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The Structural and Morphological Properties of Heat Treated Hybrid Blend ZnPc/CdS Thin Films

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Abstract
CdS Nps (inorganic material) was prepared by the chemical reaction method. ZnPc (organic material) and CdS thin films were prepared separately to compare their characterization with the hybrid BHJ blend ZnPc/CdS thin film (2ml:2ml) by spin coating technique. The structural and morphological properties of the prepared thin films have been measured by XRD and AFM respectively. The XRD pattern for both as-deposited and annealed CdS nanoparticle films shows a hexagonal structure. The crystallite size behavior of as deposited ZnPc films and annealing at 423K for 1h, 2h and 3h was approximately similar to the behavior of heat treated blended films. The grain size was measured by AFM, which decreaseds with annealing temperature for ZnPc films, while it increases with annealing for CdS films.

Keywords: Organic/inorganic hybrid, structural, morphological, CdS and ZnPc

الرقيقة المعاملة حراريا CdS/ZnPc الخصائص التركيبة و السطحية لاغشية المزيج الهجين

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الخلاصة
مركب كبريتيد الكادميوم النانوي (مادة لاعضوية) تم تحضيره عن طريق التفاعل الكيمياوي. حُضرت اغشية الزنك فثالوسيانين (ZnPc) (مادة عضوية) الرقيقة و اغشية كبريتيد الكادميوم (CdS) كلاً على حده باستخدام طريقة الطلاء البرمي وتمت المقارنة بين خواصهم وخواص اغشية المركب الهجين الناتج عن مزجهم مع بعض ZnPc/CdS (2ml:2ml). الخصائص التركيبية والسطحية للاغشية الرقيقة تم فحصها باستخدام حيود الاشعة السينية ومجهر القوة الذرية على التوالي. أظهرت نتائج الاشعة السينية لاغشية CdS النانوية الرقيقة المرسبة في درجة حرارة الغرفة والملدنة ذات تركيب سداسي. سلوك الحجم البلوري لأغشية ZnPc المرسبة والملدنة عند 423 كلفن لمدة ساعة، ساعتين و ثلاث ساعات كان تقريبا مشابه لنمط حيود الاغشية الهجينة. الحجم الحبيبي لاغشية ZnPc المقاس بمجهر القوة الذرية يقل مع التلدين والعكس يحصل في حالة اغشية CdS.

Introduction

Hybrid BHJ blend organic/inorganic systems have attracted much attention because of their potential applications as new photoelectric materials that combine the desired properties of both the organic and inorganic components [1, 2]. Organic/Inorganic blends are used as gas sensors, thin film field effect transistors, solar cell and electro photographic systems, etc. [3].

Organic materials are cheaper and more easily utilizedle compared to inorganic materials**.** Among these organic materials, phthalocyanines (Pcs) which are well-known metal organic complexes since the beginning of the last century. Phthalocyanines are a highly conjugated macrocycles with good

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thermal and chemical stability, and properties that allow them to be applied in many different fields It is an important material for organic-based electronic devices [4]. Many studies were directed to synthesize metal-Phthalocyanine (MPcs) such as CoPc, ZnPc, CuPc, etc. in order to optimize the properties of Pcs to convenient values. Generally, MPcs materials were used by the accompaniment of an inorganic semiconductor in electronic devices [5].

Cadmium sulfide (CdS) is a wide band gap II-VI compound semiconductor. It has direct band gaps (Eg) of 2.57 and 2.40 eV, at room temperature for hexagonal and cubic structures respectively I Its transmission and resistivity properties, and crystalline structure-make it a very suitable inorganic n-type material for the blending with organic materials to prepar a hybrid BHJ blend [6,7].

Many studies have been made on organic/inorganic composites and chemical methods have been often used to prepare the organic/inorganic composites [3]. A phthalocyanine/CdS pair is a perspective combination in terms of stability and cheapness for the production of solar cells, The spectral sensitization of CdS semiconductor by metal-free phthalocyanine was first shown in 1980 and various phthalocyanine/CdS bilayer structures have been produced using CdS single crystal [8].

Experimental

The Preparation of CdS nanoparticles by chemical method using cadmium chloride ($CdCl_2$), sulfur (S), Paraffin oil, and oleic acid was done following three main steps:

i. Preparation of the S-paraffin oil solution.

ii. Preparation of Cd complex solution from the mixture of $CdCl_2$ dissolved in Paraffin:Oleic acid solution.

iii. CdS nanoparticles synthesis was done by mixing the Cd and S from mixing the S-Paraffin solution and Cd-Paraffin:Oleic acid complex and heating this mixture up to 300°C then cooling it down and adding a large volume of absolute ethanol.The CdS nanoparticles colloid was then washed many times by ethanol and centrifuged The last treatment was by

i. toluene and then with ethanol using ultrasonic bath washing and centrifuged by toluene then with ethanol using ultrasonic, . to be followed by centrifuging.t The precipitate was dried at T=60°C for 30 minutes to get CdS Nps powder, then CdS Nps (0.01g) of which was dissolved with 4ml of chloroform.

Zinc phthalocyanine (ZnPc) (0.02g) was fully dissolved in chloroform (4ml), using a hot plate stirrer for (40) hours with temperature of 50oC, then the solutions is was filtered using 0.45μm and placed ing again on an ultrasonic stirrer for 10 hours and 5 hours on ultrasonic to get a homogenous solution. The same steps used were followed to get CdS solution. The n mixed ZnPc and CdS solutions were mixed together (2ml:2ml) and following ed the same steps to get a blend solution., prepared t Thin films from these solutions were prepared by the spin coating method on pre-cleaned glass substrates.

The prepared samples leaved were left in at room temperature (R.T) for one day then putted were plced in an oven at 70oC for 10 min to remove the residual solvent that may be stay still present inside the film.

This paper deals with the structural and morphological characterizations of deposited CdS , ZnPc and ZnPc/CdS blend thin films and with annealed filmsthem at 150 oC (423K) for 1 hour, 2 hour and 3 hour and.The films were examined using X-ray diffraction method (XRD) and atomic force microscopy (AFM) to understand the crystal plane spacing (d), crystallite and grain size, phase composition, preferred orientation, and to defect the structure of all the phases.

Results and Discussion

1. X-ray Diffraction

Figure-1 shows the XRD pattern for both the as-deposited and the annealed CdS nanoparticle films. The films have a hexagonal structure [9, 10] (card number of 96-900-8863 and 96-901-1664 respectively) (as tabluated and that is illustrated in Table-1.

Figure-2 showed the patterns of ZnPc (ICDD card number of 39-1882) of as- deposited ZnPc films and the annealed films at 423K for 1h,2h and 3h .They have a polycrystalline structure with the same orientation and the same 2Θ.It was confirmed that a A small diffraction peak of as-deposited and annealing ZnPc films at 2Θ of 6.90˚ appeared,which can be assigned as to (-1 0 1) plane and there is a . Another peak appeared for the same films at 2Θ of 9.25˚ with preferred orientation (1 0 1). These results were in good agreement with other reported results in the literatures [11, 12].

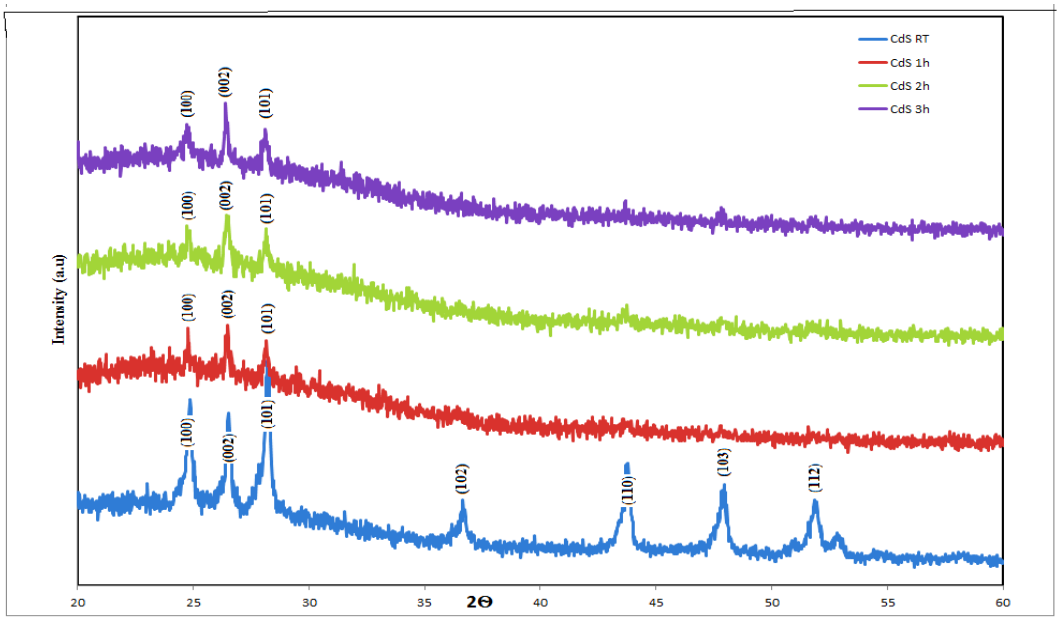


Figure 1-XRD patterns for both as-deposited and annealed CdS Nps films

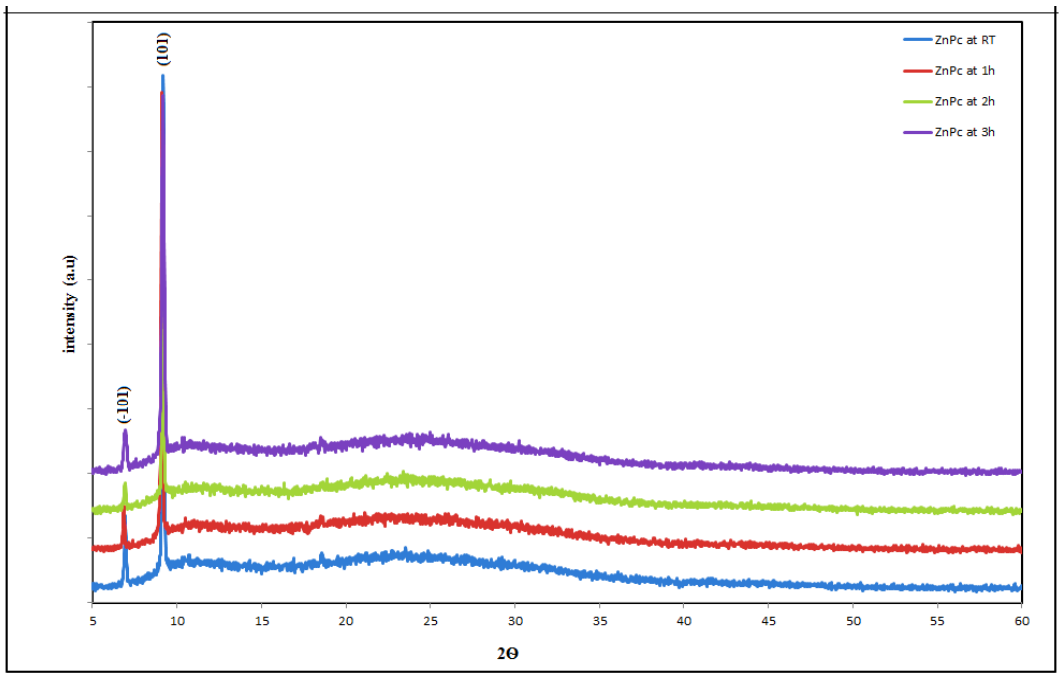


Figure 2-XRD patterns for both as-deposited and annealed ZnPc films

Figure-3 shows that the XRD patterns of as deposited and annealing ZnPc/CdS blend (hybrid) film., t The appeared same peaks as same as peaks those in the annealed ZnPc films., except for a small diffraction peak at 2Θ of 6.90˚ appeared in ZnPc as-deposited film pattern and was did not appear ed for blend as-deposited film.

The crystallite size of ZnPc films decreased s by annealing the films from 97nm at R.T to 53nm .

The crystallite size of ZnPc/CdS blend films change un unsystematically with annealing time . This is because of the blending occuring between these two different materials that have a different behavior and because of the rearrangement of particles with the time of annealing.

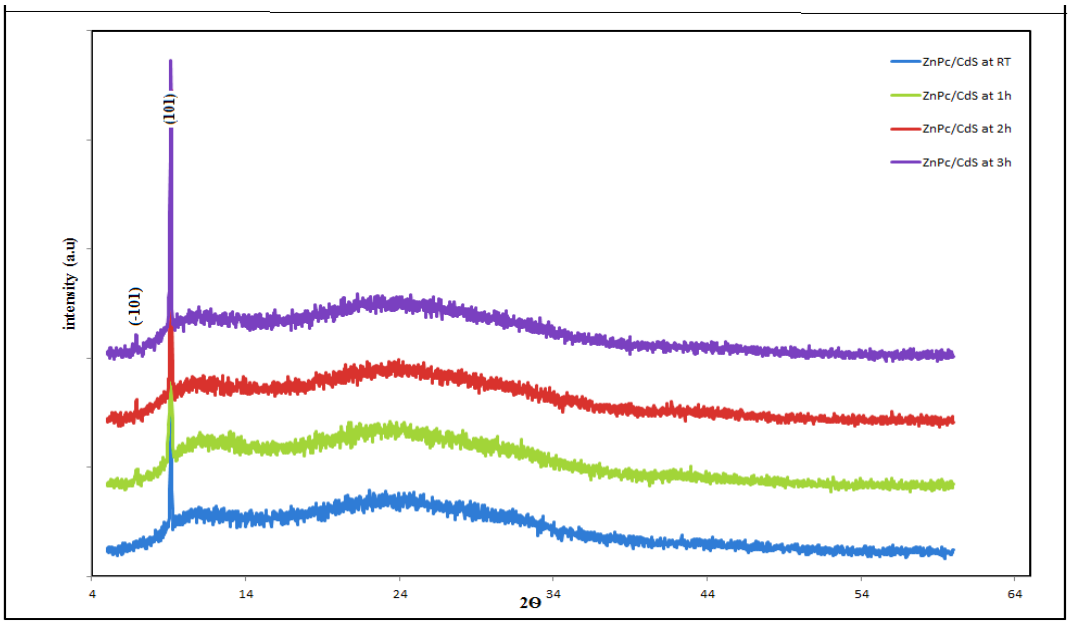


Figure 3-XRD patterns for both as-deposited and annealed ZnPc/CdS blend films

Table 1-The 2Θ , d-spacing , FWHM , and crystallite size values.

Sample	Annealing time at 150C°	2Θ	d-spacing	FWHM	Crystallite Size	Card no.
ZnPc	RT	6.98	12.63	0.119	75	39-1882
		9.18	9.62	0.092	97	
ZnPc	1h	6.82	12.94	0.125	71	
		9.06	9.74	0.113	78	
ZnPc	2h	6.94	12.71	0.139	64	
		9.19	9.64	0.119	75	
ZnPc	3h	6.87	12.85	0.212	42	
		9.15	9.64	0.167	53	
CdS	RT	24.96	3.59	0.248	32	96-900-8863
		26.51	3.35	0.267	34	
		28.17	3.16	0.289	38	
		36.73	2.44	0.450	21	
		43.72	2.06	0.376	25	
		47.87	1.89	0.512	19	
		51.86	1.76	0.542	18	
CdS	1h	24.78	3.58	0.164	55	96-901-1664
		26.53	3.35	0.243	37	
		28.11	3.17	0.314	36	
CdS	2h	24.84	3.58	0.313	29	
		26.51	3.35	0.307	35	
		28.17	3.16	0.450	20	
CdS	3h	24.76	3.59	0.382	24	
		26.51	3.59	0.193	47	
		28.17	3.16	0.315	29	
ZnP /CdS blend	RT	9.09	9.71	0.092	92	-
ZnP /CdS blend	1h	6.89	12.80	0.362	24	
		9.11	9.69	0.118	75	
ZnPc/CdS blend	2h	6.94	12.71	0.291	30	
		9.09	9.71	0.108	82	
ZnPc /CdS blend	3h	6.86	12.86	0.142	62	
		9.11	9.69	0.101	87	

2. Atomic Force Microscopy (AFM)

It is well known that AFM is one of the most effective ways for the surface analysis due to its high resolution and powerful analysis.

The three dimensional AFM images of CdS, ZnPc, and ZnPc/CdS blend as deposited and annealing films at 423K for 1h, 2h, and 3h that were prepared by the spin coating method are shown in Figures-(4,5,6 respectively).

These images show homogeneous CdS films over the substrate without any voids or cracks, and also shown a continuous granular morphology.

The grain size for as deposited CdS generally get to increased s by annealing films at 423 K from 56.22 nm to 67.12 nm. The grain size decreased s from 83.3 nm to 41.9 nm for ZnPc films by annealing , also, the grain size for ZnPc/CdS blend films get to decreased from 78.92 nm to 71.13 nm by annealing films.This behavior can be explained on as due to the change in the crystal structure.

Table-2 shows root mean square and grain size for as deposited and annealing films at 423 K for 1h,2h, and 3h

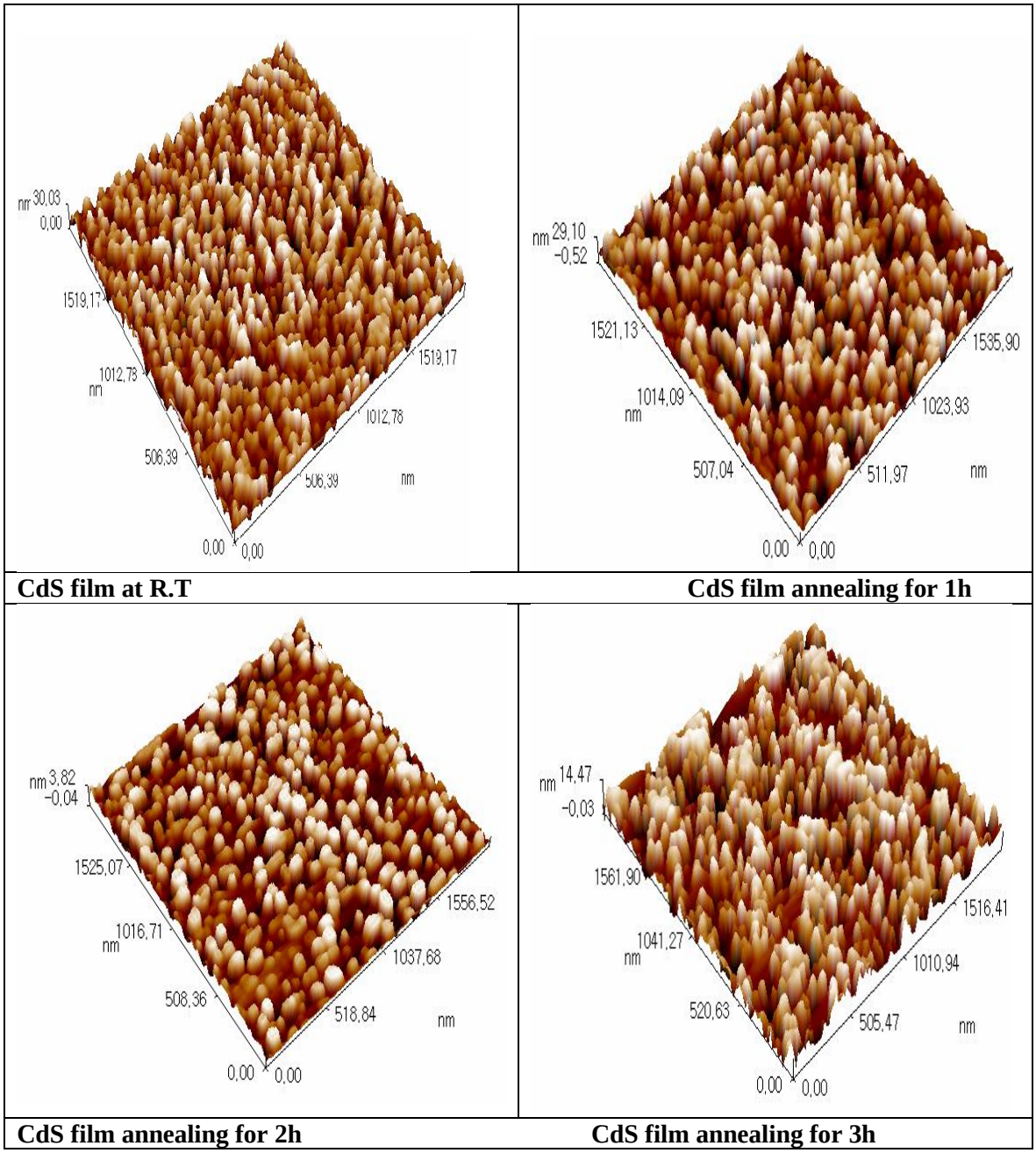
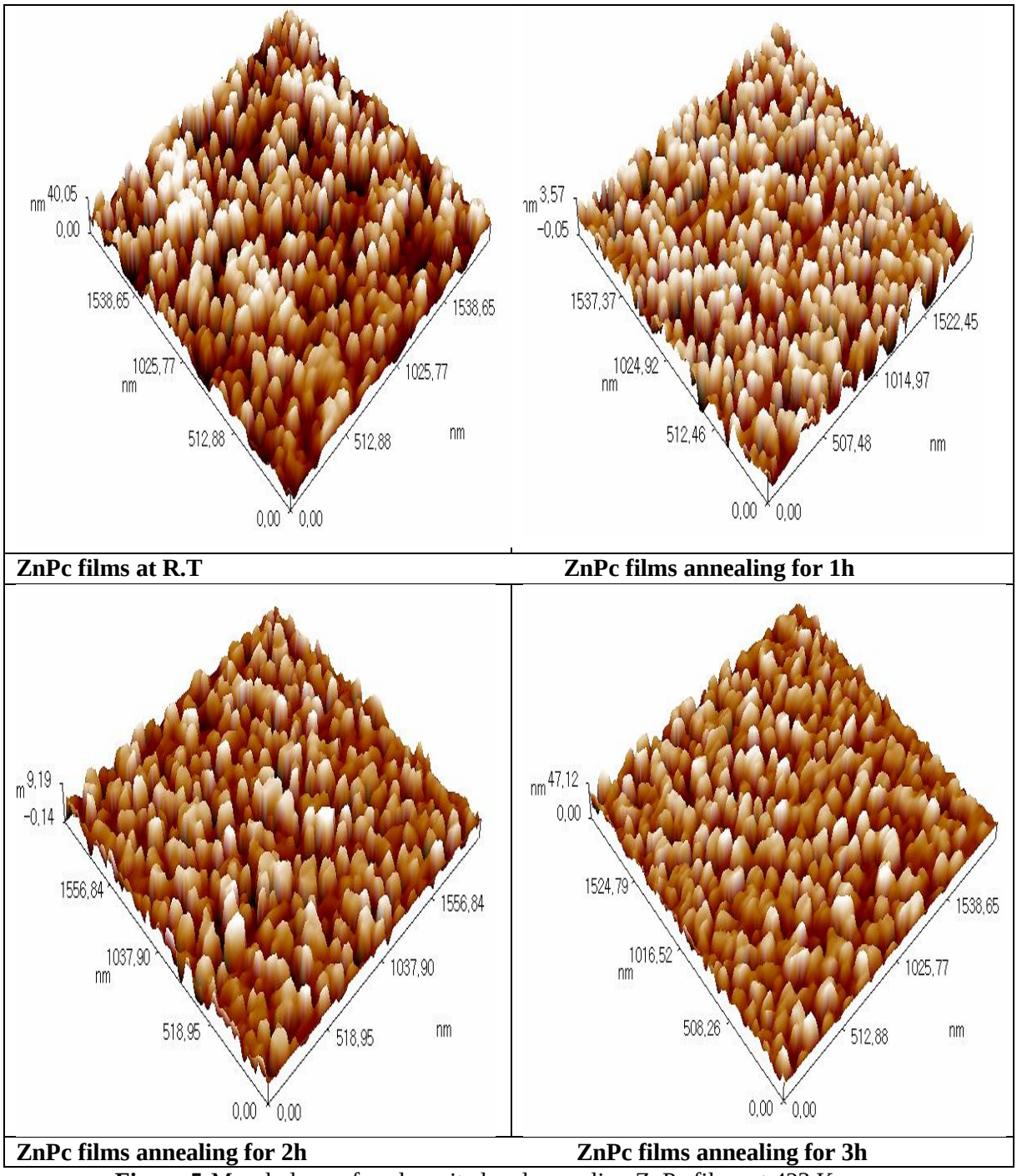
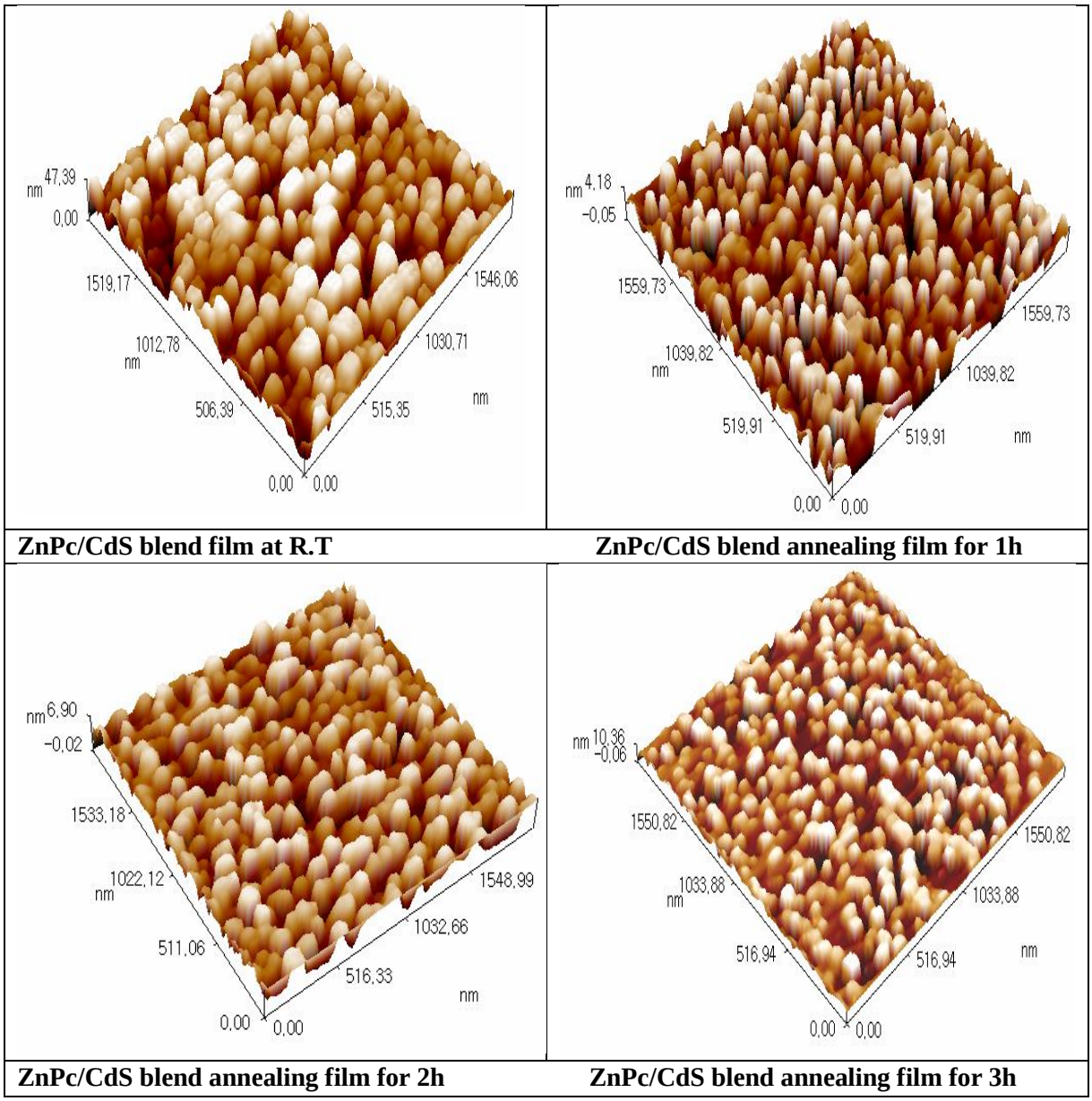


Figure 4-Morphology of as deposited and annealing CdS films at 423 K.



ZnPc films at R.T	**ZnPc films annealing for 1h**
ZnPc films annealing for 2h	**ZnPc films annealing for 3h**

Figure 5-Morphology of as deposited and annealing ZnPc films at 423 K.



ZnPc/CdS blend film at R.T | **ZnPc/CdS blend annealing film for 1h**

ZnPc/CdS blend annealing film for 2h | **ZnPc/CdS blend annealing film for 3h**

Figure 6-Morphology of as deposited and annealing ZnPc/CdS blend films at 423 K.

Table 2- root mean square, average roughness, and grain Size for as deposited and annealing films at 423 K for 1h, 2h and 3h.

Sample	Annealing time at 150C°	Root Mean Square	Grain Size (nm)
ZnPc	R.T	11.4	83.30
	1h	1	77.69
	2h	2.23	72.92
	3h	9.84	41.90
CdS	R.T	7.45	56.22
	1h	8.4	59.37
	2h	1.08	64.44
	3h	3.31	67.12
ZnPc/CdS blend	R.T	11	78.92
	1h	1.22	71.31
	2h	1.68	108.82
	3h	2.79	90.48

Conclusion

CdS nanoparticles have been was prepared by the chemical method, . i Its structural properties were examined using XRD method. Also itsIt was noticed show that the as deposited and annealed ZnPc/CdS blend films have the similar behavior as that of as deposited and annealed ZnPc films. AFM measurements show that all the samples was were homogeneous and tightly adherent films over the substrate without any voids or cracks.

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