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Structural and morphological properties of SnO_2:Sb:F thin films produced by spray pyrolysis technique at various substrate temperatures

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ABSTRACT

Doubly (antimony and fluorine) doped tin oxide (SnO_2:Sb:F/AFTO) thin films with low solution concentration and low Sb doping were deposited on the glass by using spray pyrolysis technique at different substrate temperatures. The effect of substrate temperature on properties of the prepared films was investigated. It was seen from X-ray diffraction analysis that the thin films are rutile structure with polycrystalline and orientations along (101), (200) and (210) directions for all substrate temperature. SEM and AFM images indicated that thin films were affected by substrate temperature and the surface of films was homogeneous and to be made of nanocrystalline. The films have 83% average transmittance values and E_g values are between 3.10-3.89 eV. These E_g and transmittance values changed continuously with substrate temperatures. Hence, it was concluded that properties of thin films were affected by the substrate temperature and these result mostly compatible with the results obtained from literature.

Keywords: Spray Pyrolysis, Thin films, Antimony and Fluorine doped tin oxide (SnO_2:Sb:F), Electrical Properties, PL studies

Farklı altlık sıcaklıklarında sprey piroliz yöntemiyle üretilen SnO_2:Sb:F ince filmlerin yapısal ve morfolojik özellikleri

ÖZ

Düşük çözelti konsantrasyonlu ve düşük Sb dopingli çifte (antimon ve flüor) katkılı kalay oksit (SnO_2:Sb:F/AFTO) ince filmler, farklı altlık sıcaklıklarında sprey piroliz tekniği kullanılarak cam altlık üzerinde biriktirildi. Altlık sıcaklığının hazırlanan filmlerin özellikleri üzerindeki etkisi araştırılmıştır. X-ışını difraksiyon analizinde, ince filmlerin, tüm substrat sıcaklığı için (101), (200) ve (210) yönleri boyunca yönelimli ve polikristal tetragonal bir yapı olduğu görülmüştür. SEM ve AFM görüntüleri, ince filmlerin altlık sıcaklığından etkilendiğini, film yüzeylerinin homojen olduğunu ve nanokristallerden yapıldığını gösterdi. Filmler % 83 ortalama geçirgenlik değerlerine sahiptir ve E_g değerleri 3.10-3.89 eV arasındadır. Bu E_g ve geçirgenlik değerleri altlık sıcaklıkları ile sürekli değişmiştir. Bu yüzden ince film özelliklerinin substrat sıcaklığından etkilendiği ve bu sonuçların çoğunlukla literatürden elde edilen sonuçlarla uyumlu olduğu sonucuna varıldı.

Anahtar Kelimeler: Sprey piroliz, İnce filmler, Antimon ve Flor katkılı kalay oksit (SnO_2: Sb: F) , Elektriksel Özellikler, PL çalışmaları

INTRODUCTION

Transparent on optical range, low resistivity conducting and wide optical band gap (E_g) (>3 eV) oxides (TCOs) have attracted the scientists due to their wide using in many research and industrial areas for example, low-emissivity glass [1], window defrosters [2], transparent anode layer for all general organic light emitting diodes [3] and optoelectronic devices [4-5] gas sensor [6], DSSC solar cell [7] and flat panel TV displays. This combination sort of transparency and conductivity isn't usually possible in intrinsic stoichiometric oxides; however, it is made in a non-stoichiometric composition or with appropriate dopants as Sb, F, Zn, Mo, Pr and Ta [8]. So, from 1940 year to nowadays many studies on TCOs by using different methods and by changing the conditions required to prepare them have been making to improve properties of them [1-9].

It is known that many oxide stoichiometric materials with wide gap, high T in the visible and reflective ultraviolet ranges behave as an insulator at RT. A good conductivity and transparency for these materials is getting by increasing free charge concentration in the conduction band by the state of some nonstoichiometric [9]. These properties are obtained in deposited thin films.

Although many excellent reviews of TCOs are available in literature [1, 4-5], the report about doubly doped thin films is very rare [10]. Among these doped TCOs thin films, such characteristic properties are shown easily at the tin oxides (SnO_2) doped with antimony and fluorine. Whenever depositing, an O^{2-} ion is substituted with an F^- ion and donor level is produced. Also, Sb introduces Sb^{5+} ions that act as donors but after that Sb^{3+} ions begin to replace the Sn^{4+} ions [8, 10, 11]. So, doubly doped process can be made.

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Doubly doped tin oxide thin films can be produced by many methods like as dip coating, pulsed laser deposition [12]. Thermal evaporation [13], sol-gel [14] and spray pyrolysis technique. The spray pyrolysis method is very useful technique because it is economic, cheap, re-producible and suitable for big area uniform coatings and easily adding dopant materials [10, 15].
In this study, homemade spray pyrolysis technique, which is ideal for performing multiple doping, was used in the production of antimony and fluorine doped tin oxide thin films. The effect of substrate temperature on the structural and morphological properties of these thin films was investigated using XRD, SEM, UV and PL analyzes. Analysis of these thin films revealed very interesting properties, such as p-type conductivity first time reported for doubly doping as known.

MATERIALS and METHODS

Deposition of SnO_2:Sb:F Thin Films

In the experiment, Antimony (Sb) and Fluorine (F) doped tin oxide (called SnO_2:Sb:F or AFTO) thin films were deposited on borosilicate glass substrates with (1x1x0,1) cm^3 using starting solution with low concentration by home-made spray pyrolysis technique at different substrate temperatures in steps of 40 °C. The schematic diagram of home-made spray pyrolysis technique and other details have been reported elsewhere [11]. Substrate temperature is maintained 320 °C from 480 °C ±5 using thermocouple. While host precursors for Sn are $SnCl_2.2H_2O$, Sb and F doping was obtained from $SbCl_3$ and NH_4F (Merck) precursors, respectively. Doping of Sb and F is 4 and 30 wt. %, respectively. To enhance the solubility of tin oxide, 5 mL HCl is added with the precursor solution. Totally, volume of solution with doubly deionized water is 50 mL. After deposition, the substrate temperature was decreased to 25 °C. In each process, several samples were produced simultaneously at each different substrate temperature levels. It was realized that the crystals have same properties as like [16].
The substrates were washed in ultrasonic cleaner with organic solvents and deionized water for 8 min. The substrates were pre-heated to gain the required temperature on all glass surfaces. Spray nozzle-substrate distance and angle (α) were 40 cm and 45˚, respectively. The deposition time was 20 min, speed per minute is 20 rpm and totally volume is 50 mL.

Characterization

The deposited thin films were fully characterized with XRD, SEM, optical and electrical property measurements etc. XRD patterns of these thin films were recorded by Rigaku D/Max-IIIC XRD diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV and 10 mA. Surface morphology of film analyzed with SEM and AFM, that is, by employing JEOL SEM Model 6460 Scanning Electron Microscope and by NT-MDT Atomic Force Microscope. The Optical measurements carried out in the range of 250-1000 nm using a UV-VIS spectrophotometer (Perkin Elmer, Lambda 35). The electrical measurements measured using the Vander Pauw configuration probe by Ecopia HMS5000/AMP55T Hall probe system in at room temperature. PL measurements were taken by using Jobin Yvon Horiba Spex Fluoromax-3 Spectrometer. 300 nm is excitation wavelength in all PL experiments.

RESULTS and DISCUSSION

Structural Analysis

Structural properties of SnO_2:Sb:F/AFTO thin films with low concentration (0.05 M) deposited at different substrate temperature were determined using XRD technique. XRD spectra for these AFTO thin films are studied in the 2θ of 20°-70° shown in Figure 1.
It was seen that the prepared films were polycrystalline with tetragonal (rutile) structure irrespective of substrate temperature. Three more power peaks along (101), (200) and (210) and two more lower peaks along (110) and (211) planes are clearly indicated that the films have polycrystalline mainly. Extra phases (as like SnO, Sn_2O_3 and Sb_2O_3 compounds) are not observed in the deposited films [8]. It was found that XRD patterns were compatible with the Amer. Soc. for Testing and Materials (ASTM) standard (JCPDS Card No: 71-0652 Quality C) for the tin oxide.
The films deposited at different substrate temperature have preferential orientation along the (200) plane. However, as the temperature is increased the intensity of the (200) peak increased, after 400 ˚C decreased. So, best properties regarding crystalline structure was observed on films which prepared at 400 ˚C temperature. It was understood that 400 ˚C substrate temperature was suitable for good atomization which to make good thin film on substrate. The reason of this may be due to the increase in crystallinity with increasing in the substrate temperature.

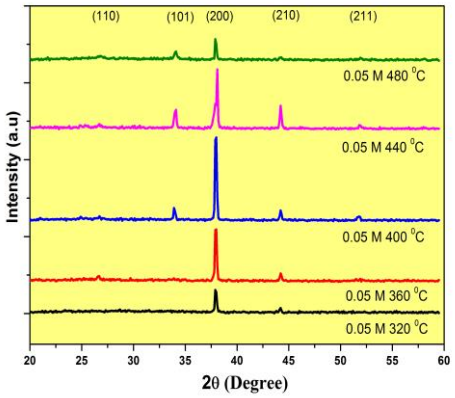

Figure 1. The XRD spectra for SnO_2:Sb:F/AFTO thin films prepared at different substrate temperatures

Because the sharp and highly intense peaks suggest that deposited films have good crystalline nature [17]. Moreover, when substrate temperature was increased, decomposition increases and good thin film growth

quality was better because of ideal deposition conditions taken place on the substrate. But, more increasing substrate temperature after 400 ˚C is risky due to solvent vaporizes before the droplets reaches the substrate or begin more dislocation on the substrate due to high vibration. Similar results have been found in the literature [8,10]. For example, Mokaripoor and Bagheri-Mohagheghi [8] have reported that tin oxide thin films with very low to high Sb doping have (110) and specific (110) and (200) direction. However, as the ratio of Sb is increased, intensity of the (110) peak decreased but intensity related to the (200) increased like present study.

Also, it was noted in the literature that if HCI was put in the solution, the thin films were clearly oriented along (200) plane. As HCl was added the solution in this study, the (200) planes were observed [17]. Finally, substrate temperature 400 ˚C was the best crystalline preparing temperature found in the present work. So, substrate temperature is more important parameter for preferential orientation in depositing thin film. Moreover, the preferred orientations depend on compounds' source, solvent and growth parameters such as solution and deposition concentration [7,19,20].

The crystallite size (D) of these AFTO thin films is calculated using Debye-Scherrer's formula, $D=0.9\lambda/(\beta\cos\theta)$ [8] where λ is the wavelength (λ=1.5418 Å), β means of the broadening of diffraction line measured at (FWHM) and θ is the Bragg angle. Structural parameters of these AFTO thin films which were calculated for only preferential orientation plane by using above formula are summarized in Table 1.

Table1. Summary of the structural parameters of SnO_2:Sb:F/AFTO thin films

$T_{substrate}$	(hkl)	2θ(˚)	FWHM	d_{std}(Å)	d_{cal}(Å)	$a_{std}=b_{std}$(Å)	$a_{cal}=b_{cal}$(Å)	c_{std}(Å)	c_{cal}(Å)	D(nm)	δ(lines/ m^2)
320 ˚C	(200)	37,9	0,23257	2,369	2,375	4,738	4,750	3,187	-	38,1	6,91E+14
360 ˚C	(200)	38,0	0,23364	2,369	2,369	4,738	4,738	3,187	-	37,9	6,97E+14
400 ˚C	(200)	38,0	0,22777	2,369	2,369	4,738	4,738	3,187	3,183	38,9	6,62E+14
440 ˚C	(200)	38,1	0,14224	2,369	2,363	4,738	4,726	3,187	3,164	62,2	2,58E+14
480 ˚C	(200)	37,9	0,20737	2,369	2,375	4,738	4,750	3,187	3,160	42,7	5,49E+14

(hkl) miller indices, 2θ-The Diffraction Angle, FWHM-Full width at half maximum, d-interplaner distance, a, b and c lattice constants, D-Crystallite size, δ-Dislocation density, cal: calculation and std: standard

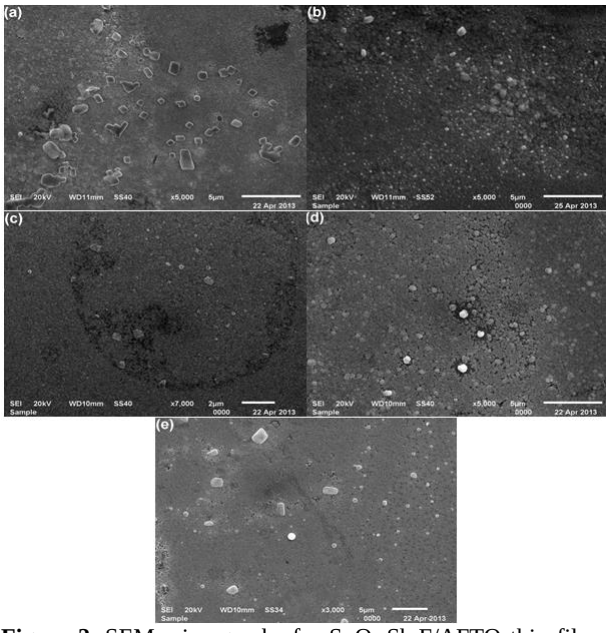

Figure 2. SEM micrographs for SnO_2:Sb:F/AFTO thin films prepared at different substrate temperature; (a) 320 °C, (b) 360 °C, (c) 400 °C, (d) 440 °C and (e) 480 °C respectively.

From the estimated crystallite size values (Table 1), it is found that the crystallite size changed depending on substrate temperature from 38.1 nm to 42.7 nm. A sudden increase at 440 ˚C can be due to the aggregation of grains (see SEM-AFM graphs). Once fluorine doping in present work comparing to earlier work [11] decreased, it was seen grain size of thin films increased in good agreement with Shinde et al [21]. So, the obtained structural values for SnO_2:Sb:F/AFTO thin films are in good agreement with the literature.

The distance of interplaner (d) for every crystal calculated (see Table 1) from XRD results by using Bragg's law; ($n\lambda = 2d\sin\Phi$). As the films have tetragonal rutile structure, the lattice constants a and c are calculated using the equation [22]; $(1/d^2)=\{[(h^2+k^2)/a^2]+(l^2/c^2)$ where (hkl) is Miller indices. Tetragonal rutile structure has $a=b\neq c$, $\alpha=\beta=\gamma=90^\circ$ formula. The calculated 'a=b' and 'c' values are well matched with the JCPDS Card No: 71-0652 Quality C. Lattices parameters (a and c) which calculated from XRD measurement were given in Table 1. It was concluded that lattice constants of these thin films were not affected much with substrate temperature but the minor increase in the lattice parameter (a) may be due to the increase in the substitutional F (133 pm) ion with the O (132 pm) ion sites. Also, if lattice parameters variety for thin films deposited by spray, automatically film grains is strained means of due to the change in the film structure and impurity concentration [23].

In this work, dislocation density (δ) was calculated with $\delta=1/D^2$ formula where D is the crystallite size [24]. The dislocation densities of these films are presented in Table 1. The small values of δ obtained in these reported study approved the good crystallinity of AFTO thin films deposited by spray pyrolysis technique [17]. Despite having the best crystal quality at 400 ˚C, the dislocation density of this crystal is higher than the crystals obtained at higher temperatures. This situation has not been understood. But, like in our previous work, it was seen that precursor concentration is the most important process parameter controlling film structural properties and reducing the defects.

Morphological Study

The surface morphological measurements of AFTO thin films which prepared at different substrate temperature were taken by using a JEOL SEM Model 6460. This SEM Micrographs displaying the surface morphology of AFTO thin films are shown in Figure 2.

It was seen from SEM graphs that the surface morphology of the films was strongly affected by the substrate temperature. The evolution in the structure of the films is evident from images presented. It is observed that the AFTO thin films were fully covered on all the substrate and nanocrystalline particles were mostly found on the film surface. It was found that as crystallinities of thin films are developing, surface morphologies are uniform and homogenous with well developed.

It was known from SEM analysis, the grain size increased when substrate temperature increased until 400 ºC. The grain size at the further temperature increasing exhibits a decreasing trend. At 440 ˚C it was found a sudden increase. These results are suit to the XRD analysis. AFTO thin films have uniform size grains with circle shape at very lower and upper temperature from 400 ˚C. At 400 ˚C which achieved the best film surface size grains have both circle shape and needle shape.

Substrate temperature is an important parameter because when substrate temperature increased, decomposition increases and good film growth quality is better because of ideal deposition conditions taken place on the substrate. But, at low substrate temperature, droplet in liquid phase which reached on the substrate decomposes without a good film growth quality according to another high substrate temperature.

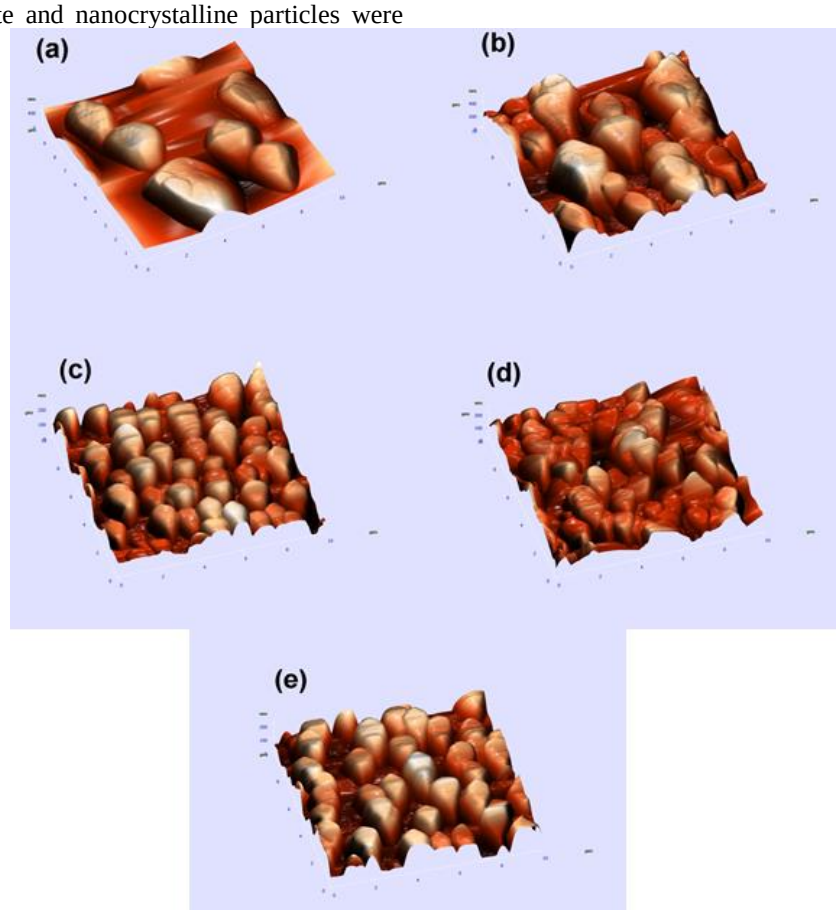

Figure 3. AFM images for SnO_2:Sb:F/AFTO thin films prepared at different substrate temperature; (a) 320 °C, (b) 360 °C, (c) 400 °C, (d) 440 °C and (e) 480 °C respectively.

Surface Study

A further increasing substrate temperature after 440 ˚C is risky due to solvent vaporizes before the droplets reaches the substrate or begin more dislocation on the substrate due to extreme vibration. Finally, it was found that best crystalline and SEM results confirmed XRD patterns. 3D AFM images at Figure 3 showed that the surface of these films have nanocrystalline particles-uniform and homogenous with well developed. The cone or cornet shapes grains can be seen on all substrates.

Most grains are slightly non-homogenous except Figure 3-c. When the substrate temperature is increased at 400 °C, the distribution of grains is more uniformly on the substrate surface. Some higher grains seem to be aggregated at 440 °C substrate temperature which confirmed SEM graphs. From the AFM images, it was understood that the surface grain size become going smaller and then larger.

The values of surface RMS (Root mean square roughness) depended on substrate temperature are seen in Table 2. These values follow the same trend like surface grain size as a function of the substrate temperature. The RMS of the films doped at 400 °C is the lowest in comparison with other films.

Table2. The RMS values of AFTO films prepared at different substrate temperature

Substrate Temperature	RMS (nm)
320 °C	113,455 nm
360 °C	74,9580 nm
400 °C	35,6588 nm
440 °C	36,8323 nm
480 °C	57,6777 nm

RMS- Root mean square roughness

Optical Properties

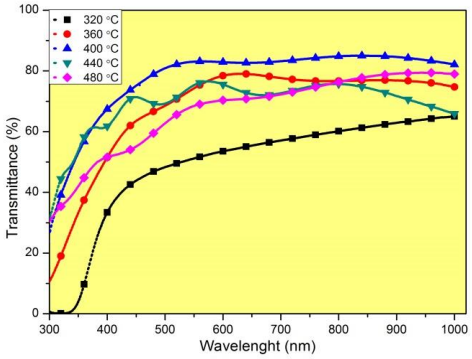

Figure 4. Optical transmission spectra of SnO_2:Sb:F/AFTO thin films prepared at different substrate temperature

The optical transmission spectras (T) of the AFTO thin films prepared at different substrate temperature in the wavelength range of 300–1000 nm are shown in Figure 4. As tin oxide and its derivatives is one of the most attractive TCOs materials, it is expected that they have high transmittance in general. In this work, the average transmittance of these thin films in the visible range is observed as between 50-85%. It is found that The AFTO thin film deposited at 400 °C exhibits the highest transparency (83% at 700 nm).

At deposited 320 °C substrate temperature, the thin films have lower transmittance from other which may be due to incomplete decomposition of the sprayed droplets. The value of T of thin films increased when substrate temperature increased from 320 °C to 400 °C due to the increasing crystalline. At higher temperature, T decreased due to solvent vaporizes before the droplets reach the substrate. These results were similar to those found in literature [8, 17].

The main absorption can be used to define the materials E_g [25]. The molar absorption coefficient (α) can be counted from the Lambert-Beer law [26]; $\alpha=\ln[(1/T)/t]$. And that coefficient changes with photon energy (hν) in term of $\alpha h\nu=A(h\nu-E_g)^{n/2}$ formula where A is related to the effective mass associated with the E_g and n is equal to 1 for a direct gap and 2 for an indirect gap material [27]. The direct E_g values were found by extrapolating the linear portion of these $(\alpha h\nu)^2$ vs. (hν) and $(\alpha h\nu)^{1/2}$ vs. (hν) plots to the zero absorption [18]. The E_g values estimated using the absorption spectra are presented in Table 3.

Table3. The T and E_g values of AFTO thin films prepared at different substrate temperature

Substrate Temperature	$T_{average}$ (%) at 700 nm	E_g (eV)
320 ºC	57,07	3,10
360 ºC	77,64	3,59
400 ºC	83,19	3,89
440 ºC	72,66	3,53
480 ºC	72,26	3,71

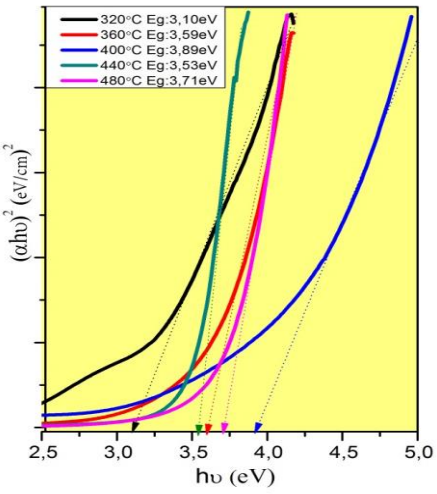

Figure 5. Plots of $(\alpha h\nu)^2$ versus (hν) for AFTO thin films prepared at different substrate temperatures

From the Table 3 it is observed that AFTO thin films have wide optical band energy about 3.10-3.71 eV at room temperature and direct band gap. Also optical band gap at 400 °C temperatures is the highest values. The reason for the increasing E_g value is due to decreasing band defects according to report declared by Senthilkumar et al. [28]. That means crystallinity of films increased with substrate temperature, diminished defects quantity and gained better crystal orientation. Hence recombination with no-light reduced and the intensity of the peak increased.

Shortly, it must be well adjusted the substrate temperature which affected T and E_g values. Moreover, due to the contribution of quantum size effect regarding thin film, the band gap of SnO_2 thin films larger than the value of 3.62 eV for the bulk SnO_2 [29,30]. Because band defects in crystal were found very low than normally value. E_g values are compatible with literature [8,17,27,31].

Electrical Studies

Ecopia HMS5000/AMP55T Hall probe technique in Vander Pauw configuration at room temperature was used determining of the sheet resistance (R_{sh}), carrier concentration (n), resistivity (ρ), conductivity (σ) and carrier mobility (μ) of these AFTO thin films deposited at different substrate temperature. They have been presented in Table 4. The Average Hall Coefficient measurements confirmed that some of these thin films have p-type conductivity and also some of them n-type conductivity.

When SnO_2 is doped with Sb, some of the Sn^{+4} ions in the lattice are substituted with Sb^{+5} ions, since the ionic radius of antimony (62 pm) is similar to tin (71 pm). This substitution of Sb^{+5} ions as donor compose a free electron in lattice which results in an increasing in the concentration of free charge carrier (electron) and decreasing the R_{sh}. When the doping ratio increases, some Sb^{+5} ions reduce to the Sb^{+3} state. So, the acceptor sites (loss of charge carries) is seen [18, 32, 33].

Sb^{+5} ions in role of acceptor (interstitial ions) can trap some free electron in higher quantity of impurities and it was resulted that decreasing in the free charge concentration and so increasing the sheet resistance [8]. Similarly in the case of fluorine doping, the F impurity ions (133 pm) substituted O^{-2} anions (132 pm) in the lattice and created free electrons.

Therefore, the films R_{sh} value decreases. But in more F ratio, the R_{sh} increases because the more F atoms cannot act as suitable substitution impurities, but act as interstitial impurity and hence increasing the error (disorder) in the lattice and finally the R_{sh} increases [10,18].

As doping agents such as antimony and fluorine in this report have their own limits to decrease the resistivity, both of these doping agents are deposited in different ratios to find for better conductivity condition [18].

Table4. Various electrical parameters of SnO_2:Sb:F/AFTO thin films prepared at different substrate temperatures

Substrate Temperatures	R_{sh} (mΩ/cm^2)	n (x10^{19}/cm^3)	ρ (Ω.cm)	σ (S/cm)	μ (cm^2/V.s)
320 °C	161	86,3	3.61E-02	2.77E+01	4.20E+00
360 °C	31,8	-7,45	1.85E-02	5.39E+01	4.09E+01
400 °C	28,8	3,84	5.98E-03	2.27E+02	3.82E+01
440 °C	149	-12,12	2.05E-02	4.87E+01	8.38E+00
480 °C	153	-23,08	2,53E-02	3,95E+01	4,03E+00

Sheet resistance (R_{sh}), carrier concentration (n), resistivity (ρ), conductivity (σ) and carrier mobility (μ)

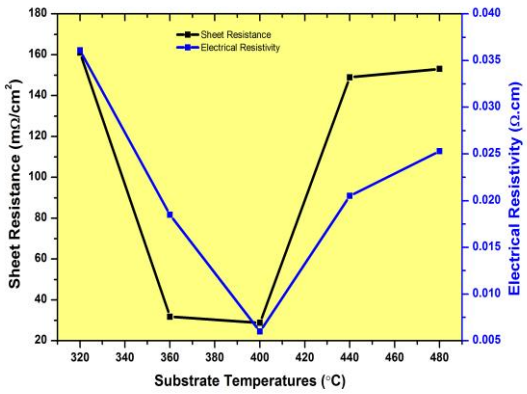

Figure 6. Some electrical parameters of SnO_2:Sb:F/AFTO thin films prepared at different substrate temperatures

The films R_{sh} depend on fluorine and antimony ion doping in SnO_2 lattice or interstitial site as a role of donor or acceptor, respectively, [34]. The variations of R_{sh} and electrical resistivity (ρ) with substrate temperature are seen in Figure 6. Both have same trend as a function of the substrate temperature like

The films R_{sh} depend on fluorine and antimony ion doping in SnO_2 lattice or interstitial site as a role of donor or acceptor, respectively, [34]. The variations of R_{sh} and electrical resistivity (ρ) with substrate temperature are seen in Figure 6. Both have same trend as a function of the substrate temperature like decreasing with increasing substrate temperature and then increasing at higher temperature. This variation compatible with XRD results is due to the proper improvement in the film crystallinity.

In the case of higher solution concentration and higher doping of F, the films have lesser R_{sh} value. It may be due to the predominant role of oxygen vacancies over the substitutional incorporation of F^- ions. Similar results were found in other studies [11, 17, 35]. On the other hand, it was reported by Chinnappa et al. [17] that which in the starting solution Sb doping does not affect R_{sh} value in the AFTO, it this work we found that Sb doping influenced (was increased) the values of R_{sh} compared to our previous study [11].

Also, it is seen that the carrier concentration (n) decreases with increasing temperature and after 400 °C increases. Therefore, the transparency values in the visible region are also high. Otherwise, transparency is reduced with an excessive amount of carrier concentration, but near IR region reflectivity has improved [36]. Kojima et al. [33] reported that T value increased due to reduced solution concentration. In short, it was concluded that the electrical properties are affected by the substrate temperature.

The negative value of the (n) prepared in 0.05 M concentration and (101) peaks dominance in thin films is reached as the result that some these films show p type conductivity instead of n type conductivity. This is the case with Gupta et al. [37] and Ravichandran et al. [38]. Already Kawazoe et al. [39] reported that research on such TCO materials continued [37]. The ideal p-type TCO materials should have higher transparency and conductivity was mentioned by Ravichandran et al. [38] and Benouis et al. [40]. For this reason, an intensive effort has made to investigate p-type conductivity studies. At the same time doubly doped tin oxide with p-conductivity was reported for the first time in this report.

Conductivity (σ) and carrier mobility (μ) is increasing with substrate temperature and then decreasing for higher temperature. The increasing reason carrier mobility is that the effect of increasing grain size or concerned to doping of Sb and F where previously discussed at Figure 5. Because, the grain boundary and ion impurity scattering effect mobility [41]. In same time, second scattering which limits the mobility is the dominant mechanism [10]. However, the mobility of the films with high doped rating was lower than that of the films with less doped due to interstitial scattering due to the excessive doped of fluorine.

These results are match with the previous reports i.e. substrate temperature decides the SnO_2 film stoichiometric variation. But, if substrate temperature increasing much the film starts non-stoichiometric state which behaviors that the surface mobility was enhanced and thus the grain size become larger. So, grain boundaries reduced and mobility enhanced [10,42].

Photoluminescence (PL) Studies

PL measurements provide information about band transitions and imperfections in the structure. To identify that, thin films excited at 300 nm. A room temperature PL spectrum of AFTO thin films was recorded as shown in Figure 7. It was found that a strong blue emission band around 347 nm (3.57 eV) and low intense three peaks around 397 nm (3.12 eV), 450 nm (2.76 eV) and 469 nm (2.65 eV) in all films.

Origin of 3.57 eV peak is exciton emission inside rutile SnO_2 structure [43]. Intensity of this peak is power than in our previous study. PL band at 397 nm can be related to the electron transfer from the donor level to the acceptor level [44]. In spray polycrystalline oxides, oxygen vacancies are accepted common defects and composed the donor level [45]. Also, some researchers have reported that SnO_2 thin films has a broad dominant peak near 396 nm (about 3.14 eV), which assigned with luminescent centers such as nanocrystals and defects [46]. Also Gnanam and Rajendran [47] said to Cheng et al. [48] proposed that 452 nm band may be concerned to crystal defects or defect levels associated with oxygen vacancies or tin interstitials. A 469 nm peak related to blue luminescence and can be assigned to singly charged O_2 vacancies or luminescent centers [49].

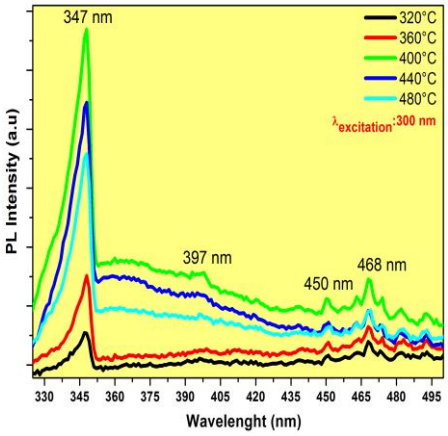

Figure 7. PL emission spectra of SnO_2:Sb:F/AFTO thin films prepared at different substrate temperature

It was found from PL graphs that maximum PL intensity of film deposited at 400 °C is located at about 347 nm and this is corresponding to about 3.57 eV (optical E_g), but it was found the E_g value of films at 400 °C was to be about 3.89 eV. This discrepancy in band gap energy value would be due to the fact more defects which located in the band gap [50]. But, any detailed explanation about these results in conflict with each other was not been identified.

The improvements in the crystal with increasing substrate temperature (diminished defect density, improved crystal orientation) have resulted in increased energy and intensity of the PL emission. But, there was so very slight shift to a UV region for strong peak due to decreasing defects with the substrate temperatures. Because, the UV shift can be attributed to the increased crystallinity and a higher carrier concentration [51]. These values are like to the results reported by previous reports [19,52,53].

CONCLUSION

In this paper, two layers of doped SnO_2:Sb:F/AFTO low doped and low solution concentration thin films have been successfully prepared by using homemade, simple and easy spray pyrolysis method at different substrate temperatures. From the XRD spectra, it was found that these films were polycrystalline and had a rutile quadrangular structure with three main peaks having planes (110), (200) and (210). The grain size of the thin films ranged between 38.1 nm and 42.7 nm. The surface morphology was investigated by SEM and AFM, and the films were found to have nano-particulate structure. Hall Effect revealed that some of these thin films had p-type conductivity (no report for doubled doped films) and some had n-type conductivity. The optical transmittance of the films was between 60% and 80%, and the optical band gap of these films varied from 3.1 eV to 3.89 eV, depending on the substrate temperature. All structural and morphological properties of AFTO thin films have demonstrated that they can have optimum properties with appropriate doping concentration and these films have the potential to be used as an alternative product in TCO applications.

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