Study the Structural and Morphological Properties of $Cd_xZn_{1-x}S$ Thin Films prepared by Chemical Spray Pyrolysis Technique (CSP)

Adel H. Omran Alkhayat[1], S.M.Thahab[2] and Salah M. Saleh[1]

[1]Department of Physics ,Faculty of Science ,University of Kufa, 21Najaf,Iraq
[2] Nanotechnology and Advanced Materials Research Unit(NAMRU)
Faculty of Engineering University of Kufa Najaf, Iraq

adilh.alkhayat@uokufa.edu.iq, Sabah.alabboodi@uokufa.edu.iq, mm.salah47@yahoo.com,

Abstract

$Cd_xZn_{1-x}S$ thin films have been prepared by the chemical spray pyrolysis method on glass substrate. The structural, compositional properties of $Cd_xZn_{1-x}S$ thin films have been investigated using X-ray diffraction. As-deposited $Cd_xZn_{1-x}S$ thin films are polycrystalline and show the hexagonal (Wurtzite) with the highly preferential orientation (002). The surface morphology and defects of $Cd_xZn_{1-x}S$ thin films have been investigated using (SEM) and (EDAX). The morphology of thesis thin films indicate that the size of the particles increased with Cd^{2+} concentration. However, EDAX spectra indicated well defined peaks corresponding to Zn, Cd and S. the surface texture of the deposited $Cd_xZn_{1-x}S$ thin film have been investigated using AFM. The AFM show deposited of $Cd_{0.5}Zn_{0.5}S$ thin film on glass substrates exhibits the smooth surface texture.

Keywords: Thin Film ; Spray Pyrolysis Deposition ; $Cd_xZn_{1-x}S$ ternary

الخلاصة

في هذا البحث تم تحضير أغشية $Cd_xZn_{1-x}S$ بتقنية الرش الكيميائي الحراري على أرضيات زجاجية بدرجة حرارة 400 ^oC . وتضمن هذا البحث دراسة وتحليل الخصائص التركيبية لأغشية $Cd_xZn_{1-x}S$ المحضرة بواسطة حيود الاشعة السينية . إن الخصائص التركيبية للأغشية المحضرة قد دُرست وحللت بإستخدام تقنية حيود الأشعة السينية (XRD). نتائج حيود الأشعة السنية تشير إلى ان تركيب الأغشية الرقيقة المحضرة هي متعددة التبلور وتمتلك طور سداسي (Wurtzite) وبإتجاه سائد على طول المستوي (002). كما تم دراسة طبوغرافية السطح لاغشية $Cd_xZn_{1-x}S$ المحضرة بواسطة المجهر الالكتروني الماسح SEM و EDAX والذي يشير إلى إن حجم الجسيمات (البلورات) يزداد بزيادة نسبة تركيز Cd^{+2} . صور EDAX تشير الي وجود قمم محددة وواضحة للعناصر Zn وCd وS. كما تم دراسة طبيعة السطح للاغشية المحضرة بواسطة مجهر القوة الذرية AFM والذي اظهر غشاء $Cd_{0.5}Zn_{0.5}S$ الرقيق المحضر على الزجاج ذو بنية سطح صقيلة.

الكلمات المفتاحية اغشية رقيقة ، الترسيب بالرش الحراري ، $Cd_xZn_{1-x}S$ ثلاثي

Introduction:

The past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other optoelectronic devices with much interest shown in the use of CdS window layer in solar cell architecture [8]. due to their favourable electrical and optical properties. Among the chalcogenide semiconductors, CdZnS is one of such type materials, which is an important materials for the development of various modern technologies of solid state devices such as light emitting diode, detector etc. because of lattice matching with absorber materials and band gap in visible reason cell [2].

The CdZnS has been prepared by various methods such as vacuum evaporating, screen printing, sintering, chemical deposition, physical vapour deposition, dip technique, electrodeposition, spray pyrolysis etc [4] Among these, spray pyrolysis method is economical, simpler and more versatile than the others and gives the possibility of obtain films with suitable properties for optoelectronic applications and also when large areas are needed [5].

In this report, the optoelectronic، structural and surface morphology properties of the spray deposition ternary semiconductor thin films of $Cd_xZn_{1-x}S$ are presented.

Experimental:

Spray pyrolysis is basically a chemical process, in which a precursor solution is sprayed onto a substrate held at high temperature, where the solution reacts and forms the desired thin film. Cadmium Nitrate, thiourea and Zinc Chloride are used as starting material for the source of Cd^{2+}, S^{-2} and Zn^{2+} ions. The precursor solution has been prepared by mixing appropriate amounts of Cadmium Nitrate and Zinc Chloride in Thiourea solution. The optimized coating parameters used in the present work as Substrate-nozzle distance-31cm, flow rate of the precursor solution-8 ml/min. The thin films have been prepared at 400℃ substrate temperature. The precursor solution is prepared by mixing aqueous solution of (0.125 M) Cd(NO3)2.4H2O, (0.150 M) of $CS(NH_2)_2$ and (0.125 M) $ZnCl_2$, to get $Cd_xZn_{1-x}S$ thin films with stochiometry $Cd_xZn_{1-x}S$, (x= 0.3, 0.5, and 0.7). The film thickness was measured by weight gain method. The structural properties of $Cd_xZn_{1-x}S$ thin films are studied by using X-ray diffractometer (XRD) using Cu-Kα radiation with wavelength 1.5406Å. Surface morphology was examined by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDAX). Surface texture was examined by atomic force microscopes (AFM).

Results and discussion:

Structural Analysis

Figure 1 shows the x-ray diffraction pattern for the composition x =0.3 $Cd_{0.3}Zn_{0.7}S$ thin films which exhibit a polycrystalline structure with hexagonal (Wurtzite) phase. All the peaks assigned to (100), (002), (102), (008), (105), (106) and (0010) orientations of hexagonal phase of $Cd_xZn_{1-x}S$. The preferential orientation at (2Θ= 26.10) for (002) planes. The intensity of XRD peaks decreases at higher concentration of Zn^{2+} .The broad peaks of $Cd_xZn_{1-x}S$ at Cd content of 0.3 value of indicate poor crystallinity and small crystalline size.

Figures 2 and 3 show the x-ray diffraction pattern of the compositions x =0.5 $Cd_{0.5}Zn_{0.5}S$ and x = 0.7 $Cd_{0.7}Zn_{0.3}S$, it can be seen that all thin films are single phase, polycrystalline and possess the hexagonal structure. The strongly preferred orientation at (2Θ =26.96) for (002) planes of the compositions x= 0.5 and at (2Θ =24.61) for (100) planes of the compositions x = 0.7.

Most of the peaks assigned to (100), (002), (101), (102) and (110), orientations of hexagonal (Wurtzite) phase of $Cd_xZn_{1-x}S$. The intensity of (002) of XRD patterns for composition x =0.5 and x =0.7 was significantly increased as compared to intensity of (002) peak of x =0.3 compositions. It was observed that the diffraction angle of (002), shifts towards higher angles with an increase in the ZnS concentration, which means that the (002) lattice constant decreases. The (002) diffraction peak gives the lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(S_{1-x}Se_x)_2$, which are used in photovoltaic solar cells[7].

The observed diffraction patterns are in good agreement with the standard JCPDS cards data 41-1049, 39-1363 and 40-0836 for CdS, ZnS, and $Cd_{0.723}Zn_{0.277}S$ respectively, Kumar *et al.*, (2009)[10]; Ravangave and Biradar, (2013)[8]; Ravangave *et al.*, (2012)[7]; Verma *et al.*, (2013)[9], reported similar hexagonal structure of $Cd_xZn_{1-x}S$.

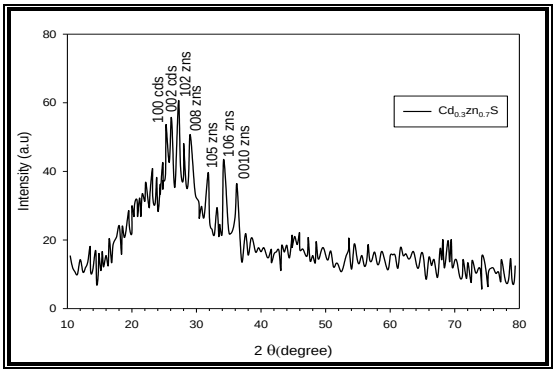

Fig. 1 The x-ray diffraction pattern of ***$Cd_{0.3}Zn_{0.7}S$*** *thin film.*

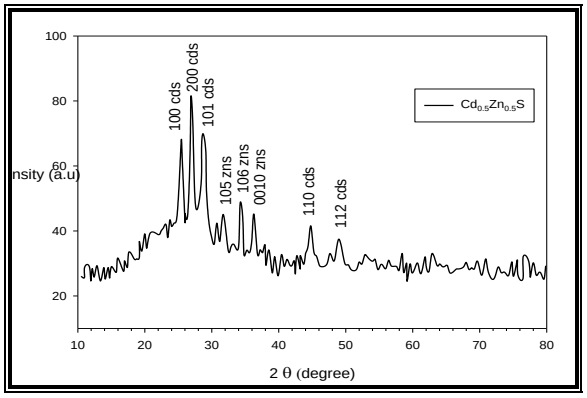

Fig. 2 The x-ray diffraction pattern of ***$Cd_{0.5}Zn_{0.5}S$*** *thin film.*

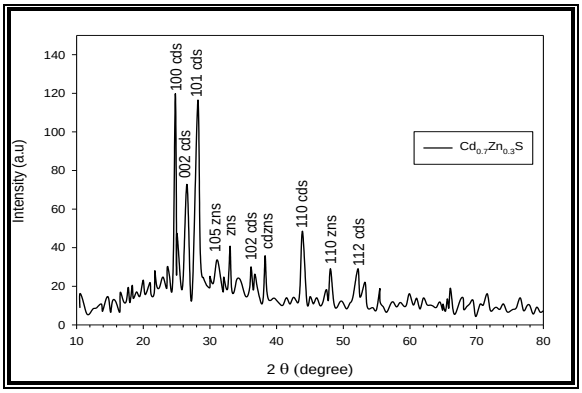

Fig. 3 The x-ray diffraction pattern of ***$Cd_{0.7}Zn_{0.3}S$*** *thin film.*

The values of lattice constant experimental „a" and „c" for hexagonal planes of the $Cd_xZn_{1-x}S$ thin films are calculated from XRD data using the following equation [1].

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{\ell^2}{c^2} \qquad \text{.....(1)}$$

where (hkl) are Miller indices, The a parameter is obtained from the plane (h00), while the plane (00 ℓ) is used to obtain c-parameter.

The values of lattice constant „a" and „c" of $Cd_xZn_{1-x}S$ thin films observed to vary as composition of Cd (from x= 0.3 to 0.7), its values varies from (3.917, 6.82) Å to (4.097, 6.655) Å respectively. The increase in the values of lattice parameters with the

composition of Cd confirmed the increase of the unit cell size [3][7] .
The grain size was calculated from XRD data using Scherriers formula [5].

$$G.Z = 0.9\lambda / B\cos\theta \quad \text{.....(2)}$$

λ: is the wavelength, B: the full width half maximum (FWHM), θ: is Bragg diffraction angle. Table 1 shows the variation of grain size with Cd composition and presented in fig. 4. It is observed that the grain size of the $Cd_xZn_{1-x}S$ increased with increase in Cd composition. The average grain size is observed decreased from (59.931 to 20.943) nm and then increase to 37.670 nm with increase in Cd composition. The average grain size values of all compositions x for $Cd_xZn_{1-x}S$ thin films gives an indicate that the prepared films were a nanocrystalline. This result was in a good agreement with the literatures Ravangave and Biradar, (2013)[8]; Verma *et al*., (2013)[9]. From XRD patterns, one can see that the diffraction angle (2θ) shifts towards a slightly higher angle with increasing (Zn content) in the thin films. This is due to the substitution of Zn^{2+} for Cd^{2+} which different ionic radius of Cd^{2+} (0.095 nm), in and Zn^{2+} (0.074 nm) leads to the increase of lattice constants of $Cd_xZn_{1-x}S$ thin films[3][6]. Table (1) shown the X-Ray analysis data of $Cd_xZn_{1-x}S$ as a function of Cd.

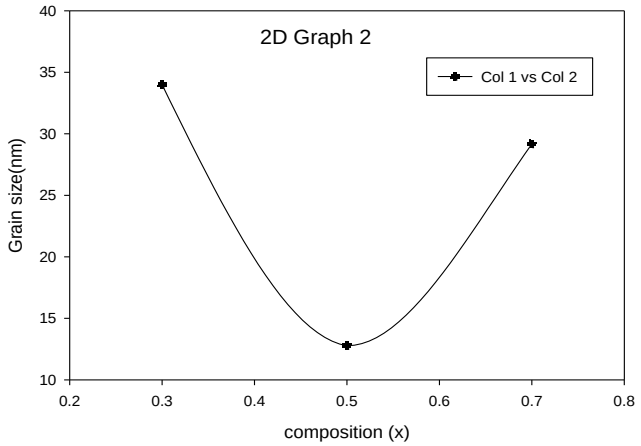

*Fig. 4 The average grain size varies **Cd** composition for **$Cd_xZn_{1-x}S$** thin films.*

Surface Morphological Analysis

The surface morphology and defects of $Cd_xZn_{1-x}S$ thin films were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX) charts it is given in Figs. 5 (a, b, and c) for three samples of $Cd_xZn_{1-x}S$ thin films with respect to composition of Cd. The composition of Cd of the thin films varies from 0.3 to 0.7. The growth of the layers is oriented in c axis normal to the substrate. The morphology of thesis thin films indicate that the size of the particles decreased with Zn concentration. However, EDAX spectra indicated well defined peaks corresponding to Zn, Cd and S. The $Cd_xZn_{1-x}S$ thin films with composition of Cd of 0.5 is otherwise uniformly, coated except few defects and this concentration is better as compared to other thin films the host.

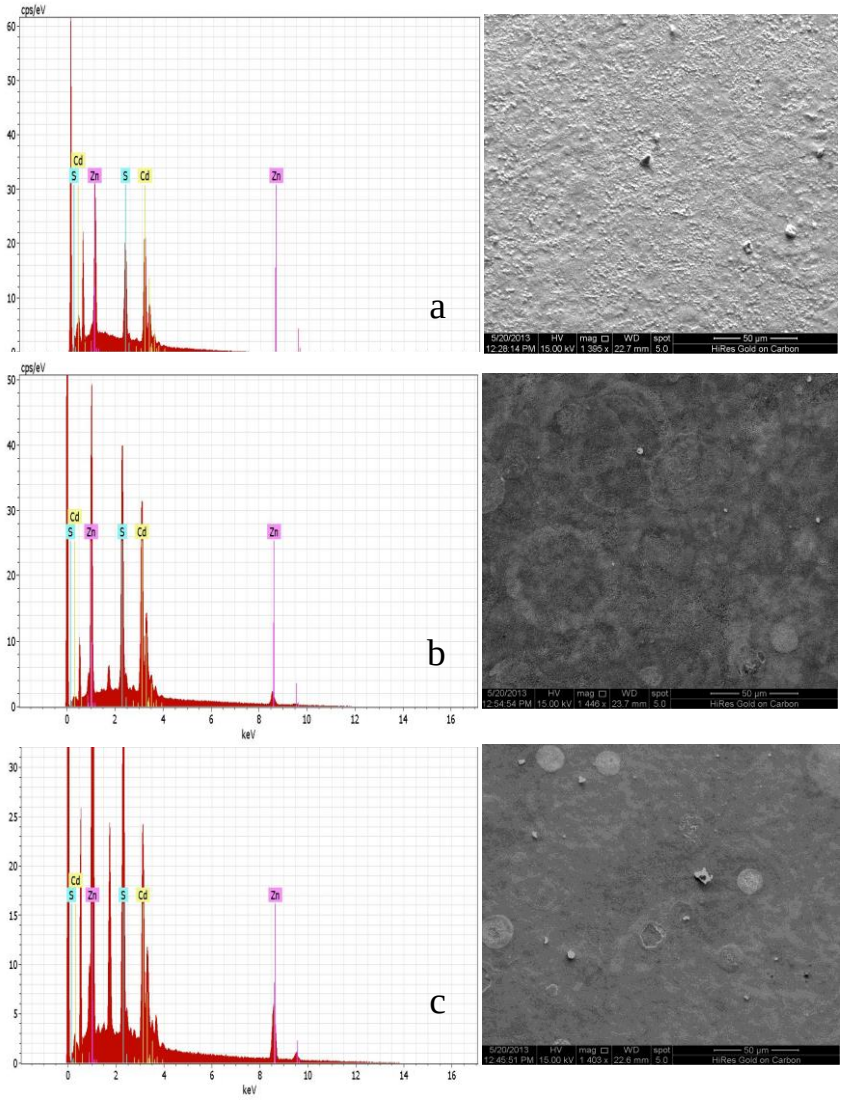

Fig. 5 (a, b, c) SEM and EDX images of ***$Cd_xZn_{1-x}S$/glass*** *thin films as a function of Cd composition (a) 0.3, (b) 0.5, and (c) 0.7.*

Surface Texture Analysis

Atomic force microscopy (AFM) is well suited for visualize the surface texture of the deposited CdxZn1-xS thin film, especially when the surface feature sizes are far below one micron. Figure 6 shows the AFM images of the $Cd_{0.5}Zn_{0.5}S$ thin films on glass, substrates. Measuring the surface texture of $Cd_xZn_{1-x}S$ thin films with horizontal length scale of less than 10 microns and a vertical length scale of 500 nm is critical for optoelectronic applications. The surface roughness profile was drawn by using the imager 4.62 software. Our investigated results show deposited of $Cd_{0.5}Zn_{0.5}S$ thin film on glass substrates exhibits the smooth surface texture with roughness 3.48 nm and root mean square 4.64 nm.

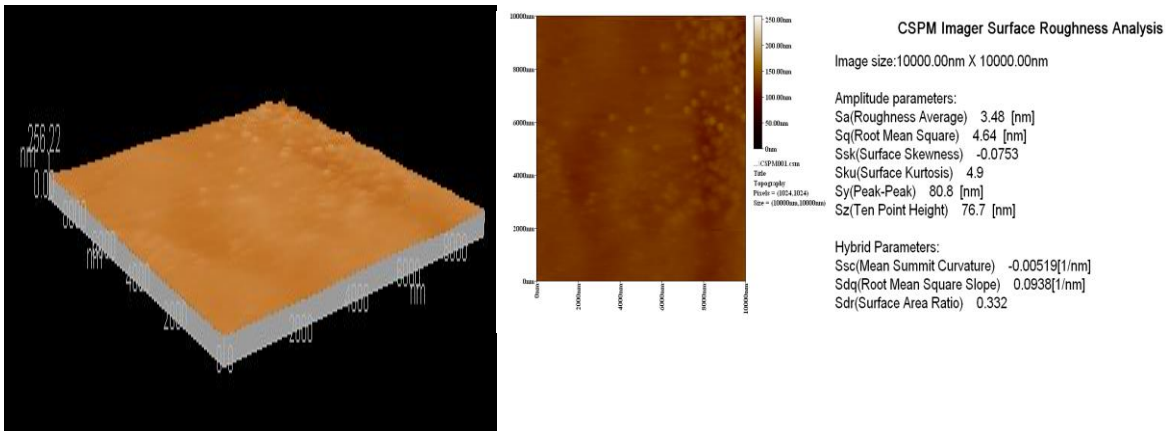

Fig. 6 show AFM images of $Cd_{0.5}Zn_{0.5}S$ thin film deposited on glass substrates.

Table 1. The x-ray data analysis data of $Cd_xZn_{1-x}S$ as a function of Cd composition.

No.	Compound *x*	2Θ	d(Aº) Observed	(hkl)	a (ºA)	c(ºA)	Grain size(nm)
1	**0.7**	24.91	3.570	(100)	4.097	6.655	37.3389
2		26.58	3.350	(002)			**29.1532**
3		28.27	3.153	(101)			23.2854
4		31.52	2.835	(105)			68.8231
5		43.87	2.061	(110)			29.5469
6		47.95	1.895	(110)			28.9960
7		52.03	1.756	(112)			46.5497
8	**0.5**	25.35	3.510	(100)	4.053	6.607	12.7294
9		26.96	3.303	(002)			**12.7650**
10		28.70	3.107	(101)			10.7951
11		31.78	2.813	(105)			22.9558
12		34.29	2.612	(106)			18.9044
13		36.13	2.483	(0010)			19.0010
14		44.66	2.027	(110)			15.9123
15		48.52	1.874	(110)			54.4888
16	**0.7**	25.6	3.586	(100)	3.917	6.82	60.3768
17		26.10	3.359	(002)			**33.9788**
18		27.48	3.2	(102)			86.1312
19		28.64	3.12	(008)			63.1015
20		31.86	2.76	(105)			77.5397
21		34.32	2.61	(106)			42.6596
22		36.13	2.49	(0010)			55.7362

Conclusion:

$Cd_xZn_{1-x}S$ thin films had been deposited by CSP method at 400°C substrates. The XRD studies showed that the hexagonal phase of the $Cd_xZn_{1-x}S$ thin films with preferred orientation (002) and the

intensity of (002) of XRD patterns for composition x=0.5 and x=0.7 significantly increased as compared to intensity of (002) peak of 0.3 compositions, which gives the lattice matching to the chalcogenide semiconductors used in solar cell devices. The grain size of the $Cd_xZn_{1-x}S$ increased with increase in Cd composition which is related to the substitution of Zn^{2+} for Cd^{2+}, average grain size value indicated that the prepared films were a nanocrystalline. The lattice constant values for all $Cd_xZn_{1-x}S$ thin films increased with the increase Cd, confirming the increase of the unit cell size .The SEM images showed the smooth morphology of $Cd_xZn_{1-x}S$ thin films was observed which indicated that the size of the particles decreased with increased in Zn concentration. While the $Cd_{0.5}Zn_{0.5}S$ thin film showed uniformed surface with few defects in which its reflected that this concentration is better as compared to other Cd compositions. The AFM images showed the smooth surface texture was observed in the deposited of $Cd_{0.5}Zn_{0.5}S$ thin films on glass substrate.

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