Structural properties of SnO_2 films dopped by Lithium

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Abstract:-

This paper the undoped Tin Oxide(SnO_2) and Lithium doped(SnO_2:Li) were prepared with doping percentage (5%) for the Molartiy (0.05, 0.1 , 0.15 , 0.2) ,were prepared by using chemical Spray pyrolysis technique (CSP) . Have been deposited on a glass substrate temperature at (400℃) , And the thickness of the prepared films were (350∓15) nm . By the X-Ray diffraction technique the nature of structure was exmined with aprefered orientation along (110) . It was found that . The prepared undoped (SnO_2) and indoped(SnO_2) have a (Tetragonal) polycrystalline structure . Also it was found that the average crystalline size increase as the increase in doping of the concentration(9.20 – 21.86) nm . AFM images the average grain size increase of the Molarity (73.60 -106.16)nm.

Key Words :- ($Sn O_2 : Li$) , Structural properties , Chemical Spray Pyrolysis .

المستخلص :

تم تحضير ثنائي أوكسيد القصدير(SnO_2) غير المشوبة والمشوبة بالليثيوم ($Sn O_2 : Li$) وبنسبة تشويب ٥% لكل من التركيز (0.05 , 0.1 , 0.15 , 0.2) باستخدام طريقة الرش الكيميائي الحراري على قواعد زجاجية وبدرجة حرارة (400℃) . وسمك الاغشية المحضرة (٣٥٠∓15)nm . وعن طريق دراسة نمط حيود الاشعة السينية تم تشخيص طبيعة تبلور الاغشية المحضرة , أذ تبين ان الاغشية المحضرة المشوبة وغير المشوبة تمتلك تركيب متعدد التبلور من النوع الرباعي, وكان الاتجاه السائد (١١٠) للاغشية غير المشوبة والمشوبة بالليثيوم في كل التراكيز المستخدمة وتبين كذلك ان معدل حجم البلورة يزداد مع زيادة التراكيز للاغشية غير المشوبة (16.58 – 96. ٢٩)nm , ويزداد ايضا معدل حجم البلوريات للاغشية المشوبة مع

زيادة التراكيز (٩.٢٠ – 21.86). صور AFM يزداد معدل الحجم الحبيبي مع تركيز التشويب(106.16 −73. 6 nm).

الكلمات المفتاحية :- أغشية ($SnO_2:Li$) , الخصائص التركيبية , التحلل الكيميائي الحراري

Introduction

The Oxides of the target are one of the transparent conductivity Oxides (stable and economic) . The filters are used to reflect in IR range . and be transparent in the visible rang [1]. Examples of this are(SnO_2-), Which is used in glass coating especially windows of cars and aircrafts It is also used for transparent coating of mirrors used in building due to its low thermal emission . Note that (SnO_2) has several application [2]. Because of its high efficiency and its electrical conduction . Therefore , it is used in electro – optical devices . And indirect – power switching devices (semiconductor - insulator – conductor) in solar collectors[2,3].

Experimental work :-

Many researches have discussed the mechanism of chimical Spray pyrolysis . In this study , the perpartion of tin oxide thin films(SnO_2) On glass basses using water tin chloride and its chemical from($SnCL_2$-$2H_2O$) from of molecular weight powder (42.39 g/mol) and concentration (0.05,0.1,0.15,0.2) . On these weights we use the following equation[4]

$$M = \frac{W_t}{M_{wt}} x \frac{1000}{V} \quad \text{----------(١)}$$

Where :-

M: the molars concentration .

W_t: The weight required to be damaged .

M_{wt} : Molecular weight of matter.

V: volume of distilled water.

The powder is dissolved in 100ml distilled water and aglass mixer is used under normal pressure . The solution was then applied to glass basses(substrate)(2.5×2.5) cm at a temperature (400℃) and thikness(350∓15) nm . to prepare tin oxide films doped lithium . aquantity of lithium was dissolved in (100ml) distilled water and solution was mixed with a solution of tin oxide and percentage of doping (5%) with Molarity (0.05,0.1,0.15,0.2) . The thickness of the prepared films was measured using a (Mettler- AE—160) Sensitive distilled water and the solution was mixed with a solution of tin dioxide and 5% with concentration

(0.05,0.1,0.15,0.2)M. The thickness of the prepared membranes was measured using a(Mettler – AE160) sensitive balanc (10^{-4} g) .It is the knowledge of the mass difference , the density of the material and the distance of the base. The condition of undoped tin oxide (SnO_2) and (SnO_2) doped lithium and a percentage of doping (5%) and a Molarity (0.05,0.1,0.15,0.2) as shown in the table (1)

Table (1) condition for the preparation of undoped Tin Oxide (SnO_2) and Lithium doped films

Pressure of the spray gas	**3bar**
Substrate temperture	**400℃**
Stop time	**60 sec**
Deposition	**8 sec**
Rate of the spray	**5 ml/ min**

Results and discussion :-

Through X- Ray diffraction (XRD) results and compared to the International Tin Oxide(SnO_2) card (JCPDS) (The Joint on Powder Diffraction Standards) with a serial number (00- 041- 1445) . It is the study of the pattern of Tin Oxide(SnO_2) diffraction angle and knowledge of the peaks that apper for all films prepared at temperature (400℃) which was deposited on the glass bases show that it has a (polycrystalline) structure of the (Tetragonal) type and this is consistent with researchers [4]. Figure (1) represents the X- ray diffraction diagram as a undoped Tin Oxide(SnO_2) and Lithium doped (SnO_2:Li) films a percentage of doping (5%) and Molarity (0.05,0.1,0.15, 0.2), shows the presence of diffraction peaks corresponding to the plans (110),(101),(200),(211),(310),(301) , the trend direction Tin Oxide undoped and Lithium doped films for all concentrations used are (110) and The results showed that the crystalline structure of the Tin Oxide films do not affect by the doping , all of the films were found to be tetragonal and polycrystalline structure . Figure (1) shows that the peak intensity of the trend direction remains constant with Lithium doping , with a decrease in Full Width of High Maximum (FWHM) for all concentration used,the reason is due to the fact that ionic radius of Lithium (Li^{+}) is (0.68Å) which is roughly equal to the ionic radius of tin (Sn^{+4}) is (0.71Å) .Table (2) shows peak loction , values of interfaces , (FWHM) values (2θ) values as undoped Tin Oxide Lithium doped films percentage doping (5%) and Molarity (0.05,0.1,0.15,0.2).

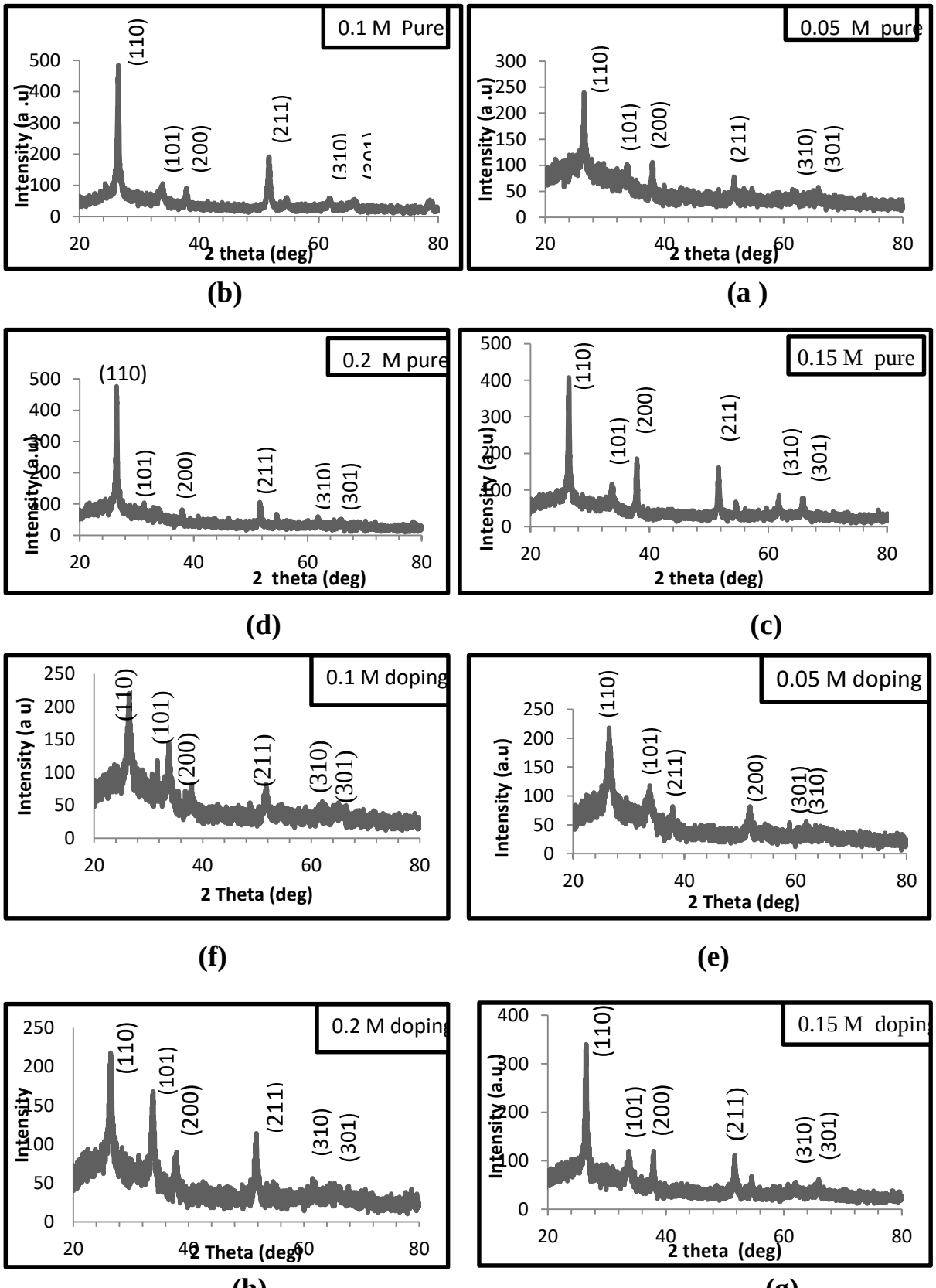


Figure (1) shows X-ray diffraction of the undoped (SnO_2) Films and doped of Lithium (SnO_2:Li) with Molarity (0.05,0.1,0.15,0.2)

Table (2)shows Loctions of peaks ,the interplaner spacing , (FWHM) and (2θ) values of the undoped (SnO_2) films and doped of Lithium (SnO_2:Li)

Sample	2θ(degree)	d_{hkl} (Å)	FWHM (deg)	h kl
((JCPDS) SnO_2)	26.6107 33.8925 37.9493 51.7796	3.3470 2.6427 2.3690 1.7641		(110) (101) (200) (211)
(SnO_2)(0.05M)	26.4984 37.9537 51.6508	3.3610 2.6506 2.3688	0.4920 ٠.٣٥٦٧ ٠.٣١٣٣	(110) (200) (211)
(SnO_2)(0.1M)	26.4940 26.2089 51.6891·	3.3615 3.3615 2.7679	0.3588 0.3588 0.2960	(110) (110) (211)
(SnO_2)(0.15M)	٢٦.4491 37.8719 51.6095	3.3671 2.3737 1.7695	0.3027 0.2830 0.2920	(110) (200) (211)
(SnO_2)(0.2M)	26.5201 26.1490 51.6775	2.8315 2.6227 2.4983	0.2774 0.2600 0.2600	(110) (110) (211)
SnO_2:Li (0.05M)	٢٦.٥٢٥٠ ٣٣.٧٨٩١ ٥١.٧٩٧٤	٣.٣٥٧٧٠ 2.٢٦٥٠٦ ١.٧٦٣٥٨	٠.٨٨٨٧ ٠.٨٦٠٠ ٠.٧٨٠٠	(١١٠) (١٠١) (٢١١)
SnO_2:Li (0.1M)	٢٦.٤٩٥٠ 33.٧٨٩١ ٥١.٦٩٧٥	٣.٣٦١٤٤ ٢.٦٥٠٦٢ ١.٧٦٦٧٦	٠.٨٦٦٧ ٠.٧٠٠٠ ٠.٧٠٠٠	(١١٠) (١٠١) (٢١١)
SnO_2:Li (0.15M)	٢٦.٥٠١٧ ٣٧.٨٩٦٠ ٥١.٦٦٨٣	٣.٣٦٠٦٠ ٢.٣٧٢٢٥ ١.٧٦٧٦٩	٠.٣٧٣٣ ٠.٣٣٨٠ ٠.٣٨٨٣	(١١٠) (٢٠٠) (٢١١)
SnO_2:Li (0.2M)	٢٦.٤٧٩٤ ٣٣.٨٠٤٠ ٥١.٧٠٥٠	٣.٣٦٣٣٨ ٢.٦٤٩٤٩ ١.٧٦٦٥٢	٠.٧١٨٠ ٠.٦٩٠٠ ٠.٦٧٥٠	(١١٠) (١٠١) (٢١١)

Of the following relationshipe is calculated the lattice constants ($a_\circ, c_\circ$) [5].

$$\frac{l^2}{c_\circ{}^2} + \frac{h^2+k^2}{a_\circ{}^2} = \frac{1}{d^2} \text{ ----------(2)}$$

d: the distance between plans atomic levels.

($a_\circ$, $c_\circ$) : lattice constants hkl : Miller coefficients

It is noted that values are consistent with lattice constants values in the standerd card for the (SnO_2) undoped films.

Table (3) shows the lattice constants values ($a_\circ$, $c_\circ$) ,the interplaner spacing and Miller coefficient values of the crystille plans with (SnO_2) undoped thin films and doped of Lithium

Sample	d (Å)	Lattice constant		hkl
		$a_\circ$(Å)	$c_\circ$ (Å)	(110)
(JCPDS) SnO_2)	3.3470	4.738	3.187	(110)
(SnO_2)(0.05M)	3.3610	4.753	3.120	(110)
(SnO_2)(0.1M)	3.3615	4.749	3.110	(110)
(SnO_2)(0.15M)	3.3671	4.761	3.138	(110)
(SnO_2)(0.2M)	3.3583	4.749	3.115	(110)
SnO_2:Li (0.05M)	3.3577	4.748	3.137	(110)
SnO_2:Li (0.1M)	3.3614	4.753	3.189	(110)
SnO_2:Li (0.15M)	3.3633	4.752	3.164	(110)
SnO_2:Li (0.2M)	3.3606	4.756	3.102	(110)

The average Grain size (D_{av}) was calculated for undoped films and doped in the trend direction (110) using (shere′ s Formula) as in the equation (3) [6].

$$G=\frac{0.9\lambda}{\beta cos\theta_B} \quad \text{----------(3)}$$

β : Full Width at Half Maximum measured in (rad) .

It has been observed that the average size of crystals increase with increasing Concenteration as shown in Fig (4) , this is consistent with the researcher (Bagheri) [7] . This is explained by the fact that the ion is impurity (Li^+) with Half crystallizeation and the size of crystals increases . This leads to the confirmation of the distance between crystalline levels (d_{hkl}) and decreases(2θ)

The texture coefficient (T_c) was calculated from relationship (4)

$$Tc = \frac{I(hkl)/I_\circ(hkl)}{\sum_N^{N-1} I(hkl)/I_\circ(hkl)} \quad \text{----------(4)}$$

Where :

N : The number of peaks in the x- ray diffraction(XRD) .

I(hkl) : Relative intensity measured for the level(hkl) .
$I_{\circ}$(hkl) : Standard intensity measured to level (hkl) takenfrom (JSPDS) .

Where the trend dirction represents the level of crystallization (hkl) with polycrystalline films . It was found that the values of the texture coefficient of level (110) is greater than one with undoped (SnO_2) films and Doped from lithium(SnO_2:Li) a percentage of doping (5%) with Molarity (0.05,0.1,0.15,0.2) as shown in the tables(4 a,b,c)

The table (4a) represents the average crystal (D_{av}) and (FWHM) and texture coefficient values ($T_{C\ (hkl)}$) For thr undoped tin oxide a percectage doping(5%) with concentractions (0.05,0.1,0.15,0.2)M

Sample	$\theta(degree)$	FWHM(rad)	D_{av} (nm)	$T_{C\ (hkl)}$	hkl
(SnO_2)(0.05M)	13.2492	0.00858	16.58	1.1	(١١٠)
(SnO_2)(0.1M)	13.2470	0.00626	22.74	1.7	(١١٠)
(SnO_2)(0.15M)	13.2245	0.00528	26.96	1.01	(١١٠)
(SnO_2)(0.2M)	13.2600	0.00484	29.42	2.3	(١١٠)

The table (4b) represents the average crystal (D_{av}) and(FWHM) and texture coefficient values ($T_{C\ (hkl)}$) For the doped tin oxide with Lithium a percectage doping(5%) with Molarity (0.05,0.1,0.15,0.2)

Sample	$\theta(degree)$	FWHM(rad)	D_{av} (nm)	$T_{C\ (hkl)}$	hkl
(SnO_2:Li)(0.05M)	13.2625	0.01547	9.20	1.4	(١١٠)
(SnO_2:Li)(0.1M)	13.2475	0.01512	9.41	1.23	(١١٠)
(SnO_2:Li)(0.15M)	13.2397	0.01253	11.36	1.3	(١١٠)
(SnO_2:Li)(0.2M)	13.2508	0.00651	21.86	1.1	(١١٠)

The table (4c) represents the average crystal (D_{av}) and (FWHM) and modulus factor values ($T_{C\,(hkl)}$) for For thr undoped tin oxide doped tin oxide with Lithium a percectage doping(5%) with Molarity(0.05,0.1,0.15,0.2)

Sample	$\theta(degree)$	FWHM(rad)	D_{av} (nm)	$T_{C\,(hkl)}$	hkl
(SnO_2)(0.05M)	13.2492	0.00858	16.58	1.1	(١١٠)
(SnO_2:Li)(0.05M)	13.2625	0.01547	9.20	1.4	(١١٠)
(SnO_2)(0.1M)	13.2470	0.00626	22.74	1.7	(١١٠)
(SnO_2:Li)(0.1M)	13.2475	0.01512	9.41	1.23	(١١٠)
(SnO_2)(0.15M)	13.2245	0.00528	26.96	1.01	(١١٠)
(SnO_2:Li)(0.15M)	13.2397	0.01253	11.36	1.3	(١١٠)
(SnO_2)(0.2M)	13.2600	0.00484	29.42	2.3	(١١٠)
SnO_2:Li)(0.2M)	13.2508	0.00651	21.86	1.1	(١١٠)

The crystal (microstrain)(s) was calculated of relationship(5)[5].

$$S = [|C_0 - C_{XRD}| / C_0] \times 100\% \text{.....(5)}$$

$C_\circ$: Lattice constant values in the card.

C_{XRD} :Calculated value of the lattice constant of (XRD) .

It was observed that the crystal (microstrain) changes were altered by changing the Molarity of the films. Due to the Deformities of the lattice with the increase of the micro – stresses resulting from the process of doping as shown in the table(5- a,b,c). The Dislocation density(δ) was also calculated of the relationship (6)[6].

$$\delta = \frac{1}{D_{av}^2} \quad \text{----------(6)}$$

It was observed that the value of the dislocation of the Lithium – doped Films increase with increased doping concentration , compared with their Value in undoped films , because the dislocation density is inversely proportional to the sqare size of the crystals. Dislocation density is a structural defect and can be eliminated by heat, table(5-a,b,c) shows the Dislocation density of all perpared films . the number of crystals ($N_\circ$) for the Area unit of the relationship(7)[7] also calculated :-

$$N_\circ = \frac{t}{D_{av}^3} \quad \textbf{----------(7)}$$ t: thin films thickeness

It was noted that the number of crystals decreasing concentration rates, because they are inversely proportional to the cube size of the crystals
As shown in the table(5a,b,c) .

The table (4a) represent (microstrain , dislocation density and numberof crystallites/area)For the undoped tin oxide a percectage doping(5%) with Molarity (0.05,0.1,0.15,0.2)

Sample	Microstrain (S)	Dislocation Density $(\delta) \times 10^{11}$ /m^2	Number of crystallites/Area $(N_\circ) \times 10^{12}$ / m^2
(SnO_2)(0.05M)	13.08	3.63	85.08
(SnO_2)(0.1M)	5.54	1.39	5.54
(SnO_2)(0.15M)	4.67	1.37	4.67
(SnO_2)(0.2M)	2.25	1.15	2.25

The table (4b) represent (microstrain , dislocation density and numberof crystallites/area) For the doped tin oxide with Lithium apercectage doping(5%) with Molarity (0.05,0.1,0.15,0.2)

Sample	Microstrain (S)	Dislocation Density $(\delta) \times 10^{11}$ /m^2	Number of crystallites/Area $(N_\circ) \times 10^{12}$ / m^2
(SnO_2:Li) (0.05M)	1.56	1.12	1.56
(SnO_2:Li) (0.1M)	0.07	1.18	0.07
(SnO_2:Li) (0.15M)	0.72	2.09	0.72
(SnO_2:Li) (0.2M)	2.60	7.74	2.60

The table (4c) represents(microstrain , dislocation density and numberof crystallites/area) For thr undoped tin oxide doped tin oxide with Lithium a percectage doping(5%) with Molarity (0.05,0.1,0.15,0.2)

Sample	Microstrain (S)	Dislocation Density $(\delta) \times 10^{11}$ /m^2	Number of crystallites/Area $N_\circ) \times 10^{12}$ / m^2
(SnO_2)(0.05M)	13.08	3.63	85.08
(SnO_2:Li)(0.05M)	1.56	1.12	1.56
(SnO_2)(0.1M)	5.54	1.39	5.54
(SnO_2:Li)(0.1M)	0.07	1.18	0.07
(SnO_2) (0.15M)	4.67	1.37	4.67
(SnO_2:Li) (0.15M)	0.72	2.09	0.72
(SnO_2) (0.2M)	2.25	1.15	2.25
(SnO_2:Li) (0.2M)	2.60	7.74	2.60

To study the topography of the surface of the perpared doped and undoped films the extent of their doping . The Atomic Force Microscope has been used to measure analyze these images and give accurate Statistical value on the rate and distribution of gransize. As well

The roughness of the surface , depending on the sqare root of the average roughness (RMS)(Root Mean Square), images and AFM results have been shown through analysis of measurements . Lithium doping clearly affects the topography surface , as shown by the $(10\times 10)\ \mu m^2$ dimension survey of the composition of the undoped and doped surfaces and all the doping concentrations . Gransize have more homogeneous surfaces with reduced roughness values . Depending on the square root of the average roughness (RMS) as shown in the table . fig (2) shows images of the tin oxide films undoped doped for Lithium percentage (5%) Molarity (0.05,0.1 ,0.15, 0.2) .

Table (6a) shows (Roughness , Root Mean Square and average diameter) For thr undoped tin oxide doped tin oxide with Lithium a percectage doping(5%) with Molarity (0.05,0.1,0.15,0.2) as measured(AFM)

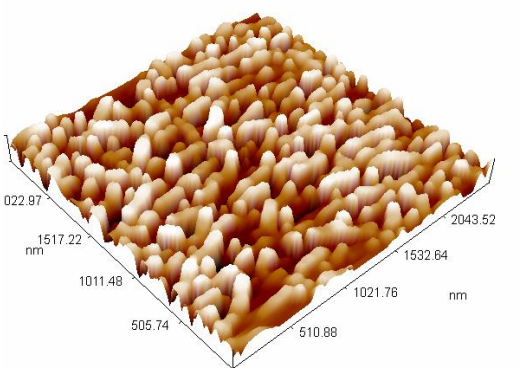
Samples	Roughines average(nm)	R . M . S (nm)	Average diameter(nm)
0.05M SnO_2	1.48	1.37	78.06
0.1M SnO_2:Li	0.2	0.244	73.60
0.15M SnO_2	22.9	26.9	87.29
0.2M SnO_2:Li	2.76	3.27	81.91
0.05M SnO_2	3.59	4.21	95.63
0.1M SnO_2:Li	17.1	20	100.72
0.15M SnO_2	1.92	2.23	114.11
0.2M SnO_2:Li	10.3	12.2	106.16

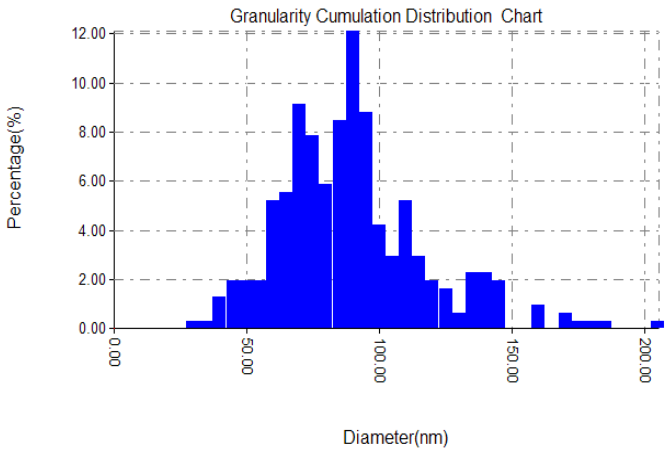
Table (6b) shows (Roughness , Root Mean Square and average diameter) For the undoped tin oxide a percectage (5%) with Molarity (0.05,0.1,0.15,0.2) as measured(AFM)

Samples	Roughines average(nm)	R . M . S (nm)	Average diameter(nm)
0.05M SnO_2	1.48	1.37	78.06
0.1M SnO_2	22.9	26.9	87.29
0.15M SnO_2	3.59	4.21	95.63
0.2 M SnO_2	1.92	2.23	114.11

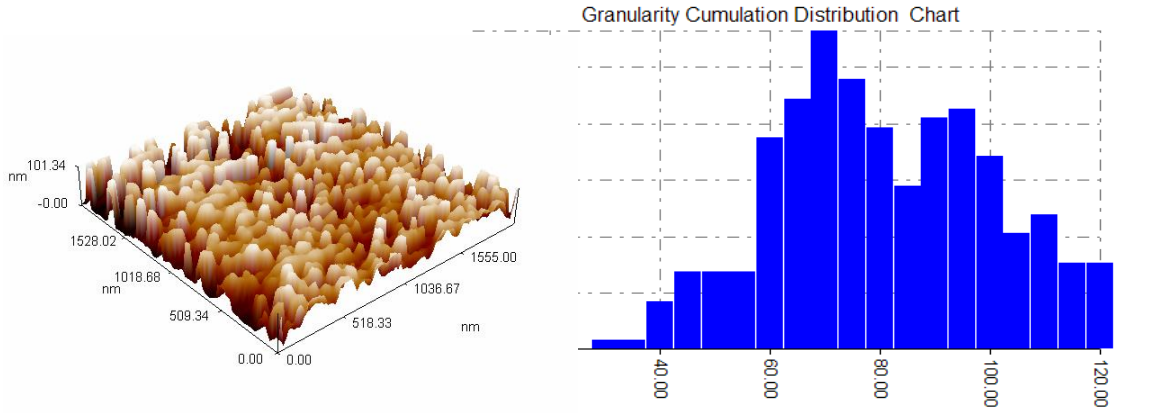
Table (6C) shows (Roughness , Root Mean Square and average diameter) For doped tin oxide with Lithium a percectage doping(5%) with Molarity (0.05,0.1,0.15,0.2) as measured (AFM)

Sample	Roughines average(nm)	R . M . S (nm)	Average diameter(nm)
0.05M $SnO_2:Li$	0.2	0.244	73.60
0.1M $SnO_2:Li$	2.76	3.27	81.91
0.15M SnO_2:Li	17.1	20	100.72
0.2M $SnO_2:Li$	10.3	12.2	106.16

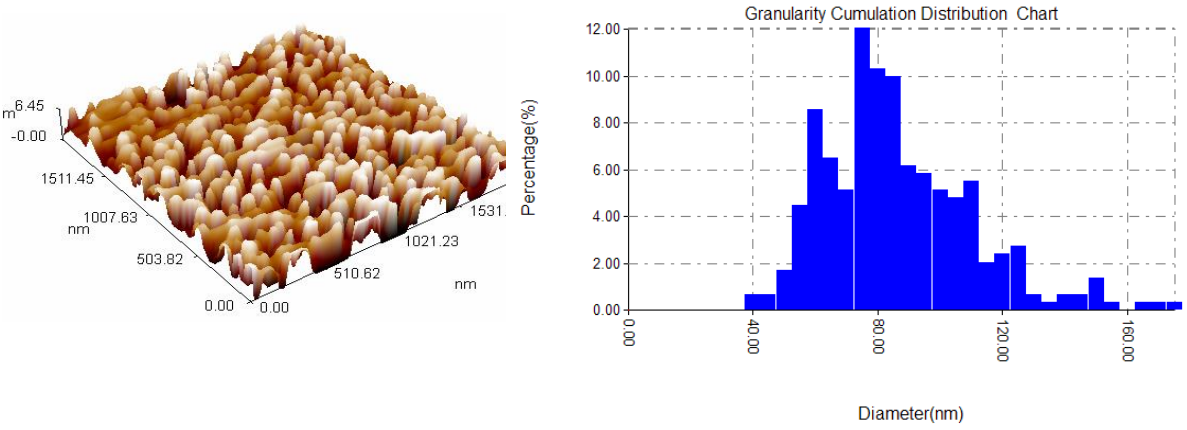




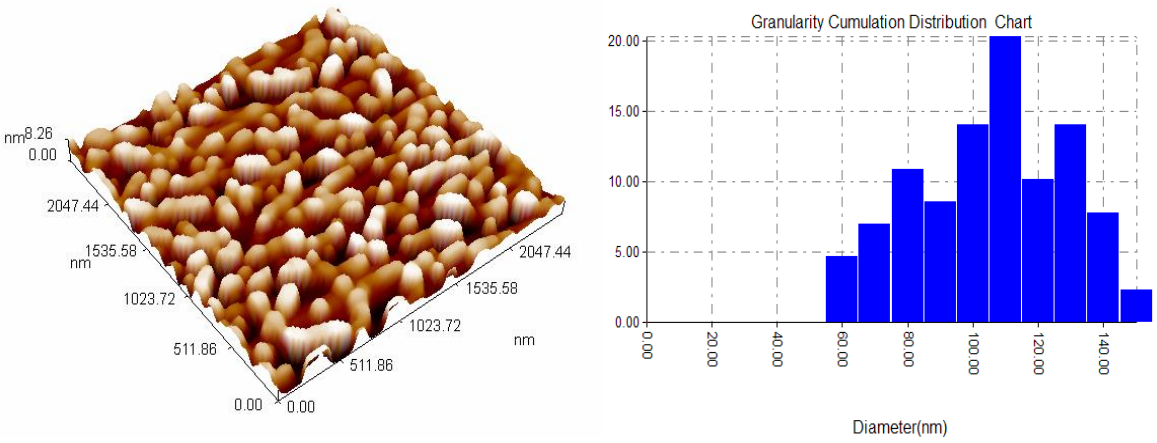
(SnO_2)(0.05M)



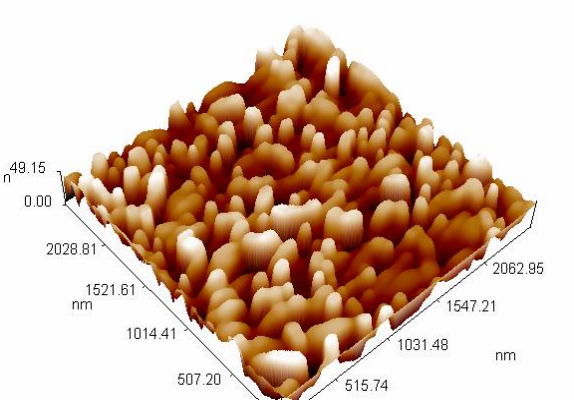
(SnO_2)(0.1M)

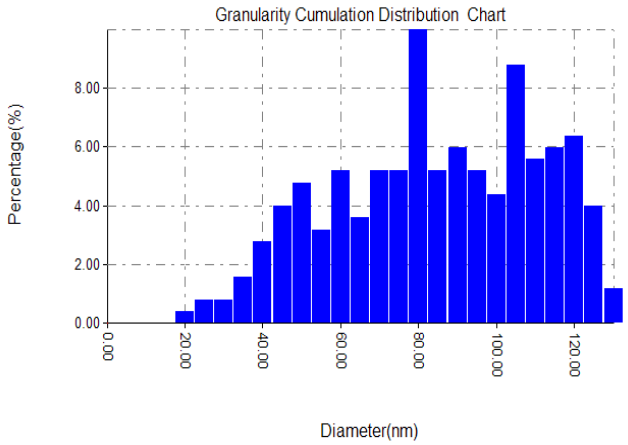


(SnO_2)(0.15M)

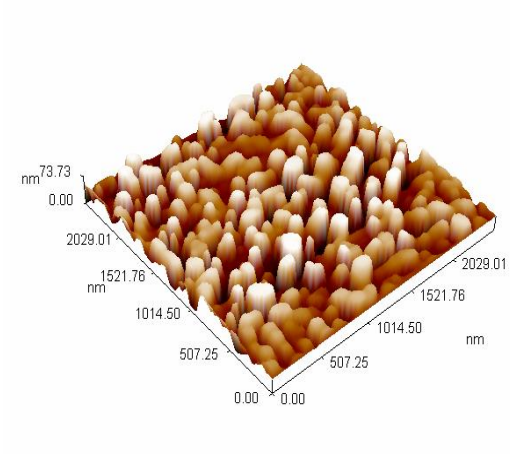


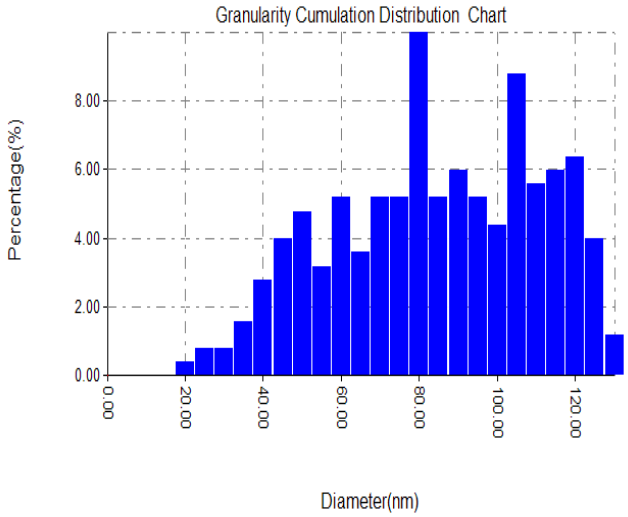
(SnO_2)(0.2M)



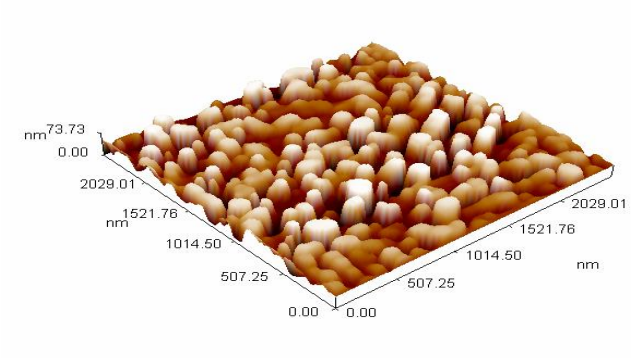


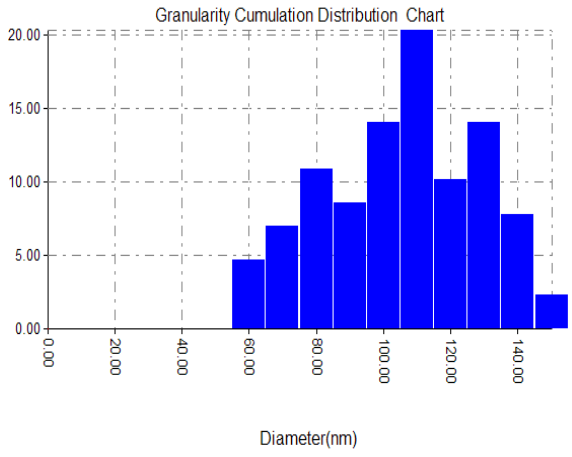
(SnO_2:Li) (0.05M)



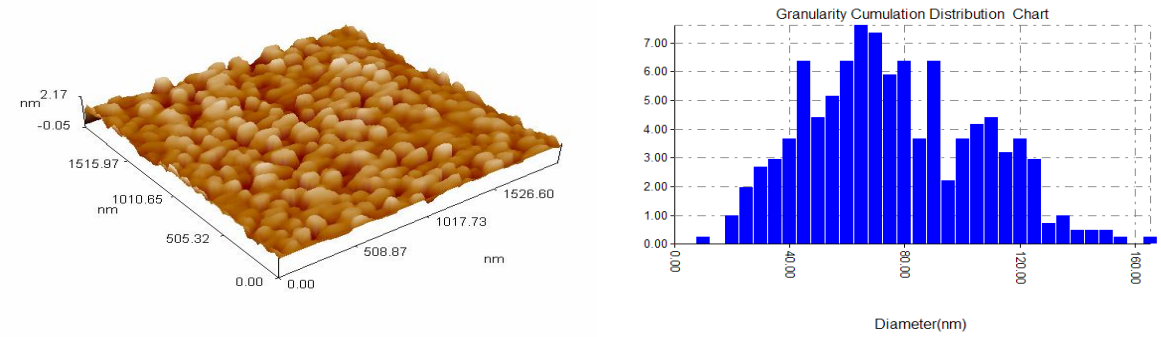


(SnO_2:Li)(0.1M)





(SnO_2:Li) (0.15M)



(SnO_2:Li) (0.2M)

Figure (2) photo of surface structure of undoped and doped tin oxide Films with 5% and Molarity (0.05,0.1,0.15,0.2) as measured (AFM)

Figure (3) shows the optical microscope images of the surface of the undoped and Lithium doped tin oxide with percentage of doping 5% And Molarity (0.05,0.1,0.15,0.2) .

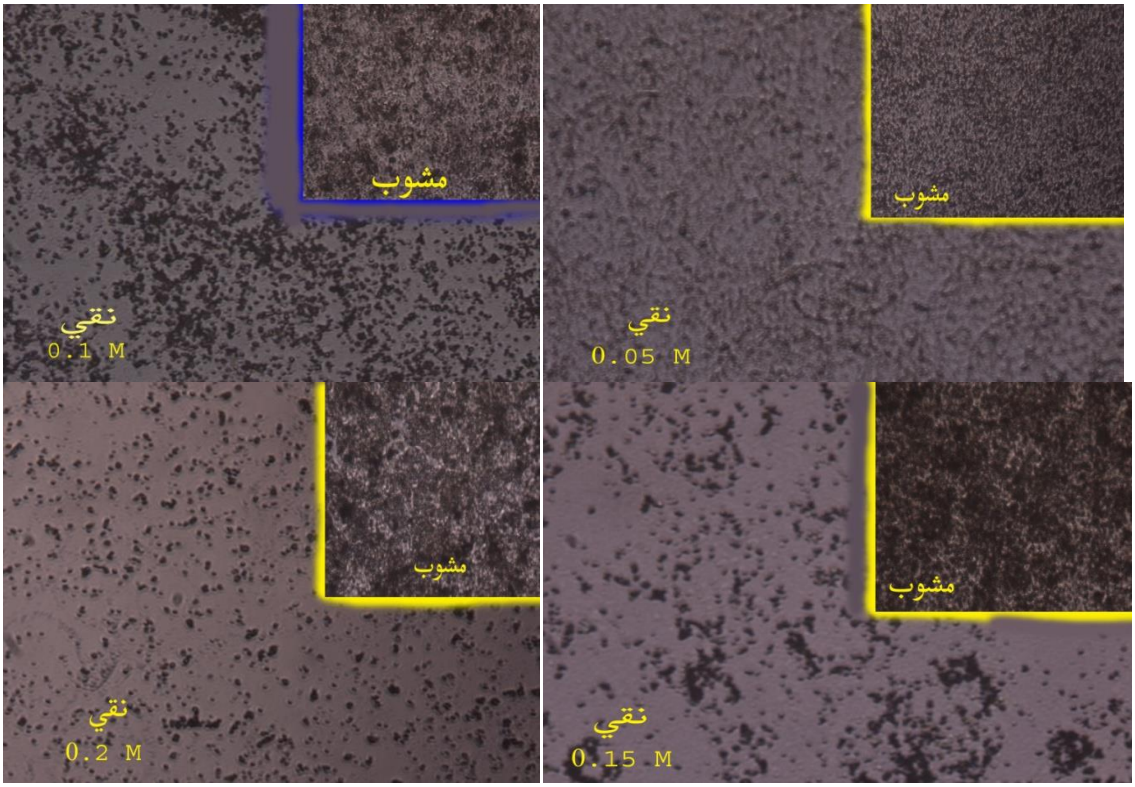


Figure (3)shows images of the optical microscope of the undoped tin oxide Films with percentage of doping (5%) and Molarity (0.05,0.1,0.15,0.2).

Conclusions:-

1- The results of X- ray diffraction showed all preperd films are and (tetragonal) type for undoped tin oxide (SnO_2) and doped for Lithium (SnO_2:Li) percentage of doping (5%) at temperature (400℃) .

2- Tend direction of undoped and doped tin oxide films with percentage of doping (5%) and concenterations (0.05,0.1,0.15,0.2)M is (110) .

3- The Atomic Force Microscope (AFM) results show the amount of roughness of the surface decreases when each concentration is doping .

4- The appearance of nano- structures of the doping of lithium .

Refernces

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