ISSN: **1991-8941**

The Effect of substrate temperature and the annealing time on the optical properties of the AgInS2 thin films prepared by chemical spray pyrolysis Technique

Mazin Abdulhameed Al-Alousi
University of Anbar - Collage of Science,
Received: 12/4/2010 Accepted: 19/9/2010

Abstract: The AgInS2 thin films were prepared on a glass substrates with different substrate temperatures (623, 573, 523 and 473) K by chemical spray Pyrolysis . For annealing temperature 473 K , different time (2, 2.5 and 3) hours have been applied .The structure test produced by used the x-ray techniques by (Diffraction and diffractometer Philips 200) system with copper target (Cu - Kα), wavelength (0.15406 nm), the average is (2000counts/sec), the voltage is (40 KV) , the scanning average is (5 deg /min) and the angle range is (2θ =20o – 60o).The optical properties of the AgInS2 films were determined from the absorbance (A) and the transmittance (T) data , using UV-Vis. Spectrophotometer at wavelength (400 – 1000) nm at room temperature.The direct band gap of (1.87 – 2.46) eV has been found that of the AgInS2 thin films according the substrate temperature , also , it is affected by annealing time and becomes (1.82 – 2.15) eV . The optical constants (α , k , n) are also changed as the substrate temperature and annealing time change .The AgInS2 films regard as active selecting films in the range (400 – 665) nm , and can be used as an absorber layers in solar cells and optoelectric devices.

Key words: substrate temperature , annealing time , optical properties , AgInS2 thin films, chemical spray pyrolysis Technique

Introduction

The development of contemporary, sophisticated technologies which increase the quality of human life is closely to the semiconducting materials. The science and technology of semiconducting thin films have a crucial role in high – tech industry.[1]
Multiparty compounds, or series of materials consisting more than two atomic species, have been extensively studied in many fields of materials science and solid state electronics. While multinary compounds are not vary popular materials in the other kinds of substances, such as dielectric, magnetic and superconducting materials [2].
AgInS2 has been crystallized in chalcopyrite phase with a strong (112) X-ray diffraction line [3], which has gap energies between 1.87 eV and 2.01 eV [3-5] and orthormic structure with gap energy 1.98 eV [4].
AgInS2 crystals and polycrystalline films have been prepared by diverse techniques . In addition, polycrystalline thin films of this material have been prepared by spray pyrolysis :
(2001) M. Ortega-L´ opez & et. al. prepared AgInS2 thin films by the spray pyrolysis technique and studied the effects of the growth temperature and the chemical composition of the solution on the structural, optical and electrical properties of the films [6].
(2005) Seungnam Baek and Kwangjoon Hong studied AgInS2 which has been grown by hot wall epitaxy method [3] .
(2006) Aissa and et. al. studied some physical investigations on AgInS2 sprayed thin films which are structural and optical properties .[4]
(2006) Okoli & et. al. studied the optical properties of AgInS2 which prepared by chemical bath deposition technique [7]
(2007) Aissa & et. al. studied the effect of S/In concentration ratio on the physical properties of AgInS2-sprayed thin films [8]
(2007) Albor Aguilera and et. al. studied the Photoluminescence of chalcopyrite and orthorhombic AgInS2 thin films deposited by spray pyrolysis technique [4].
(2008) Kong-Wei Cheng and Sheng-ChihWang studied the Effects of complex agents on the physical properties of Ag–In–S ternary semiconductor films using chemical bath deposition [9]

In the chalcopyrite structure of AgInS2, the splitting of the valence band is known to be dominated by the uniaxial lattice compression. Therefore, the uppermost valence bands of AgInS2 are profoundly influenced by the proximity of the d levels of the valence band of the noble-metal. Then, both p and d orbitals of AgInS2 are known to be partially elevated due to this degeneracy. These states participate in the photoconduction process, resulting in extending the photo-response on the higher energy side. Generally, absorption experiments are used to measure the band gap energy. This method is known to be in accurate to obtain the band gap energy due to the difficulty in defining the position of the absorption edge. Also, studies of the temperature dependence of the band gap for only a limited number of ternary chalcopyrite crystals have been reported in the literature [10].

These films can be used as a good photo-absorber in PEC applications, in solar cells and optoelectric devices . [11]

In this paper the ternary AgInS2 thin films compound, which has been investigated known to be a ternary compound semiconductor, with wide band gap in the visible region of the spectrum.

Most of the optical properties of the films have been calculated from the experimentally measured values of the absorbance (A) and the transmittance (T) according to following relations :

$$T = (1-R)^2 \exp(-A)$$
$$= (1-R)^2 \exp(-\alpha t) \text{......... ......(1)}$$

where the R is the reflectance , (α) is the absorption coefficient and (t) the film thickness [12] .

when (R) is very small ,the optical absorption coefficient (α) is determined by using the relation [13] :

$$\alpha = 2.30.3\frac{A}{t} \text{.................(2)}$$

the extinction coefficient has been calculated by [14]

$$k = \frac{\alpha\lambda}{4\pi} \text{........................(3)}$$

λ is the wavelength of photons.

The refraction index (n) of the films has been calculated by :

$$n = \left[\frac{4R}{(R-1)^2} - K\right]^{½} - \frac{R+1}{R-1} \text{.......... ....(4)}$$

Experimental Procedure

The chalcopyrite AgInS2 films have been produced by spraying the aqueous solution of (0.02 M AgNO3.2H2O) , (0.08 M InCl3) and (0.16 M (NH2)2CS) in a 4:1:1 (by volume) on to the glass substrates (25X25X1) mm , at different substrate temperatures (623,573,523 and 473) K ± 5 K , before the deposition the slid were cleaned with HCl solution , DI water and acetone .

The flow rate of solution during deposition was adjusted to be about 2.8 ml / min and kept constant throughout the experiment and the normal distance between the nozzle and the substrate is 50 cm . The natural air used as the carrier gas to spray the solution .

The thickness of the films calculated by weighting method and it was (100 ± 20) nm .The films are annealed at 473 K with different times (2,2.5 and 3) hour by using electric oven.

The absorbance & transmittance of the films have been measured by UV- Visible spectrophotometer in the range (100 - 400) nm at room temperature.

Result and Discussion :

The absorption coefficient (α) was determined from eq. (2) for the thin films under investigation. Figure (1) shows that the variation of (α) with λ for different substrate temperature. The direct band gap material for AgInS2 has been calculated to be the cutoff value of (α) has been found to be $\approx 7.5\times10^{-3} cm^{-1}$ at 675 nm same for all substrate temperature , while in the region below 675 nm the value of (α) has been found to depends on the substrate temperature . This means that the substrate temperature is not effected on the type of the primary compound but it effected on the grains of the films and It is observed that the absorption coefficient decrease with decreasing photon energy. We deduce that the absorption is not attributed to the free carriers only, but to impurities or localized electronic states. or by producing secondary phases with the primary compound as shown by figure (2) .

Figure (3) shows how the values of the absorption coefficient at 550 nm are varied with the annealing time We deduce that the some of the secondary phases are concealed with produced the AgInS2 phases .

Figure (4) has been noticed that the band gap energy were decreases when the substrate temperature decreased from 573 K to 623K , while it behaves inversely at 523K (1.87 eV at 623 K , 2.46 eV at 573 K , 2.38 eV at 523 K and 2.28 eV at 473 K).This can be attributed to the formation of a new phases , such as Ag2S and In2S3 compounds with more probable to Ag2S since the electro- negativity of Ag higher than In [15], caused to increment in Ag2S phases at some temperature below AgInS2 generation temperature .

The value at substrate temperature 623 K is in good agreement with reported values [3,4, 6].

Figure (5) has been noticed that The values of the band gap changed as (2.02, 1.85 and 1.82) eV at 623 K , (2.1, 2.05 and 2.09) eV at 573 K, (2.04 , 2.08 and 2.05) eV at 523 K and (2.15,2.1 and 2.05) eV at 473 K when annealed with (2,2.5 and 3) h, generally, the films are working in a visible range.

The band gap for the films which deposed at substrate temperature 623 K are increased with the annealing time decreasing , but at 2 hours the value of band gap decreased from 1.87 eV to 2.02 eV , this decrease was attributed to variation of stoichiometry [16] , The recovery in the value of band gap for the films which preparing at 623 K due to the recovery and the integrating in the crystal structure , this reason has done on all the recovery in the optical properties[9], the lag of the optical properties for the films which are preparing at low substrate temperatures caused by finding the indirect transitions. The annealing is the effecting on the absorption edge by increasing the grain size and decreased the crystal defects this has been caused the fading of the extra absorbance which produced by the grain boundaries, and the decreasing in the band energy gap with the treatment by the annealing has been indicated to the grain defects increased by secondary phases generation and the wilding of the crystal grains in their films caused to produced the islands [17].

Figure (6) and Figure (7) have been noticed that the values of the extinction coefficient changed with substrate temperature and with the annealing time, To explain this behavior , it may be related to a new phase of AgInS2 and the increasing and decreasing in the secondary phases.

Figure (8) and figure (9) have been noticed that The values of the refraction index changed with substrate temperature and the annealing time, The explanation of this behavior may be related to the polarization of thin film because n depends on material polarization where with increasing polarization the velocity of light was decreased so n changed [18] . In general the behavior of K and n similar the behavior of α.

The AgInS2 thin films with diract band gap energy between (1.82 – 2.465) eV with various the sabstrate temperature between (473 – 623)K , the films have been deposited by using the chemical spray pyrolysis technique .

We can consider the activ range of the produced films were at (400 – 665) nm . The experimental results show that films in this study can be used as a good photo-absorber in PEC applications.

References

1. B.Altiokka,S.Aksay," Optical Properties of $CuInS_2$ films Produced by Spray Pyrolysis Method " , Jour. of Art and Sciences Sayi , 3/ May ,2005 , pp 27-33.
2. K. Sato, "Perspective of Ternary & Multinary Compounds as Future Materials ", IPAP Books,1(2001),pp. 4-5.
3. S. Baek & K. Hong, "Band gap energy and valance band splitting of photocurrent behaviour for AgInS2 epilayers grown by hot wall epitaxy", Journal of Ceramic Processing Research. Vol. 6, No. 1, pp. 20~24 (2005).
4. Z. Aissa ,T. Ben Nasrallah, M. Amlouk , J.C. Bernède and S. Belgacem," Some physical investigations on AgInS2 sprayed thin films ",Solar Energy Materials and Solar, Cells Volume 90, Issues 7-8, 5 May 2006, Pages 1136-1146.
5. M.L. Albor Aguilera , J.R. Aguilar Hernández, M.A. González Trujillo, M. Ortega López and G. Contreras Puente," Photoluminescence studies of chalcopyrite and orthorhombic AgInS2 thin films deposited by spray pyrolysis technique",Thin Solid Films ,Volume 515, Issue 15, 31 May 2007, Pages 6272-6275.
6. M. Ortega-L´opez, A. Morales-Acevedoand Omar Solorza-Feria." Physical properties of AgInS2 films prepared by chemical spray Pyrolysis", Thin Solid Films 385,2001. 120-125.
7. OKOLI D. N , A. J. EKPUNOBI AND C. E. OKEKE, OPTICAL PROPERTIES OF AgAlS2 THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION TECHNIQUE (CBDT), Academic open Internet journal , V. 18 , 2006.
8. Z. Aissaa, M. Amlouka,_, T. Ben Nasrallaha, J.C. Berne`deb, S. Belgacem. Effect of S/In concentration ratio on the physical properties of AgInS2-sprayed thin films",Solar Energy Materials & Solar Cells 91 (2007) 489–494.
9. Kong-Wei Cheng, Sheng-ChihWang ," Effects of complex agents on the physical properties of Ag–In–S ternary semiconductor films using chemical bath deposition" , Materials Chemistry and Physics (2008) .
10. M. Ortega-López, O. Vigil-Galán, F. Cruz Gandarilla and O. Solorza-Feria," Preparation of AgInS2 chalcopyrite thin films by chemical spray yrolysis",Materials Research Bulletin Volume 38, Issue 1, 1 January 2003, Pages 55-61.
11. J.E. Jaffe and Alex Zunger “ Theory of the band-gap anomaly in ABC2 Chalcopyrite semiconductors” Physical Review B, Vol 29. No 4 (1984).
12. B.Y. Taher," the structure and optical properties of thin films for compound Cu(In1-x Alx)S2 prepared by chemical spray pyrolysis M.Sc. thesis , Al-Anbar University (2005).
13. M.Y. NADEEM, Waqas AHMED,"Optical Properties of ZnS Thin Films",. Turk J Phy ,24 (2000) , 651 - 659.c TUBITAK
14. S.M. Alnaimi and M.N. AL-Dileamy , "Determination of the Optical Constants of Cadmium Stannate (Cd2SnO4) Films" , International Journal of Pure and Applied Physics ISSN 0973-1776 Volume 3 Number 1 (2007) pp. 30–39 , Research India Publications.
15. David R. Lide, "CRC Handbook of Chemistry and Physics", Copyright Taylor and Francis Group LLC 2006 .
16. B.A. Ezekoye & C.E.Okeke," Optical Properties In PbHgS Ternary thin Films deposited by S0lution Growth Method" , The Pacific J. of Science and Technology,V(7),No. 2,Nov. 2006.
17. A. H. Jloukan , " Optical and electrical properties of CuInS2Thin Films", M.Sc. thesis , Baghdad University ,Aug.(1990).
18. Y. A. Al -Shaabani, "Studying Some Physical Properties Of Zn2xCu1-xIn1-xS2 thin Films Prepared by Chemical Spray Pyrolysis" ,D.ph. thesis ,University of Technology ,Baghdad, Jun,(2009)

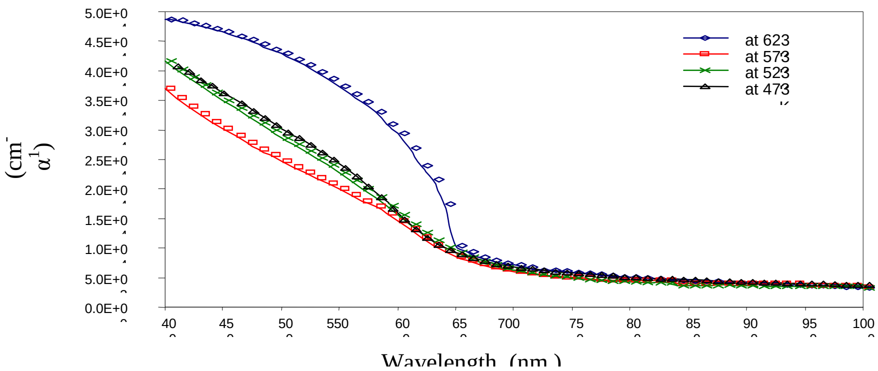

Fig. 1: **The absorption coefficient with the wavelength as function of the substrate temperature(623 ,573, 523and 473)K**

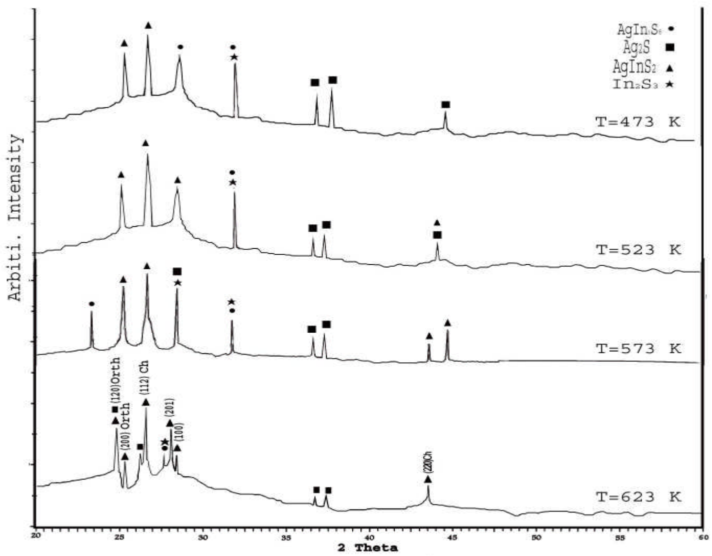

Fig. (2) : X-ray diffraction pattern of AgInS2 thin films at different substrate temperatures (623, 573, 523 and 473) K.

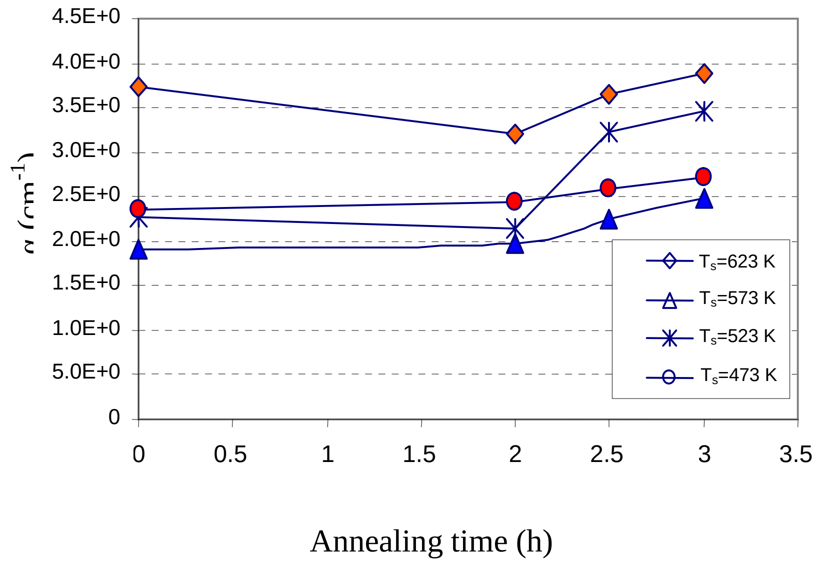

Fig. 3: **The absorption coefficient as function of the annealing time (2, 2.5 , 3) hours at 550 nm**

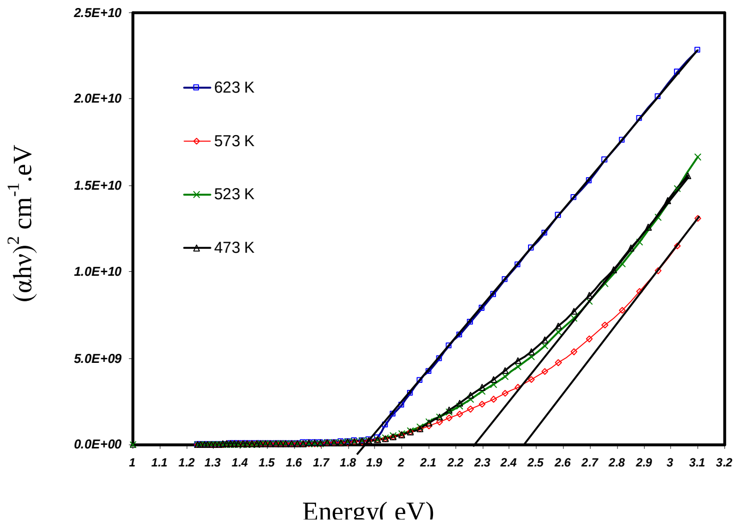

Fig.4: The band gap with different substrate temperatures (623 ,573, 523and 473)K

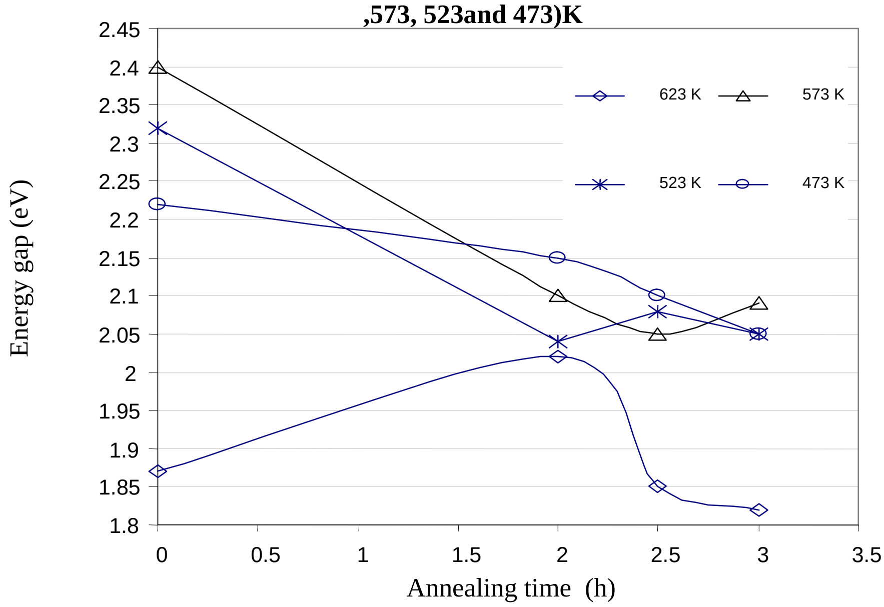

Fig. 5: The band gap is a function of the annealing time at 550 nm

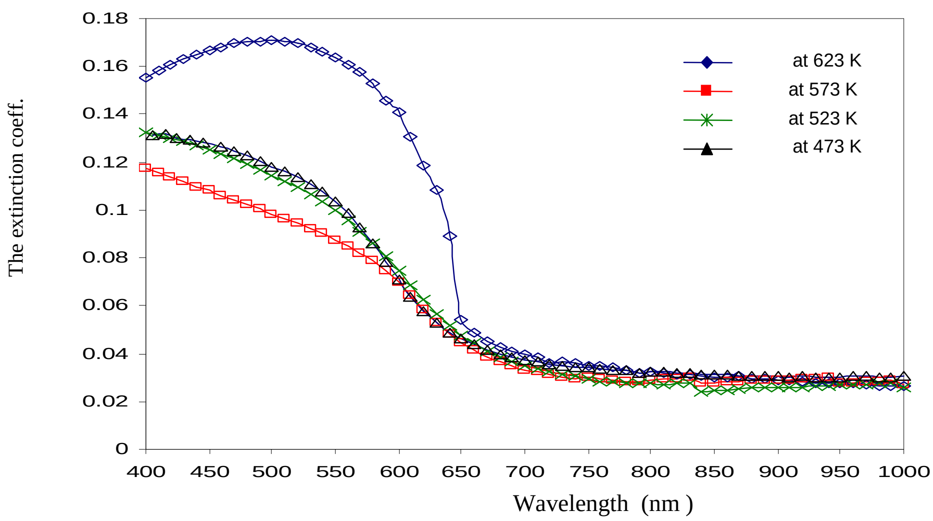

Fig . 6 The extinction coefficient with the wavelength as function of the substrate temperature (623 ,573, 523and 473)K

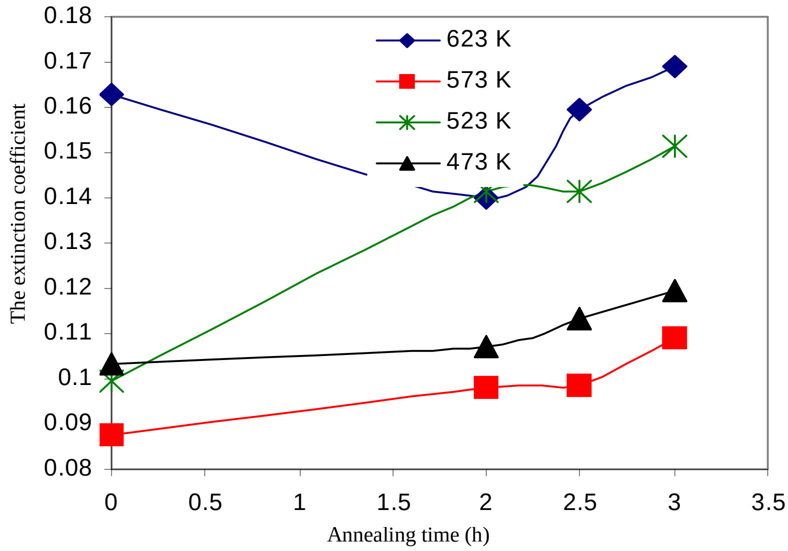

Fig . 7 The extinction coefficient as function of annealing time at 550 nm

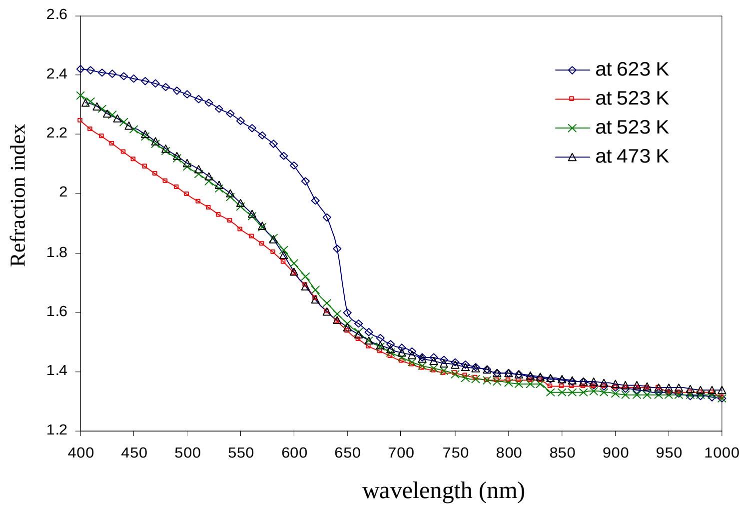

Fig . 8 The refraction index with the wavelength as function of the substrate temperature (623 ,573, 523and 473)K

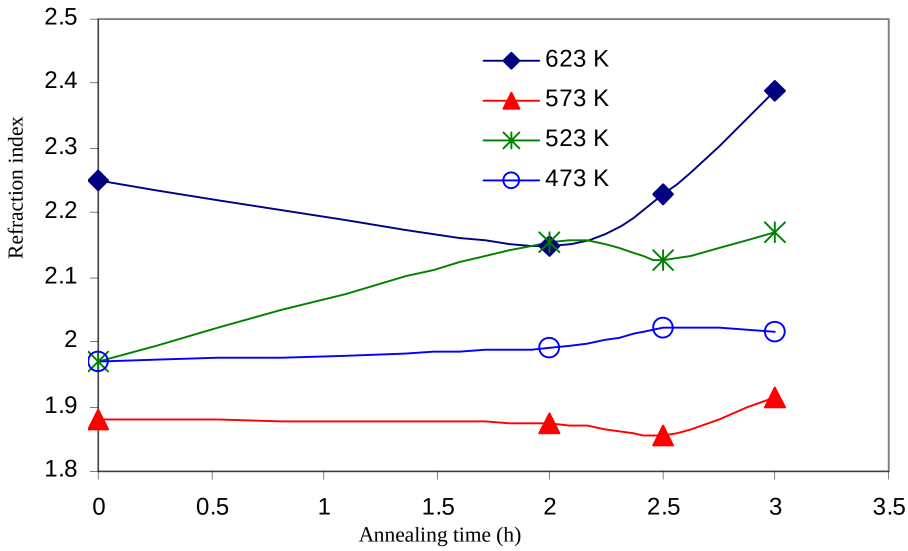

Fig . 9 The refraction index as function of annealing time at 550 nm

تأثير درجة حرارة الأساس و زمن التلدين على الخصائص البصرية لأغشية **AgInS2** الرقيقة المحضرة بطريقة الرش الكيميائي الحراري

مازن عبد الحميد عبد القادر
E.mail: mazin_alalousi@yahoo.com

الخلاصة

حضرت أغشيةِ AgInS2 الرقيقة بطريقة الرش الكيميائي الحراري على شرائح زجاجية بدرجات حرارة أساس K (473 ,523 ,573 ,623) و لدنت بدرجة حرارة (K 473) بأوقات تلدين مختلفة (2,2.5,3) ساعة .تم أجراء الفحص التركيبي باستخدام تقنية حيود الأشعة السنية باستخدام جهاز من نوع (Diffraction and diffractometer Philips 200) والمزود بهدف من مادة النحاس (Cu - Kα) والباعث للأشعة السينية بطول موجي (0.15406 nm) وبمعدل (2000counts/sec) و بفولتية (40 KV) وتيار (30 mA) ومعدل مسح (5 deg /min) ومدى زاوية (2θ =20o – 60o).الثوابت البصرية لأغشية AgInS2 حددت من معلومات الامتصاصية و النفاذية للأطوال الموجية nm(400-1000) باستخدام المطياف UV-Visible في درجة حرارة الغرفة نوع (SP-8-100 UV/Vis Pye unicam). وجد أن أغشية AgInS2 تمتلك فجوة طاقة مباشرة eV (1.87 – 2.46) حسب درجة حرارة الأساس وكذلك تأثرت بزمن التلدين و اصبحت eV (1.82 – 2.15) أن قيم الثوابت البصــرية (α , k and n) تغيرت نتغير درجة حرارة الأساس و زمن التلدين و لوحظ أن هذه الأغشية فعالة في المنطقةnm (665 - 400)، وهذه الخصائص ترشح هذه الأغشية لاستخدامها كطبقات ماصة في الخلايا الشمسية و النبائط الالكتروبصرية.