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Structural and morphological investigation of bulk heterojunction blend ($NiPc/C_{60}$) Thin films under heat treatment

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Abstract

Thin films of the blended solution of $NiPc/C_{60}$ are fabricated using spin-coating method for three different ratios (100/1, 100/10 and 100/100) according to the weight. The films are deposited on to glass substrates and treated with several annealing temperatures (373, 423 and 473)K. The structure and surface morphology of the as-deposited and annealed films using x-ray diffraction and AFM was studied and exhibited a change and enhanced crystallization and surface morphology caused by changes in heat treatment temperatures. Investigation of X-ray diffraction patterns of $NiPc/C_{60}$ indicated that it have polymorphism structure, i.e. mix between amorphous and polycrystalline structure. when heat treatment temperatures changed, led to the α-crystalline films oriented preferentially to the (100) plane. The grain size of the blend ($NiPc/C_{60}$) thin film is calculated using the Scherrer relation and the variation was nonsystematic with increased annealing temperature. AFM measurements supported the result of XRD.

Key words: Organic Semiconductors, $NiPc/C_{60}$, XRD, Morphology, Structural properties and heat treatment.

الاستقصاء التركيبي والسطحي لاغشية الخليط الحجمي الغير متجانس (NiPc / C60) الرقيقة تحت تاثير المعاملة الحرارية

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الخلاصة

تم تصنيع الأغشية الرقيقة للمزيج من NiPc / C60 باستخدام طريقة الطلاء البرمي لثلاث نسب مختلفة (1/100 ، 10/100 و 100/100) اعتماداعلى الوزن. تم ترسيب الأفلام على ركائز الزجاج وتمت معالجتها مع العديد من درجات حرارة التلدين K (373 ، 423 ، 473). تمت دراسة البنية البلورية والخصائص السطحية للأفلام المحضرة والمعاملة حراريا باستخدام حيود الأشعة السينية و مطياف القوة الذرية واظهرت تغير وتحسين في التبلور والتشكل السطحي الناجم عن التغيرات في درجات حرارة المعاملة الحرارية. أشار فحص أنماط حيود الأشعة السينية لـ NiPc / C60 إلى أنه يحتوي على بنية متعددة الأشكال ، أي مزيج بين التركيب العشوائي والمتعدد التبلور. عندما تغيرت درجة حرارة المعاملة الحرارية ، أدت إلى إنتاج الأفلام البلورية من الطور α بشكل تفضيلي للمستوى (100). تم حساب الحجم الحبيبي لغشاء الرقيق (NiPc / C60) باستخدام علاقة شيرير وكان الاختلاف غير منتظم مع زيادة درجة حرارة التلدين.. وان نتائج قياسات AFM دعمت نتائج حيود الاشعة السينية.

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1. Introduction

Organic semiconductors have been the subjects of scientific research for the past 50 years. the study of semiconductor organic matter confirmed on small organic molecules in the crystalline state [1,2] . The structural study of materials has always been a high priority, because the physical properties of materials are mainly dependent on their structure.

Organic semiconductors can be divided into two types: polymers and small molecule materials. There are significant differences between these two types of materials. small molecules can be divided into two sub-groups: pigments, not soluble in organic solvents, and dyes, which are soluble[3].

chemical and thermal stability is one of the main gains of using Pcs, and It has excellent electrical and optical properties [4], Metal Phthalocyanines (MPcs) is a group of medium sized organic molecules that have wide applications in fields that contain non-linear optics, molecular electronics, and the manufacture of electrochemical sensors [5].

Nickel phthalocyanine (NiPc) showed good sensitivity and electronic properties [6, 7]. Jacob et al. have mentioned that the NiPc nanostructures can be synthesized by using of ionic media [8]. The molecular structure of NiPc shown in Figure-1

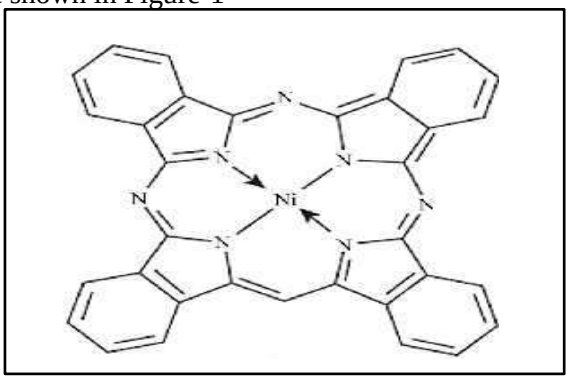

Figure 1-The structure of Nickel phthalocyanine NiPc [6]

Fullerenes are large carbon cage molecules (Fig.2) that are three-dimensional isotopes of benzene. Buckminster fullerene (C_{60}) is the most plentiful form of fullerenes with 60 carbon atoms arranged in a spherical structure. [9], It looks like football with 12 pentagons and 20 hexagons. An important characteristic of C_{60} molecule is its high symmetry.

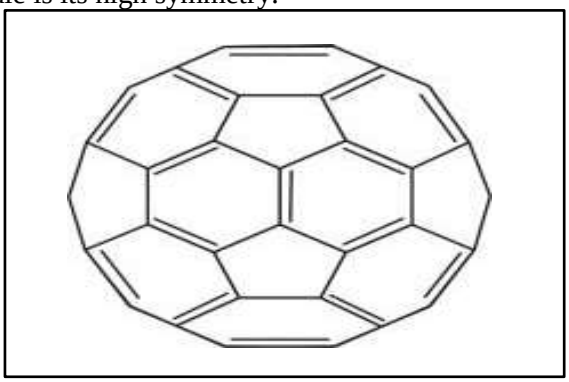

Figure 2-Fullerene C60 arranged in spherical structure with Carbon at each vertex[9]

Thin layers of fullerene are dyed from yellow to yellowish-green. The colour of fullerene solutions is due to the transition of π–π electron.

2. Experimental work

Nickel phthalocyanine (NiPc) and Fullerenes (C_{60}) purchased from sigma-Aldrich and used without additional purification. Before deposition the blend, Glass substrates cut to the size of 2.5cm×2.5cm after that clean them in an ultrasonic bath for 15 min, to avoid contaminants from the glass surface, using different steps with distilled water, liquid soap, acetone and ethanol, the substrate was dried in nitrogen gas.

Three weight ratios of (NiPc/C_{60}) used to prepared the blends and thin films which are (100/1, 100/10 and 100/100) respectively by mixing 15mg/ml of NiPc in chloroform and (0.15, 1.5 and 15) mg/ml of C_{60} in toluene. The blend solutions of NiPc and C_{60} for each ratio were putted on a hot plate stirrer for 40 hours with temperature of 50^{o}C, then the two blended solutions is filtered using 0.2 μm filter and mixed together and leaved 20 hours again on stirrer to get homogenous solution.

Now the blended solution becomes ready to spin-coated on pre-cleaned glass substrate using spin coater type CHEMAT SCIETIFIC SKW-4A2 for 2000 rpm for 1.5min. The prepared samples leaved in air for one day then putted in an oven at 70^{o}C for 15min to remove the residual solvent may be stay inside the film as Nano bubbles. The bulk heterojunction blend (NiPc/C_{60}) thin films were annealed in a vacuum oven at variable temperatures (373, 423 and 473) K for one hour to study the effect of heat treatment temperatures on structural and morphological properties.

structural analysis of the prepared thin films is completed by X-ray diffractometer (Miniflex II Rigaku company, Japan) by Cu Kα radiation (λ = 1.54 Å), full width at half maximum (FWHM) intensity of the diffraction peaks is studied, and the surface morphology of these films is studied by means of atomic force microscopy (AFM) (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS from Angstrom Ad-Vance Inc) (AFM-contact mode).

By using the Bragg's law, the lattice factors of the films were calculated:

$$n\lambda = 2d \sin\theta \quad (1)$$

By using Scherer's relation, the grain size of the crystallites was calculated from the XRD,

$$D = \lambda K / \beta \cos\theta \quad (2)$$

Where λ the wavelength of X-ray, K = 0.94 is a constant, β the full width half maximum and θ the diffraction angle.

Results and Discussion

X-ray diffraction pattern of bulk heterojunction blend (NiPc/C_{60}) thin films for three different ratios prepared by spin coating technique of as-deposited and thermally treated with different annealing temperatures (373, 423 and 473)K are presented in the Figures-(3, 4, 5). XRD pattern shows that all the samples have polymorphism structure, i.e. mix between amorphous and polycrystalline structure, The amorphous phase belongs to the fullerene (C_{60}) while the polycrystalline due to the α-phase NiPc. The XRD parameters of the as-deposited BHJ blend (NiPc/C_{60}) thin films and annealing with several temperatures were calculated and shown in Tables-(1, 2, 3).

The peaks corresponding to miller indices (100), ($\bar{1}$02), (002) and (102) in all patterns included in Figures-(3, 4, 5) belonged to α-crystalline phase of NiPc in the BHJ blend of (NiPc/C_{60}) thin film. The structure of the thin film (NiPc/C_{60}) is defined in a tetragonal with a preferential orientation along the (100) direction at 2θ = 6.8°[10-17]. The d values obtained from diffractogram are decreasing with annealing temperature increasing and in perfect match with JCPDS record. diffraction peaks are matched with the previous explanations.The differences in the values d are due to higher X-ray absorption, sample purity, particle size, preferred orientation and crystal quality. The increase in crystallization is due to the destruction of pseudomorphic layers existing in the film at high annealing temperature[10,13] .

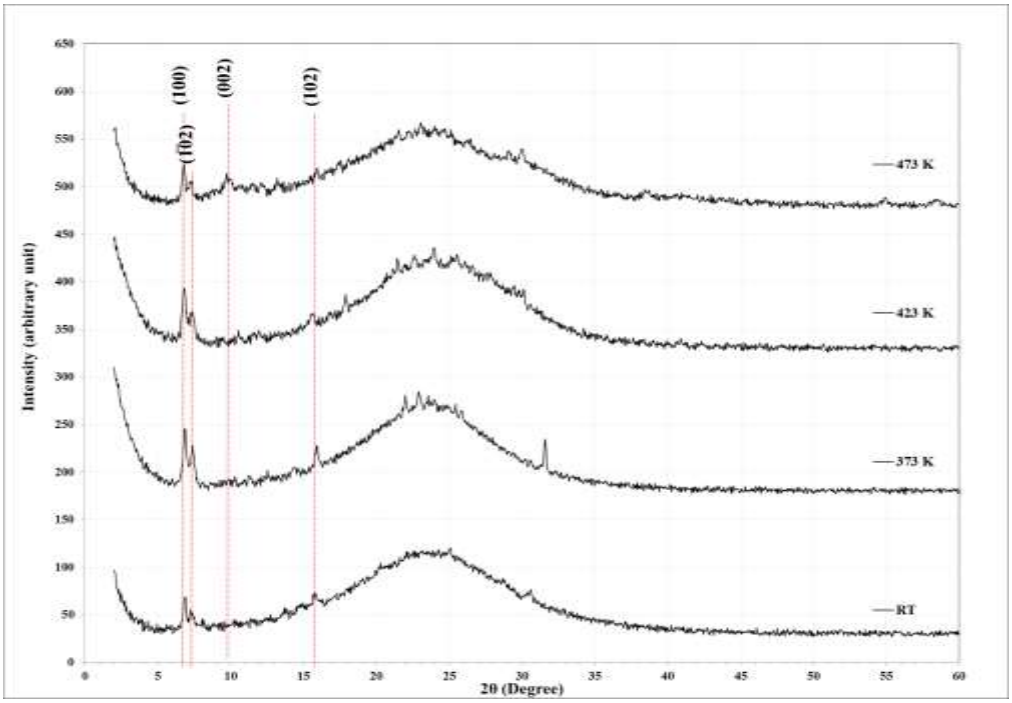

Figure 3-XRD pattern of as- deposited and annealed ($NiPc/C_{60}$)(100/1) Thin Films

Table 1-The structural parameters of as- deposited and annealed ($NiPc/C_{60}$)(100/1) thin Films

Ta (K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	phase	hkl
RT	6.853	0.237	12.8878	33.6	12.500	NiPC	(100)
	7.338	0.316	12.0376	25.2	9.791	NiPC	($\bar{1}$02)
	10.093	0.262	8.7567	30.5	8.451	NiPC	(002)
	15.800	0.500	5.6044	16.0	5.750	NiPC	(102)
373	6.865	0.285	12.8661	27.9	12.500	NiPC	(100)
	7.391	0.344	11.9514	23.1	9.791	NiPC	($\bar{1}$02)
	11.272	0.193	7.8435	41.5	8.451	NiPC	(002)
	15.905	0.262	5.5675	30.6	5.750	NiPC	(102)
423	6.811	0.240	12.9667	33.2	12.500	NiPC	(100)
	7.370	0.357	11.9854	22.3	9.791	NiPC	($\bar{1}$02)
	10.548	0.218	8.3801	36.5	8.451	NiPC	(002)
	15.587	0.388	5.6804	20.7	5.750	NiPC	(102)
473	6.785	0.249	13.0176	32.0	12.500	NiPC	(100)
	7.310	0.269	12.0832	29.6	9.791	NiPC	($\bar{1}$02)
	9.772	0.343	9.0440	23.2	8.451	NiPC	(002)
	15.953	0.251	5.5511	32.0	5.750	NiPC	(102)

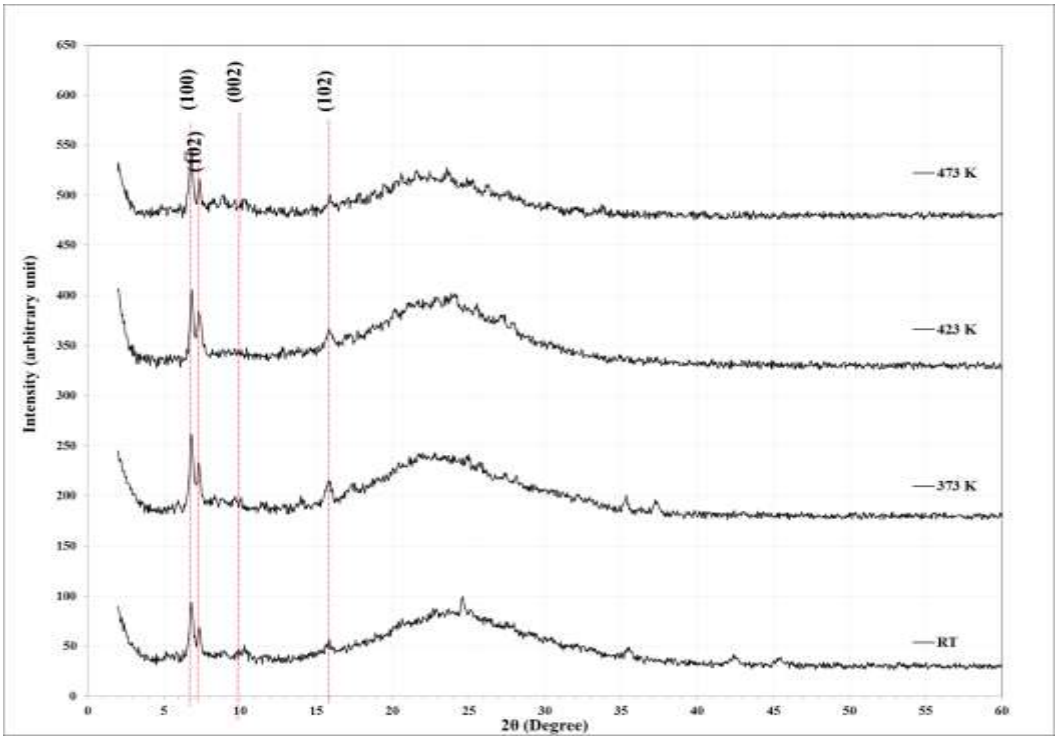

Figure 4-XRD pattern of as- deposited and annealed ($NiPc/C_{60}$)(100/10) Thin Films

Table 2-The structural parameters of as- deposited and annealed ($NiPc/C_{60}$)(100/10) thin Films

Ta (K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	phase	hkl
RT	6.832	0.291	12.9279	27.3	12.500	NiPC	(100)
	7.339	0.268	12.0358	29.8	9.791	NiPC	($\bar{1}02$)
	10.323	0.202	8.5627	39.4	8.451	NiPC	(002)
	15.346	0.262	5.7693	30.7	5.750	NiPC	(102)
373	6.823	0.282	12.9444	28.2	12.500	NiPC	(100)
	7.318	0.258	12.0695	30.8	9.791	NiPC	($\bar{1}02$)
	10.055	0.184	8.7903	43.3	8.451	NiPC	(002)
	15.833	0.370	5.5930	21.7	5.750	NiPC	(102)
423	6.832	0.251	12.9285	31.7	12.500	NiPC	(100)
	7.345	0.361	12.0267	22.1	9.791	NiPC	($\bar{1}02$)
	9.870	0.207	8.9545	38.6	8.451	NiPC	(002)
	15.862	0.422	5.5827	19.0	5.750	NiPC	(102)
473	6.802	0.280	12.9844	28.4	12.500	NiPC	(100)
	7.358	0.237	12.0053	33.7	9.791	NiPC	($\bar{1}02$)
	10.317	0.413	8.5673	19.3	8.451	NiPC	(002)
	15.901	0.383	5.5691	20.9	5.750	NiPC	(102)

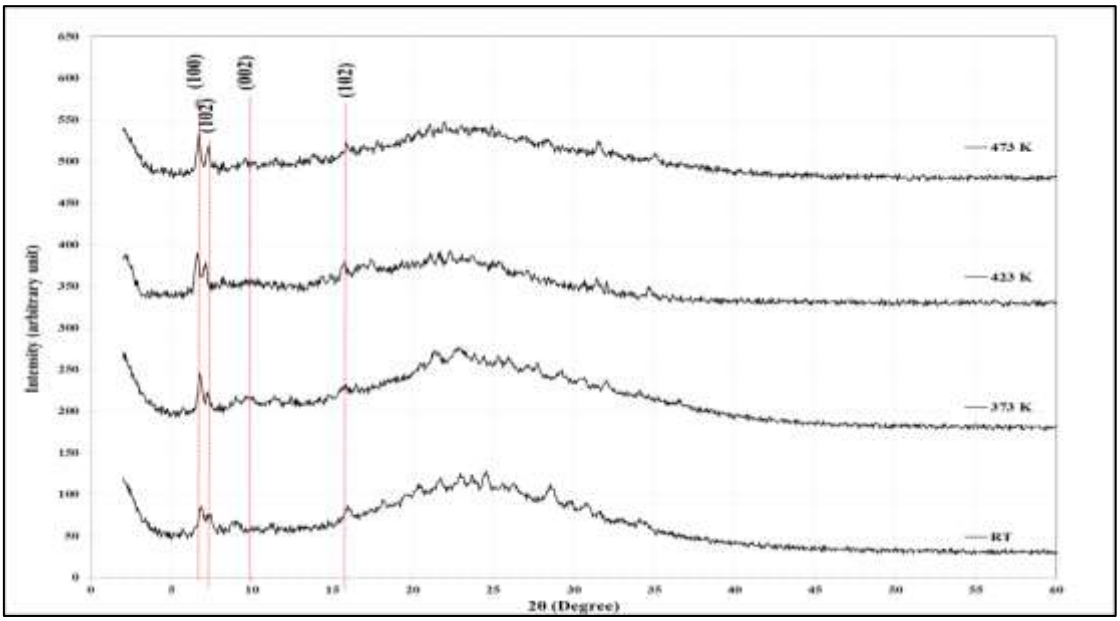

Figure 5-XRD pattern of as- deposited and annealed ($NiPc/C_{60}$)(100/100)Thin Films

Table 3-The structural parameters of as- deposited and annealed ($NiPc/C_{60}$)(100/100) thin Films

Ta (K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	phase	hkl
RT	6.850	0.392	12.8932	20.3	12.500	NiPC	(100)
	7.368	0.311	11.9890	25.6	9.791	NiPC	($\bar{1}$02)
	9.127	0.281	9.6814	28.4	8.451	NiPC	(002)
	15.926	0.430	5.5604	18.7	5.750	NiPC	(102)
373	6.783	0.289	13.0202	27.6	12.500	NiPC	(100)
	7.250	0.200	12.1833	39.8	9.791	NiPC	($\bar{1}$02)
	9.735	0.348	9.0781	22.9	8.451	NiPC	(002)
	15.733	0.577	5.6283	13.9	5.750	NiPC	(102)
423	6.599	0.273	13.3828	29.2	12.500	NiPC	(100)
	7.093	0.324	12.4525	24.5	9.791	NiPC	($\bar{1}$02)
	9.556	0.199	9.2481	40.0	8.451	NiPC	(002)
	15.731	0.310	5.6288	25.9	5.750	NiPC	(102)
473	6.713	0.273	13.1570	29.2	12.500	NiPC	(100)
	7.293	0.324	12.1119	24.6	9.791	NiPC	($\bar{1}$02)
	9.556	0.687	9.2474	11.6	8.451	NiPC	(002)
	15.867	0.465	5.5810	17.2	5.750	NiPC	(102)

It has been found there is a direct relationship between the intensity and sharpening of the prevailing peak and annealing temperature. This result showed that crystallinity and lattice quality of the films enhanced with heat treatment temperatures. The enhancement of crystal may be attributable to the annihilation of pseudomorphic layers existing in the film and increase the ability of atoms to transport towards stable locations in the lattice.

The first position and the most intense peak correspond with the peak (100) for the tetragonal crystal structure of α-NiPc. The second peak can be defined as a reflection (102) of the monoclinic crystal structure of α-NiPc. Other low-angle peaks are represented (002) and (102) reflections of tetragonal structure. All other peaks are in the upper angles formed from the polycrystalline glass substrate thin film. hump is widely in the area 2θ = 20 – 30 degrees is may be due to amorphous glass substrate and/or amorphous phase of C_{60}, this peak is completed by other well defined low intensity peaks, agreeing to lower symmetry phases C60 ordered in orthorhombic and monoclinic structures

[18,19]. From the XRD analysis, it can be determined that as-deposited thin films also contain generally of α-modification of NiPC with a quadruple crystal structure.

The grain size of the blend ($NiPc/C_{60}$) thin film is calculated using the Scherrer relation. All samples have the nonsystematic behavior i.e. the grain size decrease with increased annealing temperature upto 373K .The grain size increase with increased annealing temperature to 423K, Increased annealing temperature provides sufficient thermal energy for atoms rearrangement, resulting in improving of atoms and consequently in faster crystallite growth. As the crystallite size grows, the pseudomorphic layers formed at room temperature are destroyed by heat treatment and the crystallinity of films improves. At annealing temperature increase to 473K the grain size decrease due to structure change to nanofiber[13].

It was observed that there is only one diffraction peak at $2\boldsymbol{\theta}$ = 31.74º. However, this feature can only be a noise effect, as this result can hardly be compared with similar measurements in literature[20,21] and, moreover, the peak is very sharp and little intense. The film is amorphous and no evidence of crystalline structure can be inferred from this XRD measurement.

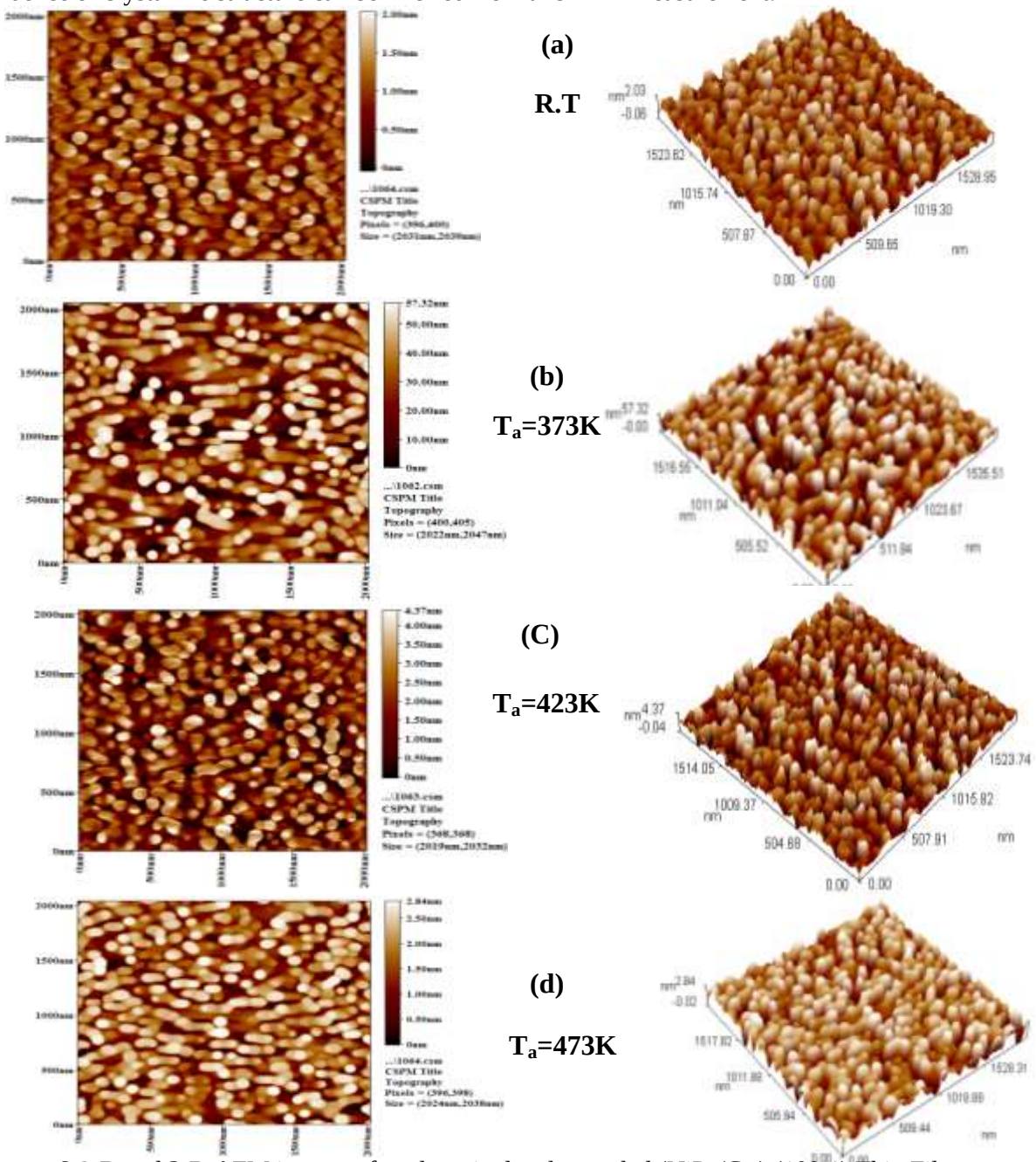

Figure 6-2-D and 3-D AFM images of as-deposited and annealed ($NiPc/C_{60}$) (100:1) Thin Films (a) R.T, (b) T_a=373K (c) T_a=423K and (d) T_a=473K.

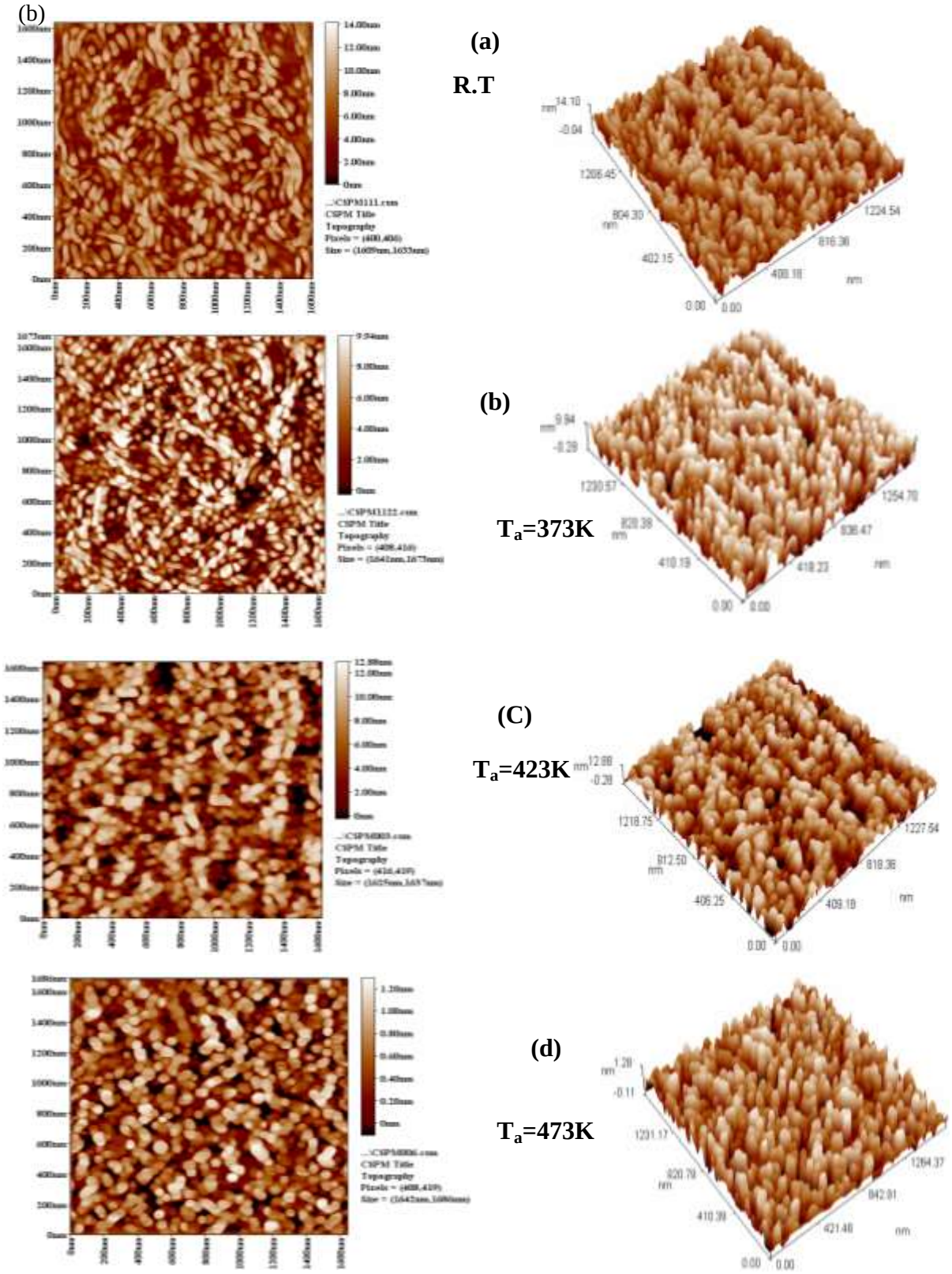

Figure 7- 2-D and 3-D AFM images of as-deposited and annealed ($NiPc/C_{60}$) (100:10) Thin Films (a) R.T, (b) T_a=373K , (c) T_a=423K and (d) T_a=473K.

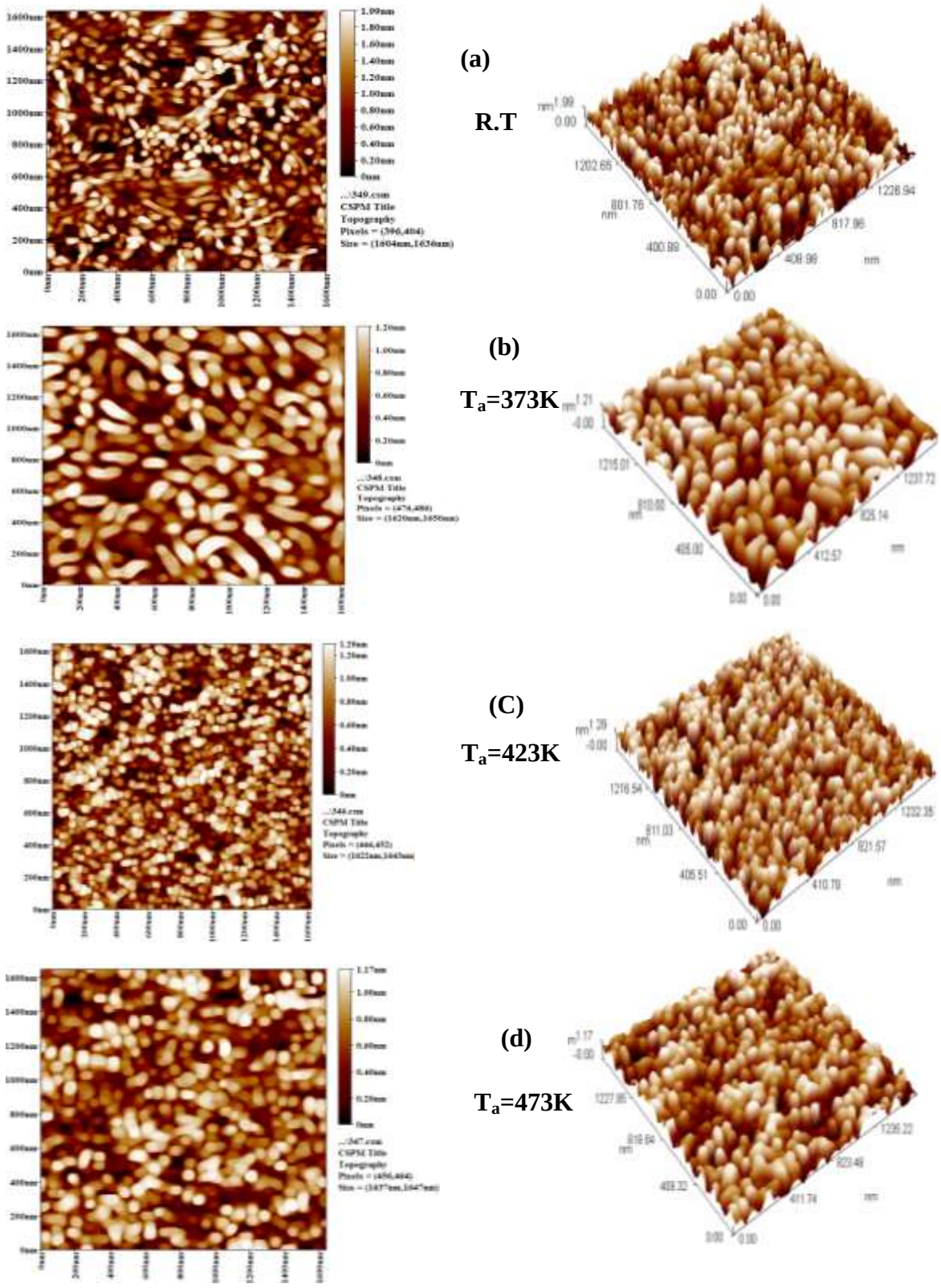

Figure 8- 2-D and 3-D AFM images of as-deposited and annealed ($NiPc/C_{60}$) (100:100) Thin Films (a) R.T, (b) T_a=373K , (c) T_a=423K and (d)T_a=473K.

Surface morphology of ($NiPc/C_{60}$) thin films for three different ratios is shown in Figures-(6, 7, 8). From the observation of these shapes we can see that the morphology of the ($NiPc/C_{60}$) thin film has a larger grain size and is uniformly distributed, referring to the crystalline nature of the film. It can be observed that due to the heating caused by the preparation of films at different annealing temperatures,

the growth of grain will occur which gives the crystal and good surface morphology [16]. These results correspond well with XRD features. The morphology of crystals and the molecular orientation change with annealing temperature. These morphological properties confirm that the annealing temperature allows to control the structural regulation of organic molecules in their solid state, which is expected to significantly improve the properties.

By using the Scherrer relation, the grain size *D* of the film was calculated, From the Tables-(4, 5, 6) it was observed that the parameters can be obtained from AFM analysis such as grain size, (r.m.s) Roughness and peak to peak. From these tables it was observed that the grain sizes variation was nonsystematic and have the same behavior as in XRD measurement and belong to same reasons which mentioned in XRD section.Tables-(4,5 and 6) shows that by increasing the annealing temperature, the grain size is increased.

Table 4-Grain size and average roughness of blend (NiPc/C_{60})(100/1) Thin Films by AFM technique

T $_a$(K)	***Grain size(nm)***	***(r.m.s)Roughness (nm)***	***(p-p) (nm)***
RT	88.24	0.654	2.79
373	78.14	0.433	2.02
423	87.91	15.1	5.69
473	82.74	1.12	4.41

Table 5-Grain size and average roughness of blend (NiPc/C_{60})(100/10) Thin Films by AFM technique

T $_a$(K)	***Grain size(nm)***	***(r.m.s)Roughness (nm)***	***(p-p) (nm)***
RT	61.37	2.78	9.64
373	56.40	2.95	10.2
423	78.01	3.39	11.7
473	63.57	0.356	1.4

Table 6-rain size and average roughness of blend (NiPc/C_{60})(100/100) Thin Film by AFM technique

T $_a$(K)	***Grain size(nm)***	***(r.m.s)Roughness (nm)***	***(p-p) (nm)***
RT	90.29	0.289	1.16
373	48.03	0.576	1.99
423	66.24	0.316	1.21
473	48.10	0.336	1.28

Conclusions

The structural of (NiPc/C_{60}) thin films fabricated by spin-coated technique on glass substrates prepared at different annealing temperatures successfully hase been investigated. Structural analysis showed an improvement in the crystallization of NiPc films and that the grain size became largest according to the increasing of heat treatment temperature. Also, AFM analysis showed that the homogeneity and morphological stability of the films improved in annealing temperature.

X-ray diffraction patterns obtained for (NiPc/C_{60}) exhibited it has a polymorphism structure, i.e. mix between amorphous and polycrystalline structure. Film is preferentially oriented (100) plane as tetragonal. It can be observed that the intensity and value of the d is sharpened, and the main peak increase with annealing temperature that shows the crystallization of the films when the heat treatment temperature is increased. The diffraction peaks obtained for films prepared at higher annealing temperatures are sharp due to the increased crystallization.

With increasing annealing temperatures, the full width at half maximum (FWHM) are reduced and the grain sizes variation was nonsystematic behavior with increased annealing temperature upto 423K.with different annealing temperatures, rearrangements of molecules are taking place. The variation in grain size shows that the structure and morphology of (NiPc/C60) are controlled its properties, depending on the increase in the annealing temperatures.

Through topographic AFM analysis, we found that there is a significant effect of annealing temperatures on surface morphology of ($NiPc/C_{60}$) films and the change in the shape of the crystal and the molecular orientation with annealing temperature. These films showed more grain size, distributed homogeneously, rough indicating the crystalline nature of the film.

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