The structural and optical properties of nonstoichiometric $AgAlS_2$ thin films prepared by chemical spray pyrolysis method

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Abstract

Nonstoichiometric $AgAlS_2$ thin film of Ag/Al: 1, 0.6, 0.5, 0.4 and 0.3 were prepared by chemical spray pyrolysis on heated glass substrate at temperature of 300 ^oC . The films structure was analyzed by XRD , All the patterns of thin films prepared are polycrystalline. UV-VIS spectroscopy was used to investigate which were. The optical energy gap of thin films equal to 2.3, 2.21, 2.15, 2.12 and 2.08 eV according to the value of Ag/Al respectively. The optical constants such as refractive index ,extinction coefficient, real and imaginary dielectrics were investigated also.

Keywords: $AgAlS_2$Thin films ,Chemical spray pyrolysis

Introduction

The I–III–VI_2 chalcopyrite semiconductors have revealed much interest as semiconductors for practical applications in opto-electronic devices and in thin film solar cell [1]. All I–III–VI_2 compounds investigated so far have been found to have direct band gaps and visible stimulated emission has been observed at low temperature . It is well know that the properties of thin films are highly sensitive to small changes in their chemical compositions and the crystallographic imperfections which in turn are controlled by the detailed mode of preparation and conditions of growth [2] . The nonstoichiometric semiconductor such as Ag/Al not equal one can be grown as either n or p type since the conduction type depends on the intrinsic defects of the structure [3] . There for the energy gap of $AgAlS_2$ may be various from 2.3 eV to another value . In this paper a nonstoichiometric thin films of $AgAlS_2$ for Ag/Al with various ratio prepared by chemical spray pyrolysis technique and its structural and optical properties are investigated .

Experimental

$AgAlS_2$ thin films prepared by chemical spray pyrolysis deposited on micro glass slides those were first cleaned with detergent water and then dipped in acetone. Spray solutions were prepared by mixing 0.1 M aqueous solution of $AgNO_3$, $Al(NO_3)_3$, and Thiourea $CS(NH_2)_2$, then mixed a certain amount of solution for each experiment by a magnetic stirrer. Automated spray solution is transferred on the hot substrate kept at the normalized deposition temperature of 300 ±10 ºC with the help of carrier gas. Filtered air is used as carrier gas, the flow rate of which is normalized to ~3ml/min. To avoid excessive cooling of substrate, spraying was achieved in periods was about 10 sec followed by 15sec wait . To deposit films of uniform thickness the distance between the substrate and spray nozzle was kept at 50cm.

Thickness measurement of the films has been carried out using optical method which equal to 400 ±20nm

To determine the nature of the growth and structural characteristics of the prepared thin films, an X-ray diffraction (XRD) obtained for diffractometer type Philips pw. 1840 with target Cu-K**α**. The UV-VIS spectrophotometer type Jenway 6800 UV/VIS was used to measure the absorptance and transmittance in the wavelength range 200-1100nm, and from these measurements, the optical parameters were calculated. The topography of $AgAlS_2$ thin film surface was inspected with optical reflected-microscope type Nikon-73346 under magnification of 108 X.

Result and discussion

1. X-Ray diffractions and Morphology studies

Figure 1 obtained the topographic of the prepared thin films with different ratio of Ag/Al which are 1,0.6, 0.5 ,0.4 and 0.3 from the topographic it is revealed that the grain size decrease with decreasing Ag amount . This may be related to there is additional phases , as reported by other authors [6-7].

Figure 2 shows the X- Ray diffraction patterns of $AgAlS_2$ of films prepared at 0.3 and 0.5 Ag/Al ratio . XRD results suggest that the films have polycrystalline structure . Also it shows that the films have many phases which are Ag_2S , Al_2S_3 and $AgAlS_2$ which different in intensities depends on the Ag/Al ratio . The two strong peak at $(2\theta) = 37.8^o$ for $AgAlS_2$ and $(2\theta)=38.35^o$ for Ag_2S at *(hkl)* = (-123), the value of intensity at $(2\theta)=38.35^o$ decrease with decreased Ag ratio in the films.

2. Optical studies

The optical absorption of the films has been studied in the wavelength range 200- 1100 nm . The absorption coefficient (α) was calculated using the following relation [8].

$$\alpha = \frac{2.303A}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where A is the absorbance and t is the film thickness .

Fig.(3) shows the plot of α vs λ for films. From this Fig. the value of $\alpha > 10^4\ cm^{-1}$ in the visible region , which indicate that the electronic transition was direct [9] .

The optical energy gap (E_g) was given by the relation [10].

$$\alpha h\upsilon = A(h\upsilon - Eg)^r \quad \ldots\ldots\ldots\ldots\ldots 2$$

Where A is a constant

The value of r for the direct transition equal $\frac{1}{2}$. From the extrapolating the straight line of $(\alpha h\upsilon)^2$ vs hυ the optical energy gap E_g was found as shown in Fig. (4) . The value of E_g was decreased with decrease Ag/Al ratio as shown in table1.

Table (1) the value of energy gap with Ag/Al ratio

Ag/Al ratio	1	0.6	0.5	0.4	0.3
E_g eV	2.32	2.21	2.15	2.12	2.08

Extinction coefficient (k) are given by the relation [11] .

$$k = \frac{a\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots 3$$

The variation of (k) values as a function of (λ) are shown in fig. (5),which Obtained the maximum value of (k) at the visible region decrease with increase(λ) , then it become nearly constant at NIR range , also the value of k depend on the ratio of Ag/Al , where the maximum value of (k) at 500 nm equal 0.4 for Ag/Al =1 , while for Ag/Al= 0.3 equal 0.85 at the same wavelength .

The refractive index (n) was calculated using the following relation [12] .

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K^2\right]^{\frac{1}{2}} \ldots\ldots 4$$

Where R is the reflectivity

The values of n vs λ were shown in Fig 6. From this figure the value of n increase with increase wavelength , the maximum value of n equal to 2.6 for all thin films.

Real and imaginary parts of dielectric constants were determined using the following equations [13,14].

$$\varepsilon_1 = n^2 - K^2 \ldots\ldots\ldots\ldots 5$$

$$\varepsilon_2 = 2nK \ldots\ldots\ldots\ldots\ldots 6$$

Where ε_1 and ε_2 is the real and imaginary dielectric constant respectively .The plots of (ε_1) and (ε_2) of thin films are illustrated in figures (7 and 8) respectively , from Fig.7 the variation of ε_1 is follow the refractive index , where increase in the region that λ > 400 nm , where the absorption of the films for these wavelength is small , but the polarization was increase . the maximum value of ε_1 equal 6.8 at 600 nm , for the ratio Ag/Al equal 1 but equal 6.7 at λ > 900 nm for the ratio Ag/Al equal 0.6 , 0.5 , 0.4 and 0.3 . Fig. 8 , shows that the shape of ε_2 is the same as ε_1 , this means that the refractive index was dominated in the behaviors . The maximum value of ε_2 increase with decrease the ratio of Ag/Al .

Conclusion

Nonstoichiometric $AgAlS_2$ thin films have been deposited by chemical spray pyrolysis technique ,the XRD show that the thin films have polycrystalline phases , the optical band gap (2.32 , 2.21 , 2.15 , 2.12 and 2.08) eV for the ratio Ag/Al equal 1, 0.6 , 0.5 , 0.4 and 0.3 , the extinction coefficient value was increase in the visible region with decrease Ag/Al , the films have refractive index equal 2.6 . All thin films prepared give a best optical properties to be used for optoelectronic application .

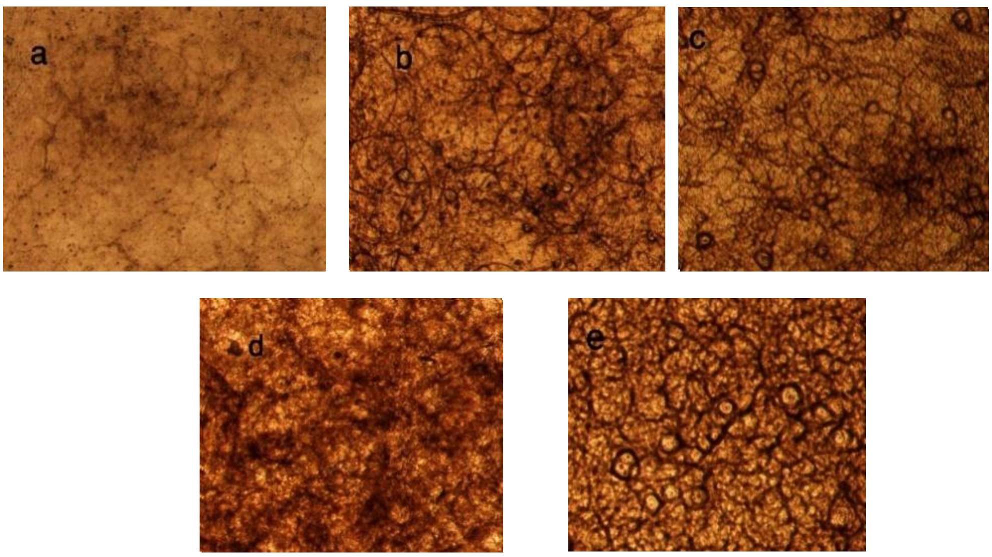

Fig. (1) the morphology of $AgAlS_2$ thin films surface where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

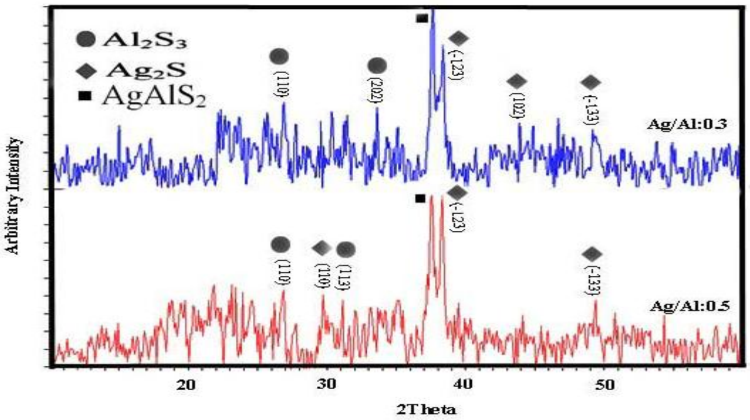

Fig. (2) The XRD pattern of $AgAlS_2$ thin films

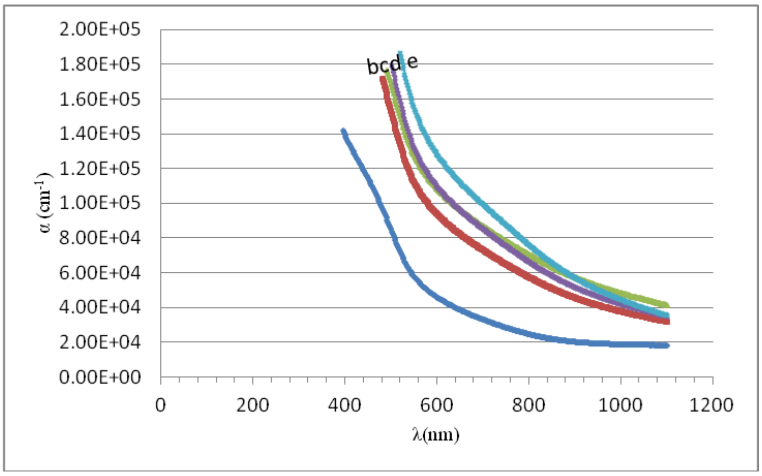

Fig.(3) the varietion of absorbtion coefficient (α)with wavelength (λ) for $AgAlS_2$ thin films where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

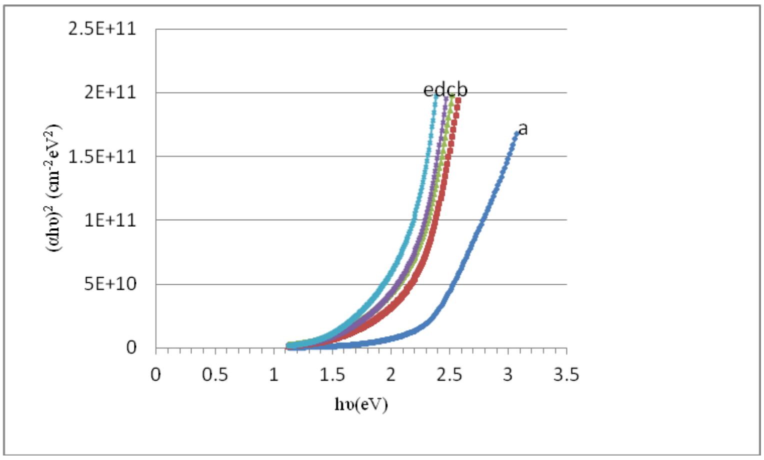

Fig (4) the optical energy gap (E_g) value for $AgAlS_2$thin films where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

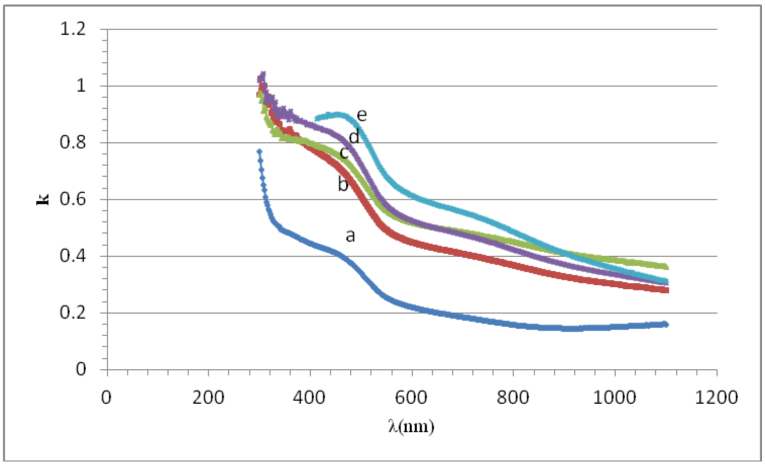

Fig.(5) The varietion of extention coeficient (k) with wavelength (λ) for $AgAlS_2$thin films where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

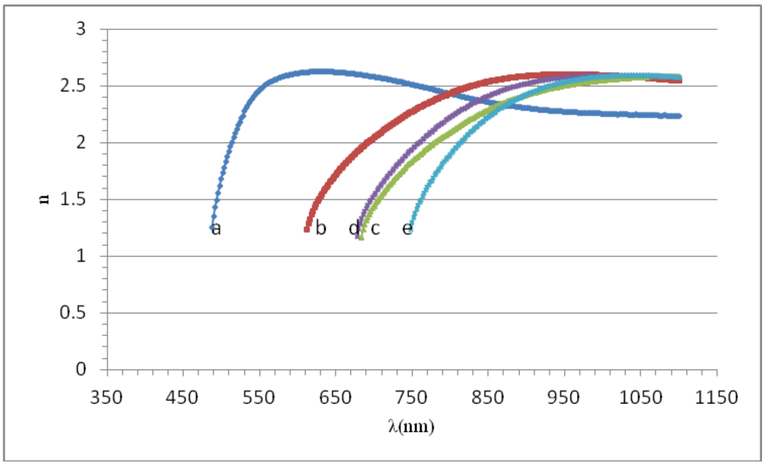

Fig.(6) The varietion of refractive index (n) with wavelength (λ) for $AgAlS_2$ thin films where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

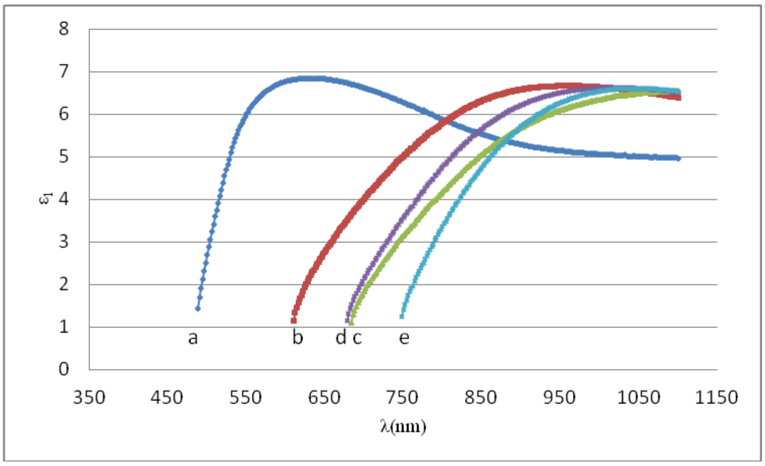

Fig.(7) The varietion of real dielectric constant with wavelength (λ) for $AgAlS_2$ thin films where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

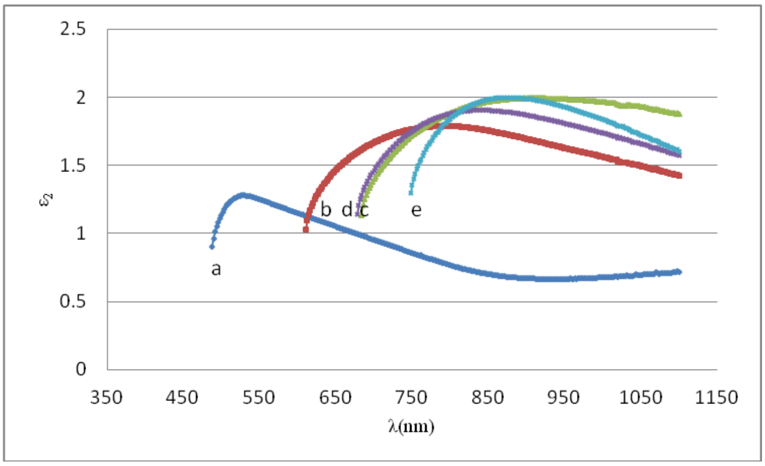

Fig.(8) The variation of imaginary dielectric constant with wavelength (λ) for $AgAlS_2$ thin films where (a) Ag/Al=1,(b) Ag/Al= 0.6,(c) Ag/Al= 0.5,(d) Ag/Al= 0.4,(e) Ag/Al=0.3

References

1- Okoli D.N , A.J. Ekpunobi and C.E. Okeke , Academic open internet journal , (2006), vol. 18 .

2- B.H.Patel and S.S. patel , Cryst. Res .echnol. ,41 (2006) , No.2 , pp 117 -122 .

3- K.W.cheny , C.M. Huoang ,G. T. Pan , P.C. Chen , T.C. Lee and T.C.K. Yang , Material chemistry and physics ,108 (2008) , pp16 –23

4- Mujdat Caglar, Saliha Ilican and Yasemin Caglar, Optics Communications vol.281, (2008) , pp1615–1624 .

5- Kong-Wei Cheng and Sheng-Chih Wang , Materials Chemistry and Physics, vol. 115 (2009), pp 14–20.

6- ShigeFusa Chichibu, Yoshiyuki Harada, Mutsumi Sugiyama and Hisayuki Nakanishi , J. of Physics and Chemistry of Solids , vol.64 (2003) , pp1481–1489.

7- M.Calixto , Material science and Engineering B174,(2010),pp 253- 256 .

8- Alaa A. Aljubory, Saeed N.T. AlRashed , Hamid S. Aljumaili , J. of university of anbar for pure science ,vol. 3 , No.3 ,(2009) , pp59-68.

9- B. Thangaraju and P. kaliannan , Cryst. Res .Technol .35 , No. 1, (2000),pp75-77 .

10-M. Ortega-Lopez, V.M. Sanchez-Resendiz , J.J. Cayente-Romero, Y. Matsumoto, M.L. Albor-Aguilera and E. Barrera-Calva, Thin Solid Films, vol.518 (2010) , pp1821–1824

11-Sho Shirakata , Tomoaki Terasako and Tetsuya Kariya, Journal of Physics and Chemistry of Solids, vol. 66, (2005) , pp1970–1973 .

12-A. Kariper, E. Guneria, F. Gode, C. Gumus, T. Ozpozan , Materials Chemistry and Physics , vol.129 (2011) , pp183– 188

13-Ping Fan , Guang-Xing Liang, Xing-Min Cai, Zhuang-Hao Zheng, Dong-Ping Zhang , Thin Solid Films 519 (2011) , pp 5348–5352 .

14-J. Joseph Sharkey , V. Dhanasekaran , Chang Woo Lee, A. John Peter, Chemical Physics Letters 503(2011),pp86–90.

دراسة الخواص التركيبية والبصرية لا غشيه $AgAlS_2$ غير المتكافئة المحضرة بطريقه الرش الكيميائي الحراري

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الملخص

تم تحضير أغشيه $AgAlS_2$ غير المتكافئة لقيم Ag/Al:1,0.6,0.5,0.4,0.3 باستخدام طريقه الرش الكيميائي الحراري على قواعد زجاجيه بدرجه حرارة 300^oC. تم فحص تركيب الاغشيه المحضرة بجهاز حيود الاشعه السينية XRD وقد تبين ان الاغشيه ألمحضره متعددة التبلور وتحتوي على مركب Al_2S_3 ومركب Ag_2S ومركب $AgAlS_2$ وتعتمد قيمهم على نسبه Ag/Al . كما تم قياس الخصائص ألبصريه باستخدام جهاز UV-VIS ضمن المدى nm (200-1100) ومنها تم حساب فجوة الطاقة البصرية والتي كانت من النوع المباشر وامتلكت قيم تراوحت بين 2.3 - 2.08 eV معتمدة على نسبه Ag/Al كما تم حساب الثوابت ألبصريه (معامل الانكسار n ومعامل الخمود k وثابت العزل الحقيقي ε_1 والخيالي ε_2) وقد بينت النتائج التركيبية والبصرية بان الاغشيه تمتلك فجوه طاقه مباشره متدرجة يمكن الاستفادة منها في تقنيات الالكتروبصريات.