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Effect of Al doping on the Structural properties of SnO2 thin films prepared by (sol-gel) method

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Abstract
Undoped and Al-doped SnO_2 thin films have been prepared by sol–gel spin coating process on glass substrate for different doping (0, 2.5 ,5 ,7.5,10)% The starting precursor was used as tin chloride dihydrate ($SnCl_2.2H_2O$), ethanol , with and without stabilizer. As annealing in a temperature 500°C for one hours, the results of (X-Ray) diffraction showed that the films have a Polycrystalline structure and increased intensity when use stabilizer and orientation was (020) with lattice constants (a=4.796, b=5.796, c= 5.193) Å.

The surface morphology of the (SnO_2: Al) thin films have been studied using atomic force microscopy (AFM) which indicated that the grown films showed good crystalline and homogeneous surface. The Root Mean Square (RMS) values and surface roughness of the films increased with increasing doped concentration specify when use stabilizer.

I. Introduction
Metal oxide semiconductors with wide band gaps have many important applications in the optics, electric and electronic industries. Transparent SnO_2 thin films have been widely used in the production of transparent electrodes, far-infrared detectors, solar cells and gas sensors [1]. SnO_2 films are inexpensive, chemically stable in acidic and basic solutions, thermally stable in oxidizing environments at high temperatures and also mechanically strong [2].Metal composite oxides $M_xSn_yO_z$ (M=Ni, Ca, Fe, Sb, Cu, Mg, Zn, etc) were also proposed to improve cycling stabililty of SnO_2 [3-6] , A variety of methods, such as magnetron sputtering [7], vacuum evaporation [8], sol-gel[9], chemical vapor deposition[10], and sonochemistry [11] have been employed to prepare SnO_2 thin films.

Sol–gel coating techniques have proved to be a popular means of fabricating nanocomposite thin films in the nanometer thickness range. Sol–gel technique is a useful method to prepare SnO_2 thin films. Comparatively, it gives a lot of advantages over other techniques by its low reaction temperature, easy process, and low cost. However, cracks on the thin films prepared by sol–gel technique exhibited adverse effects on response, so cracks on thin films prepared by this method are undesired [12] .The basis of the technique is to coat a substrate with a precursor solution containing the requisite metal components in the required proportion, which then, because of solvent evaporation and/or chemical reaction, transforms to a gel layer. The organic components of the gel are then eliminated by various heat treatments to form the desired crystalline thin film [13].

Ii. Experimental details
$SnCl_2.2H_2O$ (M=225.63g/mol) was used as precursor material, 2.25 gm of $SnCl_2.2H_2O$ was dissolved in 40 ml of absolute ethanol (C_2H_5OH). another sol prepared with a complexing agent, acetic acid ($C_2H_4O_2$) was added to stabilize the hydrolysis of $SnCl_2$ with molar ratio 1:1, The mixture was stirred at 60°C for 1 hr and then it was allowed to cool to the room temperature, After the sol was aged for 24 hr at room temperature before coating it filter, For doped samples, the sol was doped with aluminum additive by adding ($AlCl_3.6H_2O$) to the SnO_2 sol with molar ratio (2.5,5,7.5,10) %

A commercial spin coater (Vacuum Spin Coater VTC-100) was used for coating the sol on the glass substrates. The speed of the spin coater was fixed at 3000 rpm for 30 sec , the substrates were dried in oven for 80 ˚C for 20 min and annealing at 500ºC for 1h. SnO_2 formulation can be represented as [14]:

$$SnCl_2.\,2H_2O \rightarrow SnO_2 + 2H_2\uparrow + Cl_2\uparrow$$

X-ray diffraction (XRD) pattern of SnO_2 doped with Al and undoped films was recorded by system (Model: Panalytical Empyrean) using Cu Kα (λ=0.154059nm) radiation with 2θ in the range (20-70)^o ,the film surfaces were analyzed by atomic force microscopy (AFM), AFM measurements were performed with a(type AA3000, supplied by Angstrom Advanced Inc .USA).

III. Results and discussion
A- X-ray diffraction analysis:
The XRD pattern of the film shows that as the synthesized film is polycrystalline in structure nature, with the Orthorhombic phase and shows preferential orientation along c-axic (figure 1). The result is in agreement with the reported(JCPD 29-1484) data of pure SnO_2[15]. The strongest peak observed at 2θ = 31. 6975^o can be attributed to the (020) plane which are depicted in (figure 2,3), and the lattice constants recorded at (a=4.796 , b=5.796, c= 5.193) A. XRD patterns reveal that films are good crystalline specify when use stabilizer and increase intensity with increase Al –doped SnO_2. No other peaks have emerged. The high intensity of the peak suggests that these thin films mainly consist of the crystalline phase.

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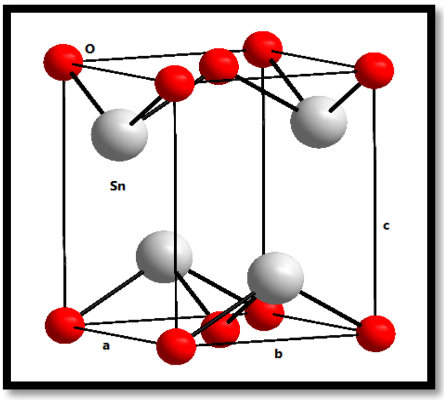

figure 1: Crystal structure of SnO_2

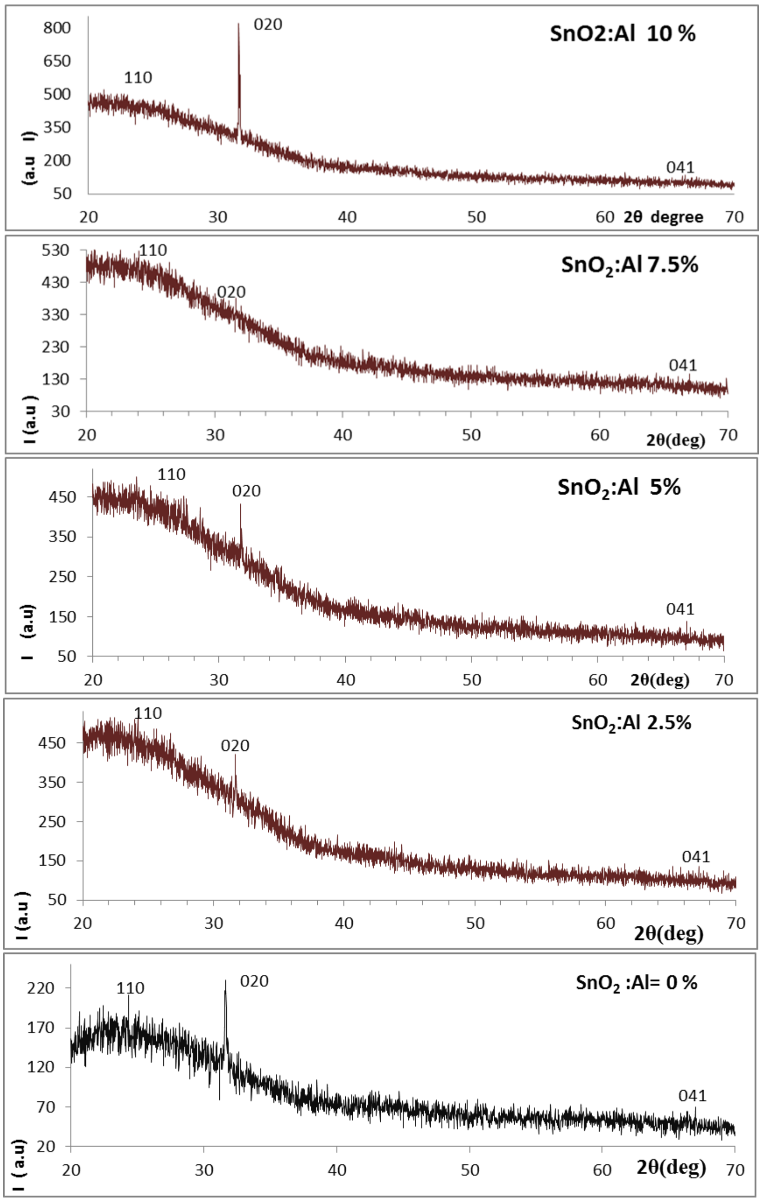

figure 2 X-ray diffraction patterns of (SnO_2:Al) thin films for different aluminum doping without stabilizer

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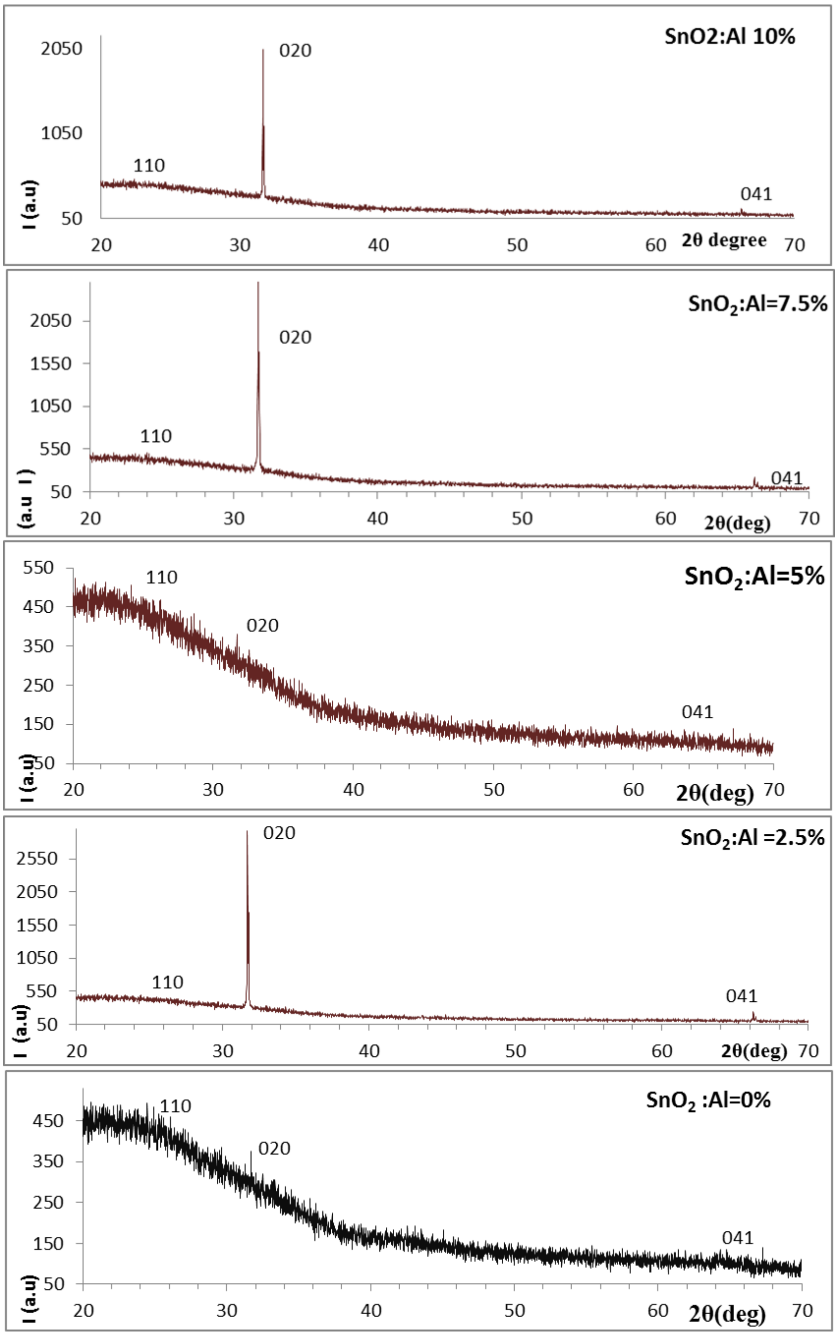

figure 3 X-ray diffraction patterns of (SnO_2:Al) thin films for different aluminum doping with stabilizer

The average grain size (D) was calculated using Scherer's formula [16]:

$D= K \lambda / \beta \cos(\theta)$

Where: **λ**: wavelength of XRD, **β**: FWHM ,θ : Bragg's angle in degree

K: The correction coefficient variation according to the diffractometer and its magnitude about (0.9 – 1), XRD parameters of (SnO_2:Al) thin films with and without stabilizer showed in table 1. The Variation of grain size with Al concentration calculated from X-ray shown in Figure (4) , when use stabilizer the grain size increased gradually, but grain size decreased to doping (2.5 ,5 ,7.5) % then increased in (10)%

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Table 1. XRD parameters of (SnO_2:Al) thin films

Sample SnO_2:Al		2θ (degree)	d_{020} (Å)	D_{av} (nm)	Dislocation Density (δ) /nm^2
Without Stabilizer	0 %	31.6975	2.820	132.3	x10^{-5}5.713
	2.5 %	31.6891	2.821	44.12	x10^{-4}5.137
	5 %	31.7357	2.8172	44.117	x10^{-4}5.138
	7.5 %	31.6741	2.8225	44.157	x10^{-4}5.129
	10 %	31.6547	2.823	176.37	x10^{-5}3.215
With Stabilizer	0 %	31.6873	2.8214	45.877	x10^{-4}4.75
	2.5 %	31.7046	2.8214	45.877	x10^{-5}3.211
	5 %	31.699	2.8203	155.61	x10^{-5}4.13
	7.5 %	31.6971	2.8206	132.338	x10^{-5}5.71
	10 %	31.7154	2.8179	176.39	x10^{-5}3.213

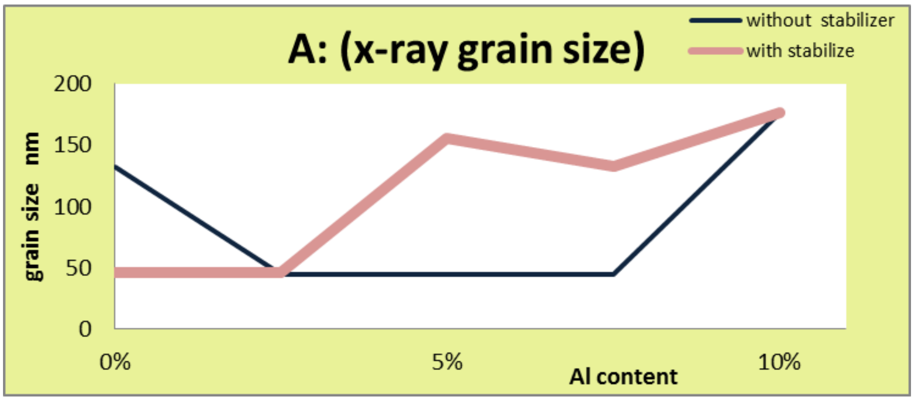


figure 4: Variation of grain size with Al concentration in X-ray

B- Surface Morphology:

The surface morphologies of the SnO_2:Al thin films, was also investigated by using atomic force microscopy (AFM). AFM study reveals that the roughness of the films is dependent on the doping concentration (5,10) % it dependent on the high and low intensity to x-ray results fig (2,3) , the surface roughness increased with increasing $AlCl_3$ concentration, it double increased specify when use stabilizer and Root mean square (RMS) roughness of the films was obtained from the AFM data (inset in Figure 5), but the grain size decreased when use stabilizer specify 10 %. The 3D images recorded at 2000 nm × 2000 nm planar in contact mode are depicted in (Figure 6,7) .

Table (2) The Obtained Result of the AFM for undoped and doped films

Sample SnO_2:Al		**Roughness Avg. (nm)**	**RMS (nm)**	**Ten point height (nm)**	**Avg. Diameter (nm)**
Without stabilizer	0%	0.193	0.223	2.24	88.84
	5%	0.311	0.357	2.48	96.27
	10%	0.609	0.766	4.34	190.13
With stabilizer	0%	0.198	0.23	1.39	96.19
	5%	0.589	0.678	2.72	138.24
	10%	1.22	1.43	7.64	103.06

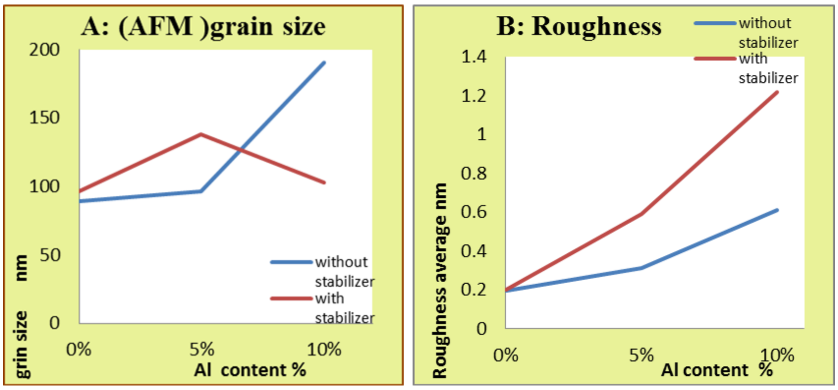
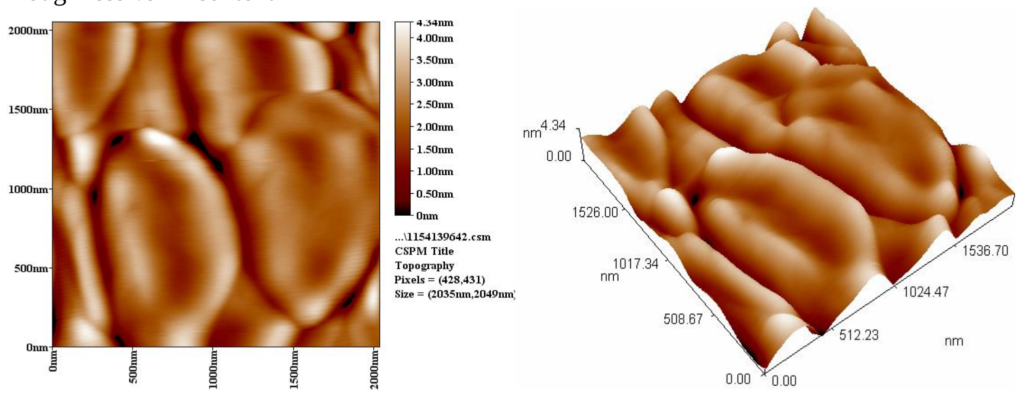
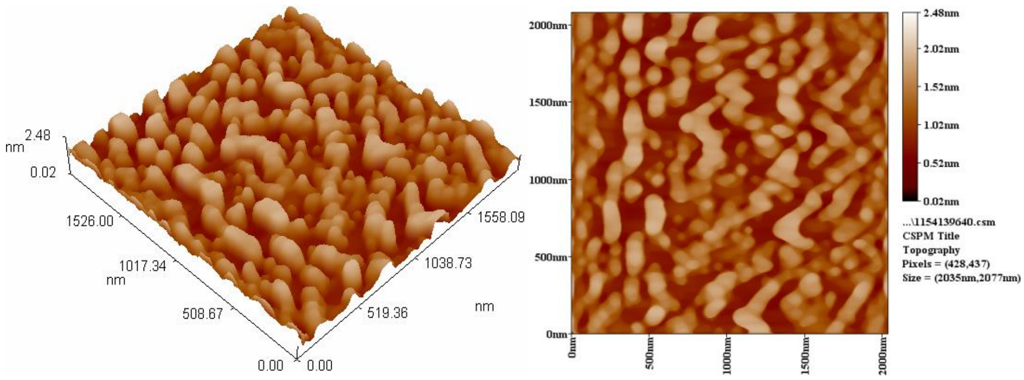


figure 5 A :Variation of grain size with Al content in AFM

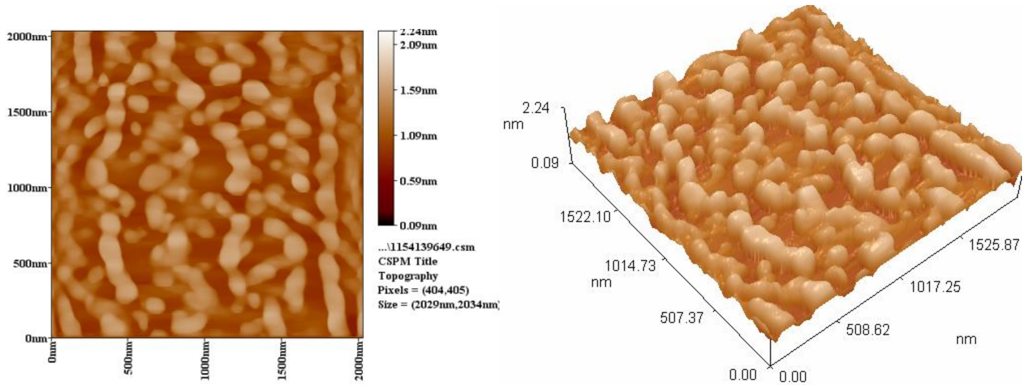
B:plot of Roughness vs Al content



c



b



a

figure 6 The AFM images of SnO_2:Al thin film for different aluminum -doping a-Al=0%, b-Al=5%, c-Al=10% without stabilizer

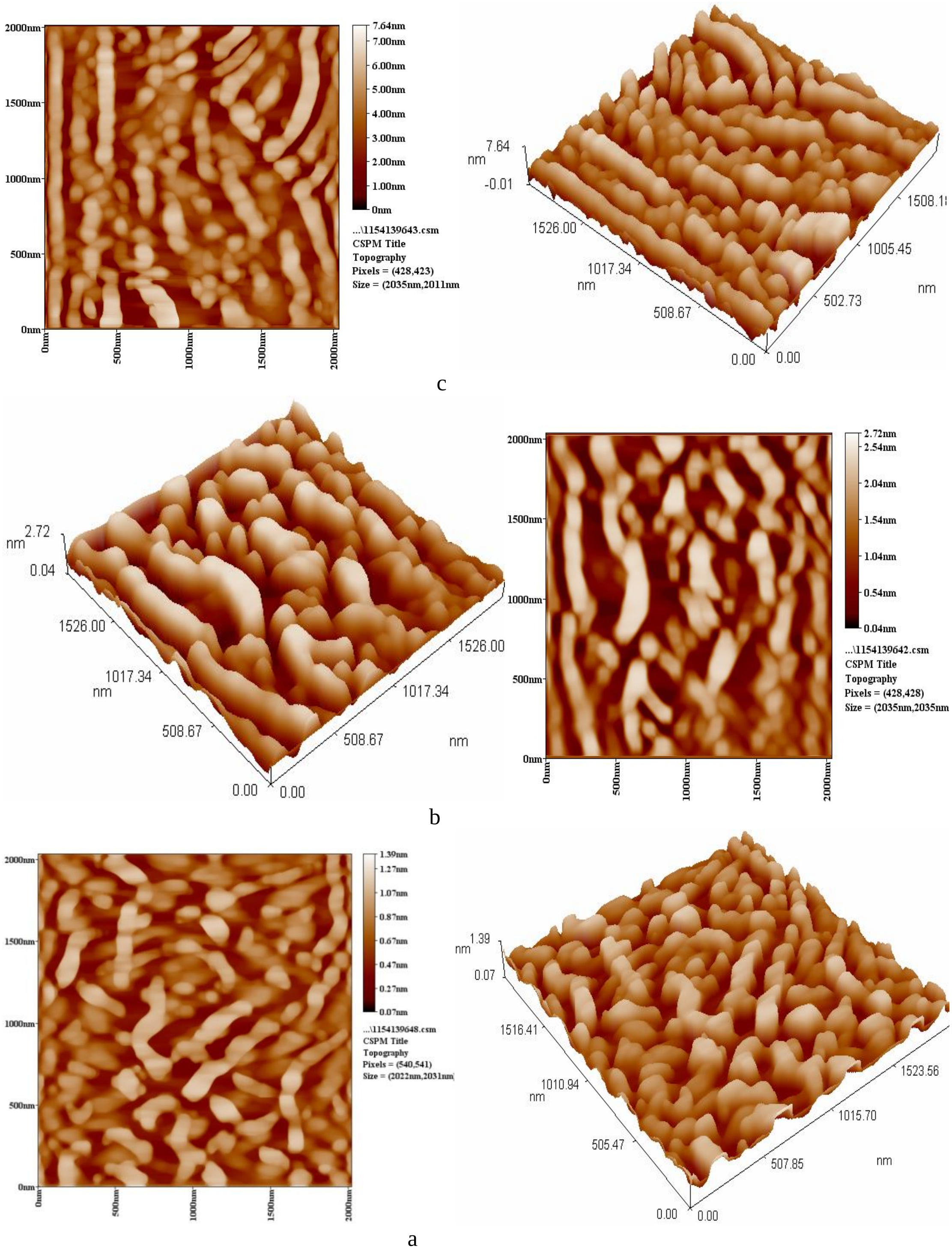


Figure 7 The AFM images of SnO_2:Al thin film for different aluminum -doping (a-Al=0%, b-Al=5% , c-Al=10%) with stabilizer

IV. Conclusions

Undoped and Al-doped Tin oxide films were prepared on glass substrates by Sol-gel Spin-coating technique , and annealing temperatures 500°C The structural analysis confirmed the prepared films are polycrystalline with Orthorhombic phase and showing a preferential orientation in the (020) direction, with lattice constants (a=4.796 , b=5.796 , c= 5.193) Å , agreement with (JCPD29-1484) data , and intensity increase with increase doping specify when use stabilizer, but grain size decreased when use stabilizer specify 10 %, the surface roughness and Root mean square (RMS) are increased with increasing doped concentration and double increased with stabilizer .

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تأثير التشويب بالالمنيوم على الخواص التركيبية لغشاء ثنائي اوكسيد القصدير (SnO_2) المحضر بطريقة (Sol-gel)

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الملخص

تم تحضير أغشية ثاني أوكسيد القصدير (SnO_2) النقية والمشوبة بالألمنيوم من ($SnCl_2.2H_2O$) وبالنسب %(0,2.5,5,7.5,10) المحضرة بطريقة (Sol–Gel) الطلاء الدوار (spin coating) وباستعمال المثبت وبدونه على قواعد زجاجية بدرجة تلدين 500 °C ولمدة ساعة واحدة اظهرت نتائج حيود الأشعة السينية أن جميع الأغشية ذات تركيب متعدد التبلور وتزداد الشدة في حالة استعمال المثبت مع ظهور الاتجاه التفضيلي (020) بثوابت شبيكة A(a=4.796 , b=5.796 , c= 5.193)

اما نتائج مجهر القوة الذرية الخاص بدراسة طوبوغرافية سطح الاغشية فبينت تبلور الاغشية وتجانسها اذ يزداد معدل خشونة السطح ومربع الجذر التربيعي للأغشية بزيادة نسب التشويب وخاصة للحالات التي يستعمل فيه المثبت.