Study The Effect of Thermal Annealing on Structural and Some Optical Properties of The $Znse_{1-X}$ Al_x Thin Film

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Abstract

The effect of both thermal annealing temperatures(373 and 473) K for one hour in vacuum furnace on optical properties of $ZnSe_{1-x}$ Al_x thin film doped with aluminum at x% (0, 2, 4, 6 and 8) was studied, which prepared by thermal evaporation method with 0.3μm thickness. The optical properties have been studied, and structure properties of $ZnSe_{1-x}$ Al_x films have been studied by X-ray diffraction .The structure was polycrystalline with cubic structure with orientation (111), the films with x% 6 and 8 and annealed at 373 K appeared new planes in (222) and (220) lead to appear the Al_2Se_3 phases. The observed results of the optical properties prepared films after heating treatment were decreased in absorption and increased in transmission. The value of the optical energy gap increased with increasing of thermal annealing from 373 to 473 K and decreasing with increasing aluminum concentration (x) from 2.85 eV to 1.99eV for all prepared samples.

دراسة تأثير التلدين الحراري على بعض الخصائص التركيبيه والبصريه لأغشيه $ZnSe_{1-x}$ Al_x الرقيقه

الخلاصة:

تمت دراسة تأثير درجتي الحراره 373 و 473 كلفن لمدة ساعه تحت الفراغ على بعض الخصائص البصريه لأغشيه $ZnSe_{1-x}$ Al_xالمطعمه بالالمنيوم بنسب مختلفه (8,6,4,2,0 %) والمحضرة بطريقه التبخير الحراري ذات سمك (0.3) مايكرومتر. تمت دراسة الخواص التركيبيه بأستخدام حيود الاشعه السينيه واظهرت ان المركب متعدد التبلور وذات تركيب مكعبي بأتجاه (111), وعند التلدين 373 و 473 كلفن وزيادة نسبة الالمنيوم الى (8,6 %) ظهر مستوي جديدة يعود للطور (Al_2Se_3). ونلاحظ الخصائص البصريه بعد التلدين معامل الامتصاص يقل والنفاذيه تزداد. لكن فجوة الطاقه تزداد بزيادة درجه حرارة التلدين من 373 الى 473 كلفن وتقل بزيادة تركيز الالمنيوم من 2.85 الى 1.99 الكترون فولت بدرجه حراره الغرفه.

INTRODUCTION

ZnSe is an ionic wide band gap II-VI semiconductor with a direct room temperature band gap of 2.67 eV, The band gap is sufficiently large to permit fabrication of injection devices that emit radiation in the blue and green regions of the visible spectrum[1]. ZnSe is a promising material for the fabrication of thin films due to its high absorption coefficient. This fact makes ZnSe useful in the

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field of optical applications such as excellent filters in the IR spectrum and coatings for high power laser windows and as antireflection coatings for solar cells fabrication [2]. The deposition techniques employed for the preparation of thin films include evaporation, chemical solution reduction process, electro-deposition and sol-gel[3] molecular beam epitaxy (MBE) [4] thermal evaporation [5] liquid phase epitaxy (LPE) [6] and pulse laser deposition[7].Because of wide band gap and transparency over a wide range, ZnSe is also suitable as window layer for thin films solar cells[8]. It exhibits a cubic structure with cell constant a = 5.668A [9].

The present study is on vacuum evaporated ZnSe thin films. In this paper, we report the composition, structural and optical properties of vacuum evaporated $ZnSe_{1-x}$ Al_x thin film.

Experiential

Preparation of ZnSe Thin Film

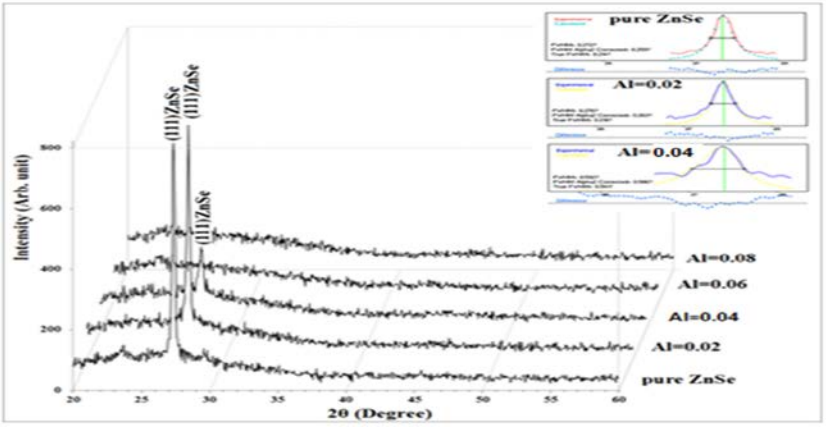
Aluminum doped ZnSe alloy has been prepared from its own constituent elements. Appropriates weights of Zn, Se and Al (99.999%) were taken in a quartz tube, which is then evacuated (10^{-2} mbar with rotary pump) and sealed. The temperature of the furnace was raised gradually to 773K and left at this temperature for about 4 h. and then, the ampoule was slowly cooled to room temperature. The ZnSe ingots was taken out form the ampoule and into fine powder and used for evaporation. Zinc selenide (ZnSe) thin films were prepared on to cleaned glass substrates using a vacuum evaporation technique under a vacuum $5*10^{-4}$ mbar. The optimized deposition parameters were used: target (material), ZnSe powder, substrate glass, room temperature (300K), substrate to target distance 15cm, current (I), deposition time 5 min. and deposition rate 1 nm/sec. After that all thin films annealed at both temperatures 373 and 374 K. Then structure was examined by X-ray diffraction (XRD) and optical properties by using UV-Visible (Cary 100) spectrophotometer

Results and Discussion

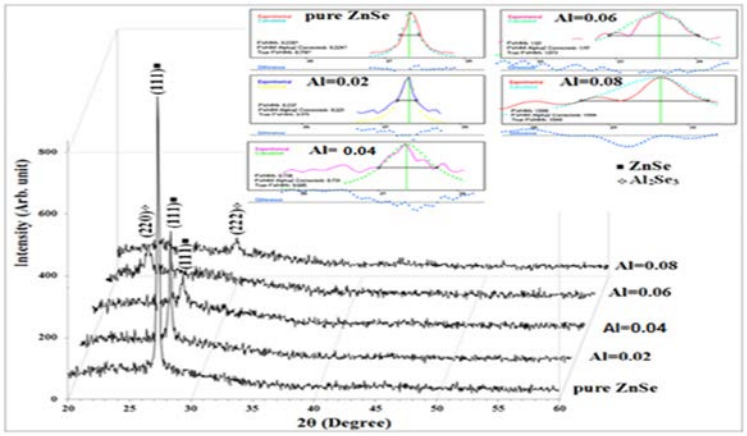
XRD Results

X-ray diffraction analysis was performed on $ZnSe_{1-x}Al_x$ films to ascertain the crystal orientation and the structure of the deposited materials. XRD spectra were taken using Cu K_α radiation on films deposited at RT, and annealed at 373K. Fig. (1) shows the XRD spectra obtained on films containing different concentration of Al. It can be seen from the figures that the films have polycrystalline nature having (111) preferred orientation and exhibiting a zinc blend (ZnSe) cubic structure at $2\theta=27.35^o$. From Figs. 2 and 3 it is also observed that spectra of the films containing Al (6 and 8 wt %) show additional peak other than those appeared for ZnSe. This indicates that the Al atoms have made solid solution with ZnSe by replacing Zn atoms or by occupying any Zn vacancy in the lattice[5]. There is another explanation, it will probably be clusters inside crystal lattice from Al_2Se_3. These bonds undesirable and can control the amount of these ties through the preparation conditions. This means effectively Al association with Se due to the negative charge dissimilarity of the electricity.

It is also observed that as the Al concentration increased the intensity of the main (111) peak gradually decreased and there are very small shifts of the peaks towards the higher diffraction angles.



Figure(1): X-ray diffraction spectra as deposited for $ZnSe_{1-x}$ Al_x thin films



Figure(2): X-ray diffraction spectra for thin films $ZnSe_{1-x}$ Al_x annealed at 373K

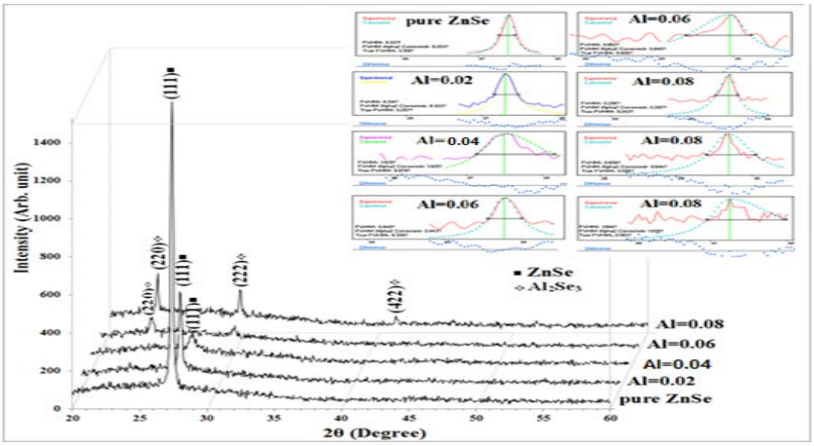


Figure (3:) X-ray pattern for $ZnSe_{1-x}$ Al_x thin film annealed at 473 K

Transmittance

We can observe from Fig.(4 a- e) that transmittance increases with increasing of annealing temperature (Ta) which means a decrease in the absorption with increasing of annealing temperatures. This is due to the heat treatment led to the reduction of crystalline defects (localized states) and increase the size of particle board and this leads to the improvement of the crystal structure of the film[5]. At Fig.(4,A) pure ZnSe in room temperature, the transmission spectrum shows oscillatory behavior because of thin film interference. The transmittance spectrum reveals at high transmission of 99.8% in the near infrared region (≥ 600nm) and a low transmission of about less than 60% in the visible region at wavelength below 450nm, It is evident that the films have good transmittance in the higher wavelength (NIR) region, similar results have been reported by Khan[12].

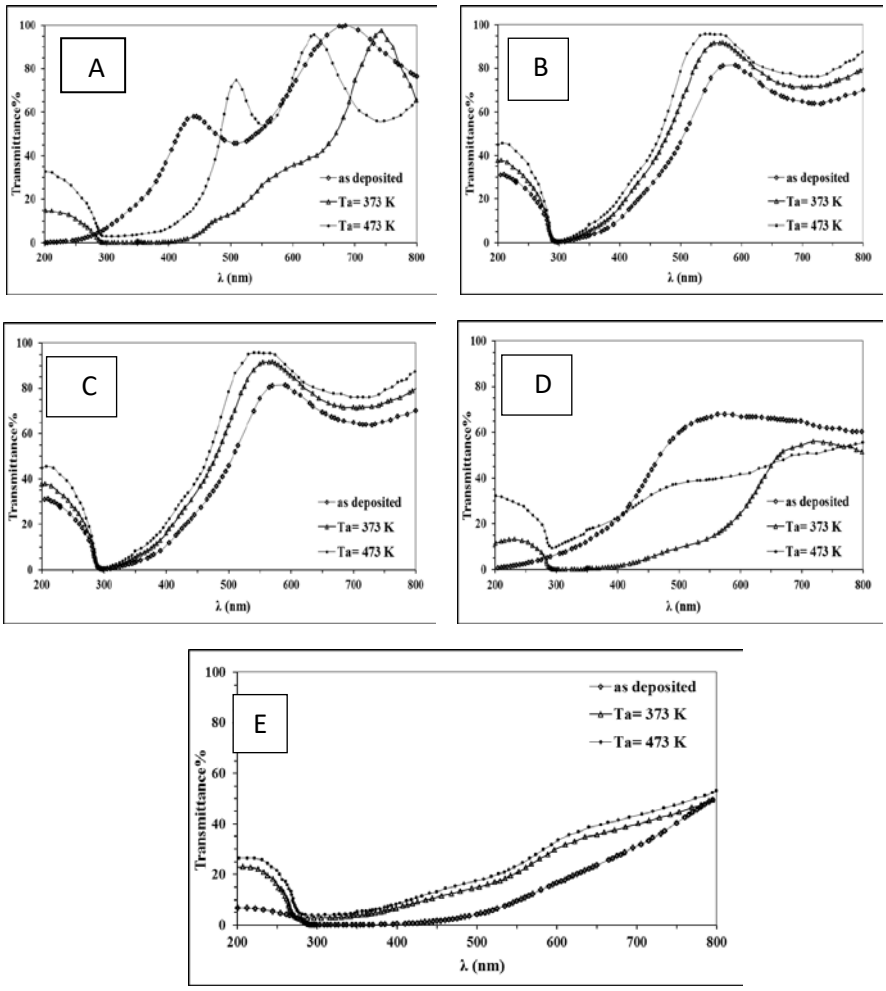


Figure (4): Transmittance spectra as function of wavelength of $ZnSe_{1-x}$ Al_x films at both Ta and x (A) 0, (B) 2, (C) 4, (D) 6 and (E) 8

Absorption Coefficient

The variation of the absorption coefficient (α) of deposited polycrystalline $ZnSe_{1-x}$ Al_x films on glass substrate deposit at room temperature and both annealing

temperatures 373 and 473K is shown in Fig (5 a, b, c, d, e). The absorption coefficient can be calculated from the equation Beer lambert[7]:

$$\alpha = 2.303\ (A/t) \qquad \ldots (1)$$

Where A: is the absorptance and t is the sample thickness.

The absorption coefficient decreases with decreasing photon energy. We deduce that the absorption is not attributed to the free carriers only, but to impurities or localized electronic states. Also, we can notice from these figures that α decreases with the increase of annealing temperature, this is due to the increasing of energy gap with annealing temperature.

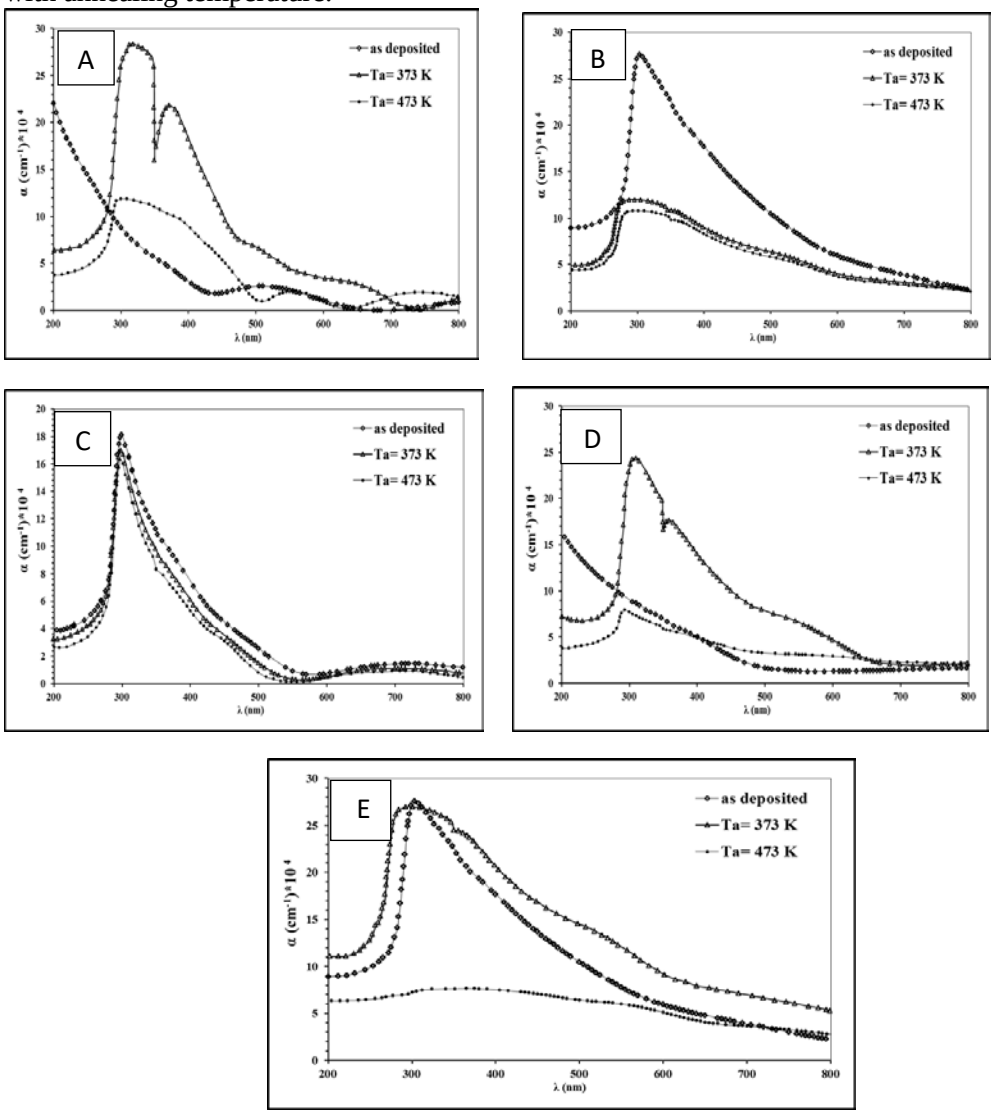


Figure.(5): Absorption coefficient spectrum as function of wavelength of $ZnSe_{1-x}$ Al_x films both Ta and at different Al wt% A) 0, B) 2, C)4, D)6, E) 8

Optical Energy Gap

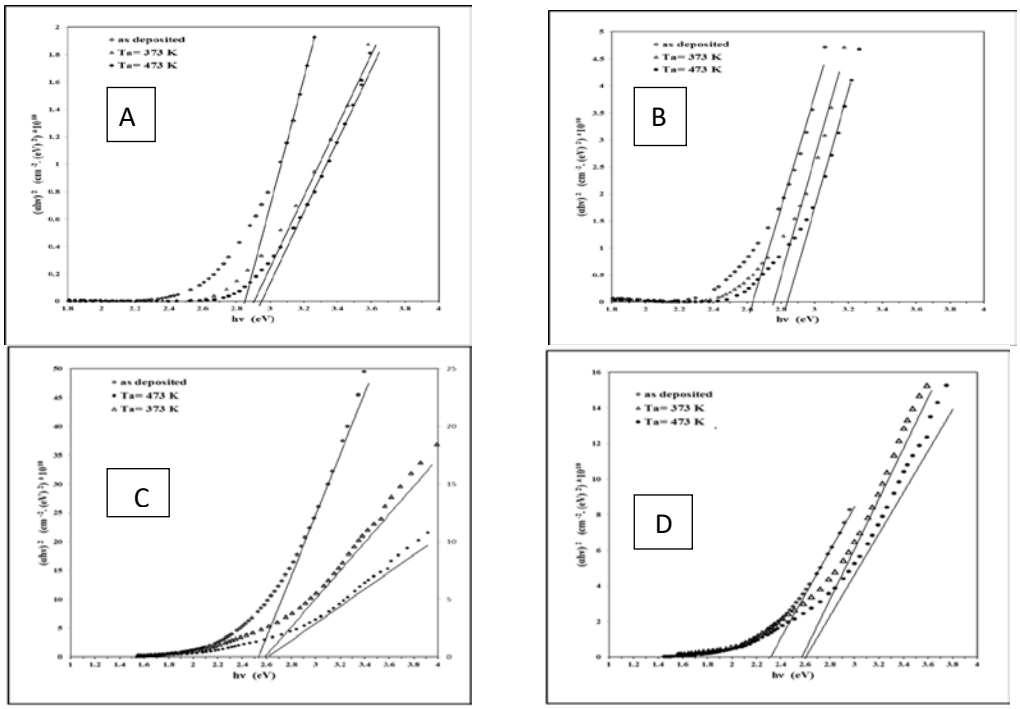
The optical energy gap values (E^o_g) for $ZnSe_{1-x}$ Al_x films have been determined by using Tauc equation which is used to find the type of the optical transition by plotting the relations of $(\alpha h\square)^{1/2}$, $(\alpha h\square)^{1/3}$, $(\alpha h\square)^{2/3}$ and $(\alpha h\square)^2$ versus with photon energy ($h\square$) and selecting the optimum linear part. It is found that the relation for r =1/2 yields linear dependence. The extrapolation i.e. E^o_g, of the portion at $[(\alpha h\square)^2 = 0]$ is shown in Fig.(6). Tauc equation[8]

$$\alpha(\square)hv=B(h\square - E_g^{opt})^r \quad \text{..... (2)}$$

The energy difference necessary for such a transition is called band gap E gap [9].

$$E \text{ photon} = h.\square = 1240/\lambda(nm) \quad \text{....(3)}$$

The value of te optical energy gap increased with increasing of Ta and decreased aluminum (x) concehntration for all samples is shown in Table(1) . Eg decreased from 2.85 eV to 1.99 eV for deposited $ZnSe_{1-x}$ Al_x films. This value of Eg in pure ZnSe at room temperature is in agreement results reported by Habubi [13].When Ta increases from R.T to 473 K, the increasing of Eg with increasing of Ta is attributed to decreasing of defect states in the band gap. This increasing in Eg in Ta may be explained by increase in crystallization and lead to decrease in crystal defects, Thus reducing the crystalline defects localized near the valance band or near the conduction band, which leads to an increase forbidden energy gap[14].



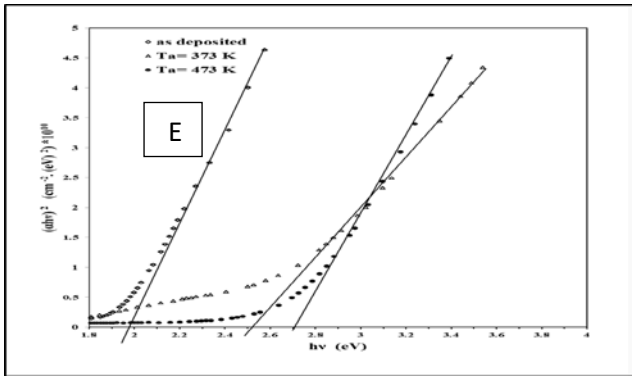


Figure.(6): $(\alpha hn)^2$ versus h□ for as deposited $ZnSe_{1-x}$ Al_x films at (373 and 473)K for different x value A)0, B)2, C) 4, D)6, E) 8

Table (1): Parameters of the optical properties of $ZnSe_{1-x}$ Al_x films at annealing temperatures and different concentration

Samples	Eg(eV)			
$ZnSe_{1-x}$ Al_x	X %	Ta=RT	Ta=373K	Ta=374K
	0	2.85	2.9	2.93
	2	2.63	2.75	2.83
	4	2.3	2.59	2.6
	6	2.19	2.59	2.79
	8	1.99	2.51	2.7

Conclusion

The results of optical measurements showed that the transmittance of the thin film is affected by annealing temperature as increased with increasing temperature, and showed that the absorption coefficient decreases with increasing the temperature and also due to increased energy gap with temperature. Found that optical energy gap that thin possess electronic transitions directly, and this energy gap decrease with aluminum concentration increase from 2.85 eV to 1.99 eV at Rt, but the energy gap decrease with temperature annealing increase.

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