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A Study on Sb and F Doped Tin Oxide Thin Films Preparing in Condition of Different Temperature and Molarity and Their Physical Comparison

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ABSTRACT: This article is about tin oxide (SnO_2:Sb:F) thin films prepared (7 samples at each experiment step) successfully on the glass substrate by using spray pyrolysis method. Different solution molarities and different substrate temperatures were used to prepare precursor solution and fabricate thin films, respectively. And then these thin film's structural, optical and morphological properties were compared. XRD patterns displayed that the deposited films were polycrystalline with tetragonal structure irrespective of molarity and substrate temperature. Each film has a transmittance of more than 60% in visible region. Optical band gap values were found to be in the range of 3.74-3.95 eV. The SEM and AFM images demonstrated that nanocrystalline particles covered all film surfaces. The best optimum property was found at thin films (0.15 M) prepared with at 520 ˚C and the grains are larger for thin films at 520 °C when compared with 480 °C. Finally, it is understood that when substrate temperature and molarity increased, more regular structure was obtained.

Anahtar Kelimeler: SnO_2:Sb:F thin films, spray pyrolysis, solution molarity and substrate temperatures

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INTRODUCTION

In latest and sophisticated technological devices like as organic light emitting diode (OLED) (Yusoff et al., 2018), dye-sensitized solar cell (DSSC) (Musyaro'ah et al., 2017), thin film transistors (TFTs) (Priyadarshini et al., 2017), flat panel display (Liu et al., 2018), gas sensor (Kou et al., 2018) and smart windows (Huang et al., 2015), transparent conducting oxide materials (TCO)s are excessively using. The reason for this is due to their excellent properties including high transparency and conductivity, low electric resistivity, chemical inertness and mechanical hardness (Ravichandran et al., 2009; Vazquez-Arreguin et al., 2016). TCOs thin films have deposited with various technique for a long time. It can be given for example spray pyrolysis (Yuwono et al., 2017), spin coating (Kadhim et al., 2017), pulsed laser deposition (Martin et al., 2004), dip coating (Carvalho et al., 2012) and sputtering (Zhu et al., 2017) methods. Among them, it was found that spray pyrolysis method have interesting properties such as simple and inexpensive experimental setup, reproducibility, easily adding of doping materials, preparing thin films with high quality (Tripathi and Shukla, 2014). The properties of TCOs thin films have been fabricated by spray can be changed with substrate temperature, spray time, spray flow rate, nozzle-substrate distance, precursors and solvents etc. (Yuwono et al., 2017). Here, we aimed to compare effect of substrate temperature and molarity on TCOs thin films by spray method (for example SnO_2:Sb:F).

MATERIALS AND METHODS

Tin Oxide Thin Film Preparation

In this work, Antimony (Sb) and Fluorine (F) doped tin oxide (SnO_2:Sb:F) thin films were prepared by using a home-made spray pyrolysis method at different substrate temperatures and different molarities. 480 ˚C and 520 ˚C degrees were chosen for different substrate temperatures. Substrate temperature is maintained ±10˚C using a k-type thermocouples. The solution molarity values were kept at 0.05M, 0.1M and 0.15M. All solvent volumes are constantly maintained at 50 mL. Doping weight ratio of Sb and F, respectively, are 4% and 30%. For precursor solution, Tin (II) chloride dehydrates ($SnCl_2.2H_2O$), antimony (III) chloride ($SbCl_3$) and ammonium fluoride (NH_4F), deionized water and hydrochloric acid (HCl) were used. All reagents and organic solvent were purchased from Merck. Glass substrates with (10x10x1) mm^3 dimensions were cleaned with Acetone, Isopropyl Alcohol and Deionized water in ultrasonic cleaner. After cleaning, the substrates were dried at 150 ˚C in an oven before being used. For making tin precursor solution, 0.564 g $SnCl_2.2H_2O$, 0.173 g $SbCl_3$ and 0.022 g NH_4F were dissolved in 5 ml of HCI. This solution was completed to 50 ml with deionized water. After dissolving, the solution was stirred at 60 ˚C for 60 min to gain homogenous solvent. A syringe filter with 0.2 micron size was used to prevent large particles. Also, in this experiment, the flow rate (10 $ml.min^{-1}$) of air used as a carrier gas, the nozzle to substrate distance (40 cm), the spray angle (α=45˚), plate rotation speed (20 $rpm.min^{-1}$) and pressure (0.2 $kg.cm^{-2}$) were fixed as a constant. To complete the deposition process, the sprayed films were allowed to cool naturally at room temperature, and some physical properties of thin films investigated and compared. The schematic diagram of this system and other experiment details has been found previous report (Battal et al., 2015).

Characterization

Rigaku D/Max-IIIC XRD diffractometer with CuKα radiation (λ=1.5418 Å), at operating voltage of 30 kV, and current of 10 mA, a JEOL SEM (Scanning Electron Microscope) Model 6460. a NT-MDT AFM (Atomic Force Microscope) and a UV-VIS (Perkin Elmer, Lambda 35) spectrophotometer were used to characterize sample's properties.

RESULTS AND DISCUSSION

Comparing of XRD Structural Analysis

Structural properties of SnO_2:Sb:F thin films prepared at different concentration and substrate temperature were recorded by Rigaku D/Max-IIIC XRD diffractometer with CuKα radiation (λ=1.5418 Å). XRD spectra for these thin films are shown in Figure 1 and Figure 2. It was observed from XRD documents that three peaks which compatible with the American Society for Testing and Materials (ASTM) standard along (110), (101) and (211) which indicated the films are polycrystalline in nature and the deposited films have tetragonal (rutile) structure irrespective of molarity of precursor in the solution and substrate temperature.

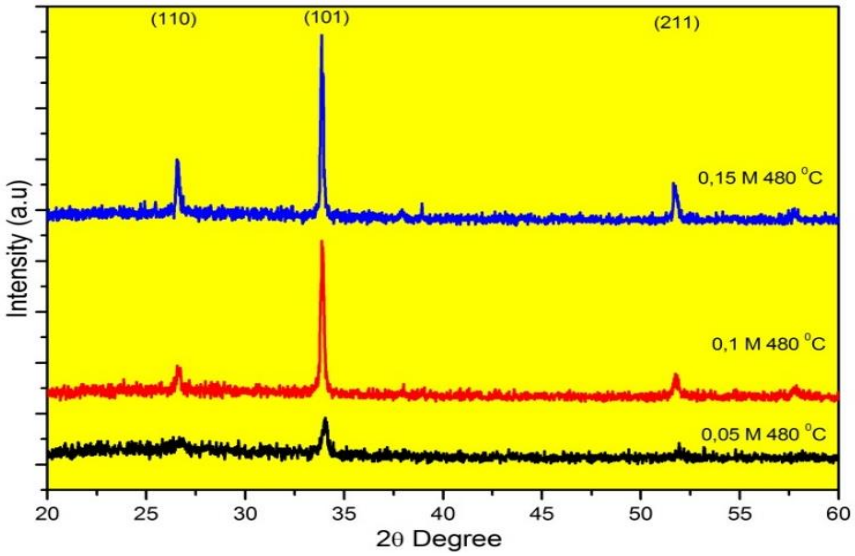


Figure1. The XRD spectra of samples prepared at different molarity and 480 ˚C substrate temperature

But, the (101) plane was preferential orientation for the deposited films. Any peaks of impurities have not seen. It was found that as molar concentration and substrate temperatures increase intensities of the all peaks increase. But, intensity of the (101) plane for thin films prepared at 520 ˚C is higher than 480 ˚C. The best optimum properties come into the open to thin films sprayed with 0.15 M and at 520 ˚C.

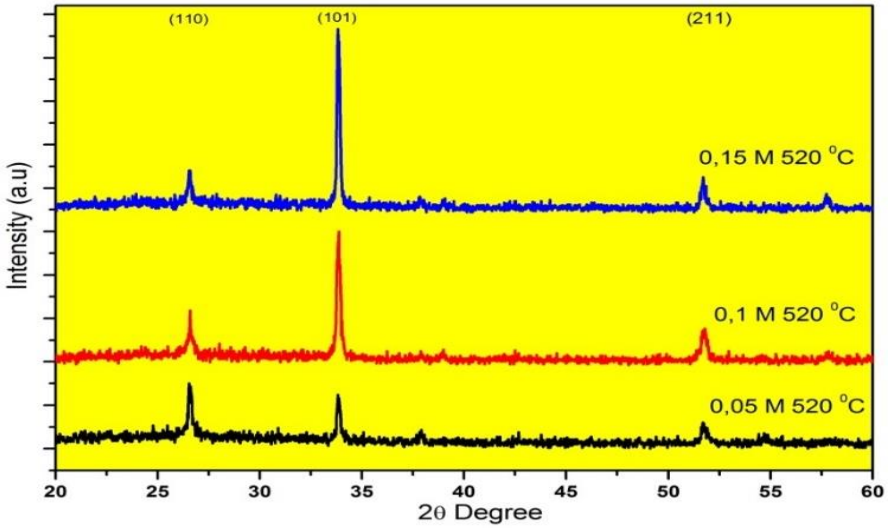


Figure2. The XRD spectra of samples prepared at different molarity and 520 ˚C substrate temperature

Also, The XRD spectra of samples deposited as a function of substrate temperatures and precursor solution concentrations can be seen in Figure 3. Structural parameters for all samples along each crystallographic plane were summarized in Table 1. The grain size (D) of these SnO_2:Sb:F thin films is estimated using Debye-Scherrer's formula (Vikraman et al., 2016), $D=0.9\lambda/(\beta\cos\theta)$ where λ is the X-ray wavelength (λ = 1.5418 Å), β is the broadening of diffraction line measured at half its maximum intensity in radians (FWHM) and θ is the Bragg angle.

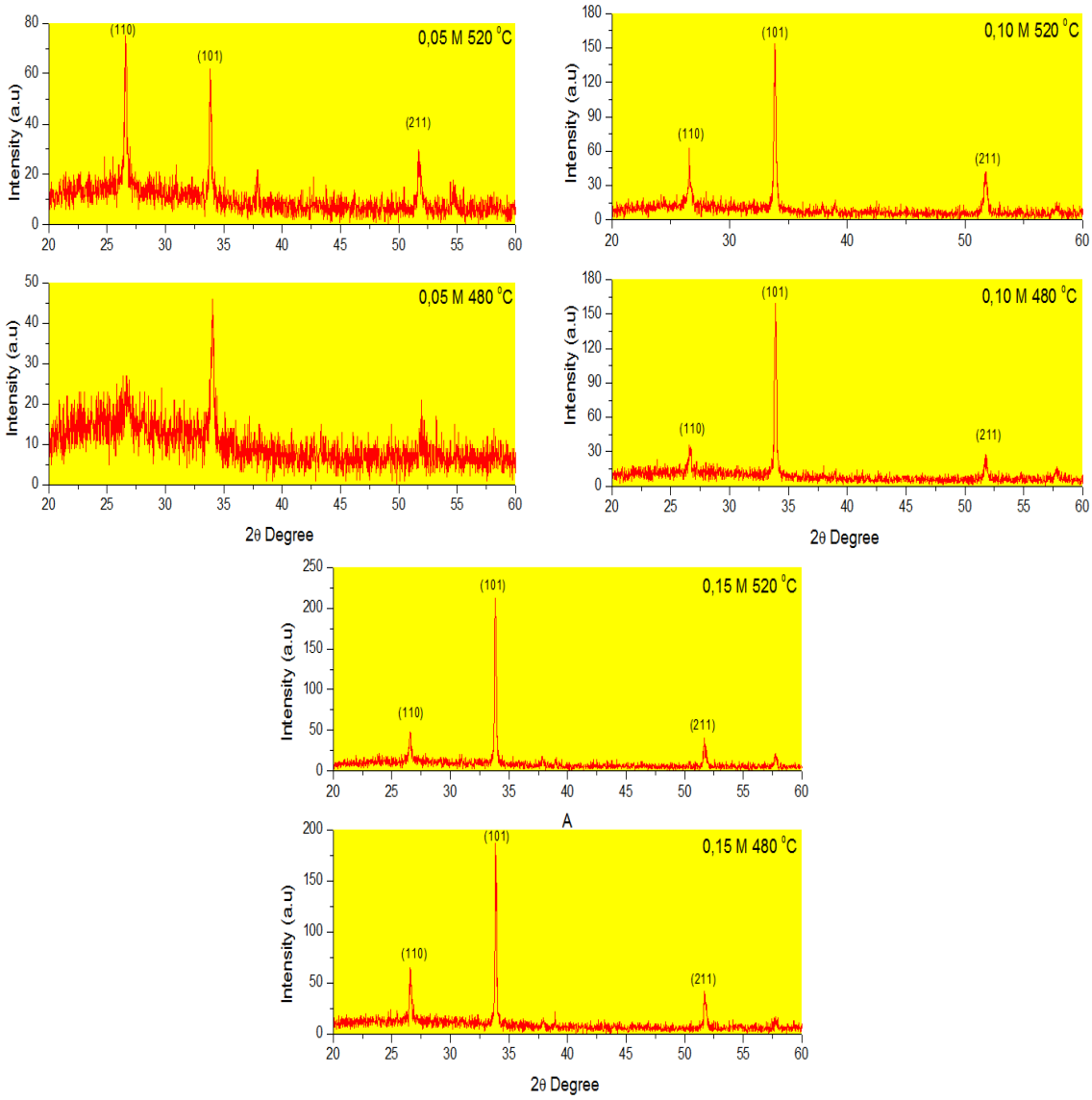


Figure3. The XRD spectra of samples prepared at different substrate temperature and molarity

The interplaner distance (d) for each samples calculated from XRD results by using Bragg's law; ($n\lambda=2d\sin\Phi$). As the films have rutile structures, the lattice constants are calculated using $(1/d^2)=\{[(h^2+k^2)/a^2]+(l^2/c^2)$ equation (Wohlmuth and Adesida, 2015); The calculated (a=b) and (c) values are compatible with the JCPDS Card No: 71-0652 Quality C. In this study, dislocation density (δ) was determined using (Ravichandran et al., 2009); $\delta=1/D^2$.

Table 1. The structural parameters of samples prepared at different molarity and substrate temperature

Samples	(hkl)	2θ(˚)	d_{std}(Å)	d_{cal}(Å)	FWHM(º)	D(nm)	δ(lines m^{-2})
0.05 M 480 ˚C	110	-	3.35	-	-	-	-
	101	34.12	2.644	2.629	0.07998	104	9.25E+13
	211	51.87	1.764	.763	-	-	-
0.05 M 520 ˚C	110	26.58	3.35	3.355	0.14578	57	3.07E+14
	101	33.86	2.644	2.648	0.20904	39.8	6.32E+14
	211	51.68	1.764	1.769	0.13331	62.4	2.57E+14
0.10 M 480 ˚C	110	26.54	3.35	3.360	0.07581	110	8.30E+13
	101	33.82	2.369	2.652	0.20889	39.8	6.31E+14
	211	51.68	1.764	1.769	0.12	63.9	2.08E+14
0.10 M 520 ˚C	110	26.72	3.35	3.337	0.05651	147	4.62E+13
	101	33.86	2.644	2.648	0.07444	112	8.01E+13
	211	51.66	1.764	1.777	0.05424	153	4.25E+13
0.15 M 480 ˚C	110	26.72	3.35	3.337	0.10746	77.4	1.67E+14
	101	33.88	2.644	2.647	0.20652	40.3	6.17E+14
	211	51.68	1.764	1.769	-	-	-
0.15 M 520 ˚C	110	26.54	3.35	3.36	0.21664	38.4	6.79E+14
	101	33.82	2.644	2.652	0.16509	50.4	3.94E+14
	211	51.68	1.764	1.769	-	-	-

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

It was shown at Table 1 that the grain size values changed and improved depending on substrate temperature and molarity. For 480 °C opposite to 520 °C, grain size of films decreased while molarity increased. For the best thin films at 520 °C, grain size is higher than 480 °C. On the other hand, dislocation density is lower than 480 °C. At lower temperatures, the situation is reversed.

In Table 2. It was found that lattice constants (a and c)were not affected much with substrate temperature and concentration. It was concluded that precursor concentration and temperature is the most important process parameter controlling film structural properties in thin films (Yuwono et al., 2017).

Table 2. Lattices parameters (a and c) of samples prepared at different molarity and substrate temperature

Molarity	$T_{substrate}$	(hkl)	d_{std}(Å)	d_{cal}(Å)	$a_{std}=b_{std}$(Å)	$a_{cal}=b_{cal}$(Å)	c_{std}(Å)	c_{cal}(Å)
0.05 M	480 ˚C	101	2.644	2.629	4.738	4.755	3.187	3.153
	520 ˚C	101	2.644	2.652	4.738	4.751	3.187	3.196
0.10 M	480 ˚C	101	2.644	2.647	4.738	4.719	3.187	3.197
	520 ˚C	101	2.644	2.648	4.738	4.745	3.187	3.191
0.15 M	480 ˚C	101	2.644	2.648	4.738	4.719	3.187	3.197
	520 ˚C	101	2.644	2.652	4.738	4.751	3.187	3.191

(hkl) miller indices, d-interplaner distance, a, b and c lattice constants, cal: calculation and std: standard

Comparing of Optical Properties

The Optical Properties of SnO_2:Sb:F thin films are investigated at RT. It was shown that the optical transmittance spectra for these thin films deposited at different substrate temperature and concentration at 300–1000 nm wavelength in Figure 4.

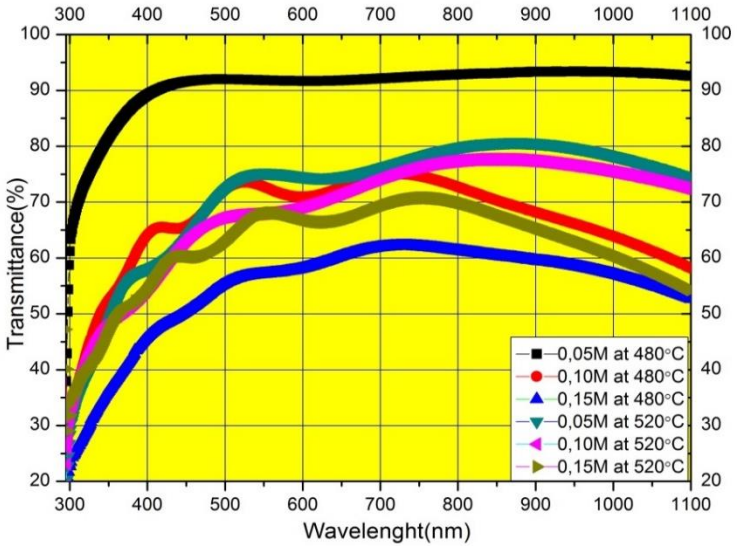


Figure 4. Optical transmittance value versus wavelength of samples prepared at different molarity and substrate temperature

It is understood from UV spectra that all samples have a transmittance of more than 60% in visible region. As the molarity increased, transmittance of films decreased due to thickness while temperature is stable. But, in the case of solution concentration is not being changed, transmittance of films at 520 °C is higher than 480 °C at higher temperature because of good crystalline. Therefore, optical properties of the thin films are depending to temperature and solution molarity. A sudden increase at 480 ˚C, 0.05 M cannot be understood.

The optical energy gap (E_g) of these thin films can be calculated from the allowed direct transition given by Tauc's eguation $\alpha h\nu=B(h\nu-E_g)^n$ (Kumar et al., 2017); where α is an absorption coefficient, h is Planck's constant, ν is the photon frequency and B is a constant.

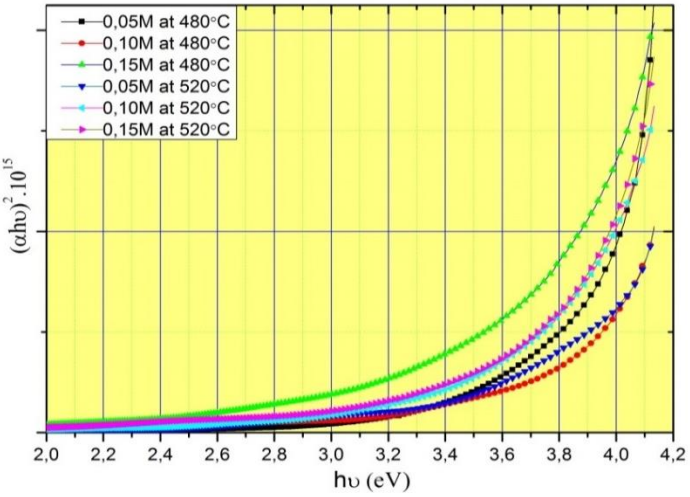


Figure 5. Tauc's Plots of samples prepared at different molarity and substrate temperature

Table 3. The T and E_g values of samples prepared at different molarity and substrate temperature

Samples	$T_{average}$ (%) at 700 nm	E_g (eV)
480 ºC 0.05 M	92.13	3.95
480 ºC 0.10 M	74.85	3.85
480 ºC 0.15 M	61.90	3.74
520 ºC 0.05 M	76.16	3.89
520 ºC 0.10 M	74.00	3.84
520 ºC 0.15 M	69.12	3.78

The optical band gap values determined by extrapolating the linear curve that intercepts the energy axis (Kumar et al., 2017) were presented in Table 3 and drawn at Figure 5. It is observed that SnO_2:Sb:F thin films have wide optical band energy. Also E_g values for these thin films were decreased with an increase in molarity. The reduction in band gap can be due to the presence of unstructured defects, which could increase the localized states of density in the band gap, thus decreasing the energy gap (Kumar et al., 2017; El-Zahed et al., 2002). As substrate temperature is increased, E_g values at 520 °C, 0.15M are higher than 480 °C well-adjusted with XRD results.

Comparing of SEM Surface Morphologic Analysis

The study of surface morphology of SnO_2:Sb:F thin films sprayed at different concentration and substrate temperature by using spray pyrolysis method has been carried out. Figure 6 are pictures displaying that surface morphologies of these thin films are strongly interrelated to the solution molarity and substrate temperature. The SEM images revealed that nanocrystalline particles covered all substrate surfaces irrespective of temperature and molarity and surface morphology is uniform and homogenous. However, it has been observed that the voids and clusters of particles in film surfaces produced at low temperatures have been reduced when the temperature and concentration which greatly affects the quality of the film are increasing.

Comparing of AFM Topographic Analysis

The AFM topographic study of these thin films was characterized by a NT-MDT AFM Microscope. Respectively, Figure 7 and Figure 8 show the 2-D and 3-D AFM images of SnO_2:Sb:F thin films deposited as a function of substrate temperatures and precursor solution concentrations. The AFM images exhibited that the prepared thin films are to be made of nanocrystalline particles, uniform, homogeneous almost all surfaces. Some of grains are like human oral teeth, another one is ice cream cone or conical shape shaped grains. The AFM images (both) clearly show that the grains are larger for thin films at 520 °C when compared with 480 °C. When temperature and molarity increased, a regular structure was obtained. These observations strongly support the results obtained from the XRD data (Table 1). The size of the grains is equal with calculated from the XRD data. On the other hand, if solution molarity is increasing, the intergranular spacing is diminishing. Some overgrown grains seem to be stacked at certain favorable sites for thin films at 520 °C and 0.10 M which confirmed SEM graph and RMS value. Such a variation in grain size values has been reported by several researchers (Moholkar et al., 2008a, 2008b); Ikhmayies and Ahmad-Bitar, 2012).

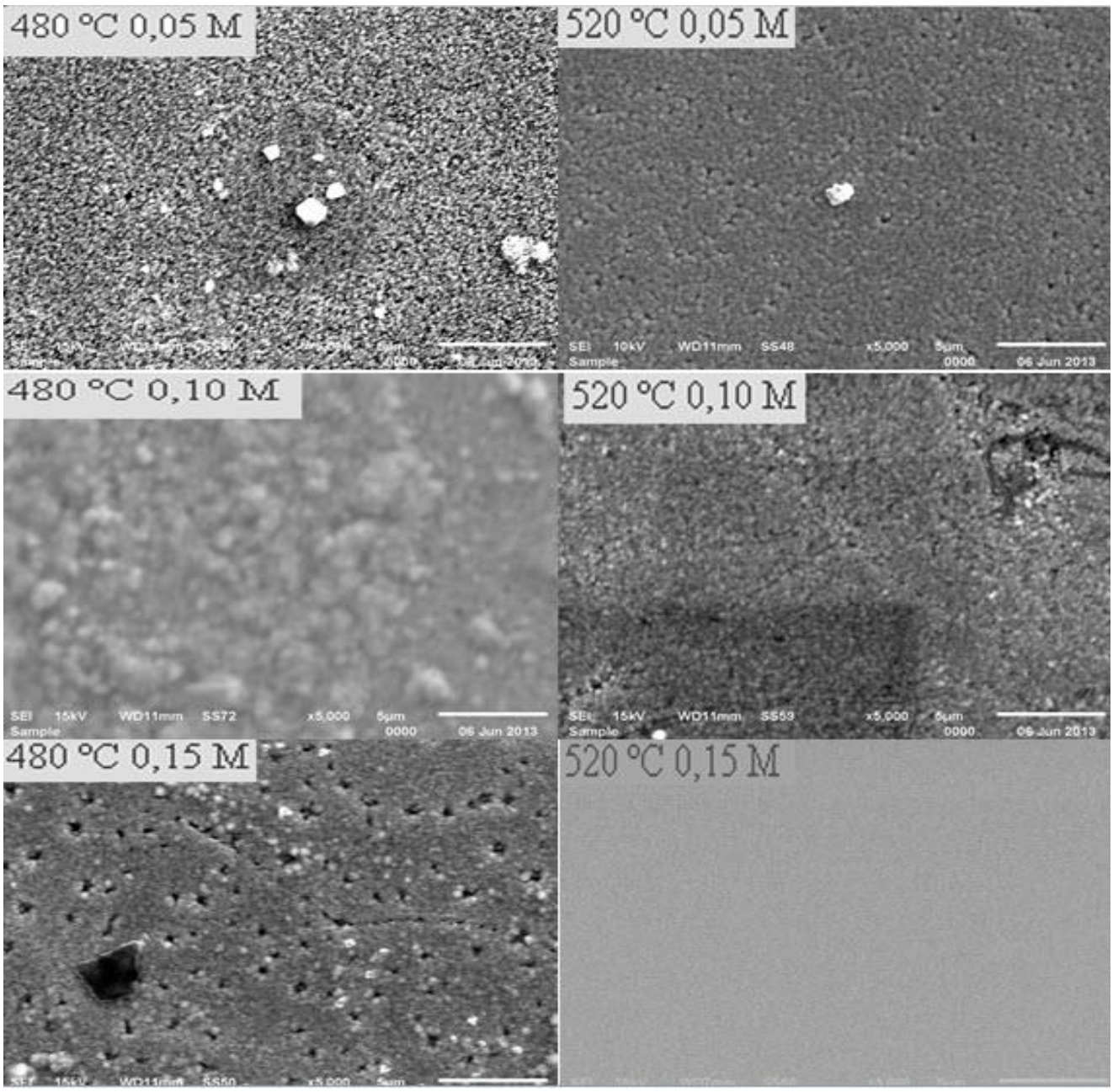
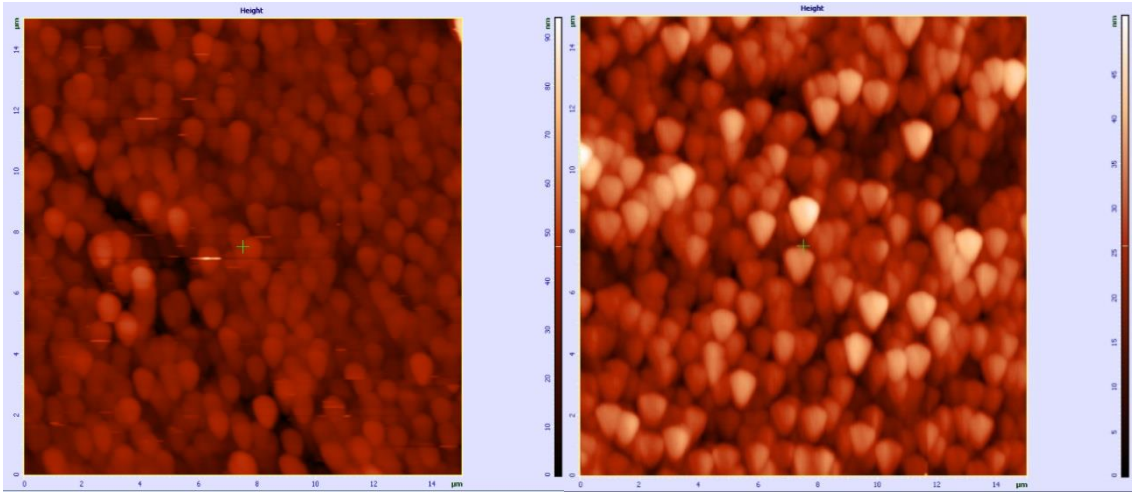


Figure 6.SEM images of samples prepared at different molarity and substrate temperature

(a)



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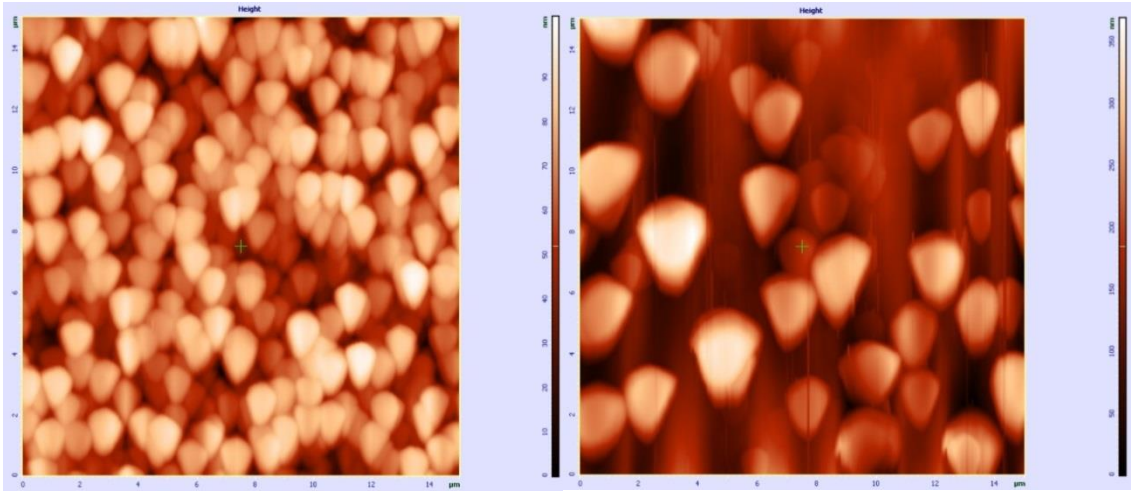

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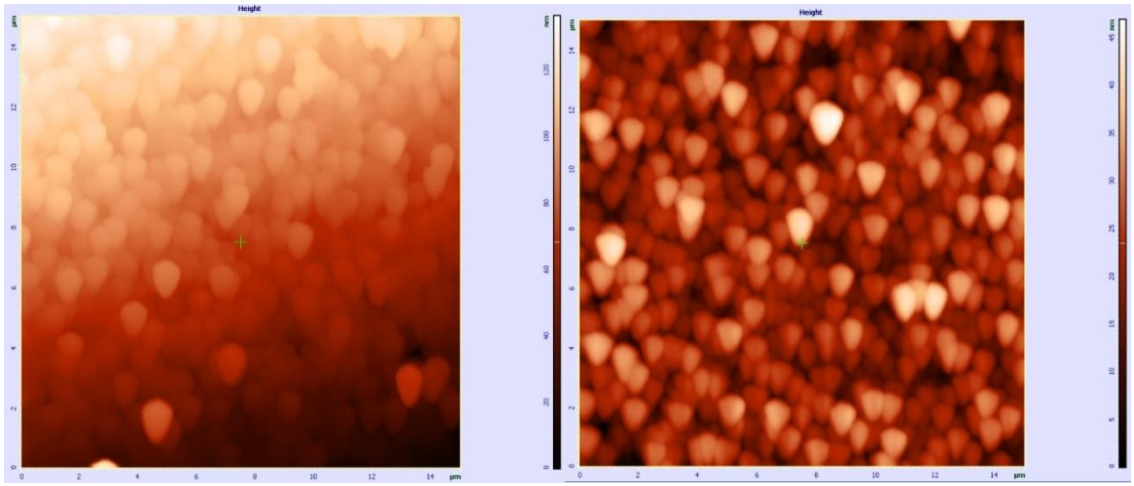
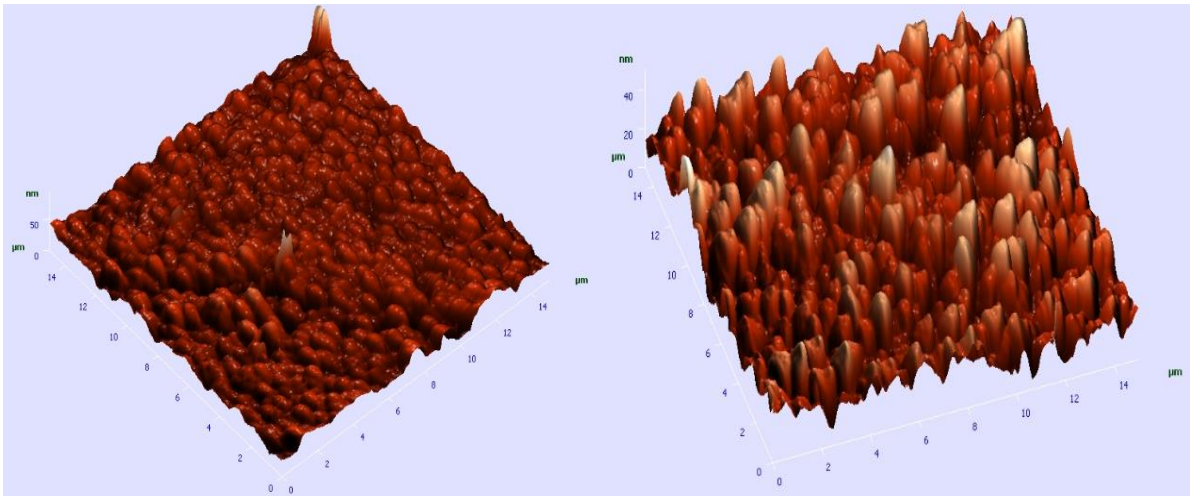


Figure 7. 2-Dimension AFM images of samples prepared at different molarity and substrate temperature (a) 0.05 M (b) 0.10 M and (c) 0.15 M at 480 ^{o}C (left) and 520 ^{o}C (right) substrate temperature

(a)



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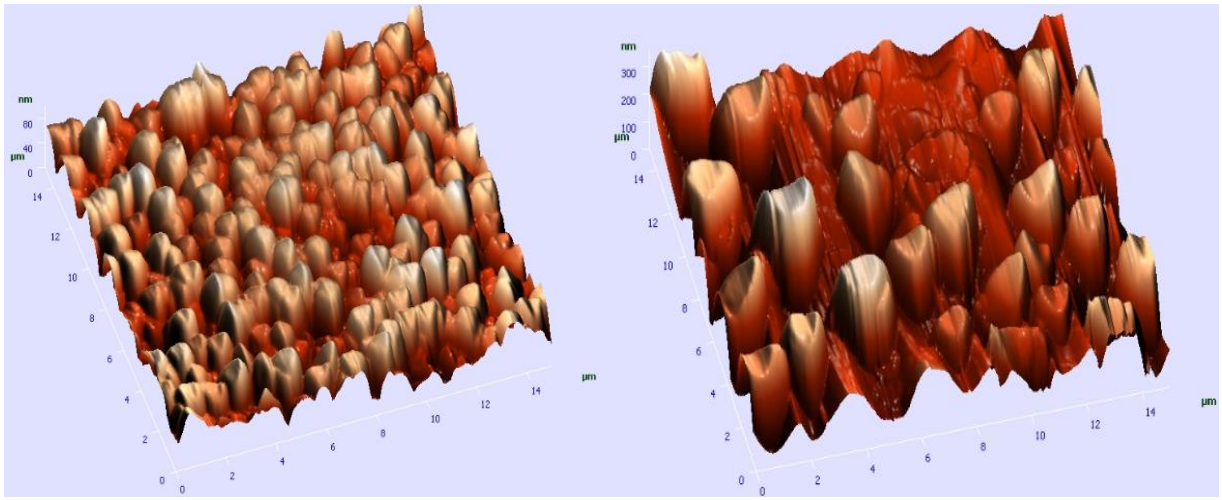

(c)

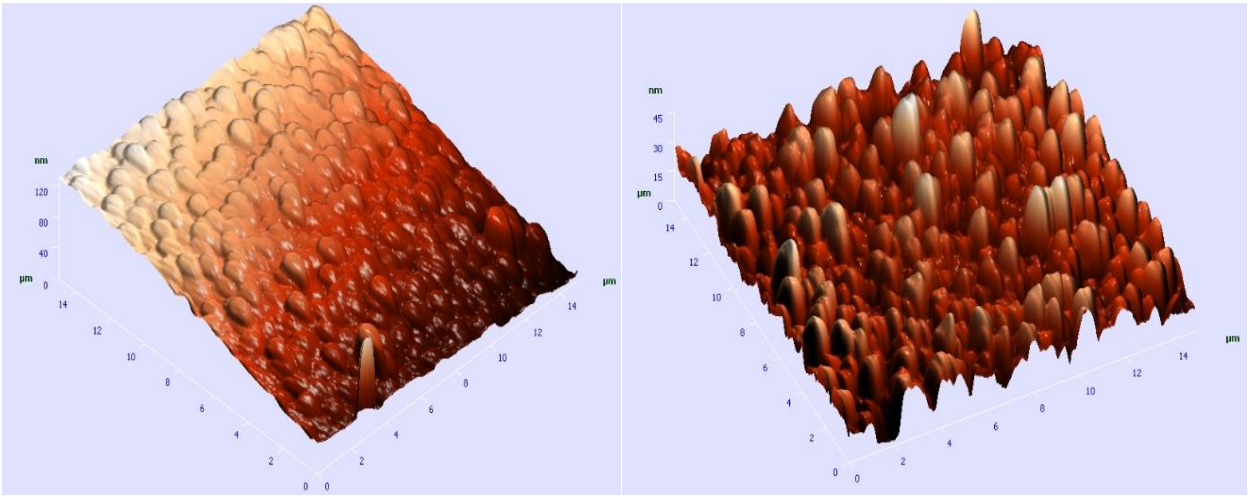

Figure 8. 3-Dimension AFM images of samples prepared at different molarity and substrate temperature (a) 0.05 M (b) 0.10 M and (c) 0.15 M at 480 ^{o}C (left) and 520 ^{o}C (right) substrate temperature

The values of surface RMS (Root mean square roughness) depended on substrate temperature and molarity are seen in Table 4.

Table 4. The RMS values of samples prepared at different molarity and substrate temperature

Solution Molarity	RMS (nm) at 480 °C	RMS (nm) at 520 °C
0.05 M	22.5383 nm	7.83088 nm
0.10 M	14.2396 nm	65.9065 nm
0.15 M	17.3141 nm	9.65524 nm

CONCLUSION

Antimony (Sb) and Fluorine (F) doped tin oxide thin films (SnO_2:Sb:F) were deposited successfully on the glass substrate by spray pyrolysis technique at different solution molarities and different substrate temperatures and their properties compared. XRD results clearly revealed that the prepared films were polycrystalline with tetragonal (rutile) structure irrespective of molarity of precursor in the solution and substrate temperature and thin films had three peaks along (110), (101) and (211). SEM and AFM images demonstrated homogeneous along almost all surfaces and some grains are like human oral teeth, another one is ice cream cone or conical shaped grains. The AFM images clearly show that the grains are larger for thin films at 520 °C when compared with 480 °C. E_g values changed 3.74-3.95 eV. Each film has a transmittance of more than 60% in visible region. As the molarity increased, transmittance of films decreased due to thickness while temperature is stable. It is found that the best optimum property was found at thin films (0.15 M) prepared with at 520 ˚C. Finally, it was understood from results that substrate temperature and solution molarity is necessary for making thin film with good atomization and optimum properties and for materials to be used on optic and electric applications area.

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