

Studying the Effects of Thermal Neutrons Irradiation on CuInGaSe₂ Thin Film

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Abstract

In this study, thermal evaporation method was used for coating CIGS thin film with about 1649 nm on a Mo layer of about 560.6 nm which in turn deposited by RF/DC sputtering method on a soda lime glass substrate. Then the samples were irradiated by an alpha neutron source ²⁴¹AmBe for continuous five days irradiation to reach a neutron flux about 9×10^{10} n.cm⁻².s⁻¹ which is necessary to activate elements of the sample, then samples annealed at 200 °C temperature in vacuum ambient at about 3×10^{-5} Torr. A structural, morphological and topographical analysis were conducted and accordingly the samples were characterized by means of XRD, SEM, EDS and AFM. As a result of thermal neutron irradiation, elemental constituent of CIGS slightly transmuted to new elements. Because of the impact energy of the neutrons the XRD peaks are changed and thin film surface average roughness factor increased to 7.97.

Keyword: CIGS (Copper, Indium, Gallium, Selenium), Irradiation, Deposition, Transmutation

دراسة تأثير التشعيع بالنيوترونات الحرارية على الاغشية الرقيقة نوع CuInGaSe₂

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الخلاصة

في هذه الدراسة استخدمت طريقة التبخير الحراري لطلاء الغشاء الرقيق نوع CIGS بسمك بلغ 1649 نانومتر تقريبا فوق طبقة من المولبدينيوم بسمك 560.6 نانومتر والتي تم ترسيبها بطريقة الرش/التردد الراديوي على لوح زجاج مختبري. تم تشعيع النماذج بواسطة مصدر نيوتروني نوع أمريشيوم - بريليوم - 241 وهو احد المصادر النيوترونية الباعثة لالفا لخمس أيام متواصلة من التشعيع لغرض الحصول على فيض نيوتروني بحدود 9×10^{10} نيوترون/سم²/ثانية. هذا الفيض ضروري لحدوث تنشيط العناصر الموجودة في النموذج المشع. بعدها تم تسخين النماذج لدرجة 200 سيليزي في بيئة مفرغة من الهواء عند ضغط سالب بحدود 3×10^{-5} Torr. أخضعت النماذج الى أختبارات البناء البلوري والتوصيف السطحي والتركيبية وأستخدمت كل من تقنية حيود الاشعة السينية وتقنية الانبعاثات الثانوية في المجهر الالكتروني وتقنية مطيافية الطاقة المتبددة إضافة الى تقنية مايكروسكوب القوى الذرية. وقد نتج عن عملية التشعيع بالنيوترونات البطيئة او الحرارية تحول عناصر بعض مكونات النماذج المشعة الاساسية الى عناصر جديدة. لوحظ من خلال استخدام تقنية حيود الاشعة السينية أن طاقة النيوترون ساهمت بتغيير قمم الاشعة السينية كما أن معدل عامل خشونة السطح قد ازداد بمقدار 7.97.

كلمات مفتاحية: CIGS (نحاس، إنديوم، كالسيوم، سيلينيوم)، تشعيع، ترسيب، تحول

Introduction

CIGS is a semiconductor and one of the ternary compounds which are representing in the form I-III-VI₂, these materials crystallizes in chalcopyrite structure with a centered tetragonal unit cell and with a lattice shape like a diamond [1], [2]. Due to CIGS thin film based solar cell properties in which the constitutional elements properties can be adjusted by replacing Indium by gallium or/and replacing selenium by sulfur to form Cu (In, Ga) (S, Se)₂. This flexible composite gives this compound an interest in the recent years, especially CIGS thin film based solar cell showed a long-term stability, relatively high conversion efficiency, less using materials, light weight, and high radiation resistivity. that's the reason behind this study which is to investigate the effect of neutron irradiation on CIGS thin film [3]. ionization and displacement defects are the main two mechanisms of radiation effects on semiconductors. The initial effect of radiation is to produce a single damage acts as single displaced lattice, called as Frankel Defect [4]. While the radiation effect by neutron is producing a specific damaged zone called clusters, each point defect is considered an energy states within the forbidden gap, accordingly, several changes can be expressed within the forbidden gap such as mobility degradation, conductivity modulation and minority life time degradation [5]. Neutrons are interacting with nucleus indirectly causing an atomic displacement, and they do not interact with the atomic electrons which are responsible for conductance, non-conductance behavior and other electrical properties. neutron rest mass about 1.00866 amu, it has two down quarks and one quark up, neutron electric charge equal to zero, its half-life is 10.4 minutes when it outside the nucleus. neutron fluence rate can be defined as number of

neutrons passes through a specific area per sec. ($n \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$). cross section of the neutron can be defined as the probability of interaction between the incident neutron and the target nucleus measured in barn (1 barn = 10^{-24} cm^2). It penetrates in matter until it undergoes a strong interaction with a nucleus. Because of the clear difference in the behavior of the neutrons, it can be refer to neutrons as 'high-energy neutrons', 'fast neutrons' and 'slow neutrons', depending on their energy. High-energy neutron means a neutron with energy larger than 1 GeV. For fast neutrons, the most probable way of interacting is by elastic scattering on the nuclei of the medium. The energy loss of neutrons is mainly due to elastic scattering, and for slow neutrons the most probable interactions are elastic scattering and neutron capture. But neutrons can also interact in other ways with nuclei:

(1) Inelastic scattering: the nucleus is left in an excited state, which later decays by gamma emission or some other forms of radiation. This process will only become significant for neutrons with more than 1MeV of energy.

(2) Radiative neutron capture: the nucleus absorbs the neutron and finds itself in an excited state, which decays by gamma emission.

(3) Neutron capture followed by emission of a charged particle or followed by fission. For many isotopes the capture cross section is inversely proportional to the speed of the neutron, and becomes very large for thermal neutrons (Interactions of neutrons with matter) [6]. This work aims to study the effects of thermal neutrons on the structure and surface morphology of CIGS thin films. A structural, compositional and topographical properties were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) and atomic force microscopy (AFM).

Experimental Detail Materials

Soda lime glass was used as a substrate, molybdenum (Mo) was used as back contact material, A pure Mo (99.95%) with 2.00 inch diameter and 0.250 inch thickness from Kurt, J, Lesker Company. high purity (99.99%) constituent elements Cu, In, Ga and Se were deposited together by using thermal evaporation method to form the CIGS thin film.

Preparation Method

After finishing the glass substrate cleaning, molybdenum (Mo) is a common used as a back contact metal among other metals such as Pt, Ag, Au and Cu. Because its stability against temperature, a good resistance for alloying with Cu or In and the typical low resistance value of Mo is about $5 \times 10^{-5} \Omega \text{ cm}$ (while the desired resistance value is lower than $0.3 \Omega \text{ cm}$) [7]. Mo thin film deposition process was conducted in Hydrogen Technology Research and Application Center Laboratory at physics department of Süleyman Demirel University ISPARTA-TURKEY. By using RF/DC magnetron sputtering system, VAKSIS 4T1M. Two layers structure of Mo were used to enhance the adhesion of the absorbance layer to the back contact. A quartz crystal monitor was used to monitor the thickness of the deposited film by means of in-situ measurements which was 560.6 nm for two deposition layers, argon (Ar) gas was used as a sputter gas, a mass flow controller was used to control the gas flow rate [8]. The deposition process of Mo thin film started with evacuating the main chamber of VAKSIS system to a negative pressure around 1×10^{-5} Torr. the CIGS absorber thin film growth was carried out by thermal evaporation method for the high purity (99.99%) constituent elements Cu, In, Ga and Se of CIGS thin film were produced and analyzed at Hydrogen Technology Research and Application

Center Laboratory at physics department of Süleyman Demirel University ISPARTA-TURKEY. CIGS is a semiconductor type, tetrahedrally bonded transformed to zinc blende form by heating.

In thermal evaporation process the source material will be heated, therefore, the surface atoms of the source will travel in a straight line towards the substrate surface, at this time the atoms will adhere to the substrate due to the low vapor pressure near this surface, and the thickness of the deposited film depends on the geometry of source/substrate, temperature of heating and evaporation time[9].

Characterization Technique

Different analytical techniques which includes XRD (Bruker D8 Advanced Twin-Twin), SEM (FEI Quanta FEG 250), EDS (EDAX) and AFM (Nanomagnetics ez-AFM) were used for structural and morphological analysis of grown CIGS thin films after neutron irradiation and annealing. The CIGS thin films were deposited by using thermal co-evaporation method by using VAKSIS 4T1M physical vapor deposition system. The samples were irradiated by an alpha neutron source type ($^{241}\text{AmBe}$) with a neutron flux about $2.1 \times 10^4 \text{ n.cm}^{-2}.\text{s}^{-1}$ for five days irradiation to reach a cumulative neutron flux about $9.01 \times 10^9 \text{ n.cm}^{-2}.\text{s}^{-1}$. Finally, the irradiated samples were annealed under vacuum at temperature of $200 \text{ }^\circ\text{C}$. The XRD results of grown films confirmed the CIGS chalcopyrite structure belong to PDF 00-062-0057 chalcopyrite CIGS with lattice parameters; $\mathbf{a} = 5.68030$, $\mathbf{c} = 11.29090$, with a preferred orientation of 112 peak corresponding to CIGS compound. Tetragonal lattice orientation, through a comparison were performed between the reference theoretical pattern and the experimental diffraction curve peaks which are listed in table (1) and shown in figure (1).

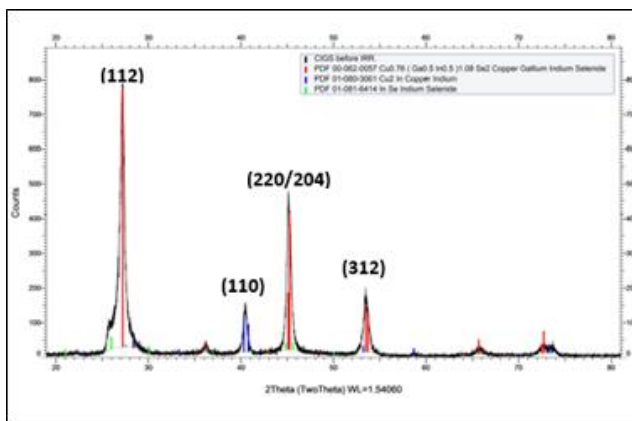


Figure (1) Crystallinity of as Deposited CIGS thin film

Table (1) The Crystal Parameters of as Deposited CIGS thin film

* 2θ (Degree)	** d value (Å)	Intensity	hkl
27.227	3.27270	999	112
45.109	2.00828	222	220
45.256	2.00210	522	204
53.490	1.71170	180	312

* θ is the angle of incidence

**d is the interplanar spacing of the crystal

According to the experimental details there is a relationship between the displacement energy and lattice constant in which the displacement energy is inversely proportional to the lattice constant [10]. Which means as much as low lattice constant as much more displacement energy required. After neutron irradiation there was very small change in the results of 2θ, d value a, FWHM, and XRD Intensity. The reason

might be this; the thermal neutron does not destroy the crystal structure of the irradiated CIGS thin film sample which can be seen in Figure 2.a). After annealing at 200 °C there was an increase in peaks intensity, this indicates that the crystalline behavior of the CIGS film was improved by increasing temperature [11]. Figure 2.b) shows the annealing effect on the CIGS thin film and related parameters are listed in Table (2).

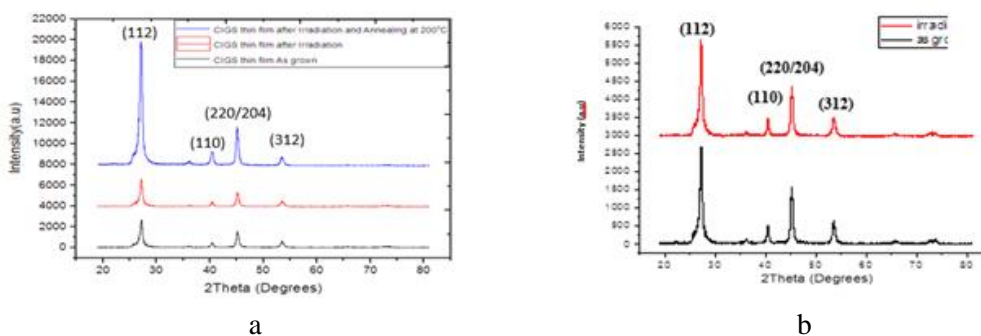


Figure (2) CIGS thin Film Crystallinity

a) After Thermal Neutron Irradiation and

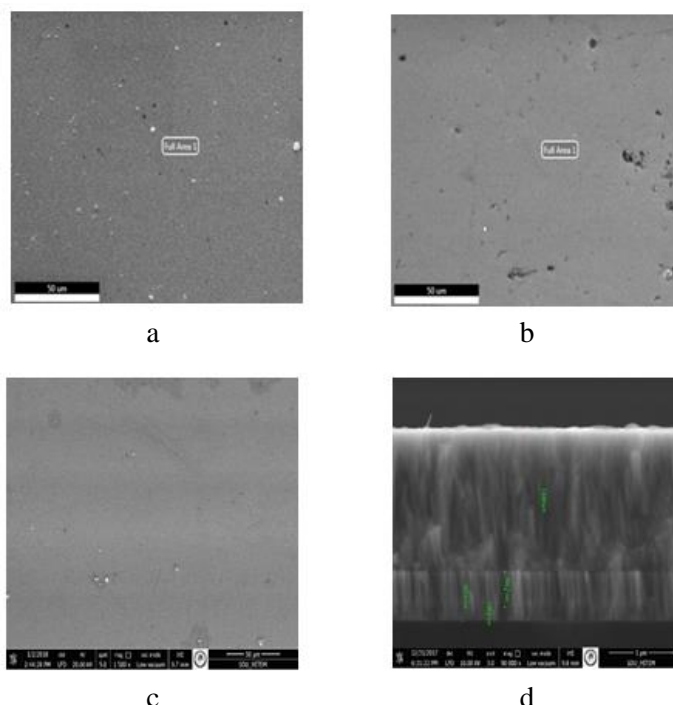
b) After Annealing at 200°C

Table (2) The Crystal Parameters of Neutron Irradiated and Annealed CIGS thin film

2 θ			FWHM			XRD Intensity Value		
Deposited film	Irradiated film	Annealed at 200°C	deposited film	Irradiated film	Annealed at 200°C	deposited film	Irradiated film	Annealed at 200°C
27.227	27.114	27.074	0.499	0.463	0.491	2397	2388	2831
53.490	53.549	53.507	0.622	0.687	0.677	583	479	191
65.684	65.746	65.663	0.456	0.483	0.508	84.5	69.0	16.3

SEM images shown in figure (3) showed a good coverage of CIGS absorber layer with approximately 1649 nm thickness deposited on Mo layer of about 560.6 nm (Figure 3.d). There was a very small change in the sample surface after neutron irradiation through the glassy and shiny

surface may be it has attributed to the rapid increase of surface temperature due to neutron flux bombardment. After annealing at 200 °C in a vacuum ambient the sample texture is slightly transformed to grain boundary [12].

**Figure (3)** SEM surface images of the CIGS thin film

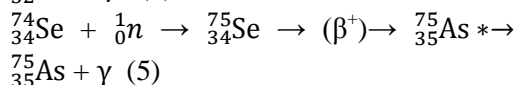
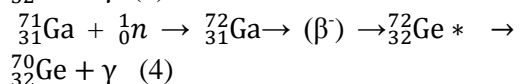
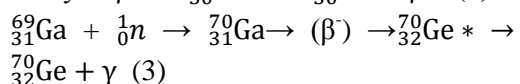
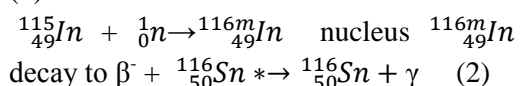
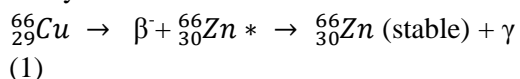
a) Deposited Film **b)** After Neutron Irradiation **c)** Neutron Irradiation + 200 °C Annealing **d)** Cross Sectional Image of CIGS and Mo Layers

The energy dispersive X-ray spectroscopy (EDS (EDAX)) which is attached to SEM system was used to determine elemental composition of CIGS thin films. By EDS system it is possible to perform analysis which includes spectrum showing peaks related to elements of the composition with true composition percentages. Furthermore, elements

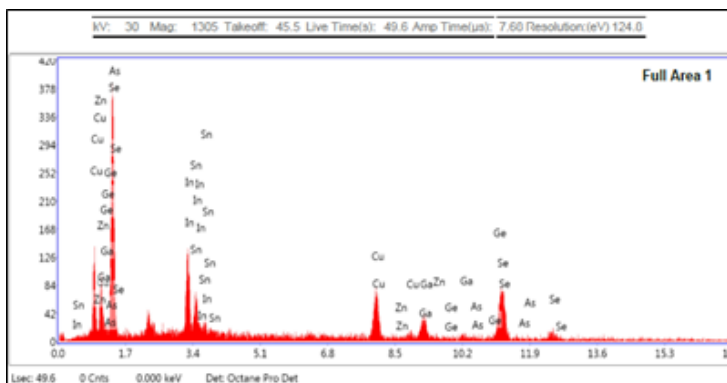
mapping and image analysis of the specimen, were available.

The EDS results and elemental composition of the as deposited, irradiated and annealed CIGS thin films respectively are shown in Figure (4). The elemental composition for deposited CIGS thin film, after neutron irradiation, and after annealing are shown in Figure 5. Tables (3, 4 and 5) shows the weight % of as

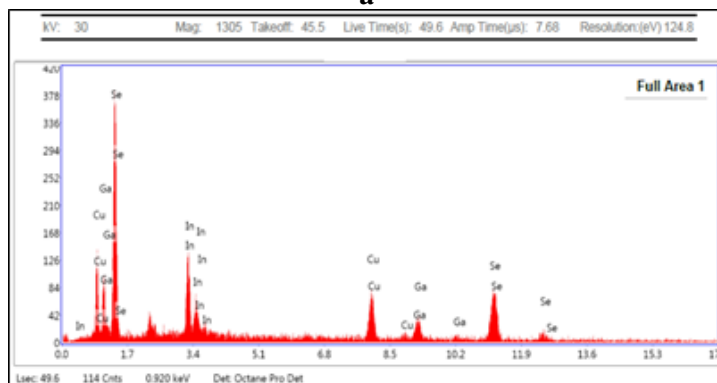
deposited, irradiated and annealed CIGS thin film elements respectively. After neutron irradiation, a new element with a higher mass number should be created after capturing a thermal neutron by the nucleus of the original element this called neutron transmutation doping [13]. Concerning the CIGS thin film, when a natural Cu, In, Ga and Se were irradiated by thermal neutrons, after neutron absorption, the proposed new elements were formed according to the following interactions. (1), (2), (3), (4) and (5). ${}^{65}_{29}\text{Cu} + {}^1_0\text{n} \rightarrow {}^{66}_{29}\text{Cu} + \gamma$ then the nucleus ${}^{66}_{29}\text{Cu}$ decayed to:



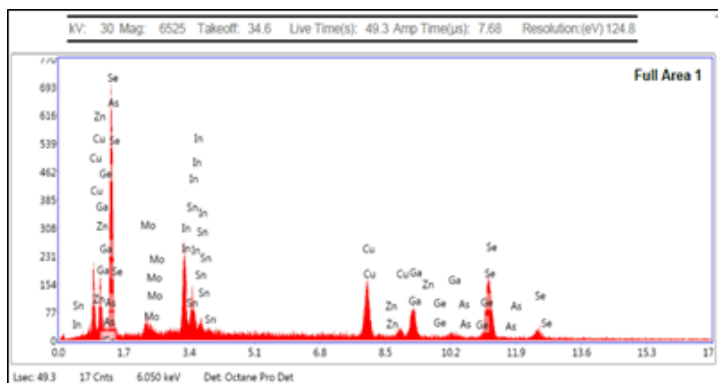
The resulted elements are (${}^{66}\text{Zn}$, ${}^{116}\text{Sn}$, ${}^{70}\text{Ge}/{}^{72}\text{Ge}$ and ${}^{75}\text{As}$) all of them are stable elements. Figure 4. b). 5. b). Table 4. the weight % of original elements were decreased after neutron irradiation. That's give an indication of transmutation effect caused by neutrons. After annealing the CIGS thin film was measured again to examine any changes could may occur in the chemical composition. Accordingly, there was a slight decrease of weigh % values for all elements after annealing at 200 °C. This may have attributed to the effect of annealing temperature on the film because the incident neutron may change the film properties such as producing voids, dislocations, impurities, film temperature rising during neutron irradiation and transmutation. it is clear that the post-annealing process trends to relocate atoms by making element diffusion more easily and more uniform [14]. Also annealing can reduce the mismatching in lattice which finally increases device performance [15].



a

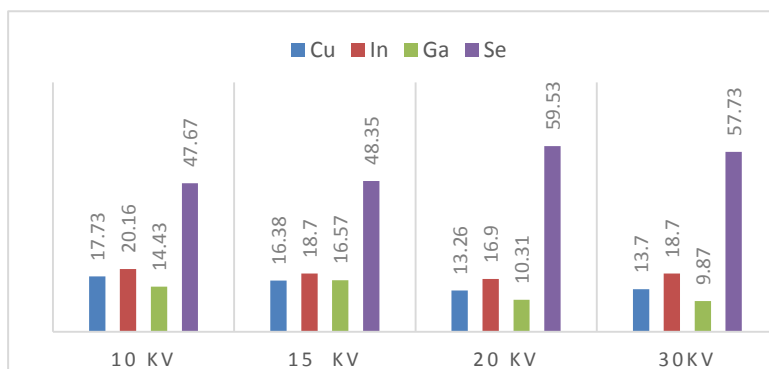


b

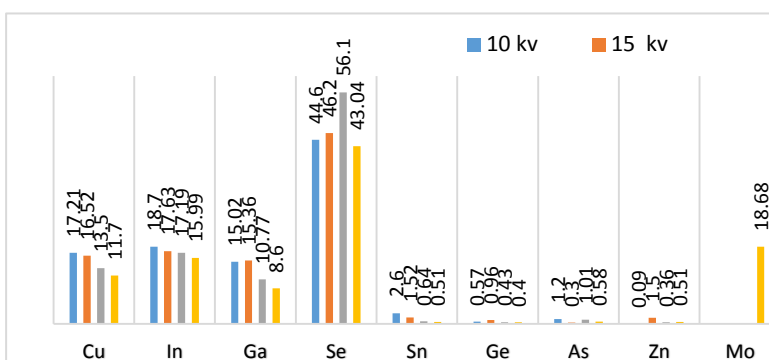


c

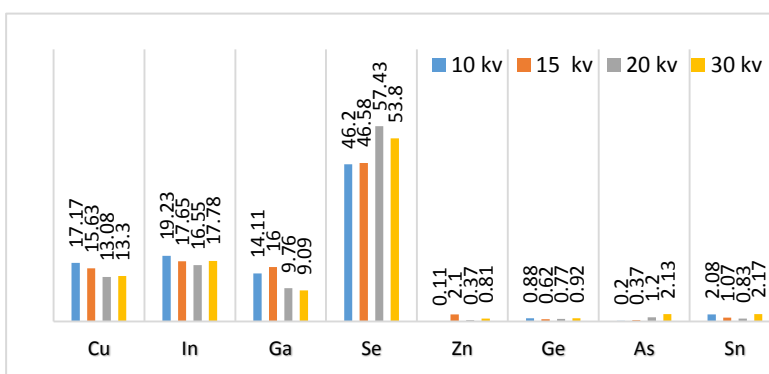
Figure (4) EDS Results, a) deposited film, b) after irradiation and c) after annealing



a



b



c

Figure (5) The Elemental Composition of as Deposited CIGS thin film

a) Deposited b) After Neutron Irradiation and c) After Annealing

Table (3) The Weight % of deposited CIGS thin film

Scan power	10 kV		15 kV		20 kV		30 kV	
Element	Weight %	Error %	Weight %	Error %	Weight %	Error %	Weight %	Error %
Cu	17.73	10.94	16.38	25.24	13.26	15.91	13.70	9.41
In	20.16	26.85	18.70	16.81	16.90	14.75	18.70	13.26
Ga	14.43	14.12	16.57	12.56	10.31	24.21	9.87	12.80
Se	47.67	7.85	48.35	7.72	59.53	18.14	57.73	6.82

Table (4) The Weight % of CIGS thin film after neutron irradiation

Scan power	10 kV		15 kV		20 kV		30 kV	
Element	Weight %	Error %	Weight %	Error %	Weight %	Error %	Weight %	Error %
Cu	17.17	11.40	15.63	23.84	13.08	15.42	13.30	10.21
In	19.23	26.63	17.65	16.91	16.55	13.84	17.78	14.19
Ga	14.11	13.80	16.00	12.47	9.76	23.12	9.09	17.77
Se	46.20	8.07	46.58	7.85	57.43	18.26	53.80	6.97
Zn	0.11	99.99	2.10	73.01	0.37	73.69	0.81	62.43
Ge	0.88	85.35	0.62	89.66	0.77	75.39	0.92	64.37
As	0.20	99.99	0.37	99.99	1.20	71.11	2.13	60.23
Sn	2.08	65.06	1.07	66.32	0.83	65.60	2.17	49.85

Table (5) The Weight % of CIGS thin film after annealing at 200 °C

Scan power	10 kV		15 kV		20 kV		30 kV	
Element	Weight %	Error %	Weight %	Error %	Weight %	Error %	Weight %	Error %
Cu	17.21	9.47	16.52	17.68	13.50	13.55	11.70	7.03
In	18.70	21.09	17.63	13.68	17.19	63.10	15.99	10.02
Ga	15.02	11.37	15.36	11.35	10.77	15.90	8.60	11.07
Se	44.60	7.25	46.20	7.29	56.10	11.69	43.04	5.68
Sn	2.60	61.40	1.52	60.88	0.64	63.10	0.51	67.13
Ge	0.57	86.29	0.96	74.49	0.43	72.08	0.40	65.80
As	1.20	73.31	0.30	99.99	1.01	68.24	0.58	63.12
Zn	0.09	99.99	1.50	69.08	0.36	67.64	0.51	61.79
Mo							18.68	47.66

According to the elemental results for CIGS thin film materials, there was a small percentage of the transmuted elements have been noticed. The reason is attributed to many factors such as; neutrons cross section for each element, in which the probability of neutron interaction may increase or decrease. And the density of the entire element also it's an important factor for occurring such an interaction, also the concentration of the deposited film and the film thickness. All those conditions must be considered when somebody need to get this type of semiconductor doping by neutron transmutation. Studying the surface

morphology of thin film is so important issue, due to its impact on electrical and/or optical properties of thin film. AFM measurement was carried out for this study and measurement parameters are given in Table 6. In this work AFM images show a good homogeneity and smoothness with a few grains distributed in non-systematic way. It is reported in the literature that the light absorption via thin film surface increase with the increasing surface roughness, due to surface reflectance decrease more light will penetrate and trapped into the film, in this way they increased the film efficiency.

Table (6) The AFM measurement parameters

Tip quality factor	470
Osc. Amp.	2V
Laser power	1.5V
Scanning time	30 min.
Scan Area	5 × 5 μm

The AFM results can explain many aspects related to surface topography such as surface roughness and lower transmittance highlight scattering.

Figures (5, 6 and 7) show the 2D/3D images of the as grown, irradiated and annealed CIGS thin film.

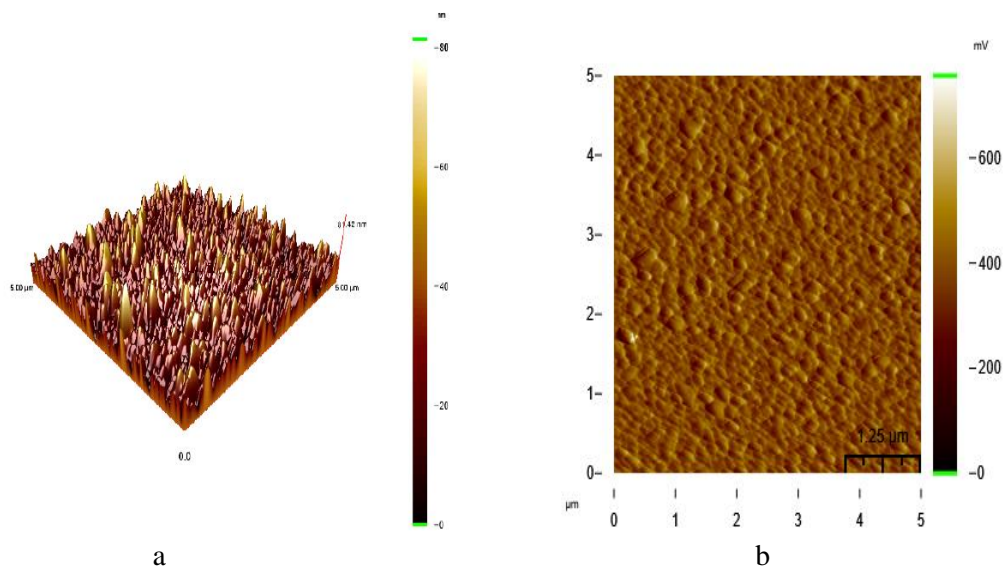


Figure (6) AFM images for deposited CIGS thin film a) 3D and b) 2D

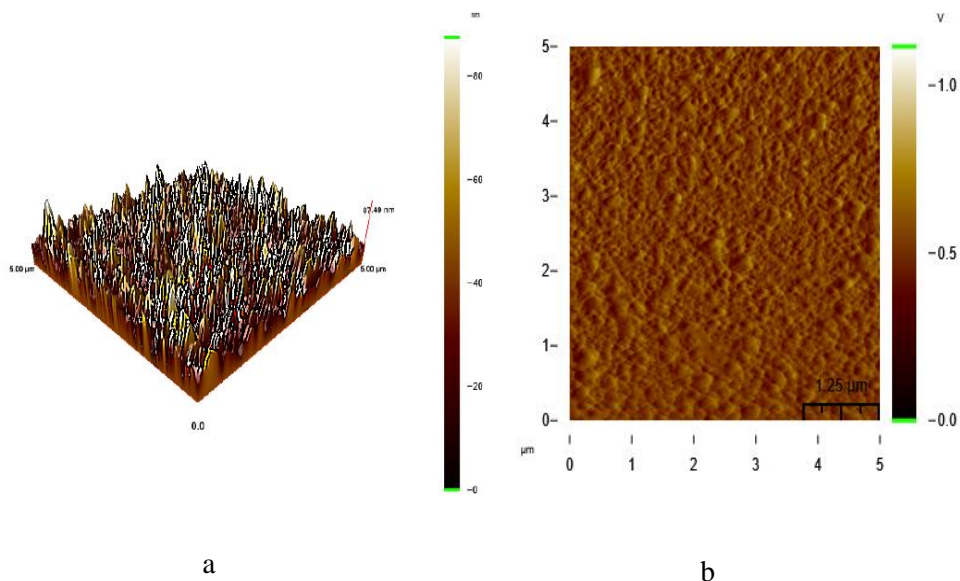


Figure (7) AFM Images for the Irradiated CIGS thin film a) 3D and b) 2D

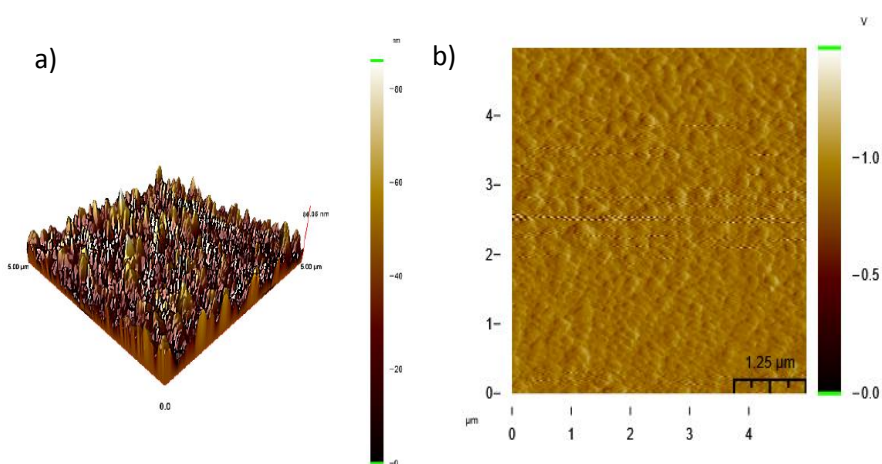


Figure (8) AFM images for the irradiated and annealed CIGS thin film a) 3D and b) 2D

From Figures 5, 6 and 7, we observed that the average roughness and root mean square of CIGS thin film were increased after neutron irradiation with about 1.68 nm and 2.15 nm respectively. This increase can be attributed to the neutron impact on sample surface, where the neutron flux bombardment could rise the surface temperature which in turn reform the surface topography. After annealing the diffusion of atoms resulted island formation by coalescence of neighbor island driven by thermal energy

that acquired from annealing temperature [16], as a result the crystallinity of the film was improved and the surface became smoother and the grain boundaries obtained from AFM images are in accordance with those resulted from XRD and SEM measurements. Table (7) illustrates the AFM parameters for the measured film.

Table (7) The AFM Parameters for the measured film

No.	AFM parameters for CIGS thin film	Average Roughness R_a (nm)	Root mean square R_q (nm)
1	Deposited thin film	6.29	8.15
2	After neutron irradiation	7.97 ↑	10.30 ↑
3	After annealing at 200 °C	7.60 ↓	9.75 ↓

Conclusion

After neutron irradiation there was a small decrease in the results of 2θ , d value a , FWHM, and intensity due to neutron irradiation effect. A very small decrease in the parent nucleus (Cu, In, Ga and Se) which they were transmuted into (^{66}Zn , ^{114}Sn , $^{70}\text{Ge}/^{72}\text{Ge}$ and ^{75}As) respectively after neutron irradiation. After annealing at 200 °C the crystalline behavior of the CIGS film was improved and a polycrystalline behavior was slightly observed which may increase the thin film performance. SEM images showed a good coverage of CIGS absorber layer. The XRD results of the deposited films

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