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Effect of thermal annealing and laser radiation on the optical properties of $AgAlS_2$ thin films

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Abstract

Effect of the thermal annealing at 400°C for 2 hours and Argon laser radiation for half hour on the optical properties of $AgAlS_2$ thin films, prepared on glass slides by chemical spray pyrolysis at 360°C with (0.18±0.05) µm thickness .The optical characteristics of the prepared thin films have been investigated by UV/Vis spectrophotometer in the wavelength range (300 – 1100)nm .The films have a direct allow electronic transition with optical energy (E_g) values decreased from (2.25) eV for untreated thin films to (2.10) eV for the annealed films and to (2.00) eV for the radiated films. The maximum value of the refractive index (n) for all thin films are given about (2.6). Also the extinction coefficient (K) and the real and imaginary dielectric constants ($€_1$ & $€_2$). The results indicate the films have good characteristics for optoelectronic applications.

Key words

Optical properties,

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تأثير التلدين الحراري والتشعيع بالليزر على الخواص البصرية لأغشية $AgAlS_2$ الرقيقة

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الخلاصة

في هذا البحث تم دراسة تأثير التلدين الحراري بدرجة حرارة(400°C) لمدة ساعتين والتشعيع بليزر الاركون لمدة نصف ساعة على الخواص البصرية لأغشية $AgAlS_2$ الرقيقة المحضرة على قواعد زجاجية بطريقة الرش الكيميائي الحراري بدرجة حرارة(360°C) وبسمك µm (0.18±0.05). الخصائص البصرية لهذه الأغشية المحضرة قد درست بواسطة جهاز المطياف للطول الموجي 1100)nm – 300). هذه الاغشية تمتلك انتقالات الكترونية مسموحة مع فجوة طاقة تتناقص من eV (2.25) للغشاء الأصلي ليصل إلى eV (2.10) للغشاء الملدن وeV (2.00) للغشاء المشعع. القيمة العظمى لمعامل الانكسار لكل الأغشية حوالي (2.6) ، قيم معامل الخمود وثوابت العزل الكهربائي والخيالي تتشابه من حيث السلوك . هذه النتائج تبين أن الأغشية تمتلك خواص جيدة للتطبيقات الالكتروبصرية .

Introduction

Most of the I-III-VI_2 compounds are direct gap semiconductors and they crystallize with the chalcopyrite structure [1-4].They have attracted a lot of attention due to their potential applications in opto-electronic and photovoltaic devices. Although the information on Ag chalcopyrite compounds are scarce compared with Cu compounds, there is many studies about Ag compounds are found [3-6].

Among the various thin film deposition techniques, spray pyrolysis is one of the principle methods used to produce a large area and uniform coating at simple and low cost [7].It is well known that the optical properties of thin films are highly sensitive to the preparation conditions and treatment conditions [2].

The interaction of laser beams with solid surfaces produce a variety of surface morphology changes, many of which show ripple structure with periods comparable to optical wavelength [8]. Energy-beam shaping can be used to prevent heterogeneous nucleation and promote growth of long individual grains. Argon laser offers the potential for good control over the recrystallization process because of the ability to produce a narrow molten zone and to shape the beam with a variety of optical techniques [8]. In this paper, deposition of $AgAlS_2$ thin films by chemical spray pyrolysis and the effect of thermal annealing and laser radiation optical properties of thin films are studied.

Experimental

$AgAlS_2$ thin films were prepared using the chemical spray pyrolysis method .The films deposited on micro glass slides , which were first ,cleaned with distilled water and then dipped in acetone .Spray solution are prepared by mixing 0.08M of AgNo3 , $Al(NO_3)_2.9H_2O$ and thiourea{ $CS(NH_2)_2$} with ration of 1:1:2 respectfully. Then mixed the amount of solution by a magnetic stirrer. We used filtered air for spraying the solution an square slide glass at temperature 350^{o}C.

The film thickness was measured by optical method .The UV-Vis spectrophotometer type JENWAY (6405 UV/Vis) was used to measurement the absorption and transmission for prepared thin films in the range (300 – 1100) nm, the optical parameters were calculated .Some the prepared films was annealing at 400^{o}C for 2 hours. by thermal furnace .

The other thin films was exposed to Argon laser (Ar) radiation, its power (150)mW and wavelength (540)nm for (30) min with distance (100) cm.

Results and discussion

The absorption coefficient (α) of the prepared $AgAlS_2$ thin films also of the thermal annealing and of which irradiated by laser radiation were found from the following relation [9]

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

where (A) is the absorbance and (t) is the film thickness.

Fig. (1) shows the plot of (α) with wavelength (λ), which obtained that the value of $\alpha > 10^4\ cm^{-1}$ for all films in the visible region , this means that the transition must corresponding to a direct electronic transition [7] , and the properties of this state are important , since they are responsible for electrical conduction. Also, fig.(1) shows that the value of (α) for the annealed and irradiated films are greater than that untreated films. The increase in absorbance after annealing the thin films at 400ºC for 2 hours and radiated by Argon Laser for (30)minutes , may be due to the increase in grain size and

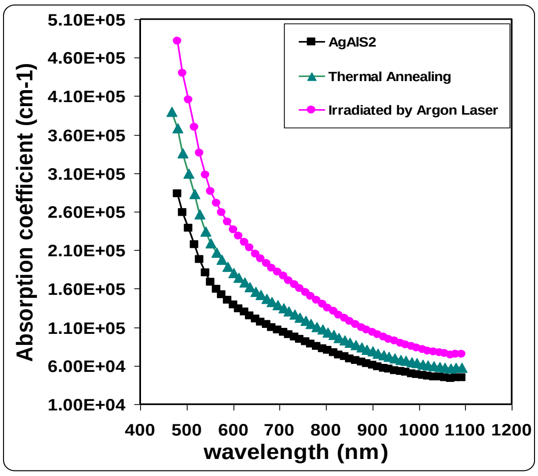

Fig. (1). The variation of absorption coefficient (α) with (λ) for thin films decrease in the number of defects as explained by Ezema[10]

The optical energy gap (E_g) has been calculated by the relation [11]

$$(\alpha h\upsilon)^2 = C(h\upsilon - E_g) \quad \text{........(2)}$$

where (C) is constant. By plotting $(\alpha h\upsilon)^2$ vs photon energy ($h\upsilon$) as shown in fig.(2).

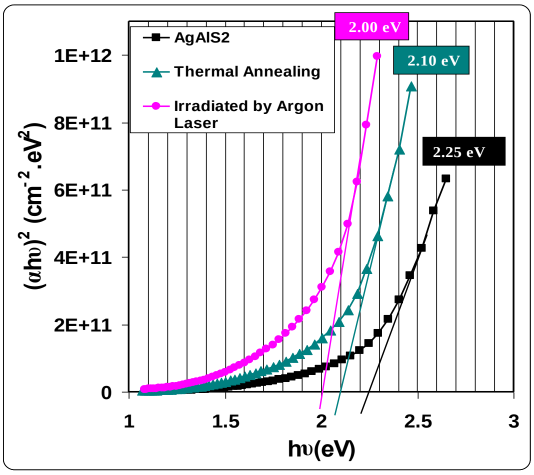

Fig. (2).The optical energy gap (E_g) value of thin films

And by extrapolating the straight thin portion of the curve to intercept the energy axis , the value of the energy gap has been calculated [11] . the value of (E_g) obtained was (2.25) eV , which is approach the value of (2.30) eV reported elsewhere [3] .

The value of(E_g) was decreased from (2.25) eV to (2.10) eV at thermal annealing and to (2.00) eV at laser radiated . The decreasing of (E_g) may be related to decrease in grain boundaries and their density due to the heating effect of the polycrystalline thin films. It was observed that the different structures of the films confirmed the reason for the band gap shifts. The behavior of (E_g) was agreement with researcher [10, 12].

Extinction coefficient (K) was calculated using the related [9].

$$K = \lambda\, \alpha / 4\pi \quad \text{........... (3)}$$

The variation at the (K) values as a function of (λ) are shown in fig. (3).

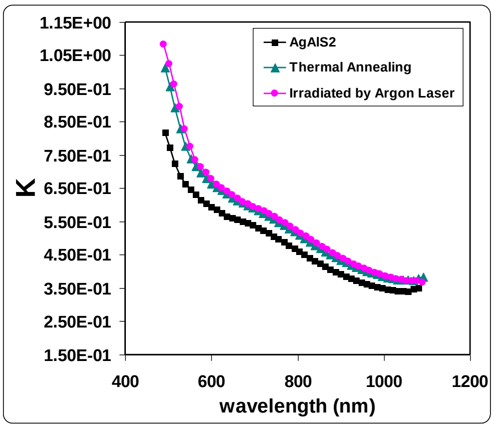

Fig.(3).The variation of extinction coefficient (K) with wavelength (λ) for thin films

It is observed that the spectrum shape of (K) as the same shape of (α).Fig.(3) obtained the value of (K) at the visible region was depend on the film treatment method , where the value of (K) at (500) nm for untreated film is (0.72) while for annealed film at the some wavelength equal (0.88) and for irradiated film equal to (0.96) at the same wavelength ,this difference in (K) value become smaller at NIR region .

The refractive index (n) is the relative between speed of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation [9]:

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

Where (R) is the reflectivity. The variation of (n) vs (λ) is shown in fig.(4).

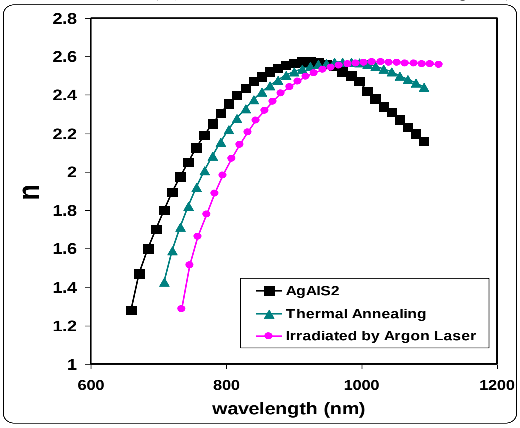

Fig.(4). The variation of refractive index (n) with wavelength (λ) for thin films which shows that the maximum value of (n) is (2.6) for all films at the same wavelength which is agreement with ref.[3]. Also we can show that the value of (n) begin to increase in the region of spectrum while (K) in its region became constant .Also (n) value decrease with annealing and with irradiated , this means that the film become more transparent in the (near infrared(0.7 – 1 μm)(NIR) region.

Fig.(5) shows the variation of the real dielectric constant ($€_1$) with wavelength of $AgAlS_2$ thin films, which calculated from the relation [9]

$€_1 = n^2 – K^2$ …………… (5)

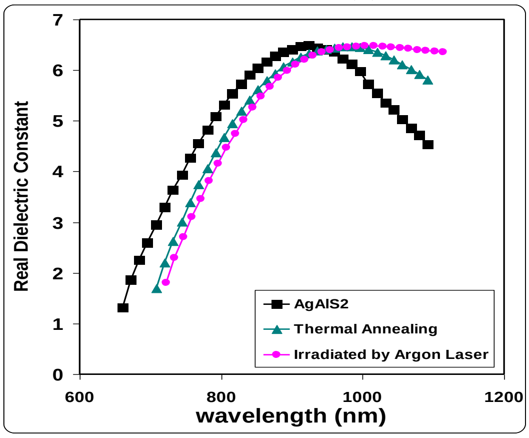

Fig. (5).The variation of ($€_1$) with wavelength (λ) for thin films

Where the real the dielectric ($€_1$) is the normal dielectric constant .From fig (5) the variation of ($€_1$) is follow the refractive index, where increased in the region that λ > 650 nm, where the absorption of the film for these wavelength is small, but the polarization was increase. The maximum value of ($€_1$) equal to (6.5) for all films at wavelength near (950) nm . The effect of thermal annealing and laser irradiation of thin films decreased ($€_1$)in the region below (950) nm wavelength .

The imaginary dielectric constant ($€_2$) vs (λ) was shown in fig.(6) this value calculated from the relation [9]:

$€_2$= 2nK ………(6)

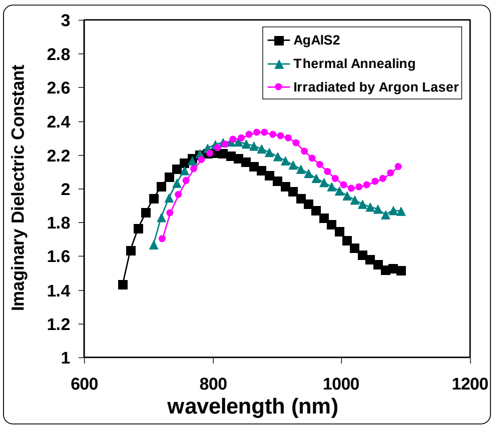

Fig.(6). The variation of ($€_2$) with wavelength (λ) for thin films

($€_2$) represent the absorption associated with free carriers [13] .As shown in fig(6) the shape of ($€_2$) is the same as ($€_1$), this means that the refractive index was dominated in these behavior . The maximum values of ($€_2$) are different according to the treatment operation , so the maximum value of($€_1$) for untreated thin film equal to (2.2) at (800) nm , while $€_2$= 2.3 at λ = 850 nm for annealed thin film, and $€_2$ = 2.35 at λ = 900 nm for laser irradiated thin films , these behavior may by related to the different absorption mechanism for free carriers.

Conclusions

$AgAlS_2$ thin films deposited by thermal spray pyrolysis show band gap (2.25) eV which under thermal annealing in oven was found to be (2.10) eV and (2.00) eV at irradiated by Argon laser.

Under these treatment the film shows a red shift of (0.15) eV for annealing and (0.25) eV for laser radiation in its optical spectra .Such dependence has been attributed to the structure of the film. The extinction coefficient value was increased in the visible region with treatment. The films give refractive index value equal to (2.6) in the NIR region .Hence, these treatment for thin film give a best optical properties to be used for optoelectronic applications.

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