Study of Some Structural and Optical Properties of $AgAlSe_2$ Thin Films

Iman H. Khudayer
Bushra H. Hussien

Dept. of Physics/ College of Education For Pure Science (Ibn Al-Haitham) /University of Baghdad

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Abstract

The structural properties of ternary chalcopyrite $AgAlSe_2$ compound alloys and thin films that prepared by the thermal evaporation method at room temperature on glass substrate with a deposition rate (5±0.1) nm s^{-1} for different values of thickness (250,500 and 750±20) nm, have been studied, using X-ray diffraction technology. As well as, the optical properties of the prepared films have been investigated. The structural investigated shows that the alloy has polycrystalline structure of tetragonal type with preferential orientation (112), while the films have amorphous structure. Optical measurement shows that $AgAlSe_2$ films have high absorption in the range of wavelength (350-700 nm). The optical energy gap for allowed direct transition were evaluated, which decreases with film thickness increasing, i.e. it decreases from 2.5 eV to 2.2 eV when thickness varies from 250±20 nm to 750±20 nm.

Keywords: $AgAlSe_2$, thin films, energy gap, structure and optical properties.

Introduction

In recent years, many groups worked on chalcopyrite semiconductors with a wide band gap to increase solar cell conversion efficiency by using an absorber close to solar spectrum [1]. Wide gap chalcopyrite materials are required for tandem solar cells and high-voltage devices [2]. Photovoltaic research has moved beyond the use of single crystalline materials such as group IV like Si and group III-V compounds like GaAs to much more complex compounds of the group I-III-VI_2 with chalcopyrite structure. The ternary ABC_2 chalcopyrites (A = Cu,Ag; B = In, Ga or Al; C= S, Se or Te) form a large group of semiconductor materials with diverse structural and electrical properties. These materials are attractive for thin film photovoltaic application for a number of reasons [3]. Cu based chalcopyrites are most intensively studied, but few experimental and theoretical studies of ABC_2 type semiconductors where group A element is Ag and the group B element is Al have been carried out [4]

Ag chalcopyrites has several advantages over Cu chalcopyrites such as:

The band gap energy of Ag chalcopyrites films is wider than Cu chalcopyrites [5] and the melting point of the Ag chalcopyrites film is lower than Cu chalcopyrites which make them commercially more preferable [6]. Most of the I-III-VI_2 compounds are direct gap semiconductors and they crystallize with the chalcopyrite structure [7]**.** This research aim to analyzes the effect of thickness on the structural and optical properties of $AgAlSe_2$ thin films prepared by thermal evaporation method.

Experimental

$AgAlSe_2$ films of different thicknesses (250, 500 and 750) nm were prepared by the alloy which is obtained by fusing the mixture of the appropriate quantities of the elements Ag, Al and Se of high purity (99.999%) in evacuating fused quartz ampoules, heated at (1200 K) for five hours, $AgAlSe_2$ films were prepared onto a glass slide substrate by thermal evaporation technique in vacuum system of $3x10^{-6}$ Torr using the Edward coating unit model (E 306) from molybdenum boat. The distance from molybdenum boat to the substrate was about 15 cm. The deposition rate was about 5 nm/sec for all the films in room temperature (R.T).

X-ray Diffraction (XRD), was used to the position and intensity of diffracted intensity spectra versus Bragg's angle θ, using (Shimadzu6000 X-ray Diffraction with copper target of the wavelength (λ=1.5406)Å, gives information on the crystal structure such as phase crystalline, polycrystalline, amorphous, crystalline size, and lattice parameter. The inter planer distance d (hkl) for different planes was measured by Bragg's law [8]:

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

where n is the order of diffraction, λ is the wavelength of the X-rays, d is the spacing between consecutive parallel planes and θ is the angle of incidence.The average crystalline size can be calculated using the Scherrer's Formula [9]:

$$C.S = \frac{0.94\lambda_{X-Ray}}{B_{(FWHM)}\cos\theta_B} \quad \text{.....(2)}$$

where λ is the wavelength of the X-ray and β is the full width at half maximum intensity in radians.

Optical experiments measurement have been done using UV-Visible 1800spectro photometer,. The optical absorption spectrum is used to determine the optical energy gap and the absorption coefficient. Knowledge of these band gaps is extremely important for understanding the electrical properties of a semiconductor, and is therefore of great practical interest [10]. The Tauc formula, equation [11]:

$\alpha h\nu = B\,(h\nu - E_g^{opt})^{1/r}$ .....(3)

where, B is a constant inversely proportional to amorphousity, hν is the photon energy (eV), E_g^{opt} is the optical energy gap (eV) ,and r is constant and may take values 2, 3,1/2, 3/2 depending on the material and the type of the optical transition. There are two types of the optical transitions, direct and indirect transition, according to the type of materials and optical transition.

The optical behavior of a material is generally utilized to determine its optical constants [refractive index (n_o), extinction coefficient (k) and, real (ε_r) and imaginary parts (ε_i) of dielectric constant]. The absorption coefficient value can be calculated from the formula [12]:

$$\alpha = 2.303\frac{A}{t} \quad \text{.....(4)}$$

where A is the optical absorbance and t is the film thickness.

The refractive index value can be calculated from the formula [13]:

$$n_o = \left[\frac{4R}{(1-R)^2} - k^2\right]^{\frac{1}{2}} + \left(\frac{1+R}{1-R}\right) \quad \text{.....(5)}$$

where k represents the extinction coefficient, which is calculated by the relation [12]:

$$k = \frac{\alpha\lambda}{4\pi} \quad \text{.....(6)}$$

where R is the reflectance. which is calculated by the relation:

R=1-A-T……(7)

The real ε_r and imaginary ε_i part of dielectric constant can be calculated by using the following equations[14]:

$$\varepsilon = \varepsilon_r - i\varepsilon_i \quad \text{.....(8)}$$

$$\varepsilon_r = n_0^2 - k_0^2 \quad \text{.....(9)}$$

$$\varepsilon_i = 2n_0k_0 \quad \text{.....(10)}$$

Result and discussion

X-ray diffraction pattern of $AgAlSe_2$ alloy is shown in Figure (1). The spectrum is seen to exhibit sharp peaks at (101) (112), (211), (220), (204), (312), (400), (404), and (415) corresponding to **2θ** equal to 16.94, 26.78, 34.56, 42.78, 45.206, 51.149, 62.11, 72.366 and 80 polycrystalline structure tetragonal unit structure of $AgAlSe_2$ were absolved as compared with the standard values in ASTM cards. . The X-ray diffraction parameters inter planer spacing (d), Miller indices and crystalline size) for $AgAlSe_2$ alloy are listed in Table (1). The prefer orientation at 112 plane.

The experimental absorption spectra for the $AgAlSe_2$ thin films with different thicknesses were made at room temperature in the spectral range (350-1100) nm are shown in Figuree (2). All spectra show better absorption in the ultraviolet and visible regions. When the thickness increases the absorption increases and close for visible region. The behavior of the absorption spectra is opposite completely to that of the transmission and reflection spectra as shown in Figures (3 and 4).

From Figure (5) it is observed that the absorption coefficient (α) values, which were calculated using equation (4), were fairly have high values reached above 10^4 cm^{-1}, which indicated the optical transition in the extended band region. The coefficient absorption values increase with the increase of optical energy gap. This result agrees with that shown by other research [15].The coefficient values decrease with increase of thin thickness that it varied from 5.7×10^4 to $2.7\times10^4 cm^{-1}$ increased from 250 to750 nm respectively. This behavior agrees with that shown by other researcher [16]. This behavior attributed to the variation of the crystal structure and that the films atoms density increases with film thickness.

The absorption coefficient decreases with increase of the thickness as shown in Figure (5) this is due to the relationship between α and the absorbance if we consider the direct proportionality of the absorbance with respect to thickness as shown in Figure (2) It is obvious that A increases with the increase of the film thickness and that can be attributed to the increase of the defects and localized centers [16].

The optical energy gap of material can be determined by using the equation (3), by plotting of $(\alpha h\upsilon)^2$ versus hυ for $AgAlSe_2$ thin films with different thicknesses is shown in Figure (6). The plot is linear at the absorption edge which confirms that $AgAlSe_2$ is a semiconductor with a direct band gap. Extrapolation of the line to the hυ axis gives the direct optical band gap and the transition is allowed direct.

It can be noticed from the values of E_g^{opt} that it decreases with the increase of thickness as shown in table (2). This is due to an increase in practical size [17], and one can notice the E_g^{opt} value for film with thickness 250 nm has 2.5 eV, this value is in good agreement with Sharma . et al (4).

As well as for thin films, it varies with thickness due to the changes in barrier height at grain boundaries with the increase of film thickness. This is due to the increase in localized density of states near the band edges and in turn decreases the value of E_g^{opt} with thickness. Also, the decrease of direct band gap with the increase of film thickness can be attributed to the increase of particle size, decrease of the strain and increase of lattice constant [18].

The variation of the refractive index (n) as a function of the photon energy for $AgAlSe_2$ films at different thicknesses is shown in Figure (7), which indicates that n decreases with the increase of thicknesses This behavior is may be due to decrease in the reflection which the refractive index depends on it.

Graph of extinction coefficient (k) as a function of photon energy for different thicknesses of $AgAlSe_2$ films is plotted in Figure (8). This figure revealed that k in general decreased and then increased as film thickness increased (250,500 and 750) nm. The variation of k with film thickness is non- systematic, as shown Table (2). This is attributed to the same reason mentioned previously in the absorption coefficient because the behavior of k is similar to α.

The dielectric constant consists of a real (ε_r) and imaginary part (ε_i) depends on the frequency of the electromagnetic wave. The variables of ε_r and ε_i versus photon electron at different thicknesses are shown in Figures. (9 and 10) respectively. The behavior of ε_r is similar to that of the refractive index because of the small value of k^2 compared with n^2,while ε_i behavior is similar to that of extinction coefficient because it mainly depends on the k value, which is related to the variation of absorption coefficient. The variation of ε_r and ε_i with film thickness are non-systematic. This means that this material possesses a specialized property with thickness.

Conclusions

$AgAlSe_2$ alloy was prepared successfully and used for preparation of thin films by thermal evaporation method. XRD tests for alloy showed that polycrystalline and have the tetragonal structure with preferential orientation in the [112] direction respectively. The influence of thickness on the values of optical parameters of $AgAlSe_2$ thin films is investigated. All thin films exhibited allowed direct optical energy band gap and high absorption in the ultraviolet and visible regions, thus, making the films suitable for optoelectronic devices, for instance as window layers of solar cells.

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Table (1) Structural parameters of $AgAlSe_2$ alloy

Crystalline size (nm)	FWHM (deg.)	2θ(stand.) (degree)	2θ(exp.) (degree)	d (stand) (Å)	d(exp) (Å)	hkl	a,c (ASTM) (Å)	a,c (exp.) (Å)
49.4432	0.188	16.89	16.94	5.26	5.267	101	a=5.968 c=10.77	a=5.967 c=10.755
		26.83	26.78	3.32	3.325	112		
		34.603	34.56	2.59	2.59	211		
		42.822	42.78	2.11	2.11	220		
		45.400	45.206	1.99	200	204		
		51.314	51.149	1.78	1.78	312		
		62.07	62.11	1.49	1.49	400		
		72.478	72.366	1.303	1.304	404		
		79.947	80	1.199	1.1979	415		

Table (2) The optical parameters (E_g^{opt}, α, k, n, ε_r and ε_i)for $AgAgSe_2$ thin films for different thicknesses at λ =380nm.

λ=380nm							
t(nm)	E_g^{opt} (eV)	Absortion٪	$\alpha\times10^4$ $(cm)^{-1}$	n	k	ε_r	ε_i
250	2.5	62.25	5.7	2.18	1.73	1.78	7.5
500	2.3	70.95	2.9	1.89	0.89	2.77	3.4
750	2.2	80.3	2.7	1.64	0.82	2.02	2.7

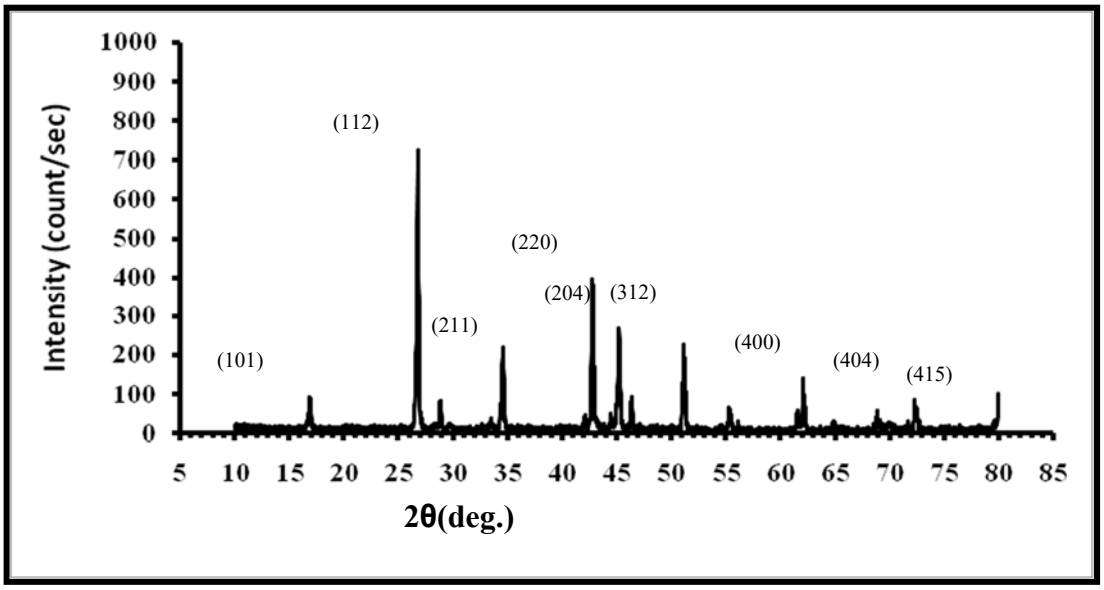


Figure (1) X-ray diffraction pattern of $AgAlSe_2$ alloy.

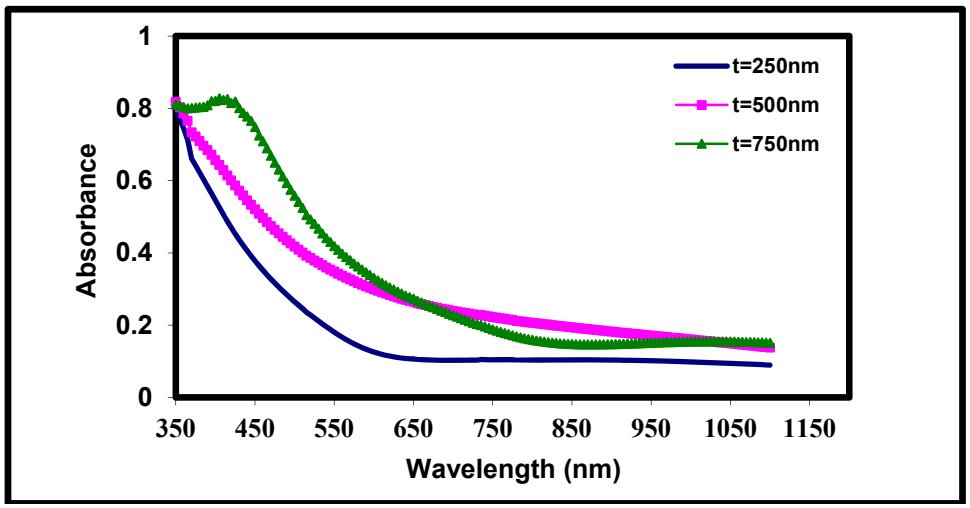


Figure (2) Absorbance spectra for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750) nm.

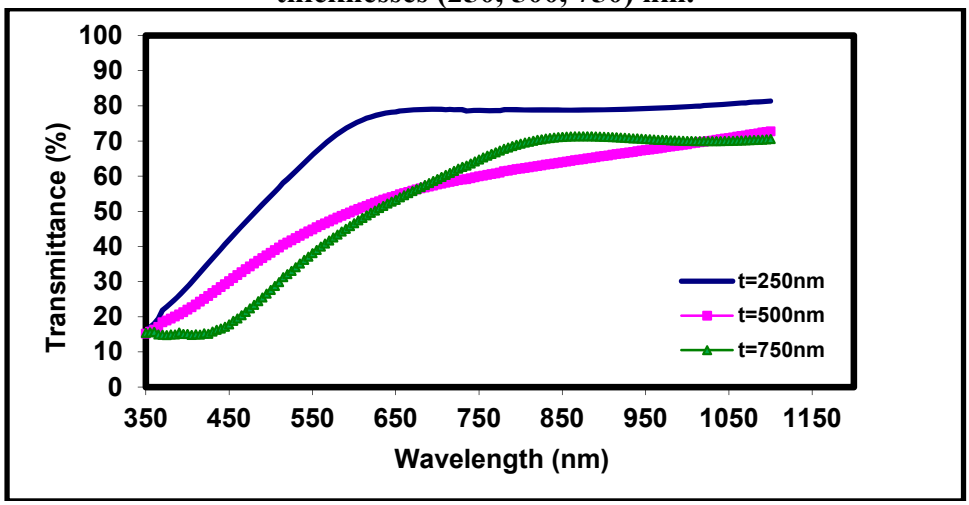


Figure (3) Transmittance spectra for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750) nm.

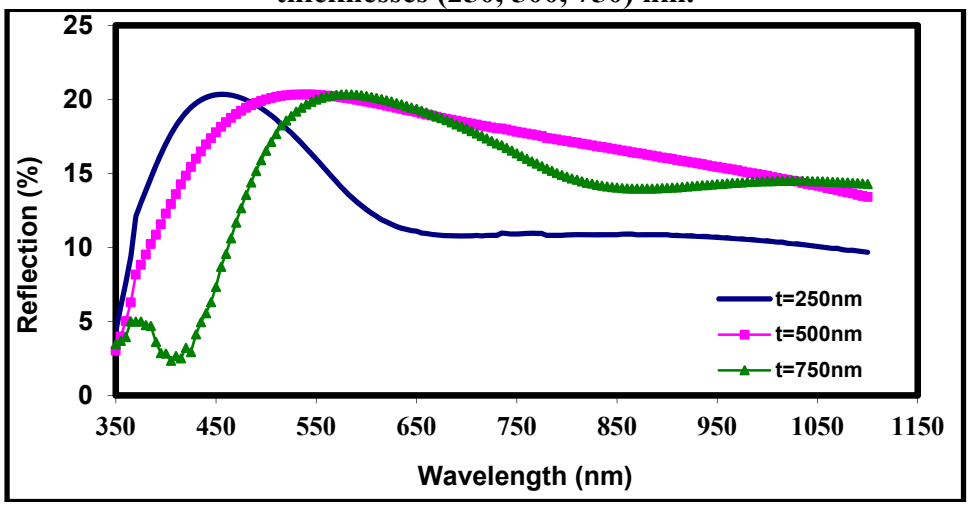


Figure (4) Reflectance spectra for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750) nm.

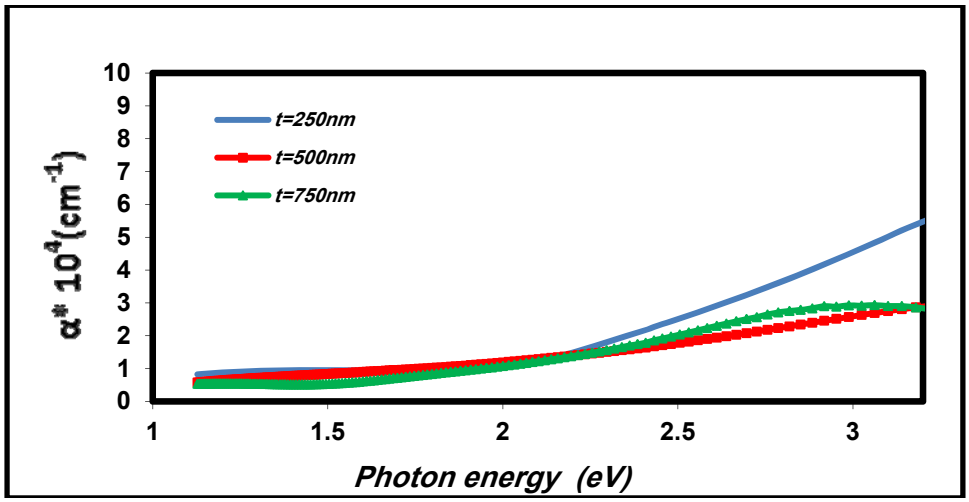


Figure (5) Variation of absorption coefficient with photon energy for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750) nm.

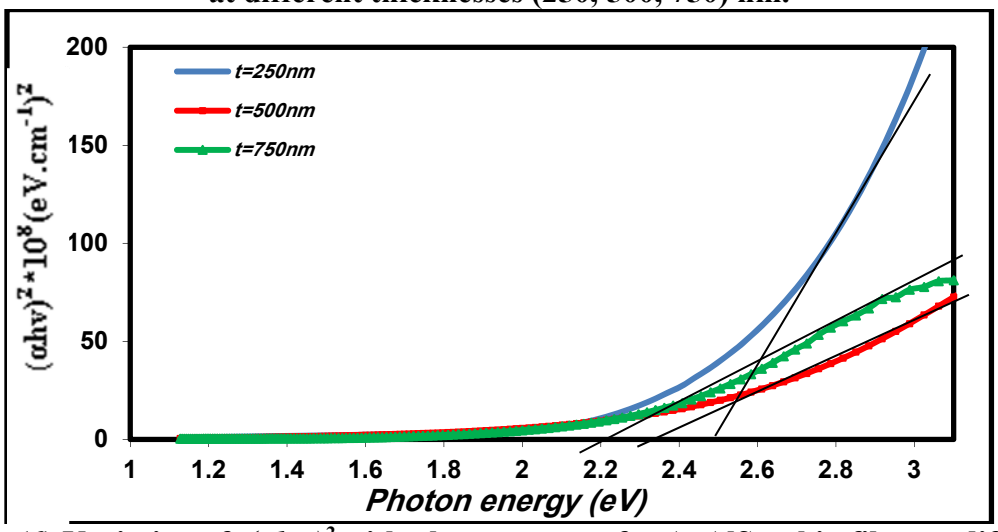


Figure (6) Variation of $(\alpha h\nu)^2$ with photon energy for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750)nm.

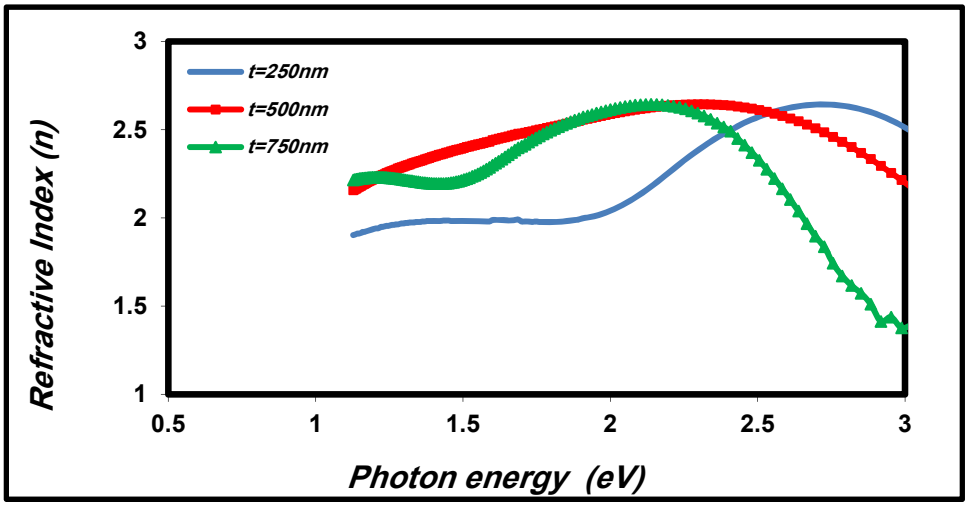


Figure (7) Variation of refractive index with photon energy for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750) nm.

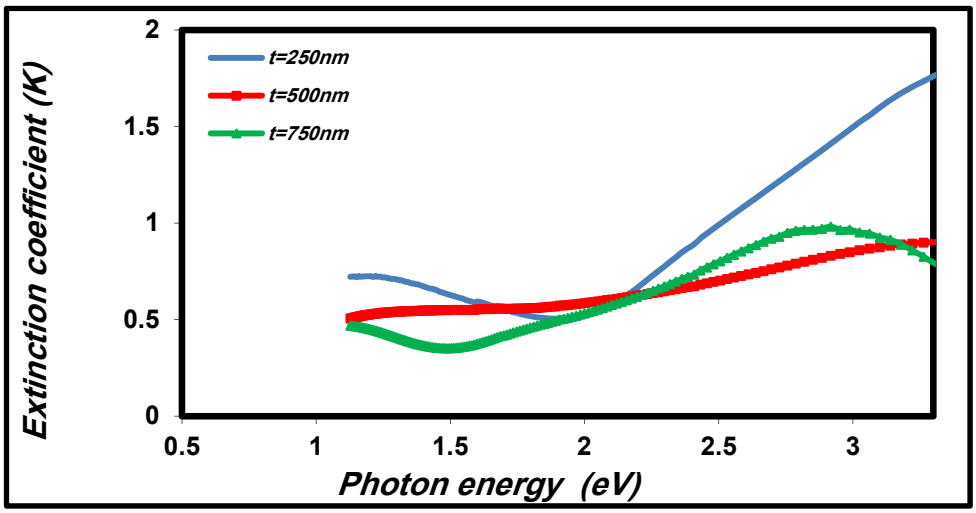


Figure (8) Variation of Extinction coefficient with photon energy for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750)nm.

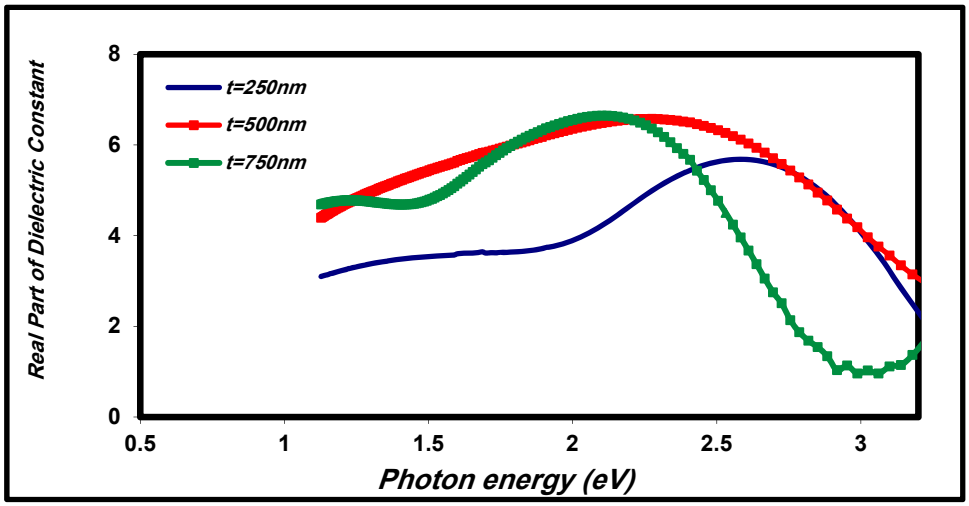
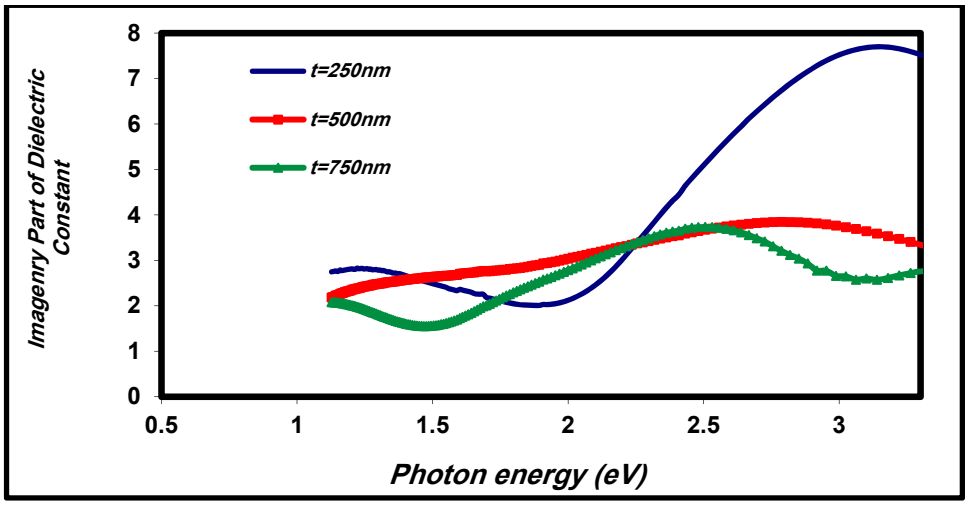


Figure (9) Variation of *real part of dielectric constant* with photon energy for $AgAlSe_2$ thin films at different thicknesses (250, 500, 750)nm.



$AgAlSe_2$ thin

Figure (10) Variation of of imaginary part of dielectric constant with photon energy for films at different thicknesses (250, 500, 750)nm

دراسة بعض الخواص التركيبية والبصرية للأغشية الرقيقة $AgAlSe_2$

ايمان حميد خضير
بشرى هاشم حسين
قسم الفيزياء / كلية التربية للعلوم الصرفة (ابن الهيثم)/ جامعة بغداد

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الخلاصـــة

درست الخواص التركيبية لسبيكة المركب الثلاثي $AgAlSe_2$ واغشيته التي حضرت بوساطة طريقة التبخير الحراري في الفراغ عند درجة حرارة الغرفة على قواعد من الزجاج بمعدل ترسيب (5 ± 0.1) nm sec^{-1}. وبسمك مختلف $(750,500,250\pm20)$نانومتر بأستعمال تقنية حيود الأشعة السينية كما درست الخواص البصرية للأغشية المحضرة. بينت الفحوصات التركيبية أن السبيكة تملك تركيبا متعدد التبلور من النظام البلوري الرباعي (Tetragonal) مع هيمنة الاتجاه (112) ، بينما تمتلك الأغشية المحضرة تركيبا عشوائيا. أوضحت القياسات البصرية أن أغشية $AgAlSe_2$ ذات امتصاصية عالية للأطوال الموجية في المنطقة المرئية (350-700) نانومتر. وتم حساب فجوة الطاقة ذات الانتقال المباشر المسموح، وان قيمة هذه الفجوة تتناقص مع تزايد السمك،اذ قلت من (2.5eV) إلى (2.2eV) بزيادة السمك من (250 ± 20) نانومتر الى (750 ± 20)على التوالي.

الكلمات المفتاحية: $AgAlSe_2$, اغشية رقيقة, فجوة طاقة, الخواص التركيبية والبصرية.