Journal of Ovonic Research Vol. 5, No. 3, June 2009, p. 63-69

NANOCRYSTALLINE DOUBLY DOPED TIN OXIDE FILMS DEPOSITED USING A SIMPLIFIED AND LOW-COST SPRAY TECHNIQUE FOR SOLAR CELL APPLICATIONS

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A simplified and low-cost spray technique using perfume atomizer is employed for the fabrication of nanocrystalline antimony + fluorine doped tin oxide films (SnO_2: Sb:F) from aqueous solutions of $SnCl_2$ precursor. The structural studies showed that the grain size of the films increases from 32 *nm* for undoped film to 71 *nm* for doubly doped films. The AFM images depict that the films are homogeneous and uniform. The optical transmittance in the visible range is 76 % and the optical band gap is 3.55 *eV*. The sheet resistance is found to be minimum (4.74 Ω /□) for the doubly doped film, for which doping levels of Sb and F are 2 and 40 at. % respectively. This value is lesser than those reported by many researchers for fluorine or antimony doped tin oxide films by employing different versions of spray pyrolysis technique. The films fabricated by the simplified technique have desirable figure of merit (1.36×10^{-2} $(\Omega/\ sq)^{-1}$) comparable with their conventional spray counterparts. Hence this simplified and in- expensive spray technique may be considered as an economic alternative to the conventional spray method for the mass production of solar cell TCO layers and transparent electrodes for optoelectronic devices.

(Received May 30, 2009; accepted June 15, 2009)

Keywords: Tin Oxide thin films, Spray pyrolysis, Double doping, Nanocrystal, Optical studies.

1. Introduction

Low electrical resistivity and high visible transmittance are the key elements for solar cell TCO (Transparent and Conducting Oxide) layers, gas sensors, hybrid microelectronics and opto-electronic devices [1-4]. TCO coatings can also act as heat mirrors due to their high reflectivity in the infrared range. Among the various TCOs, tin oxide (TO) films doped with fluorine or antimony are most promising due to their chemical inertness and mechanical hardness along with low electrical resistivity and good optical transmittance. In this study, an attempt is made to decrease the sheet resistance of the TO films by simultaneously doping antimony and fluorine. Even though, Thangaraju has reported [5] some properties of the doubly doped TO films, detailed reports on these films are hardly available in the literature. In the present work, antimony + fluorine doped tin oxide (AFTO) films have been fabricated from aqueous solutions of $SnCl_2.2H_2O$ by an inexpensive and simplified spray technique using perfume atomizer.

Doped and undoped tin oxide films have been deposited by several researchers by various methods such as sputtering, chemical vapour deposition , spray pyrolysis etc.[5-9]. Among these

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methods, spray pyrolysis is simple and inexpensive. In addition to this, it has the advantages like ease of adding doping materials, high growth, minimum wastage of source materials, mass production capability for uniform large area coatings which are very much desirable for many industrial applications [10]. In this study, a further simplified and low cost spray pyrolysis technique using a perfume atomizer (generally used for cosmetics) is employed for the fabrication of doubly doped tin oxide films. Along with low the cost, perfume atomizers have several other advantages: fine atomization, lesser substrate temperature is enough when compared with conventional spray technique, atomization is based on hydraulic pressure without using any carrier gas, enhanced wettability between the sprayed microparticles and the previously deposited layers and intermittent spraying [11-17]. Perfume atomizers avoid deposition of annoying large droplets, which often takes place in conventional spray pyrolysis depositions. The structural, surface morphological, electrical and optical properties of the sprayed SnO_2 and SnO_2: Sb: F films have been studied and compared in this paper.

2. Experimental details

The precursor solution for tin oxide film is prepared from $SnCl_2.2H_2O$ (1.0*M*). The simultaneous doping of antimony and fluorine was achieved by adding $SbCl_3$ (2 *at.%*) and NH_4F (40 *at.%*) to the host precursor. These doping ratios of antimony and fluorine are optimized by depositing several sets of films with different combinations of doping ratios of antimony and fluorine. The host and dopant precursors are dissolved in 5 ml of concentrated HCl and the solution is diluted to 50 *ml* by doubly deionized water**.** This aqueous solution was magnetically stirred for 1 *hr*, which was followed by an ultrasonic agitation for 1 *hr*, to get a clear solution. The precursor solution thus obtained was sprayed intermittently by means of a perfume atomizer on pre-heated glass substrates of dimensions 25×25×1.35 mm^3. The substrates are maintained at a temperature of 350±5 °*C* using a temperature controller and a chromel-alumel thermocouple. In the case of conventional spray pyrolysis method, in general, tin oxide films are deposited only at a substrate temperature (T_s) ≥ 400 °*C* [2,3,10,18]. But in this simplified technique using perfume atomizer, comparatively lesser T_s is employed, even without any compromise in the quality of the films such as electrical conductivity, optical transmittance and crystallinity, etc. The intermittent spray deposition followed in this study is a two-step procedure: a spray and a 10 *s* interval. The spray interval enables the substrates to reach the required temperature before the start of the next spray. The substrates were precleaned ultrasonically with organic solvents and doubly deionized water for degreasing and to remove the contaminations if any on the substrate surface. The experiment is repeated several times for each film to confirm the reproducibility of the films.

X-ray diffraction patterns were recorded using X–ray diffractometer (PANalytical- PW 340/60 X' pert PRO) which was operated at 40 *kV* and 30 *mA* with X-ray source of CuK_α radiation having wavelength 1.5406 *Å*. AFM images were obtained by employing Atomic force microscope (Veeco-di CP-II). UV-Vis-NIR double beam spectrophotometer (LAMBDA- 35) is used to record transmission spectra in the range of 300 - 1100 *nm*. The carrier concentration, Hall mobility and resistivity of the films were determined using Hall probe technique. The thickness of the films were measured by employing a profilometer (Surftest SJ-301).

3. Results and discussion

Structural studies

The thickness of the films are found to be in the range of 700 nm and are given in Table 1. Fig.1 shows the XRD patterns of the undoped and doubly doped TO films which depict that the films are highly crystalline in nature. The preferential orientation is along the (200) plane for the undoped as well as for the doubly doped TO films. The intensities of (200) and (110) peaks become stronger due to doping (Fig. 1 (b)). The XRD patterns reveal that the preferential

orientation does not change due to double doping, but the degree of preferential orientation is increased due to doping. The matching of observed and standard interplanar distance (*d*) values confirms that the deposited films

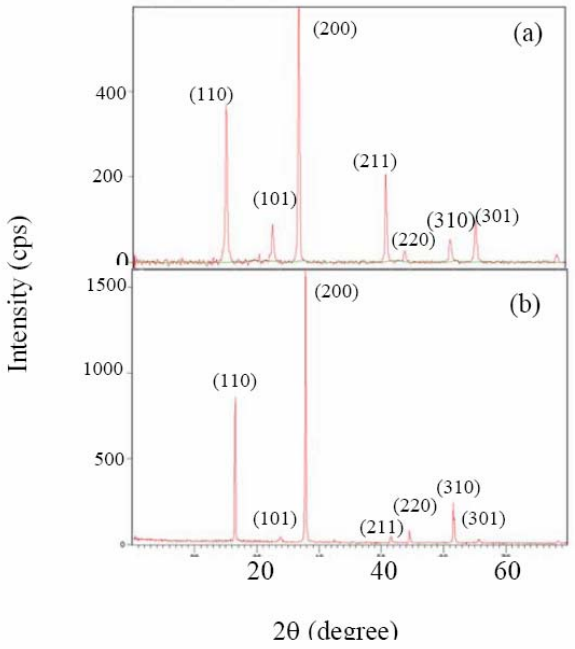

Fig.1. XRD Patterns of (a) Undoped and (b) Doubly doped TO films

are of SnO_2 with tetragonal structure. It is observed that the lattice parameter (a and c) values (Table 1) do not get altered much due to doping. The average crystallite size (D) of the films is determined using the Laue-Scherrer formula [19] which shows that the size of the crystallites are in the nano range. The number of crystallites per unit area (*N*) of the films was calculated from the formula, $N = t / D^3$, where *t* is the thickness of the film. The dislocation density (δ), defined as the length of dislocation lines per unit volume, has been estimated using the equation, $\delta = 1/ D^2$. The calculated structural parameters are summarized in Table 1.

The surface morphology of the films is examined using the atomic force microscopy of the films (Fig. 2). The AFM images depict that the deposited doubly doped TO films are uniform and homogeneous with well-developed and finely visible needle shaped grains. The AFM images clearly show that the grains are larger for the doubly doped films when compared with the undoped films. These observations strongly support the results obtained from the XRD data (Table 1).The size of the grains are grater than that calculated from the XRD data. This discrepancy in size would be due to the fact that two or more crystallites may be fused together to form a larger grain. Such a discrepancy in grain size values has been reported by several researchers[20, 21].

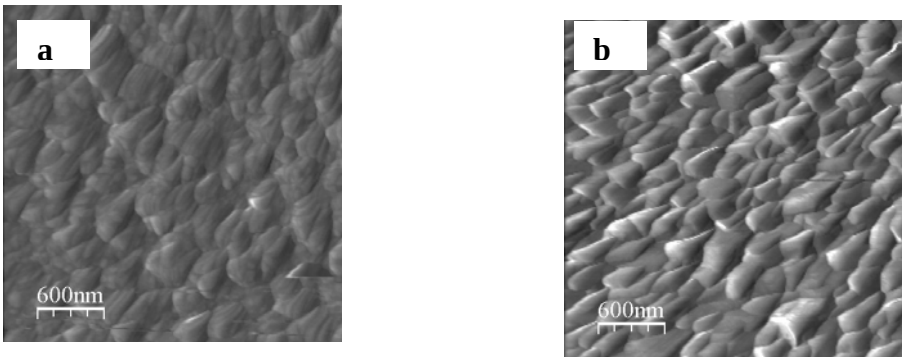

Fig. 2.AFM images of (a) undoped and (b) doubly doped TO films.

Table 1. Structural Parameters (Thickness (t), Grain size(D), Number of grains/unit area (N), Dislocation density (δ) and Lattice constants a and b) of doubly doped TO films

Doping ratio of Sb+F *(at.%)*	t	D	N	δ *($x10^{14}$)*	a*	c*
	(nm)	*(nm)*	($x10^{15}$)	*(lines/m^2)*	*Å*	
0 + 0	675	32	20.6	9.77	4.748	3.186
2 + 40	690	71	1.93	1.98	4.753	3.193

** Standard data: a = 4.737 Å, c = 3.187 Å (JCPDS Card No.: 21-1252)*

Optical and electrical studies

The optical transmission spectra of the doubly doped and undoped TO films are presented in Fig. 3.

From the spectra it is observed that the transmittance in the visible range is 76 % for the doubly doped TO films grown by this simplified technique. The absorption coefficient (α) can be calculated from the transmittance (T) values at the absorption edge from the Lambert's law $\alpha = \ln(1/T)/t$ [22]. The variation of absorption coefficient against photon energy (hν) has the form of $\alpha = A(h\nu - E_g)^{n/2}$, where E_g is the band gap, A is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct-gap material and four for an indirect-gap material [10]. To determine whether the doubly doped TO films deposited using perfume atomizer have direct or indirect band gap, $(\alpha h\nu)^2$ vs. (hν) and $(\alpha h\nu)^{1/2}$ vs. (hν) plots were drawn. Since better linearity was obtained in the $(\alpha h\nu)^2$ vs. (hν) plots, the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis. The optical band gap values are also estimated using the dT/ dλ vs λ plots (Fig. 4). The average optical transmittance and the estimated E_g values are presented in Table 2.

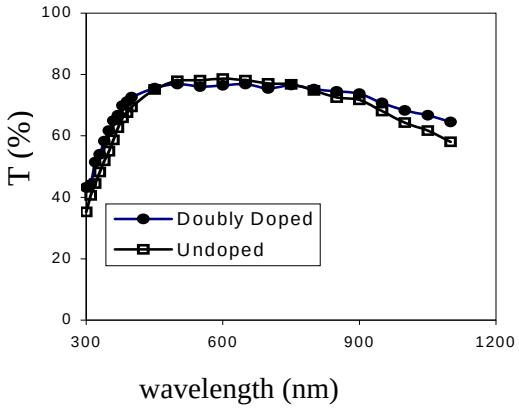

Fig.3. Transmission spectra of undoped and doubly doped TO films.

Table 2. Optical and electrical parameters of undoped and doubly doped tin oxide films

Doping ratio of Sb+F *(at.%)*	***T***	**Figure of Merit** ϕ 10^{-3}	***R***	**Optical Band Gap** E_g
(M)	*(%)*	$(\Omega/\square)^{-1}$	(%)	*(eV)*
0+0	80	2.05	61.2	3.51
2+40	76	13.5	95.1	3.55

(T - Transmittance, R- Reflectivity)

The n- type conductivity of the films is confirmed by the Hall measurements. When SnO_2 is doped with Sb some of the Sn^{4+} ions in the lattice are replaced by Sb^{5+} ions, since the ionic radius of antimony (62 pm) is compatible with that of tin (71 pm). This substitution results in the incorporation of free electrons in the lattice. Hence the sheet resistance (R_{sh}) decreases with the increase in Sb doping ratio [5]. But, this decrease in resistance stops at a particular doping level, beyond which, the resistance begins to increase. The reason for this is that, when the doping level increases, a part of the Sb^{5+} ions reduces to the Sb^{3+}state, resulting in the formation of acceptor sites and consequent loss of charge carries [23]. Similarly in the case of fluorine doping, the F impurity ions (ionic radius of F^{1-} = 133 pm) substituted O^{2-} anions (ionic radius 132 pm) in the lattice and created free electrons. Therefore, the sheet resistance of the films decreases. But beyond a particular level of F content (solubility limit of F in the tin oxide lattice), the R_{sh} increases since the excess F atoms do not act as proper substitutional impurities, but behave as interstitial impurity ions and thereby raise the disorderliness in the lattice. Consequently, the sheet resistance increases [5]. Thus, both of these doping agents (antimony and fluorine) have their own limits in the act of decreasing the resistivity of the TO films. Hence, in this work, both of these doping agents are simultaneously used in different proportions to try for better conductivity.

The electrical resistivity of the film is drastically falls from $35.3 \times 10^{-4} \Omega\, cm$ for undoped film to $3.27 \times 10^{-4} \Omega\, cm$ for the doubly doped film. The carrier concentration (n), Hall mobility (μ), resistivity (ρ) and sheet resistance values are given in Table 3. The carrier concentration found to increase considerably as expected due to double doping, which causes a steep decrease in sheet resistance and resistivity. The decrease in resistivity of the doped films can also be correlated with the grain size variation as follows: The grain size is found as larger for doped films than undoped films (Fig. 2). Since the charge transport is predominantly intra- grain in the case of larger grain films, there is a substantial improvement in the conductivity, whereas in the case of smaller grain film, the higher number of grain walls may act as low conductivity blockades [24]. The Hall mobility decreases slightly for doped films (14.4 $cm^2/V\,s$) when compared with undoped films (17.7 $cm^2/V\,s$), which may be due to the increase in carrier concentration, since Hall mobility in doped AFMiconductors is predominantly limited by ionized impurity scattering [5,15,25].

Table 3. Carrier density (n), Hall mobility (μ), Sheet resistance (R_{sh}) and Resistivity (ρ) of the undoped and doubly doped TO films

Doping ratio of Sb+F *(at.%)*	**n** $(\times 10^{20}/cm^3)$	**μ** (cm^2/Vs)	**R_{sh}** $(\Omega/\square)$	**ρ** $\times 10^{-4}$ (Ωcm)
0 + 0	2 .6	17.7	52.3	35.3
2 + 40	14.7	14.4	4.74	3.27

Sheet resistance (R_{sh}) is an important parameter in comparing thin films, particularly, those of the same material deposited under similar conditions. R_{sh} is found to be minimum (4.74Ω

/□) for the film deposited from the starting solution having doping ratio of antimony and fluorine 2 *at. %* and 40 *at.%* respectively. This may be the least value obtained for fluorine or antimony doped tin oxide film prepared from aqueous solution (without methanol or ethanol) of $SnCl_2$ using spray pyrolysis technique. With methanol as the main solvent, Elangovan et al., [3] achieved the lowest R_{sh} for antimony doped TO films from $SnCl_2$ precursor. Even though they obtained lowest R_{sh} , the transmittance of that films was poor (<50%). This may be due to the higher thickness of their films (1.2 μm). But, in the present work, the thickness of the films is kept approximately at 700 *nm* to get much better transmittance (>76%). Both low resistivity and high transmittance are equally important for TCO layers, especially in the case of solar cell applications. Because a TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between these properties is required. The Haacke's figure of merit $\phi = T^{10}/R_{sh}$ [26] is a good criterion to define the quality of highly transparent and conductive thin films. The doubly doped TO film prepared in this study was found to has desirable ϕ value (Table 2) suitable for solar cell applications [5,27].

For doubly doped TO films, the transmittance at near infrared range is found to decrease considerably (Fig. 3) which may be attributed to the higher reflectivity of the doubly doped films than the undoped TO films. This result is strongly supported by the reflectivity (R) values estimated from the relation $R = (1+2\varepsilon_0 C_0 R_{sh})^{-2}$, where $1/\varepsilon_0 C_0 = 376\ \Omega$ which is valid over a wide range in the IR region [28]. The calculated R value is 95.1 %. This high reflectivity along with the fairly good transmittance (76%) make these doubly doped TO films desirable candidates for photothermal conversion of solar energy [29]. The calculated R_s, resistivity (ρ), ϕ, and R values are given in Table 2.

4. Conclusion

Nanocrystalline doubly doped (antimony +fluorine) tin oxide films deposited by employing a low cost and simplified spray technique using perfume atomizer were found to have very good structural, optical and electrical properties. The preferential orientation is along the (200) plane. The degree of preferential orientation is found to be higher for doubly doped films. The films are found to be nanocrystalline. Wide optical band gap (3.55 *eV*), good visible transmittance (76 %), reasonable figure of merit $13.5 \times 10^{-3}\ (\Omega/\square)^{-1}$ and high IR reflectivity (95.1 %) make these doubly doped films desirable candidates for low-cost solar cell TCO layers.

Acknowledgements

The authors are grateful to the Secretary and Correspondent, Principal, Dean of sciences and Head, Department of Physics, AVVM Sri Pushpam College (Autonomous), Poondi for their excellent encouragement and support. One of the authors, K.Ravichandran is very much grateful to the University Grants Commission for the financial assistance through the minor research project (MRP-2380/06 (UGC-SERO)).

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