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Low-cost and simplified fabrication technology to deposit transparent conducting tin oxide films for solar cell applications

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Abstract

An inexpensive and simplified fabrication technology using perfume atomizer is employed to deposit transparent conducting thin films of SnO_2: Sb (antimony doped tin oxide) onto glass substrates, by varying the antimony doping concentration. The structural studies reveal that the films are polycrystalline in nature with tetragonal crystal structure. The preferred orientation is along the (110) plane for all the doping levels and the degree of preferred orientation increases with the increase in doping concentration in the starting solution. The fine quality SEM and AFM images of the antimony doped tin oxide (ATO) films obtained in this work show that the films are homogeneous and uniform. The sheet resistance is found to decrease with the increase in antimony doping level, attains a minimum value (6.34 Ω/) when the doping concentration is 1.5 at. % and then increases for further doping. Good visible transmittance (>80 %), wide optical band gap (3.52 eV) and the desirable figure of merit (4.39 Ω^{-1}) observed in this investigation make these films suitable for low-cost solar cell window layers and other opto-electronic applications.

Keywords : antimony doped tin oxide, solar cells, spray pyrolysis, thin films, transparent conducting oxide

INTRODUCTION

The primary sources of energy (petroleum, natural gas and coal) -excepting wood- have finite supplies and their lifetime is estimated to range from 15 years for natural gas to nearly 300 years for coal (Rai, 1999). Therefore, mankind must turn its attention to longer-term alternative to these non-renewable energy sources. Among the other significant sources, nuclear energy requires advanced technology and costly means for its safe and reliable utilization and it may have undesirable side effects. But solar energy on the other hand, does not require highly technical and specialized means for its widespread utilization. In addition to that, solar energy is environment friendly-involves no significant polluting effects- and is available in abundance. India, having a total land area of 3.28×10^{11} m^2 receives 5kW/m^2 solar energy per day over 300 days per annum. Even if 1 % of this land is used to harness solar energy for electricity generation at an overall efficiency of 10 %, 492×10^9 kWh/year electricity can be generated. The most useful way of harnessing solar energy is by directly converting it into electricity by means of solar photovoltaic cells.

Transparent conducting oxide (TCO) thin films with high optical transmittance and low electrical resistivity are key elements for thin film solar cells and opto-electronic devices (Elangovan and Ramamurthi, 2003). Such films are essential as substrates for the deposition of semiconductor overlayers such as Si, TiO_2, Cu (In,Ga)Se_2 and CdS/CdTe. Since the international oil crisis of 1973-74, there has been a phenomenal rise in the researches on low-cost solar cell materials. In the present study, a low-cost and simplified spray pyrolysis technique is employed for the deposition of highly transparent conducting antimony doped tin oxide (ATO) films.

Tin oxide films have been prepared by several methods such as chemical vapour deposition (Kim *et al*., 2003), electron beam evaporation (Shamala *et al*., 2004), sputtering (Moriga *et al*., 2004), thermal evaporation (Patel *et al*., 1995), sol-gel (Sunitha *et al*., 2002), successive ionic layer adsorption and reaction technique (Deshpande *et al*., 2008) and spray pyrolysis (Thangaraju, 2002). Among the various deposition techniques, the conventional spray pyrolysis is well suited for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement. In this study, we have further simplified this technique by employing a perfume atomizer in the place of spray gun, compressor and solution reservoir, because the perfume atomizer can collectively performs the functions of all the above-mentioned components. This technique requires simple apparatuses, which are low in cost but highin throughput, which is the prerequisite for the commercial production of solar cells (Fukano and Motohiro, 2004). Along with low cost, perfume atomizers have several other advantages: lesser substrate temperature is enough when compared with conventional spray technique, atomization based on hydraulic pressure without

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using any carrier gas, intermittent spraying and fine atomization (Ravichandran and Philominathan, 2008a). Furthermore, perfume atomizers avoid deposition of annoying large droplets, which often takes place in conventional spray pyrolysis depositions (Ravichandran and Philominathan, 2009).

MATERIALS AND METHODS

The block diagram of the simplified and inexpensive spray pyrolysis technique employed in this work is given in Fig. 1. The precursor solution is prepared by dissolving high pure $SnCl_2.2H_2O$ with a very small amount of HCl (0.1mol/l) and then diluting it by doubly deionized water. Antimony doping was achieved by adding suitable proportion of $SbCl_3$ (0.5-2.5 at. % in steps of 0.5 at.%) in the starting solution. This aqueous solution was magnetically stirred for 30 min, which was followed by an ultrasonic agitation for 30 min, 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 75×25×1.35 mm^3. The substrates are maintained at a temperature 320 ± 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 (Shanthi *et al.*, 1999). But in this simplified technique using perfume atomizer, a comparatively lesser T_s is employed, even without any compromise in the quality of the films such as crystallinity, transmittance and conductivity etc. The intermittent spray deposition followed in this study is a two step procedure: a spray and a 10 sec interval. The spray interval enables the substrates to attain the required temperature before the start of the next spray. The substrates were pre-cleaned 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 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*. SEM and AFM images were obtained by employing scanning electron microscope (HITACHI S-3000 H) and Atomic force microscope (Veeco-di CP-II), respectively. UV-Vis-NIR double beam spectrophotometer (LAMBDA- 35) is used to record transmission spectra in the range of 300 - 1100 *nm*. The sheet resistance values are observed with the use of a four point probe with vander Paw configuration.

RESULTS AND DISCUSSION

Structural studies

The structural analyses of the deposited ATO films are performed with the use of X-ray diffraction patterns. Figure 2 shows the diffraction patterns of the ATO films. The diffraction peaks reveal that the films are highly crystalline with the preferential orientation along the (110) plane. The other prominent peaks in the patterns are (101), (200), (211), (220), (310), (301) and (400). The preferred orientation remains predominant irrespective of the doping concentration of antimony in the starting solution and at the same time, the degree of preferred orientation increases with the increase in doping ratio. But, the intensities of the second and third stronger peaks (211) and (200) decrease gradually with the increase in doping concentration.

The matching of observed and standard interplanar distance (*d*) values confirms that the deposited films are of SnO_2 with tetragonal structure. The lattice parameter values '*a*' and '*c*' are calculated from the equation (Cullity, 1978),

$$1/d^2 = (h^2 + hk + k^2)/a^2 + l^2/c^2 \quad (1)$$

and the values are listed in Table 1. It is observed that the lattice parameter values do not get altered much when the doping concentration in the starting solution is varied. The average grain size (D) of the films is determined using the Laue-Scherrer formula (Adnane *et al.*, 2005),

$$D = 0.94\,\lambda/(\cos\theta\ \ \beta^2 - \beta_0^2) \quad (2)$$

where λ is the wavelength of the X-ray used (1.5406 Å), β is the full-width at half - maximum (FWHM) of the peak which has maximum intensity, β_0 is the full width at half maximum of the same peak for the standard diffraction and θ is the Bragg angle.

The number of grains per unit area (*N*) of the films was calculated with the use of the following formula :

$$N = t / D^3 \quad (3)$$

where *t* is the thickness of the film.

The strain in the crystalline ATO films is evaluated from the equation,

$$\epsilon = \beta \cos\theta / 4 \quad (4)$$

The dislocation density (δ), defined as the length of dislocation lines per unit volume, has been estimated using the equation (Ravichandran and Philominathan, 2008b),

$$\delta = 1/D^2 \quad (5)$$

Since δ is the measure of the amount of defects in a crystal, the small values of δ obtained in the present study confirmed the good crystallinity of the ATO films deposited using the perfume atomizer (Prabahar and Dhanam, 2005). The calculated structural parameters

Table 1. Lattice Constants of ATO films

Doping Ratio Sb/Sn (at.%)	Observed Values (Å)		Standard Values* (Å)	
	a	c	a	c
0.5	4.750	3.195		
1.5	4.749	3.194	4.737	3.187
2.5	4.749	3.196		

are summarized in Table 2.

Surface morphology

The surface morphology of the films is examined from the scanning electron micrographs and AFM images of the films. The SEM and AFM images of the film deposited from the starting solution having doping ratio Sb/Sn = 1.5 at. % are presented in Fig. 3 (a and b). The images clearly depict that the deposited ATO films are uniform, homogeneous and pin-hole free with well developed and finely visible flower petal shaped grains.

Optical studies

The optical properties of the ATO films were investigated using the transmission and absorption spectra observed in the wavelength range 300 nm-1100

Table 2. Structural Parameters *(Grain size(D), Number of grains/unit area (N), Dislocation density (δ) and Strain (∈))* of ATO films

Doping Ratio Sb/Sn (at.%)	D (nm)	N ($\times 10^{15}$)	d ($\times 10^{16}$)(lines/m^2)	$\bar{\imath}$ ($\times 10^{-4}$)
0.5	70.2	2.598	2.041	5.158
1.5	76.8	2.513	1.731	4.716
2.5	76.2	2.349	1.721	4.750

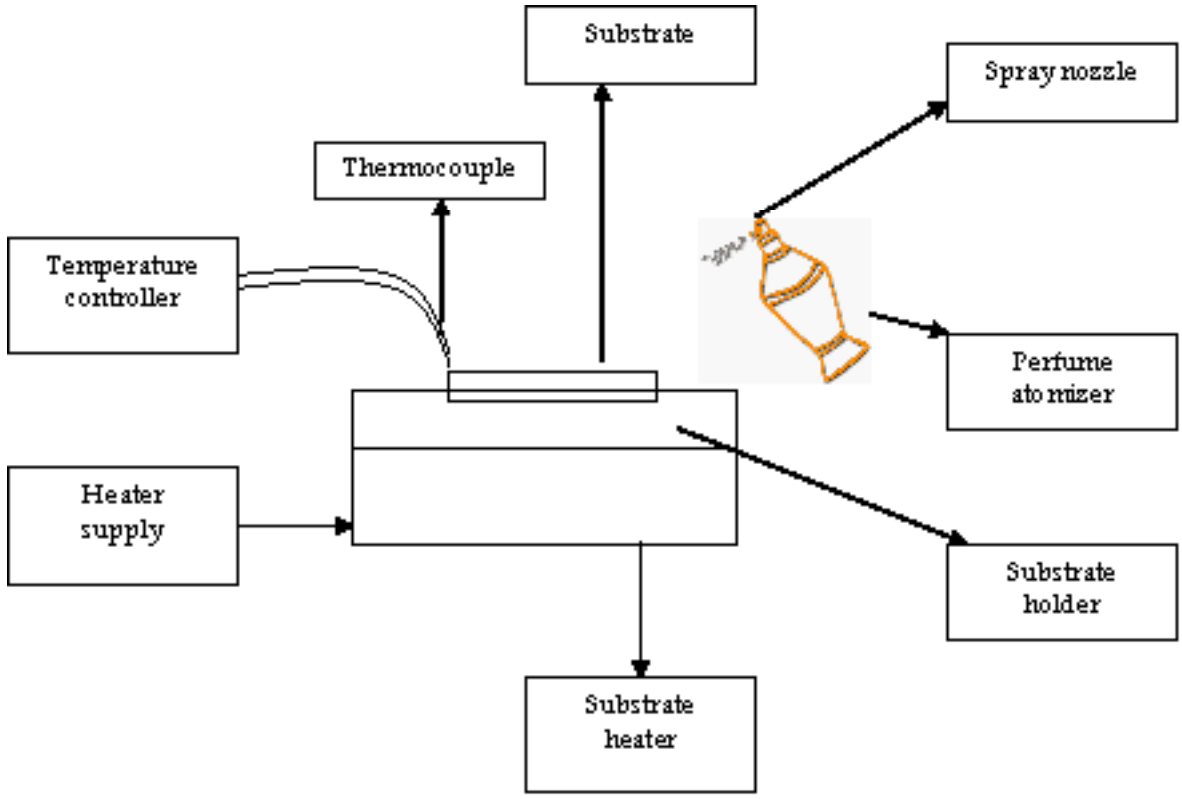

Figure 1. Block diagram of simplified spray pyrolysis unit employed in this study

Table 3. Electrical and optical parameters

Doping Ratio Sb/Sn	Thickness t	Sheet Resistance R_{sh}	Resistivity r	Transmittance T	Figure of Merit f	Optical Band Gap E_g
(at.%)	(nm)	(W/□)	(W.cm)	(%)	(W^{-1})	(eV)
0.5	1025	6.79	6.96	88	4.09	3.54
1.5	1014	6.34	6.43	85	4.39	3.59
2.5	1031	9.51	9.80	79	2.93	3.58

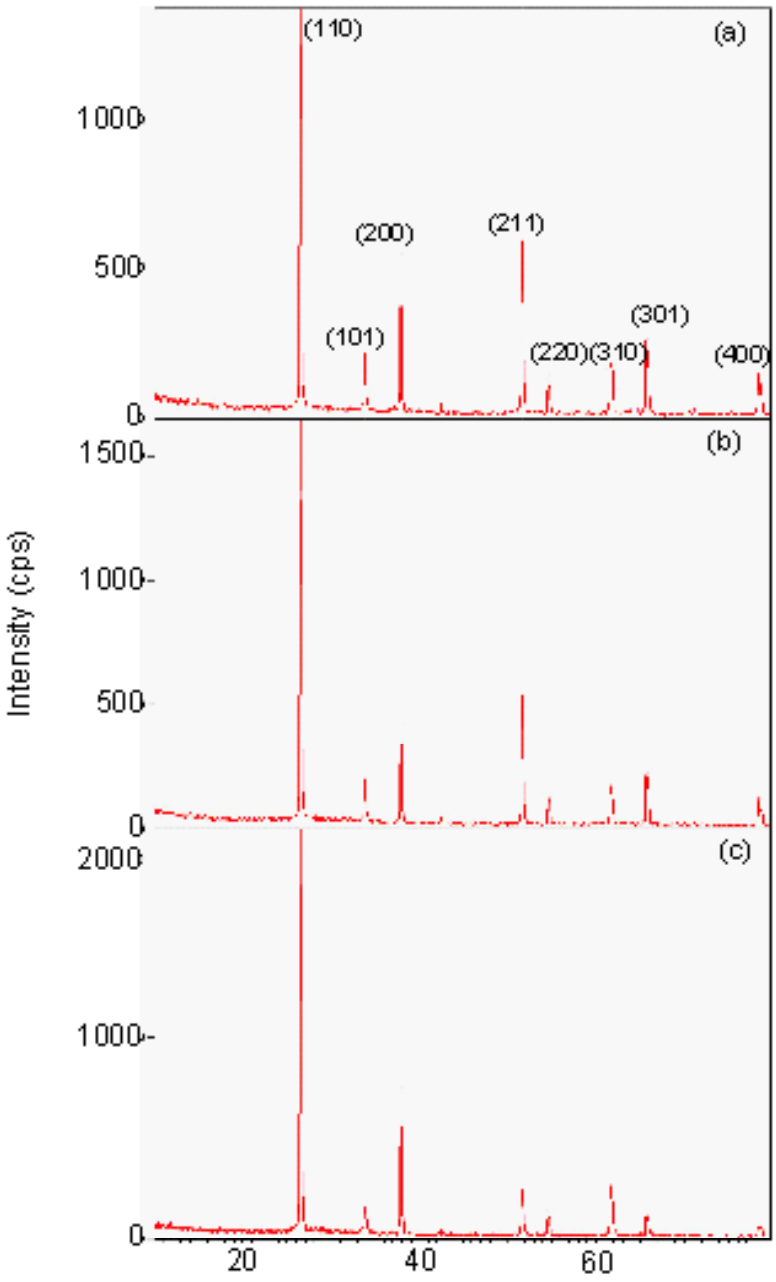

Figure 2. XRD patterns of ATO films deposited from starting solutions having Sb/Sn = (a) 0.5 at.% (b) 1.5 at.% and (c) 2.5 at.%

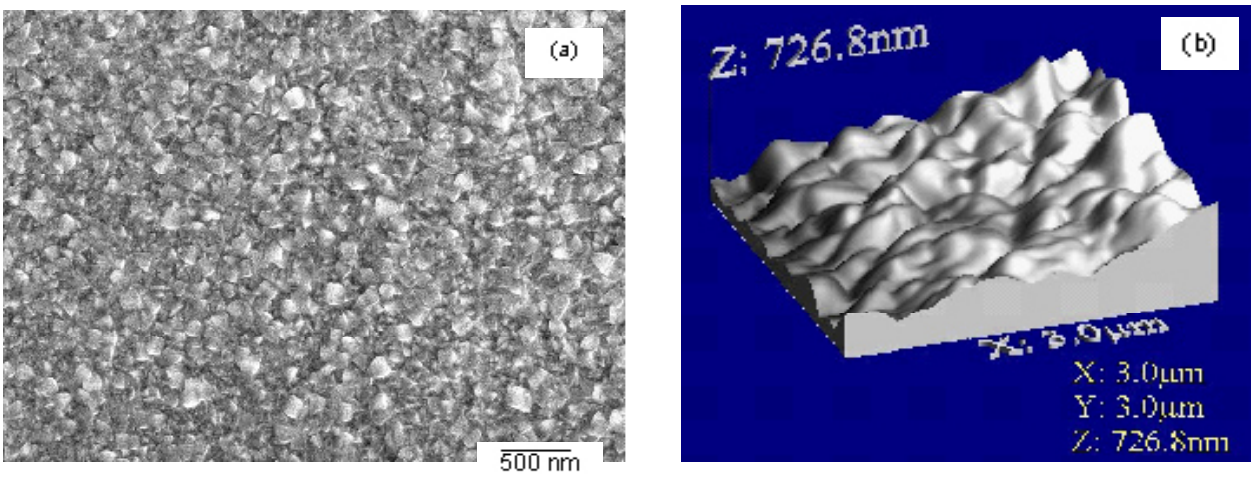

Figure 3 (a) SEM and (b) AFM images of ATO film deposited from starting solution having Sb/Sn = 1.5 at.%

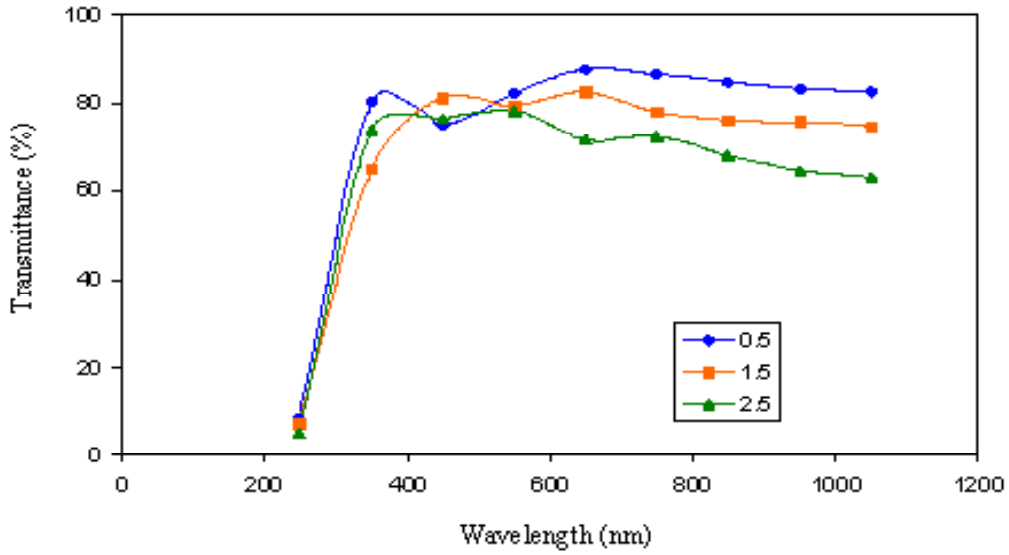

Figure 4. Transmission spectra of ATO films deposited from starting solutions having different atomic percentages of Sb/Sn

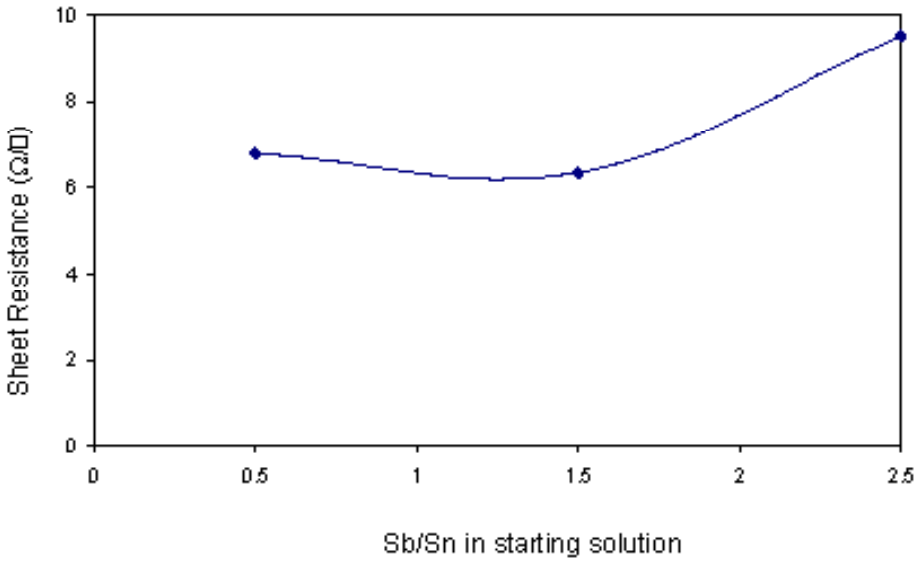

Figure 5. Variation in sheet resistance as a function of antimony doping ratio in tin oxide films

nm. The transmission spectra recorded for different doping levels of antimony in tin oxide films are shown in Fig. 4 which depict that the transmittance in the visible range is >80% for ATO films grown by this simplified technique, making them suitable for solar cell applications (Elangovan and Ramamurthi, 2005).

The fundamental absorption, which clearly shows itself by a rapid rise in absorption, can be used to determine the optical band gap of materials. The absorption coefficient (α) can be calculated from the transmittance (T) values (Manifacier *et al.*, 1977) at the absorption edge from the Lambert law $\alpha = \ln(1/T)/t$. The variation of absorption coefficient against photon energy ($h\nu$) has the form of $\alpha = A (h\nu - Eg)^{n/2}$, 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 (Cetinorgu *et al*., 2006).

To determine whether the ATO films deposited using perfume atomizer have direct or indirect band gap, $(\alpha h\nu)^2$ vs. $(h\nu)$ and $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ plots were drawn. Since better linearity was obtained in the $(\alpha h\nu)^2$ vs. $(h\nu)$ plots, the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis. The average optical transmittance and the estimated E_g values are presented in Table 3. The values are found to be comparable with the earlier reports (Manifacier *et al*., 1977).

Electro-optical studies

Sheet resistance (R_{sh}) is a useful parameter in comparing thin films, particularly, those of the same material deposited under similar conditions. The plot of sheet resistance as a function of dopant concentration in the spray solution of ATO film is shown in Fig. 5. R_{sh} is found to be minimum for the film deposited from starting solution having doping concentration Sb/Sn = 1.5 at.%. The figure of merit $\phi = T^{10}/R_{sh}$ (Moholkar *et al*., 2007) is a good criterion to define the quality of highly transparent and conductive thin films.

The ATO films prepared in this study were found to have desirable ϕ values (Thangaraju., 2002; Ravichandran *et al*., 2009) suitable for solar cell applications. The calculated R_{sh}, ϕ and resistivity (ρ) values are given in Table 3.

CONCLUSION

Transparent conducting ATO films fabricated using a low-cost and simplified spray method were found to have good crystalline characteristics with preferential orientation along the (110) plane. The higher optical transparency (>80 %), low sheet resistance (6.34 Ω/) and consequently, the desirable figure of merit (4.39 Ω^{-1}) of the films make them suitable candidates for solar cell window layers and transparent electrodes for many opto-electronic devices. Hence, this simple and low cost fabrication technology deserves due consideration, for alternative to conventional spray technique.

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