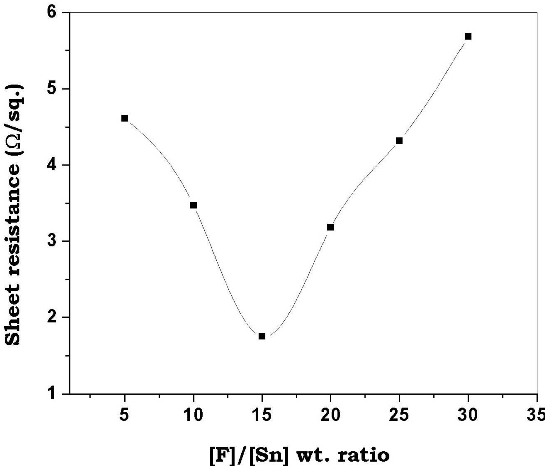

Fig. 2. Variation of sheet resistance as a function of fluorine concentration of SnO_2:F films prepared at 400 °C.

Table 1. List of the values of sheet resistance (R_{sh}) of SnO_2:F thin films prepared by spray pyrolysis from $SnCl_2$ precursors.

Reference	Year	Doping % (NH_4F)	R_{sh} (in Ω/□)
This work	2002	15 wt. %	1.75
″	″	20 wt, %	3.18
″	″	5 wt. %	4.61
[1]	2002	10 wt. %	5.65
[49]	1996	4.5 wt. %	16.40
[44]	1994	0.7 mole %	30.00

When fluorine is incorporated in tin oxide films, each F^- anion substitutes an O^{2-} anion in the lattice and the substituted O^{2-} anion introduces more free electrons. This results in an increase in free electrons and decreases the value of R_{sh}. This can be attributed as the reason for decreasing R_{sh} with increasing fluorine doping. The increase in the value of R_{sh} beyond a certain doping concentration of fluorine probably represents a solubility limit of fluorine in the tin oxide lattice. The excess F atoms do not occupy the proper lattice positions to contribute to the free carrier concentration while, at the same time, enhance the disorder of the structure leading to an increase in sheet resistance. This was observed for our films beyond 15 wt. % of NH_4F.

3.2. Optical properties

The transmittance and reflectance spectra recorded for the films in the wavelength range of 300-2500 nm are shown in Figs. 3 and 4, respectively. A plain glass plate and an alumina-coated glass were used as a reference in the transmittance and reflectance measurements, correspondingly. The transmittance (T) of the film increases with increasing fluorine concentration. The transmittance of the pure tin oxide film is only 42 % (Fig. 6. - at 800 nm) whereas it increases to 85 % (at 800nm) on doping 30 wt. % of NH_4F. This transmittance value of fluorine doped tin oxide films are in good agreement with the earlier reports [20,22,43,53,54]. The reflectance spectra obtained for 5, 15, and 30 wt. % of NH_4F doping are shown in Fig. 4. It is apparent from the figure that the reflectance of all the films is less than 10 % in the wavelength range of 300 to 1500.

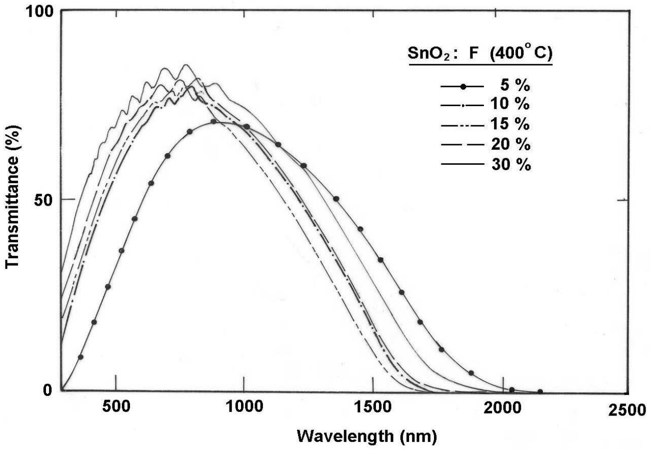

Fig. 3. Transmittance spectra of SnO_2:F thin films as a function of wavelength for different fluorine doping concentration (wt. %).

The films doped with 15 and 30 wt. % NH_4F show increase in reflectance above ~1500 nm, whereas the film with low doping (5 wt. %) show the increase only after 2000 nm. The films show increase in reflectance with increase in NH_4F doping at higher wavelengths (> 2000 nm). The films doped with 15 and 30 wt. % show the maximum reflectance of ~50 % at 2500 nm whereas the films doped with 5 wt. % show the maximum of about 20 % at the same wavelength.

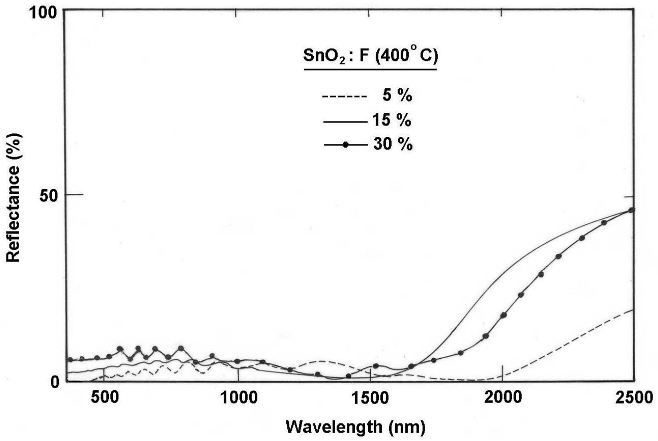

Fig. 4. Reflectance spectra of SnO_2:F thin films as a function of wavelength for different fluorine doping concentration (wt. %).

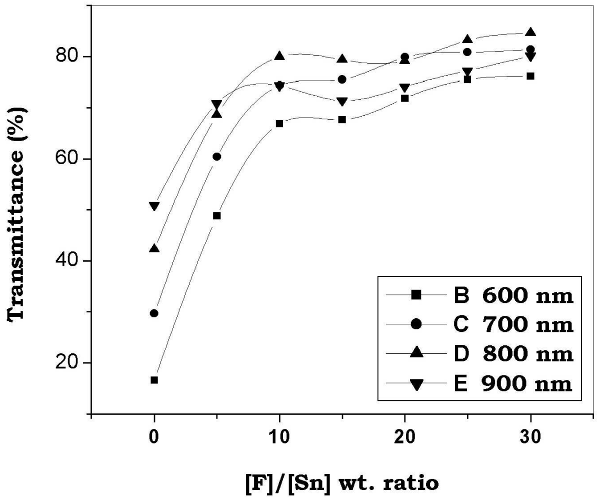

Fig. 5. Transmittance as a function of fluorine concentration of SnO_2:F films for different wavelengths.

The colour of the undoped tin oxide thin film is white which turns colourless on doping 15 wt. % of NH_4F. When the doping concentration is increased to 30 wt. %, a light trace of black colour is seen in the colourless films, but the transmittance of the films was not affected significantly. The transmittance values of the films have been plotted as a function of [F]/[Sn] wt. ratio for 4 discrete wavelengths (600, 700, 800, and 900 nm) as shown in Fig. 5. From the figure it is clear that the transmittance of all the films increases with the fluorine content at all the chosen wavelengths. The transmittance at 900 nm also increases initially but later falls to a minimum at 15 wt. % beyond with the transmittance increases steadily. We do not understand the exact reason for this behaviour. The comparison of transmittance and reflectance of pure and the doped film with lowest R_{sh} (15 wt. %) is shown in Fig. 6. This shows that the transmittance of pure tin oxide in the visible region (till 900 nm) increases on fluorine doping whereas the reflectance decreases.

The refractive index (R.I) of the films was calculated from the transmission spectra using the relation [55]

$$n^2 = \left(\frac{n_a^2 + n_g^2}{2} + 2n_a n_g T_0 \right) + \left\{ \left(\frac{n_a^2 + n_g^2}{2} + 2n_a n_g T_0 \right)^2 - n_a^2 n_g^2 \right\}^{1/2} \tag{3.3}$$

where,

$$T_0 = \left(\frac{T_{\max} - T_{\min}}{T_{\max} \times T_{\min}} \right)$$

n_a = Refractive index of air
n_g = Refractive index of glass

The R.I for SnO_2:F films with different levels of F doping was found to be in the range of 1.70-1.74. This shows that there is no significant change in the R.I as a result of fluorine doping. The observed value is low compared to the reported values for similar films [56]. As suggested by Arai [33], this low value of refractive index may probably due to the smaller density of the films. The density of the films has been calculated by assuming that Lorentz-Lorenz model is valid for the films in the present study. The density N is proportional to $(n^2 - 1)/(n^2 + 2)$. The reduction in density of the crystal (D) can be defined as $(N - N_s) / N$ and is given by

$$D=\left\{\frac{\left(\frac{n^2-1}{n^2+2}\right)-\left(\frac{n_s{}^2-1}{n_s{}^2+2}\right)}{\left(\frac{n^2-1}{n^2+2}\right)}\right\} \tag{3.4}$$

where letters with index s denotes the values of sample and those without index denotes the values of standard crystal.

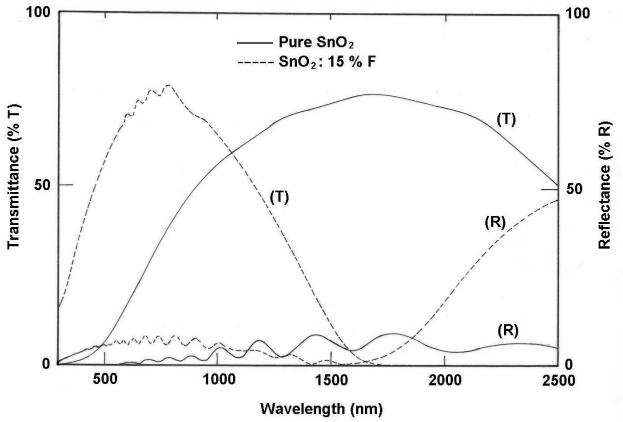

Fig. 6. Comparison of transmittance and reflectance spectra of pure and highly conducting fluorine doped SnO_2 thin films

3.3. Optoelectronic properties

The figure of merit (ϕ) that relates R_{sh} and T can be calculated using Haacke's equation [57], $\phi = T^{10}/R_{sh}$. Thangaraju [1], reports a maximum transmittance of 70 % at (800 nm) for films of thickness ~1 μm. We observed a significantly better value (~85 % at 800 nm) even for films of thickness ~1.2 μm. The improvement in the film transparency and lower resistance value, as discussed earlier in section 3.1, may be attributed to the shorter spray duration and longer spray interval employed in the present study. This has resulted in complete decomposition of the precursor and hence continuous, dense and pore free films are achieved. This is reflected in the figure of merit values that is an order higher than that reported earlier [1]. The figure of merit values for the different wavelengths obtained in the present study is shown in Table 2. The comparison of the optoelectronic properties of pure and fluorine doped tin oxide thin films reported in literature are given in Table 3.

Table 2. Figure of merit values obtained for different wavelengths.

Doping NH_4F (wt. %)	Figure of merit ϕ (Ω^{-1})			
	600 nm	700 nm	800 nm	900 nm
0	4.28×10^{-10}	1.37×10^{-7}	4.73×10^{-6}	3.04×10^{-5}
5	1.64×10^{-4}	1.40×10^{-3}	5.02×10^{-3}	6.9×10^{-3}
10	5.15×10^{-3}	1.49×10^{-2}	3.06×10^{-2}	1.49×10^{-2}
15	1.10×10^{-2}	3.45×10^{-2}	5.67×10^{-2}	1.97×10^{-2}
20	1.15×10^{-2}	3.31×10^{-2}	3.02×10^{-2}	1.58×10^{-2}
25	1.39×10^{-2}	2.76×10^{-2}	3.67×10^{-2}	1.74×10^{-2}
30	1.14×10^{-2}	2.23×10^{-2}	3.30×10^{-2}	1.91×10^{-2}

As mentioned in the introduction, the high IR reflectivity is one of the main requirements for a high quality solar window material. Further, the efficiency of flat plate collectors reduces considerably [62] because of the escape of thermal energy in the form of IR radiation. This problem is overcome by the use of high IR reflectivity transparent conducting oxides. The reflectivity (R) of the films can be calculated using the relation of Frank et al. [63]

$$R = (1 + 2\, \varepsilon_0\, c_0\, R_{sh})^{-2} \tag{3.5}$$

where $\varepsilon_0\, c_0 = 1/376\ \Omega^{-1}$. This relation is valid over a wide range in the IR region. The estimated values of R values are in the range 94.41 – 97.74 %. This combination of high R and T values make these films suitable for the photothermal conversion of solar energy [57,63,64].

Table 3. Comparison of the electro-optical properties of tin oxide thin films by various researchers.

Ref.	Method	Film	t (μm)	λ (nm)	R_{sh} (Ω/□)	ϕ (× $10^{-3}\ \Omega^{-1}$)
This work	Spray	SnO_2:F	1.21	800	1.75	56.7
[58]	Spray	SnO_2:F	0.85	750	14.5	48.5
[1]	Spray	SnO_2:F	1.00	800	5.65	2.5
[59]	Spray	SnO_2:F	0.60	650	9.2	52.6
[60]	Spray	SnO_2	0.59	500	8.5	1.3
″	Spray	SnO_2:F	0.53	550	10.6	18.5
[61]	Spray	SnO_2:F	0.13	~ 600	18.0	15.1

4. Conclusions

In an attempt to prepare low-cost transparent and conducting oxides, spray pyrolysis technique has been employed to prepare pure and fluorine doped tin oxide thin films from $SnCl_2$ precursor. The sheet resistance that is achieved for fluorine doped tin oxide films (1.75 Ω/□) is lower than the reported values for these films prepared from $SnCl_2$ precursor. The optical transmittance is found to increase with increase in the fluorine concentration to a maximum of 85 % at 800 nm (30 wt. % of NH_4F). The figure of merit calculated for the films are quite high ($3\text{-}5 \times 10^{-2}\ \Omega^{-1}$) and comparable to earlier reported values. The high transmittance together with high conductivity makes these films suitable for window materials in thin film solar cells.

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