Synthesis and study the optical properties of thin film $CdCr_2S_4$ on glass formed by chemical spray pyrolysis

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الخلاصة

لقد تم تحضير غشاء ($CdCr_2S_4$) بطريقة الرش الكيميائي الحراري على قواعد زجاجية نظيفة مسخنة بدرجة حرارة (673K) وبسمك (430nm) . اطياف الاشعة المرئية - فوق البنفسجية للاغشية درست باستخدام حسابات الامتصاص البصري والتي اخذت من المنطقة الطيفية من (300nm الى 1100nm) . ومن هذه الاطياف ثم حساب الثوابت البصرية مثل فجوة الطاقة البصرية للانتقال المباشر المسموح والممنوع ومعامل الامتصاص الخمود ومعامل لانكسار . وان معامل الامتصاص للغشاء اكبر من (10^4cm^{-1}) وهو ما يدل على حدوث انتقالات الكترونية مباشرة . وكانت قيم فجوة الطاقة البصرية لانتقال المباشر المسموح(3.325eV) وللانتقال الممنوع (2.16eV.)

Abstract

($CdCr_2S_4$) thin film has grown on cleaned glass substrate at (673k) temperature using spray pyrolysis deposition technique of thickness (430nm) . UV-VIS. spectra of the film was studied by using the optical absorbance measurements which were taken in the spectral region from (300-1100)nm . Optical constants such as optical allowed and forbidden energy band gap of direct transition , absorption coefficient , extinction coefficient and refractive index were evaluated form these spectra. $CdCr_2S_4$ has high value of absorption coefficient ($\alpha > 10^4$ cm^{-1}) which conducive to increasing the probability of occurrence direct transitions .Optical allowed band energy for direct transition was (3.325eV) and the forbidden one was (2.61eV) .

1-Introduction

Spray pyrolysis technique is basically a chem ical deposition technique in which the fine droplets of the solutioncontaining the desired species are sp rayed on

preheated substrate . The thermal decomposition taken place on the hot substrate giving rise to a continuous film [1,2,3]. We used this method in this study because of it's preeminent features of deposition are large area , deposition with homogenous , low fabrication cost , simplicity , fast , non-vacuum system and low deposition temperature [4,5] . Also this method is convenient for preparing pinhole free, homogenous , smoother thin films with the required thickness [6] .

The optical properties of thin films are markedly different from these of the specimen bulk and are dependent on many parameters such as film thickness, film substrate and substrate temperature [7,8] .

2-Experimental Details

The $CdCr_2S_4$ thin films were prepared by spraying a aqueous mixing solutions of 30 mm of $Cd(No_3)_2 .4H_2O$, 30mm of $Cr(No_3)_3$ and 30mm of thiourea$(NH_2)_2CS$ which they prepared as follows :-

1- Preparing $Cd(NO_3)_2.4H_2O$ solution :-

The $Cd(NO_3)_2.4H_2O$ solution was prepared with (0.1M) by dissolving

(6.1694gm) of it in (200ml) of distilled water

2- Preparing $Cr(NO_3)_3$ solution :-

The $Cr(NO_3)_3$ solution was prepared with (0.1M) by dissolving

(8.0029gm) of it in (200ml) of distilled water.

3-Prepation of $(NH_2)_2CS$ Solution :-

The Thiourea Solution was prepation with 0.1M by dissolving (1.5224gm) of it in 200ml of distil water

The resulting mixed solution was sprayed on preheated glass substrates to 673K , the formed CdS and Cr_2S_3 films .

The diameter of the solution tip of the nozzle is 1mm . The substrate to nozzle distance was kept at 30cm .

The resulting films were yellow in color , free from pinholes and have a good adhesive properties , $CdCr_2S_4$ thin films were prepared with different thickness , the selected thickness was 430nm . The absorbance and transmittance of prepared thin film was measured using shimadzu 157UV.VIS . spectrophotometer in the wavelength range (320-1100)nm.

3-Result and Discussion

Absorption Coefficient

From the absorbance date, the absorption coefficient (α) was calculated in the fundamental absorption region using Lambert law [3,9,10] :

$$Ln (I_0/I) = 2.303A = \alpha d$$

$$\alpha = 2.303 A/d \text{ - - - - - - - - - - - - } (1)$$

Where I_0 and I are the intensity of incident and transmitted light respectively, A the optical absorbance and d the film thickness. Fig.(1) shows the variation of absorption coefficient with photon energy for $CdCr_2S_4$ thin film , the Fig. also shows the variation of absorption coefficient in the low energy range then it's value increases exponentially beyond absorption else region (2.5-3.55)eV . We can evidently see that $CdCr_2S_4$ thin film has high value of absorption coefficient ($\alpha > 10^4$ cm^{-1}) which be conducive to increasing the probability of occurrence direct transitions .

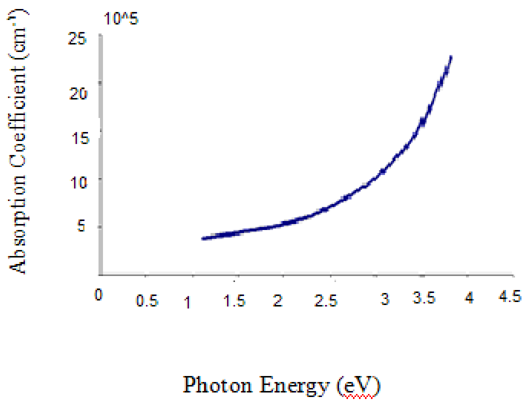

Fig.(1) Absorption coefficient vs. photon energy of $CdCr_2S_4$ thin film .

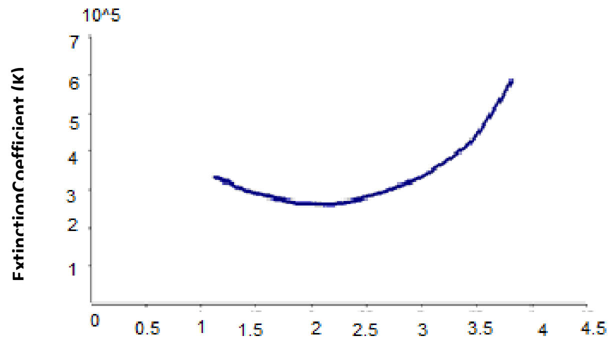

Fig.(2) Extinction coefficient vs .photon energy of $CdCr_2S_4$ thin film .

Extinction Coefficient

Extinction coefficient (k) of prepared films was calculated by using the relation[11,12]

$K= \alpha\lambda/4\pi$ ------------------ (2)

Where λ is the wavelength of incident photon . Variation of extinction coefficient as a function of photon energy is shown in Fig.(2) ,the extinction coefficient of prepared film has values in the ranges (260000-600000) . It can also be seen that the exponential increase in extinction coefficient beyond absorption edge region because of the occurrence direct transitions .

In the case of polycrystalline films , extra absorption of light occurs at the grain boundaries [3] . This leads to non-zero value of K for photon energies smaller than the fundamental absorption edge .

Reflctance

Fig.(3) shows the optical reflectance spectra for $CdCr_2S_4$ thin film . The reflectance has been found by using the relation ship :

R+T+A=1-------------------------------(3)

The figure also shows that the film reflectance increases rapidly at the low energies and then makes peaks at the energies which are corresponding to the energy gap of the film , then the reflectance decreases at the photon energy which is larger than the energy band gap which are attributed to the low absorbance of the film at the photon energies less than the forbidden energy gap , and when it becomes larger or equal to the energy band gap a clear value of absorbance appears and increases because with the material electrons interaction with the incident photon which has enough energy to make the electronic transition take place [3,4] .

There is some difference in calculation the value of forbidden energy gap from reflectance and absorbance curves because of the difference in thin films surface nature

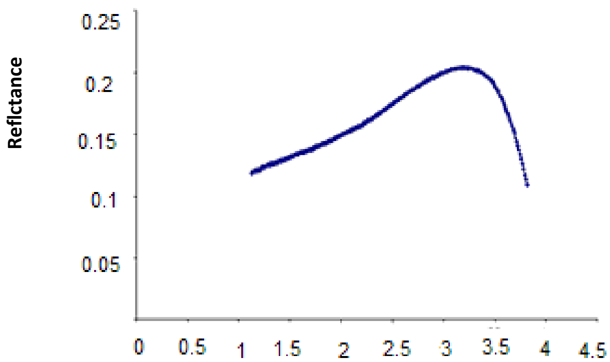

Fig.(3) Reflectance vs. photon energy of $CdCr_2S_4$ thin film .

Refractive Index

Form the reflectance data , the refraction index (n) was calculated by using the following relation ship [13] :

$n= (1+(R)^{1/2})/(1-(R)^{1/2})$ ---------------------(4)

where R is the reflectance

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The behavior of this fig. is similar to the behavior of reflectance spectra in fig.(3) , because of the strong dependence calcul-ation of the refractive index values on the reflectance value as above relations-hip ,where the refractive index increases rapid ly at the low energies which is corresponding to the energy gap of the film.

Then (n) decreases at the photon energy which is larger than the energy band gap because of the increasing the direct electronic transitions at that energies . The results show that the refractive index values of prepared film have values in the rang (2.1-2.6)eV . It can be also said that at every lowest value of refractive index there is highest value for extinction coefficient [14] .

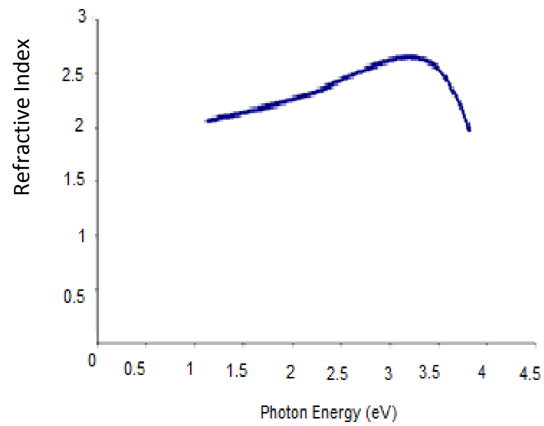

Fig.(4) Refraction index Vs. photon energy of $CdCr_2S_4$ thin film

Energy Gap

Study of material by means of optical absorption provides a simple method for explaining some features concerning the band structure of material. The nature of transition (direct or indirect) is determined by using the relation [5,15] .

$\alpha h\nu = A(h\nu - Eg)^n$ -------------------------(5)

gap energy , A the optical absorbance and n are constants . For allowed direct transition , n=1/2 and for forbidden direct transition , n =3/2 . The plot of $(\alpha h\nu)^2$ vs . hν is show in Fig.(5) for $CdCr_2S_4$ thin film . of the plot indicates the existence of direct transitions .

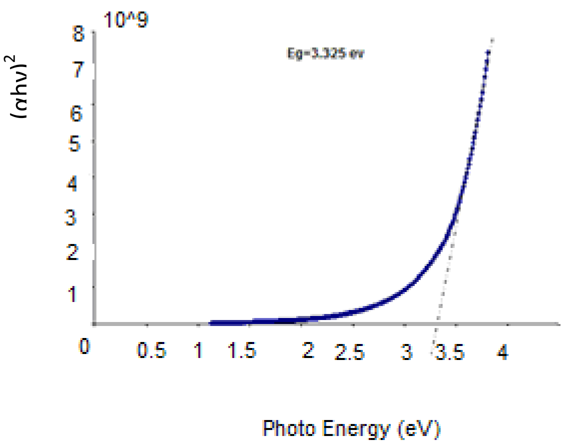

Fig.(5) variation of $(\alpha h\nu)^2$ with photon energy for $CdCr_2S_4$ thin film .

In Fig.(5) . from the straight line obtained at high photon energy the direct allowed energy gap could be determined which was equal (3.325eV).

The plot of $(\alpha h\nu)^{2/3}$ vs . hν is shown in Fig.(6) of $CdCr_2S_4$ thin film for forbidden direct transition was equal (2.61eV) .

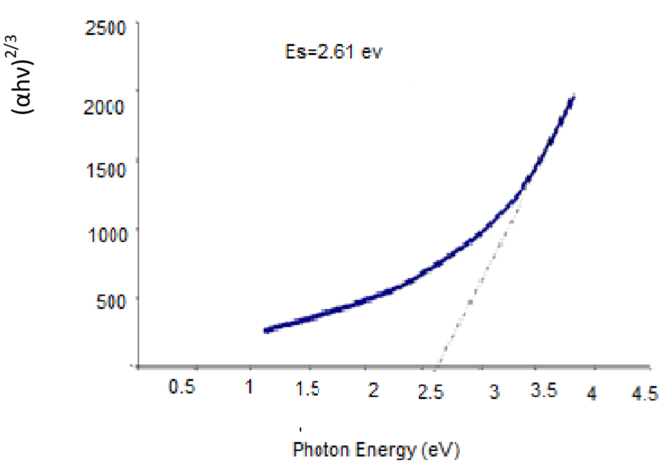

Fig.(6) variation of $(\alpha h\nu)^{2/3}$ with photon energy for $CdCr_2S_4$ thin film .

4-Conclusion

$CdCr_2S_4$ film was prepared by a spray pyrolysis technique using .

the mixing of three solution :

$Cd(NO_3)_2.4H_2O$, $Cr(NO_3)$ and thiourea $(NH_2)_2CS$, The film was deposited on glass substrate af thickness (430nm) has been characterized by using optical measurements to obtain optical properties as R spectra , optical band gap energy , refractive index , absorption and extinction coefficient . The variations of these parameter with incident photon energy wavelength have been studied .

The film shows a direct transition which was (3.325eV) for allowed energy gap and (2.61eV) for forbidden one . In conclusion , spray pyrolysis techiqe s a good methode foe product and preparation of thin films which are suitable for scientific studies and for many applications in technology and industry .

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