Study the effect of doping for various materials (F, Sb) on the properties of tin oxide (SnO_2) film

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ABSTRACT

In this research doped and undoped SnO_2 was prepared by using cold wall atmospheric pressure chemical vapor deposition (APCVD) system at substrate temperature (450 ^{0}C) and flow rate of O_2 gas (1.5) L/M for (15) min using ($SnCl_2.5H2O$) and different percentage from (NH_3F) , ($SbCl_3$) as source for (Sn, F, Sb). Several films were prepared by using different ratios of antimony (Sn:Sb) as fallowing: (1: 0.3, 1: 0.5, 1:0.7, 1:1 Wt. %) and (SnO_2:F) in ratios of (1: 0.1, 1: 0.3, 1:0.5, Wt.%). X-ray diffraction (XRD) spectra shows changing in structures for (Sb, F) with shift in peaks. Also roughness average values have been increased with increase of doping ratio. Optical properties have been studied by using UV-Vis spectroscopy. Electric properties had been studied. through spectroscopic study of these films was found to have a high transmittance in the visible region.

Keywords: SnO2, SnO_2-F, SnO_2-Sb thin films, APCVD.

دراسة تأثير التشويب لمختلف المواد (فلور ، انتيمون) على خصائص غشاء اوكسيد القصدير

الخلاصة:

في هذ البحث تم تحضير اغشية اوكسيد القصدير المطعمة والغير المطعمة باستخدام منظومة الترسيب بالبخار الكيمياوي ذو الجدار البارد عند درجة حرارة اساس (450) درجة مئوية ومعدل جريان غاز($SbCl_3$) , (NH_3F) ($SnCl_2.5H2O$)الاوكسجين كان (1,5) لتر / دقيقة باستخدام بنسب مختلفة كمادة اولية ، حيث تم تحضير الاغشية لمختلف النسب لكلا الفلور والانتيمون . اظهرت نتائج الاشعة السينية تغيير بالتركيب باضافة كل من الفلور والانتيمون مع ازاحة بالقمم. مع ازدياد نسب التشويب تزداد خشونة السطح. جميع الاغشية شفافة وهذا ما م قياسه باستخدام المطيافية المرئية-وفوق البنفسجية. الخصائص الكهربائية تم قياسها ايضا.

الكلمات الافتتاحية : منظومة APCVD, اغشية nO_2-F, SnO_2-Sb

INTRODUCTION

The tin oxide(is a wide band gap semiconductor (energy bandgap 3.6 eV), and it has only the tin atom that occupies the centre of a surrounding core composed of six oxygen atoms placed approximately at the corners of a quasiregular octahedron. In the case of oxygen atoms, three tin atoms surround each of them, forming an almost equilateral triangle. SnO_2 is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. Due to these properties, apart from gas sensors, SnO_2 is being used in many other applications, such as electrode materials in solar cells, light-emitting diodes,

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flat-panel displays, and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics, such as transparent field effect transistors [1]. SnO_2 owing to a wide band gap is an insulator in its stoichiometric form. However, due to the high intrinsic defects, that is oxygen deficiencies, tin oxide (SnO_{2-X}) possesses a high conductivity. It has been shown that the formation energy of oxygen vacancies and tin interstitials in SnO2 is very low. Therefore, these defects form readily, which explains the high conductivity of pure, but non stoichiometric, tin oxide. SnO2 thin films have been deposited using different techniques, such as spray pyrolysis [2], sol-gel process [3], chemical vapor deposition [4], sputtering [5], and pulsed laser deposition [6].

The presence of the impurities inside the crystalline structure effected the physical properties due to direct impact on crystal size and shifted the peaks locations in corner orientations within diffraction curve to high or less values depending on the ionic radius for doping atom combatable with hosting atom[7]. Doping of tin oxide films with a suitable ion creates a donor level in the band gap resulting in an enhanced conductivity of these films. Especially fluorine (F), antimony (Sb) [8].

Material and method

Doped and undoped Tin oxide thin film prepared by homemade cold wall reactor atmospheric pressure chemical vapor deposition (APCVD) with glass substrate, figure (1) , substrate temperature (450 ^{0}C) with flow rate (1.5) L/M for (15) min using ($SnCl_2$.5H2O) and different percentage from (NH_3F) , ($SbCl_3$) as source for (Sn, F, Sb) . The glass slides substrate were cleaned ultrasonically by Trichloroethylene (TCE), acetone, ethanol followed by distilled water and dry with N2. X-Ray diffraction (CuKα) radiation with a wavelength λ =1.5418 Å at 2θ values between 20° and 60 was used to study the crystal structure. (AFM) were used for investigate the morphology and roughness of surface. The optical properties were studied by UV-Visible spectroscopy. the electric measurement was made directly .

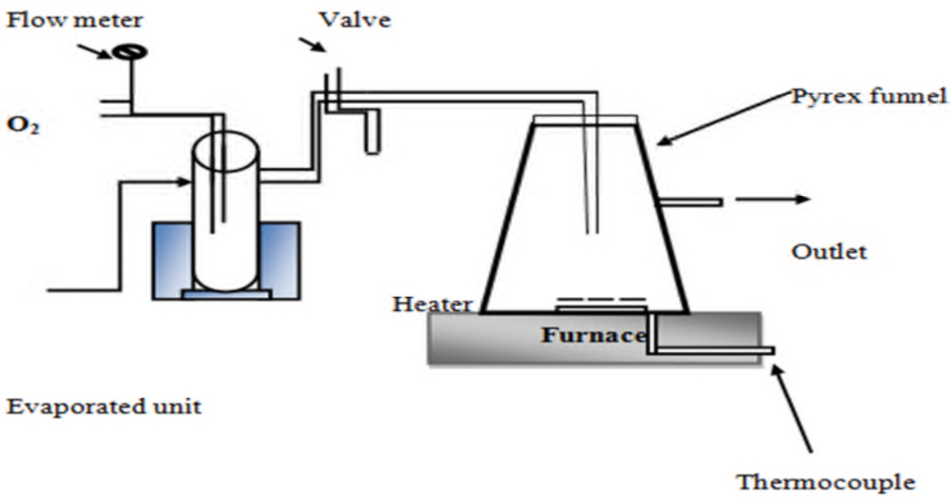


Figure (1) atmospheric pressure chemical vapor deposition (APCVD) system.

Results and discussion

Doping with antimony (Sb)

In this study, many different concentrations have been used to prepare (SnO_2: Sb) film. The ratio of (Sn:Sb) as fallowing: (1: 0.3, 1: 0.5, 1:0.7, 1:1 Wt. %) . The result of (XRD) for the films that prepared on glass substrate has showed that undoped (SnO_2) film polycrystalline of tetragonal type with preferential orientation along the (110), (101),(200),(211) directions. For doped films there is an additional peaks for some phases for Antimony oxides were appeared. It is clear from result shown in figure(2) that by doping with Sb , all the peaks of diffraction are shifted towards the higher angle (2θ) with increase of the doping ratio beside there is a change in preferred direction for peaks. This mean that the (Sb) atoms merge with tin oxide film contains, for (0.5) the preferred direction is (101) while for other ratios the intensity of this plane disappears or has less intensity , furthermore the structure is changed to amorphous for (0.3 and 0.7) ratios this is clear with AFM image measurement. Atomic force microscopy (AFM) measurements show thickness homogeneity for the prepared films depending on its size as well as building structure for film surface appearances which was clear. Root mean square (RMS) and roughness average values have been increased with increase of doping ratio, this mean increasing in grain size and decrease the grain bounders as shown in figure (3).

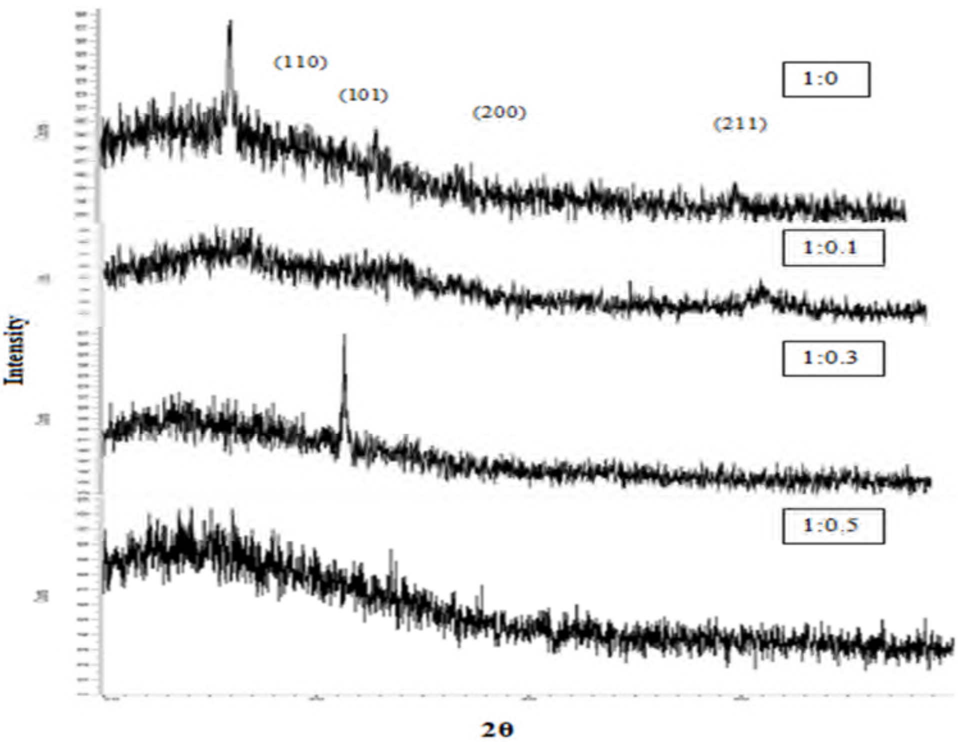
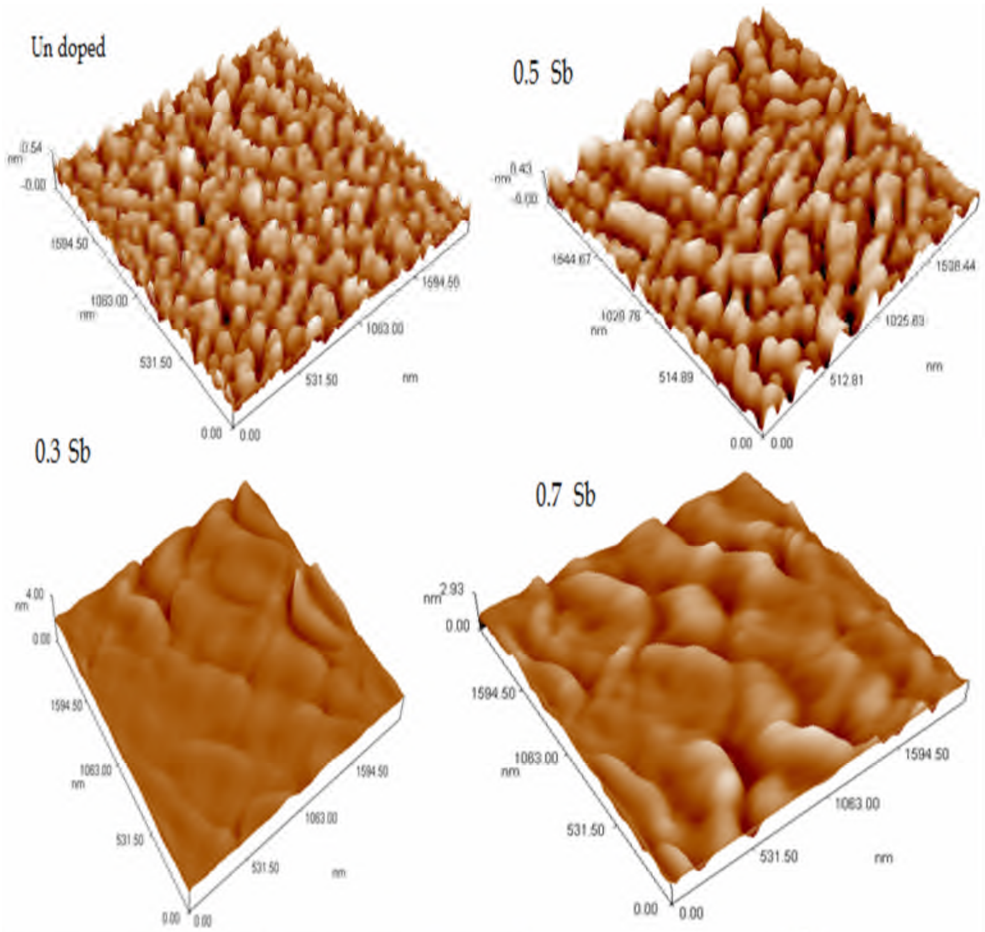


Figure (2) XRD spectra of the undoped SnO_2 and doped with antimony (Sb) films.



Sample(Sb: Sn)	G.S (nm)	RMS(nm)	Roughness Ave.(nm)
0:1	45	0.111	0.092
0.3:1	100	0.190	0.099
0.5:1	105	0.113	0.126
0.7:1	110	0.223	0.191
1:1	110	0.312	0.23

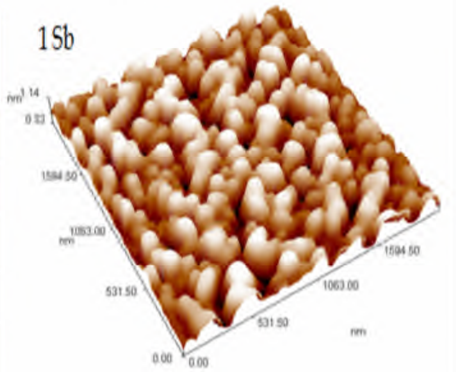


Figure (3) AFM image for (SnO_2) and (SnO_2: Sb) for different ratios and table for its measured parameters.

Depending on transmittance values for the wavelength (300-1100) nm , transmittance curve as a function to the wave length had been recorded for (SnO_2: Sb) films at substrate temperature (450) ^{0} C. The results show that (SnO_2: Sb) films has high transmittance in the visible region increase sharply and this called principle absorption edge , that mean this films have high energy gap, moreover it is clear that from figure (4),by increasing the doping percentage there is increase in transmittance except (1:1) ratio which reduce the transmittance because with this ratio material became opaque .

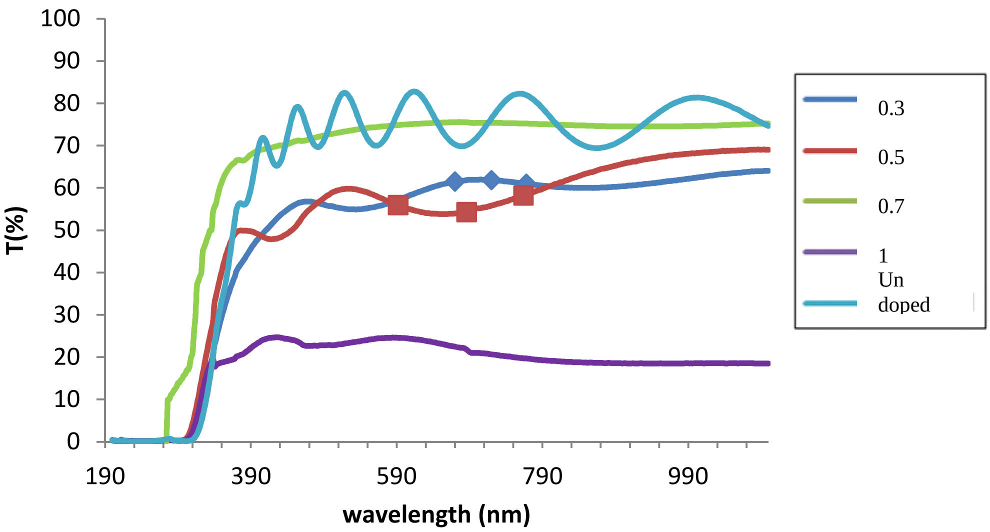


Figure (4) transmittance curve for undoped (SnO_2) and doped (SnO_2: Sb) films with different doping ratios

Doping with fluorine (F)

SnO2:F in ratios of (1: 0.1, 1: 0.3, 1:0.5, Wt.%) thin films have been prepared by the (APCVD) technique at substrate temperature (450 ^{0}C) with flow rate (1.5) L/M for (15) min using ($SnCl_2$.5H2O) and ammonium fluoride (NH_4F) as precursors. The aim of this work is to study effect of doping on the crystal growth orientation and some physical properties of (SnO_2: F) thin films, such as the electrical, structural and optical properties. The XRD patterns recorded for SnO_2: F (FTO) thin films as function of different fluorine ration are shown in Figure (5).The result of (XRD) for the films that prepared on glass substrate has showed that undoped (SnO_2) film preferential orientation along the (110), (101),(200) and (211) directions Since the peaks are sharp and it is evident that the films are polycrystalline in nature and are of cassiterite tetragonal structure. The most conspicuous feature from the XRD analysis is that the films in the present study are oriented along the (101) plane at (Sn:F= 1:0.3) ratio. SnO2: F films (Sn: F= 1:0.1, 1:0.5) ratios has amorphous structure. That means (in our opinion) that the preferential orientations of crystal growth are strongly affected by adding of fluorine.For different ratios to (F) atom the ruslts different from amorphous to crystalin in various manner[9].

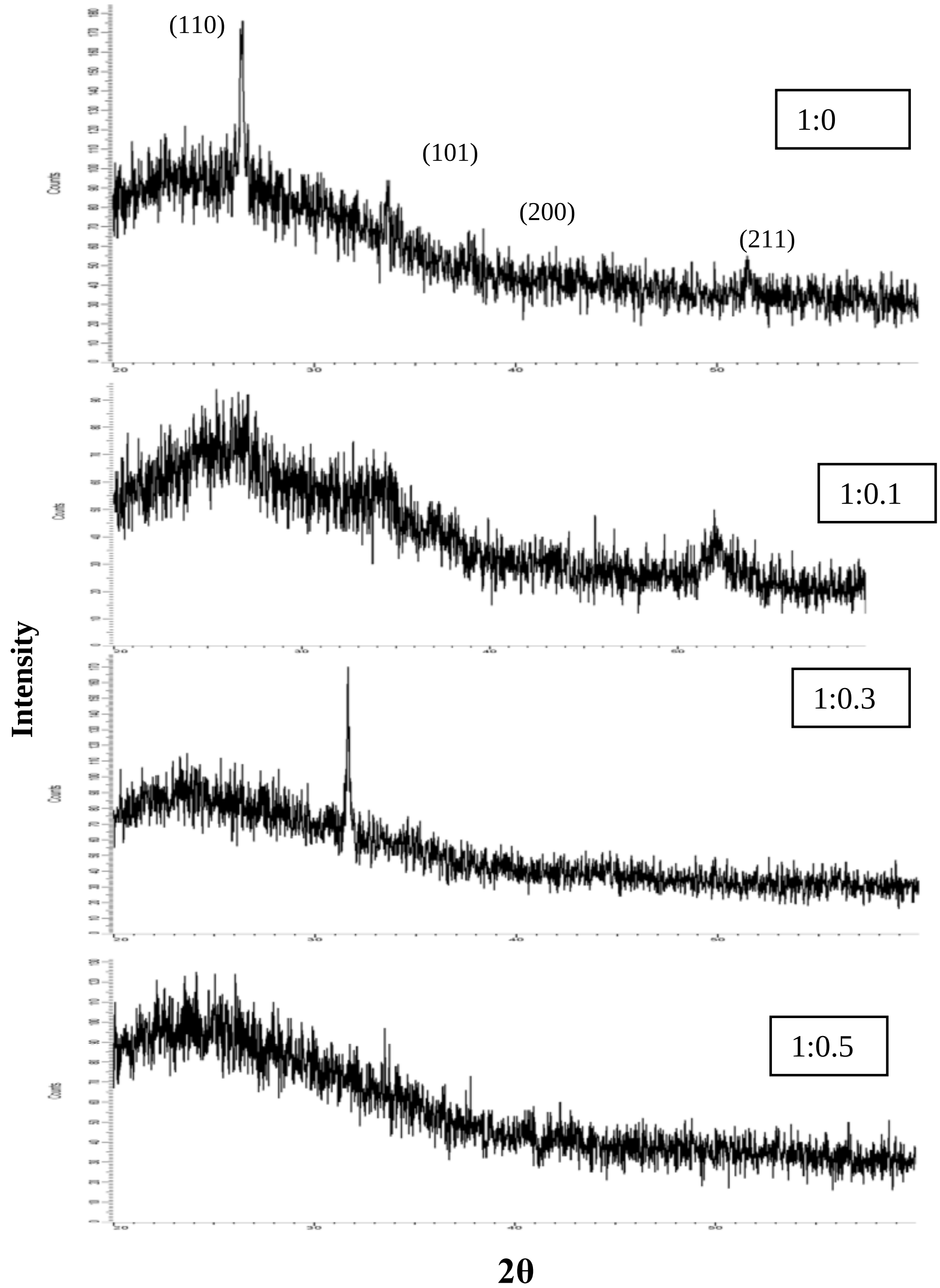


Figure (5) XRD spectra of the FTO films deposited on optical glass at different ratios (Sn: F= 1:0, 1:0.1, 1:0.3, 1:0.5)

The surface morphology of the films was studied also by AFM. From the AFM images, it was observed that the grain size becomes larger with increase of (Sn:F) ratio. AFM surface 2D images of FTO films prepared at various (Sn:F) ratios are shown in Figure (6). When the (Sn:F) ratio are increased, the distribution of grains is uniform on the substrate surface. The root mean square (RMS) values of surface roughness of the films increased with the increase of (Sn: F) ratios as shown in table (1).

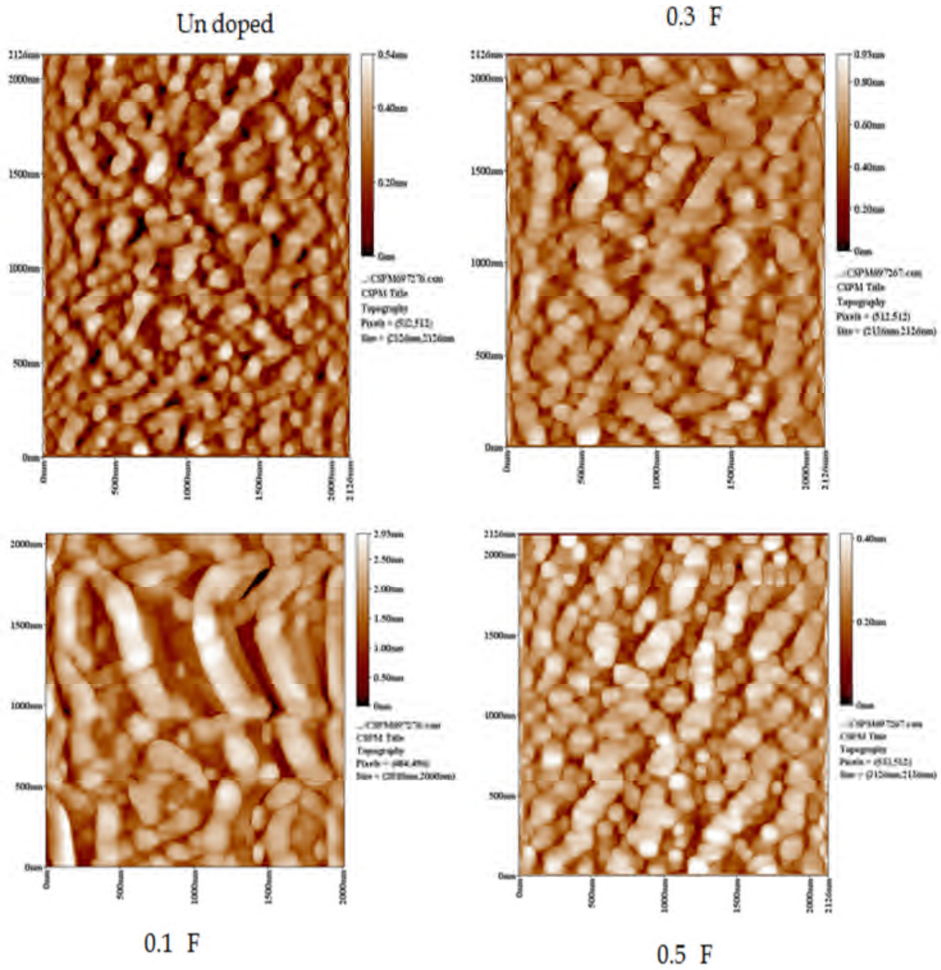


Figure (6) AFM 2D images of FTO films prepared at various (Sn:F) ratios

Table (1) the structural properties of FTO thin films at various (F: Sn) ratios; Crystallite size; RMS- Root mean square.

Sample(F:Sn)	G.S(nm)	RMS(nm)
0:1	45	0.111
0.1:1	100	0.13
0.3:1	105	0.192
0.5:1	110	0.224

Transmittance curves were made in the wavelength range of 290−1100 nm for all films and they are displayed in Figure (7) .It is noticed that, first, the transmittance of the undoped (SnO_2) films is larger than doped films. Second, the introduction of F − impurity to the SnO_2 films does effect significantly the transmittance of the samples. Third, tailing towards longer wavelengths is more evident on the transmittance curves of the (SnO_2: F) films and with increase of the (Sn: F) ratio transmittance increases in visible region and decreases in IR region. All of these observations confirm that high quality films.

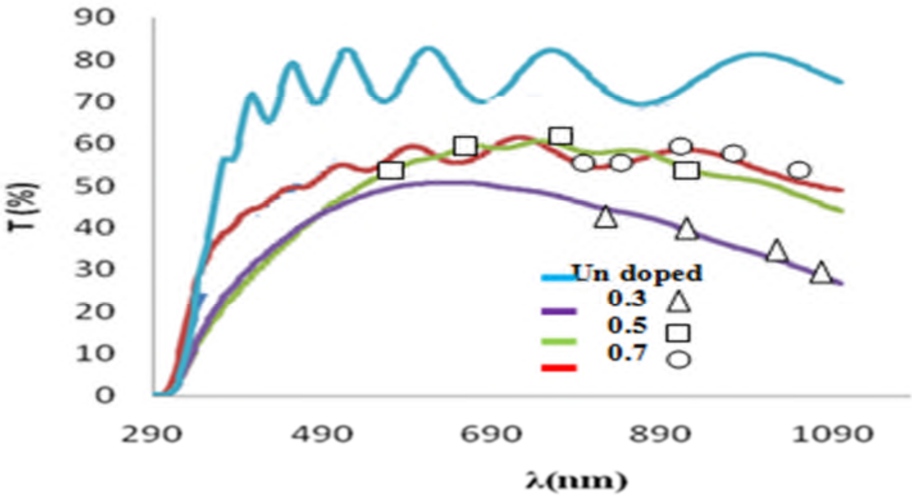


Figure (7) Transmittance curves of SnO_2: F thin films doped by using NH_4F deposited at substrate temperature of 450 ^{0}C

The electrical resistivity of the film, doped with (F,Sb), decreases with increasing of doping ratio as a results in increase of carrier constrations. The number of grain boundaries decreases and hence less grain boundary scattering will occur. This would explain the tendency of the resistivity to approach to a constant value (0.6) after this ratio , resistivty valus Increases . As it's clear from figure (8).

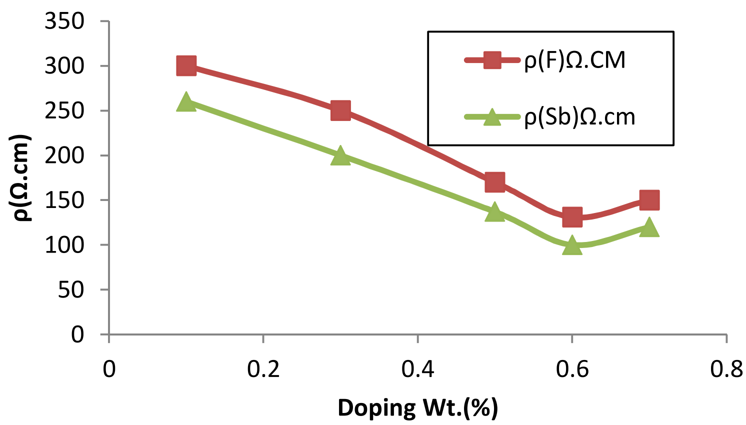


Figure (8) Resistivity curves of SnO_2: F,Sb thin films with different doping ratio

CONCLUSIONS

1- Doped and undoped SnO_2 was successfully prepared by using cold wall atmospheric pressure chemical vapor deposition (APCVD) system .

2- All doped and undoped films are transparent for visble region with all ratios.

3- Roughness average values have been increased with increase of doping Ratio for (Sb, F) in same manner.
4- Changing in structures for amorphous phase with all doping ratios for (Sb, F) .
5- Decrease in resistivity with increase in doping ratio till it reach to (0.6) ratio.

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