Tikrit Journal of Pure Science Vol. 26 (2) 2021

TJPS

IASJ

المجلات الاكاديمية العراقية

Tikrit Journal of Pure Science

ISSN: 1813 – 1662 (Print) --- E-ISSN: 2415 – 1726 (Online)

Journal Homepage: http://tjps.tu.edu.iq/index.php/j

Preparation CdSe thin films by vacuum thermal evaporation and studying the effect of annealing time on structural, electrical and optical properties.

Kawkab D. Salim , Hanan Ridha

Department of Physics, College of Education for Pure Sciences, Tikrit University, Tikrit, Iraq

https://doi.org/10.25130/tjps.v26i2.123

ARTICLE INFO.

Article history:

-Received: 8 / 11 / 2020

-Accepted: 21 / 12 / 2020

-Available online: / / 2021

Keywords: Thin films, X-ray diffraction (XRD), vacuum thermal evaporation.

Corresponding Author:

Name: Kawkab D. Salim

E-mail: kawkab_badri@tu.edu.iq

Tel:

ABSTRACT

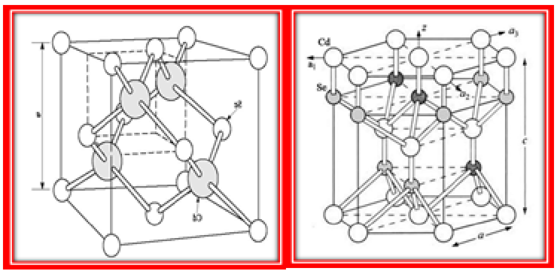
CdSe thin films were deposited on a glass substrate by using vacuum thermal evaporation technique. The deposited films were annealed to 350°C for (10, 20, 30) minutes respectively. Structural, morphological, optical and electrical properties of the films were studied by using X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy; and Atomic force microscope (AFM). The X-ray diffraction pattern showed that the film has a cubic phase with preferred orientation (111), the grain size was found to be in the range of(31-46)nm. The UV tests explain that the energy bandgap decrease with increasing of annealing time from 2.43eV to 2.17eV after 20minute annealed.

1- Introduction

CdSe is a semiconductor from (II-VI) group, and it belongs to the (Chalcoginides) group. It has two phases; the first one has a cubic phase and called (Sphalerite), the second has a hexagonal phase (called Wurtzite) [1, 2]. The first structure is unstable (metastable phase) and is formed mainly from the electrochemical process, while other has a stable thermodynamic structure which is indirectly formed by annealing the cubic phase process or directly by other methods of preparation [3].

There are Four cadmium atoms (Cd) are associated with one atom of selenium (Se) with equal length bonds and the length of the closest contact between Cd and Se is equal to both the cube and hexagon. Selenide Cadmium CdSe is a donor semiconductor type (n-type). Both w.CdSe and c.CdSe have a direct energy gap. The refractive index and the coefficient of inertia as well as the absorption coefficient are a function of the wavelength in the high absorption areas [4,5].

The first successful attempts to develop Crystals (CdSe) came from Frerichs, where the gas phase reaction between cadmium (Cd) and selenium(Se) halide was used[6]. The best method used to obtain a single crystal of (CdSe)was of good quality using Bridgman-Stockbarger techniqueBy (Rais Enterprises), and CdSe thin films can be deposited in more than one way, including Evaporation Vacuum, Hot-Wall Flash Evaporation, Molecular Beam Deposition, Electrodeposition, chemical bath deposition, Sputtering [7,8]. And because of CdSe has a high absorption factor and has suitable optical properties, its thin films have many applications, including High efficiency solar cells, Photo detectors, Thin Film Transistors, Sensor Gases, Gamma-ray detectors [9].



a b

Fig. 1: Crystalline structure of Selenide cadmium, (a) cubic phase (b) hexagonal phase

2- Experimental

The thin films of the CdSe were prepared from the (German company, Fluka and Benqawa

(99.998%)) to achieve the equal weight ratio (50%: 50%) for both Cadmium (Cd) and Selenium (Se) respectively (Se_50 Cd_50) and (3gm) of the whole alloy using a sensitive electronic balance, type (Precisa) with four decimal grade.

The weights equal to 1.762gm and 1.238gm for cadmium and selenium respectively were placed in a quartz glass tube with an internal diameter of 1.1cm and 30 cm to avoid explosion due to high selenium vapor pressure. To be thoroughly cleaned by water and liquid soap followed by alcohol, CdSe thin films were prepared by applying a quantity of pure powder material that achieves the 300 nm thickness. The powder was put in Mo boat which has a cover to prevent volatilization of the thin film material during deposition. When the pressure reaches the maximum value10-5 mbar the deposition process begins; the first stage the electric current pass through the boat, and it must be notice that the increase in current is gradually and slowly to occur The thermal equilibrium within the bell while observing the pressure gauge, because the rapid rise in the degree of temperature leads to big pressure in the vacuum champer. After the deposition process is finished, the samples are left in the evaporative chamber until they reach a room temperature to ensure the completion of the crystallization process.

3- Result and discussion

Here, there is analyzes and discusses the results obtained from this study for the structural, optical and electrical properties of pure (CdSe)thin films that prepared by vacuum evaporation technology on glass bases at room temperature and with thickness of 300 nm and deposition average of (0.7 ± 0.1nm / sec).

1-3- Structural properties

The results of the X-ray diffraction test showed that all pure and annealed a CdSe at 350 for (10,15,20) minutes were monocrystalline, of CdSe (cubic) of the type with an atomic growth towards (111) as in figures (2,3,4,5). When comparing the results obtained from surface clearance d (hkl), crystalline reticle constants (a, c) and crystalline diffraction angles (2θ) corresponding to the peak positions of pure CdSe film with the values given in the numbered card (00-019-0191).The results were largely identical as shown in (table 1).

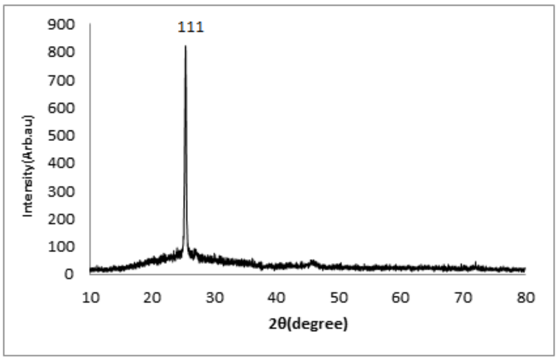


Fig. 2: XRD pattern of CdSe film before annealing

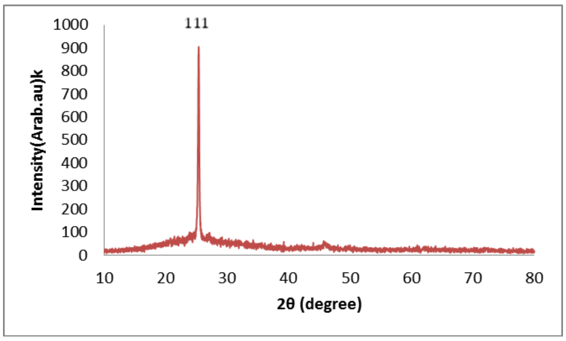


Fig. 3: XRD pattern of CdSe film after anneling at 350°C for10min

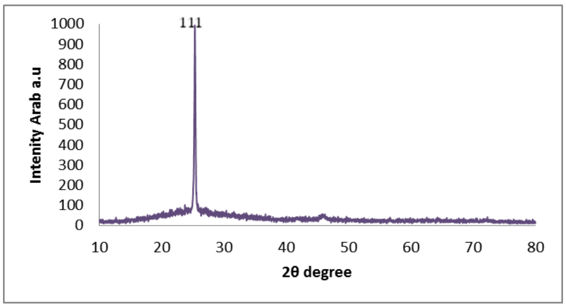


Fig. 4: XRD pattern of CdSe film after anneling at 350°C for15min

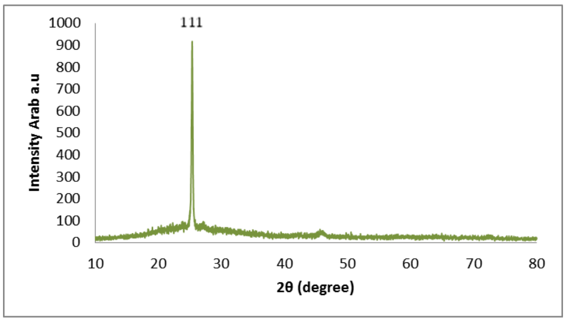


Fig. 5: XRD pattern of CdSe film after anneling at 350°C for20min

Table 1: some of XRD structural properties of CdSe Thin films prepared by thermal evaporation method

Annealing time (min)	2θ (degree)	d(hkl)	D (nm)	σ	ϵ
0	25.4098	111	31.84	0.000986	0.001136
10	25.4202	111	35.00	0.000816	0.001034
15	25.3912	111	37.30	0.000718	0.00097
20	25.011	111	46.18	0.000469	0.000784

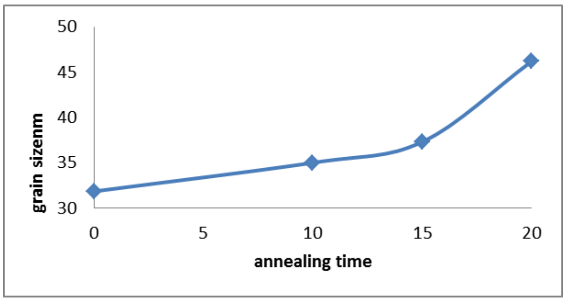


Fig. 6: The relation between grain size of CdSe paperd film by thermal evaporation method with the anneling time at 350˚C

As for the intensity, it turns out that there is a very clear increase in the intensity of the first characteristic directional summit (111). Thin films after annealing, where this increase in intensity refers to the increased degree of crystallization of the material and to improve the crystal structure. Figure(7) shows an(AFM) picture of prepared CdSe thin film before annealing process, the grain size was (66) nm. Also There are figures (8),(9) and(10) explain the effect of annealing time on the topography properties of prepared thin films, The AFM pictures declare that the value of grain size decreased with increasing the time of annealing for (10,15,20) minutes respectively. The grain size was 58nm after annealing for 10min, and54nm after annealing for15min and 61nm after annealing for 20 min.

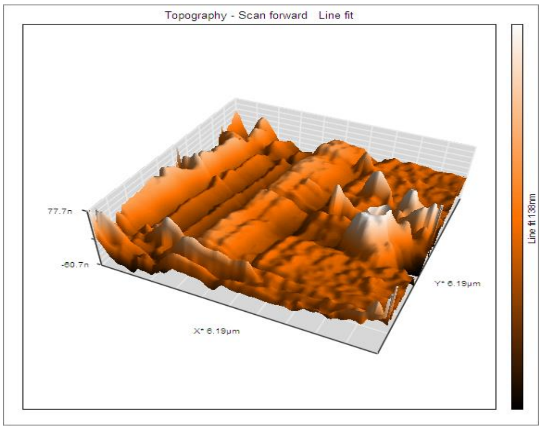


Fig. 7: AfM picture before annealing

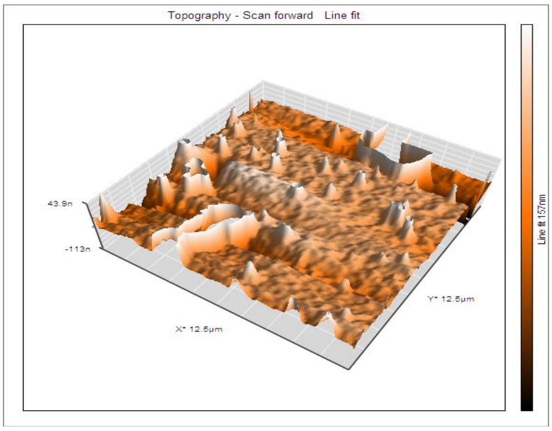


Fig. 8: AFM picture after annealing for 10min

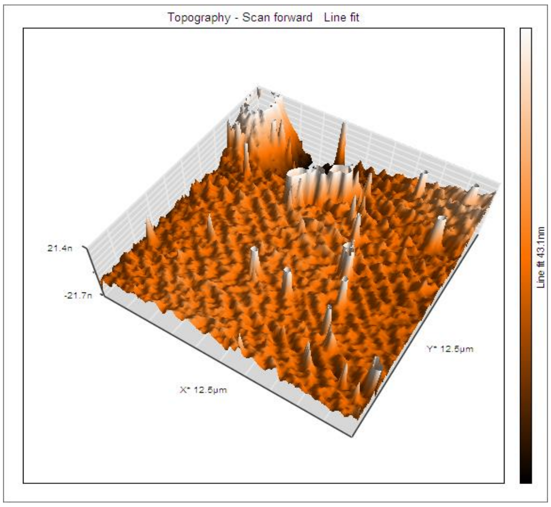


Fig. 9: AFM picture after annealing for 15min

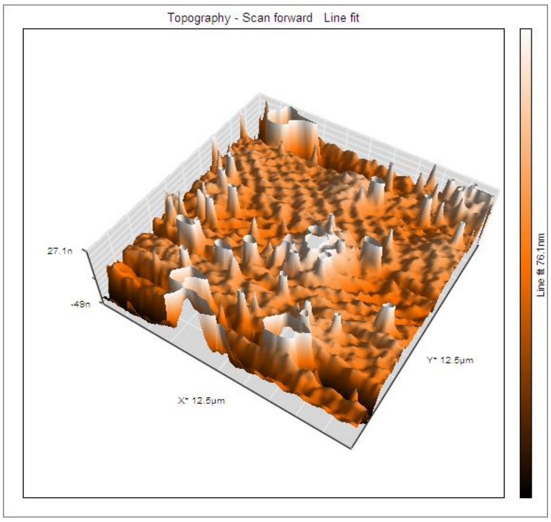


Fig. 10: AFM picture after annealing for 20min

3-2 Optical properties

Absorption spectrum measurements were made for prepared CdSe thin film befor annealing and after annealing at 350˚C for (10,15,20) minutes. Figure (11-a) shows the absorption spectrum change as a function of the wavelength of (CdSe) thin films prepared at a thickness of 600nm before annealing, It can be seen from the figure that the absorption spectrum behavior of any prepared thin film is as great as possible at short wavelengths (high photon energies) and then decreases when approaching long wavelengths. Figure (11-b) explains the behaviore f prepared thin films after they has annealed at 350˚C for (10,15,20) minutes, it is clear that all filmes had got decrease in the value of absorbtion that mean there is increaseing in the transmisiion which is it necessary for photovoltaic applications.

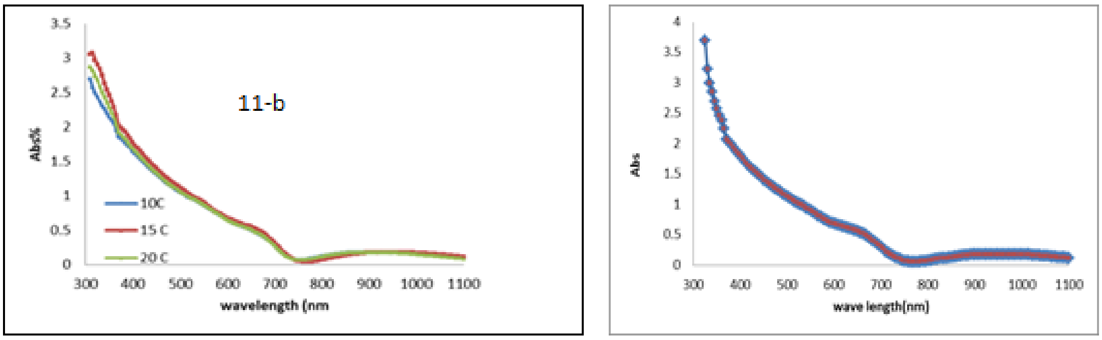


Fig. 11: (11-a) the absorption spectrum of prepared CdSe film by thermal evaporation method before annealing process, (11-b) Behavior of absorption spectrum of CdSe thin film after annealing at 350 for (10,15,20) minutes.

It was found from fig (12-a) that the energy gap value was equal to (2.43eV). The energy gap is shown by increasing annealing time, reaching a minimum value (2.17eV) after 20 minutes as in figs (12b,12c,12d) which that show the decreasing in the value of energygap afterannealing at350˚C for (10,15,20) minutes respectively. Fig(13) explains the relation between annealing time and the value of energygap; thus there is increasing in energy gap value with the time of annealing due to (Quantum size effect), i.e. if the grain size is much larger than the Bohr radius and equal to the half-ankstrom, then the quantum effect will appear and the energy gap value will change proportionally to the square of the grain radius according to the Schroedenker equation for any energy level[11].

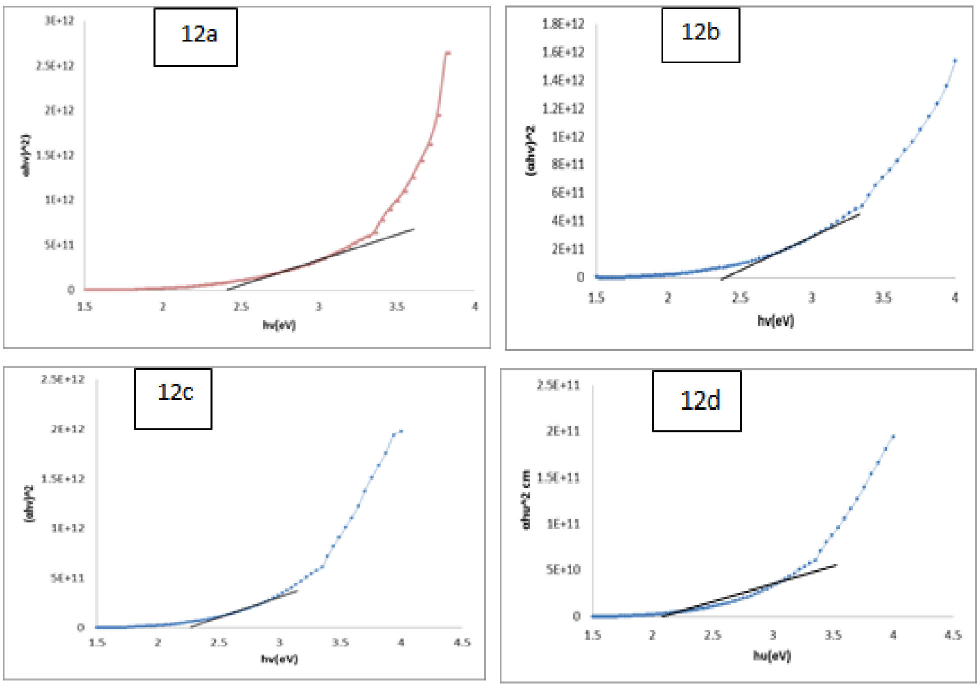


Fig. 12: the variable values of energygap of prepared CdSe by thermal evaporatiom method before annealing and after annealing at 350˚C for (10,15,20)minutes

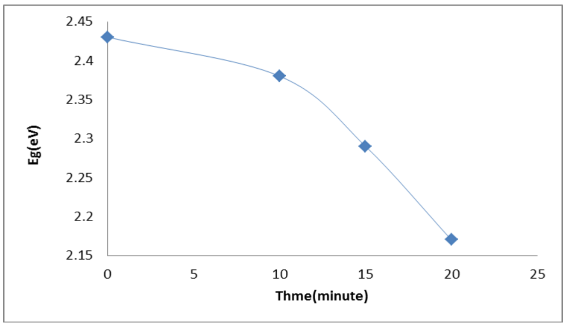


Fig. 13: the relation between annealing time and the value of energygap

3-3- Electrical properties

Figure(14b) illustrates the changing of electrical resistivity as a function of the absolute temperature invert of prapered pure (CdSe) thin films where it is clear from the figure that the resistance of films decreases with increasing time of annealing due to the presence of defects and dislocations and due to the decrease in the concentration of defects represented by (density of dislocations and micro-stresses formed by increasing annealing time.

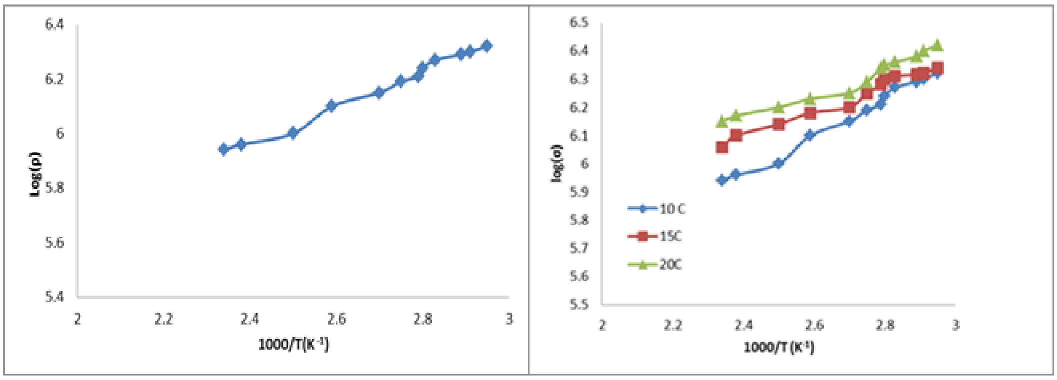


Fig. 14: (14-a) declare the electrical resistivity as a function of the absolute temperature before the annealing process, (14-b) explain the effect of annealing time on the relation between electrical resistivity and invert of absolute temperature.

Conclusion

The annealing process is a simple way to improve the properties of prepared thin film by different techniques, the effect of annealing time on CdSe thin film was studied and it had obtain a noticeable improvement in structural, optical, and electrical properties of CdSe thin films which deposited on glass substrates by thermal evaporation method at room temperature. All prepared film have got cubic phase with preffered orientation (111) according to the numbered (card 00-019-0191). The grain size was 31.84nm before annealing process and it increased with increasing the annealing time at 350˚C, the grain size became 46.18nm after 20 minutes under 350˚C. Energy bandgap decreased from 3.43eV before annealing process to 2.17eV after annealing for 20 minutes. Also the absorption spectrum decreased with annealing time and this refers to increasing in transmission spectrum, so the two improvements in energygap and spectrum are very necessary in photovoltaic aplications.

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تحضير الغشاء الرّقيق CdSe بطريقة التّبخير الحراري بالفراغ ،ودراسة خواصه البصرية والكهربائية والتّركيبية

كوكب داود سالم ، حنان رضا

قسم الفيزياء ، كلية التربية للعلوم الصرفة ، جامعة تكريت ، تكريت ، العراق

الملخص

تمّ في هذا البحث ترسيب أغشيةٍ رقيقةٍ من مادة سيلينايد الكادميوم (CdSe) على قواعد زجاجيّةٍ باستخدام تقنية التّبخير الحراري بالفراغ. وتمّ تلدين هذه الأغشية الرّقيقة إلى درجة حرارة (350℃) لمدّة (10,20,30 minutes) على التّوالي. ولقد دُرِسَتْ الخصائص التّركيبيّة ،والمورفولوجيّة، والبصريّة والكهربائيّة للأغشية بواسطة حيود الأشعة السّينية (XRD)، والتّحليل الطّيفي (المرئي– الفوق بنفسجي)، ومجهر القوّة الذّريّة (AFM) على التّرتيب. حيث أظهر نمط حيود الأشعة السّينيّة أنّ الأغشية لها طورٌ مكعبيّ وذات اتجاهية (111)، كما أنّ حجم الحُبَيبات كان في حدود nm (31-46). امّا اختبارات الأشعة فوق البنفسجية فقد أوضحت أنّ هناك تناقصًا في قيمة فجوة الطّاقة مع زيادةِ وقت التّلدين من (2.43eV) إلى (2.17eV) بعد عشرين دقيقة من التّلدين.