Preparation and Characteristics Study of ZnS Thin Films by Chemical Bath Deposition Method

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Abstract

Thin films of zinc sulfide (ZnS) have been deposited by chemical bath deposition technique using the zinc nitrate salt($Zn(NO_3)_2$) was used as a source of zinc ions(Zn^{+2}) and thiourea ($SC(NH_2)_2$) as a source of negative sulphide ions(S^{-2}). The effect deposition temperature on the structural and optical properties is described. The XRD studies revealed that the deposited films have a polycrystalline and the hexagonal structure and the grain size increases from 22 nm to 45 nm with increasing deposition temperatures. The average transmittance of ZnS films in the visible region was between 40–701% with direct optical energy decreases from 3.66eV to 3.38 eV with increasing deposition temperature.

***Keywords**: ZnS films, chemical bath deposition, effect deposition temperatures , structural and optical properties.*

Introduction

Zinc Sulphide is an important II–VI compound semiconductor with a large band gap n-type semiconductor, whose bandgap was reported to be about 3.6 eV[1,2] . It is used as a key material for light-emitting diodes [3], cathode-ray tubes [4], thin film electroluminescence [5], and buffer layers in photovoltaic cells [6]. In general, Zinc sulfide exists in two forms, cubic (zinc blende) and hexagonal (wurtzite) [7].ZnS is highly suitable as a window layer in hetrojunction photovoltaic solar cells; because the wide band decreases the window absorption loses and improves the short circuit current of the cell . In the area of optics, ZnS can be used as a reflector, because of its high refractive index (2.35), and a dielectric filter because of its high transmittance, in the visible range [8]. Several techniques such as SILAR, electrodeposition, chemical bath deposition , spray pyrolysis , vacuum evaporation and pulsed laser deposition have been used to produce ZnS films.[9-14]. Among them, CBD is the least costly and is a low temperature technique. The CBD process uses a controlled chemical reaction to effect the deposition of ZnS film by precipitation. In the most typical experimental approach, substrates are immersed in an alkaline solution containing the chalcogenide source, metal ions, an added base and a complexing agent. The deposition of ZnS by using CBD is a more difficult proposition than the deposition of CdS. It is evident that there is a much wider range of conditions in which the concurrent deposition of ZnS and zinc oxide can occur [15]. When the ZnS film is doped with a small amount of metallic ions, it emits light in the visible region, which is characteristic of the incorporated impurity. Therefore, it forms a very important class of phosphors for the fabrication of electroluminescent devices. For example, ZnS:Cu has turned out to be a good CRT phosphor and is applied in, for example, colour TVs and oscilloscopes. Therefore, the luminescent properties of ZnS phosphors doped with metallic ions have been discussed extensively in the literature, and information on the properties of such phosphors can be found in many books dealing with luminescence [16–18].

In the present work, we report the chemical bath deposition of ZnS thin films and their characterization. The effect of deposition temperatures on structural and optical properties of these films is investigated with the objective to optimize the conditions of the deposition process.

Experimental.

Zinc sulfide thin films have been deposited on glass substrates using the chemical bath deposition technique. Glass slides (75×25×1 mm) were used as substrates. The slides were cleaned with soft cotton and washed with double distilled water and dried in air. The ZnS films was grown on glass substrate by using the Zinc nitrate salt[$Zn(NO_3)_2 .6H_2O$] in molarity of 0.06 M as a source of zinc ions(Zn^{+2}) and 0.1M thiourea [$SC(NH_2)_2$] as a source of sulphide ions (S^{-2}). Ammonia solution (NH_4OH) 30 % was added slowly to form the complex and pH was adjusted between 10 and 11. The solution was stirred to ensure homogeneous dissolve about 5 minutes. The deposition was carried out in a 100 ml beaker at different bath temperatures of 50, 60,70 and 80 ^oC for a deposition time of 12 h. The glass substrate was held by Teflon holder when they were immersed vertically in the chemical bath. After the deposition, the samples were taken out from the bath, washed in distilled water and dried at 80 ^oC for 15 min in a hot air oven. The film thickness was measured by laser interferometer. The X-ray diffraction(XRD) analysis was carried out using X-ray 6000(Shimadzu) diffractometer with Cuk_α radiation (λ=1.541 Å) at 40 kV and 30 mA .The optical transmission spectra were investigated by UV-Visible Spectrophotometer (Cintra 5) GBC-Astrural

Results and discussion

1-Reaction Mechanism

The CBD is based on the formation of the sold phase from a solution, which involves two steps as nucleation and particle grown. In the nucleation, the cluster of molecules formed undergo rapid decomposition and the particle combine to grown up to certain the thickness of the film by homogeneous reactions at the substrate surface [19]. The reaction mechanism for the formation of ZnS could be understood as follows.

Ammonia hydrolyzes in water can give out OH^-:

$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$…………………… (1)

The source of Zn^{2+}:

$Zn(NO_3)_2 \longrightarrow Zn^{2+} + 2NO_3^-$……………………(2)

Zn^{2+} and NH_3 form a complex species of cadmium $[Zn(NH_3)_4]^{2+}$ (to slowly release Zn^{2+}):

$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$ ……………………(3)

Then

$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$……………………… (4)

Thiourea hydrolyzes in alkaline solution to give S^{2-}(The source of S^{2-}):

$SC(NH_2)_2+2OH^- \longrightarrow S^{2-}+CN_2H_2+2H_2O$.............. (5)

Zinc sulfide is formed:

$[Zn(NH_3)_4]^{2+} + S^{2-} \longrightarrow ZnS + 4NH_3$ …………...(6)

Fig. 1 shows the variation of ZnS film thickness as a function of the deposition temperatures. The thickness increases from 160 to 330 nm when the deposition temperature decreases respectively from 50 ^oC to 80 ^oC.The increase in deposition rate refers that in any chemical reaction the reaction rate is proportional to the temperatures of the reacting species .

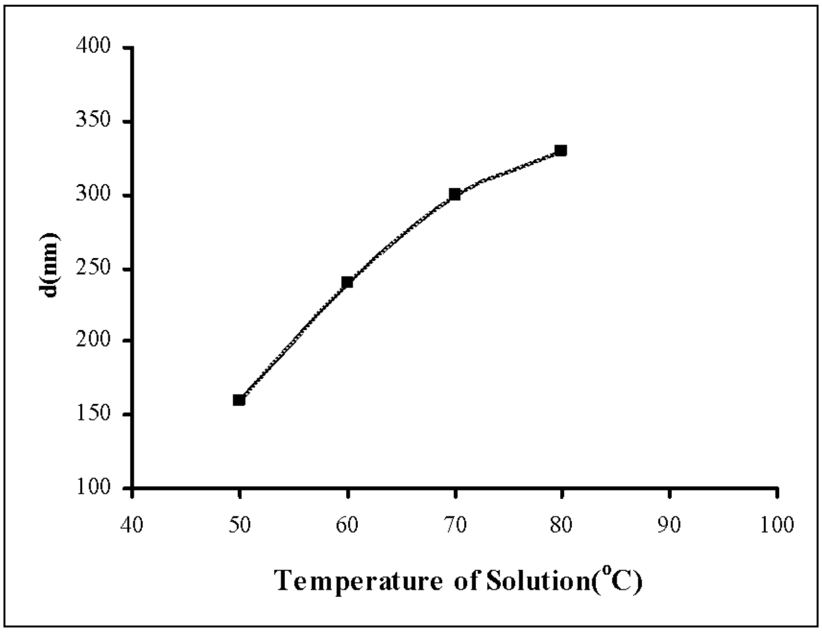

Fig.(1) :Terminal thickness of ZnS films as a function of the deposition temperature.

2-X-Ray Diffraction

All the deposited ZnS films were white, homogeneous with a good adherence to the substrate. Generally ZnS material has the hexagonal, wurtzite type structure or cubic, zinc blende-type structure. X-ray diffraction patterns of ZnS thin films prepared with different deposition temperatures are shown in Fig.2. Comparison of interplaner (d) values with JCPDC data show that phase present in the deposited films belongs to pure hexagonal wurtzite structure without any impurity phases. It is also noted that as the temperature of solution increases, the intensity of (002) peak increases and this peak becomes narrower indicating an improvement of the crystallinity. This behavior appreciably a constant procedure for all films were prepared by CBD as reported in literatures [7,18,20].

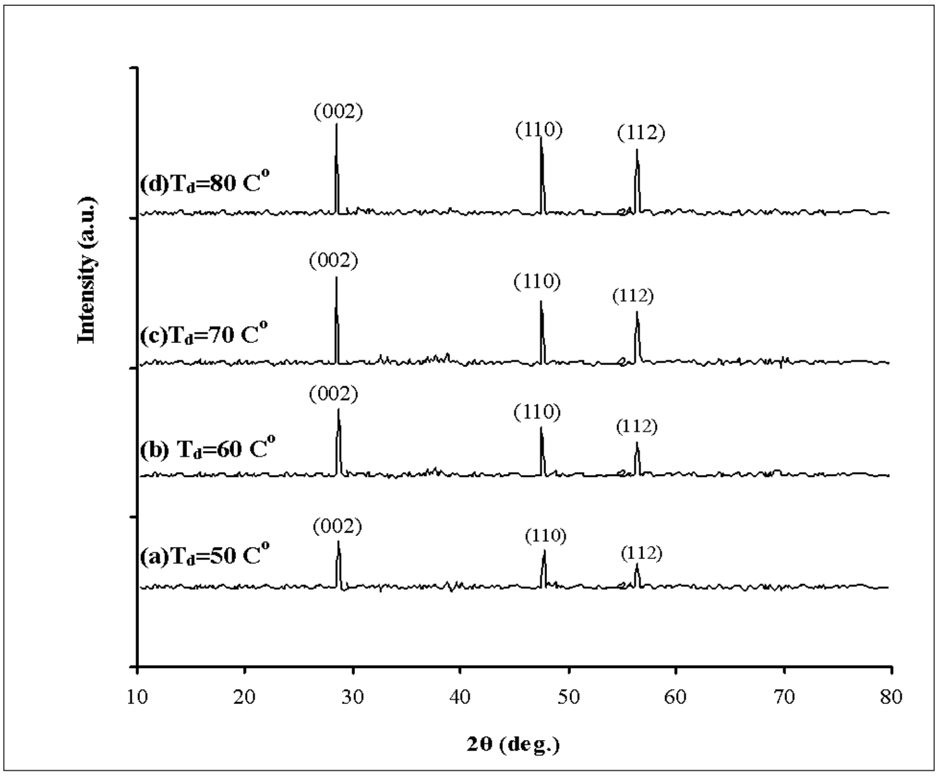

Fig.(2) :The X-ray diffraction patterns of ZnS films deposited at different bath temperatures .

The average grain size of ZnS film was calculated from the following Scherrer's equation for the (002) direction[21].:.

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Where k is a constant taken to be 0.94, λ is the X-ray wavelength ,β is the full-width at half-maximum (FWHM) of the peak, and θ is the reflection angle[18].The grain sizes of the ZnS films increase from 22 nm to 45 nm , when the deposition temperature increases, as shown in figure(3) where increasing temperature of solution causes to increasing in grain size .Several authors have reported the nature of the films having such grain sizes [22-26].

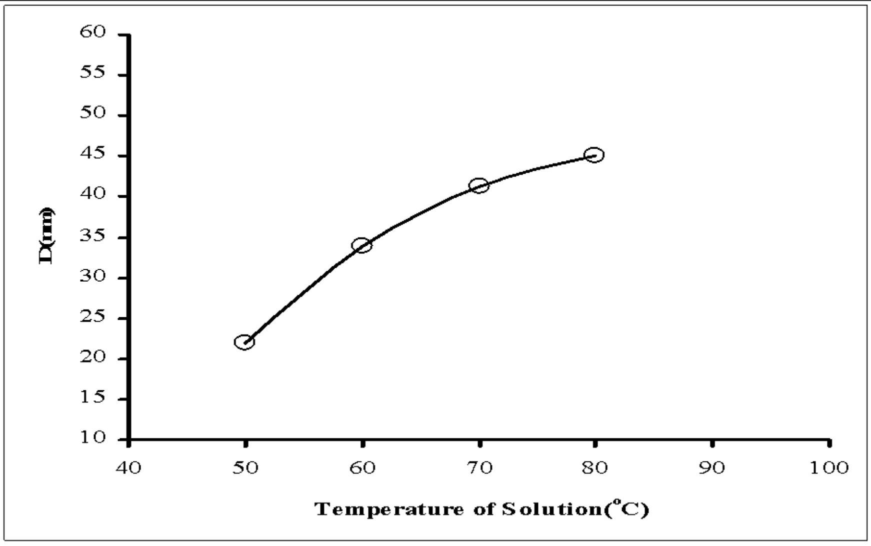

Fig.(3) :Grain size of ZnS films as a function of the deposition temperature.

3-Optical Properties

Fig.4 shows the effect of the temperature of solution on the transmission spectra in for the range 200 – 800 nm. The transmittance of the films in the visible and near-IR regions decreases with increasing deposition temperature (from 77 % to less than 40%) causes an increase of grain size as a result of increasing the film thickness and the optical transmittance spectra also show the shifting of the band edge to lower energy (red shift) as the temperature of solution increases.

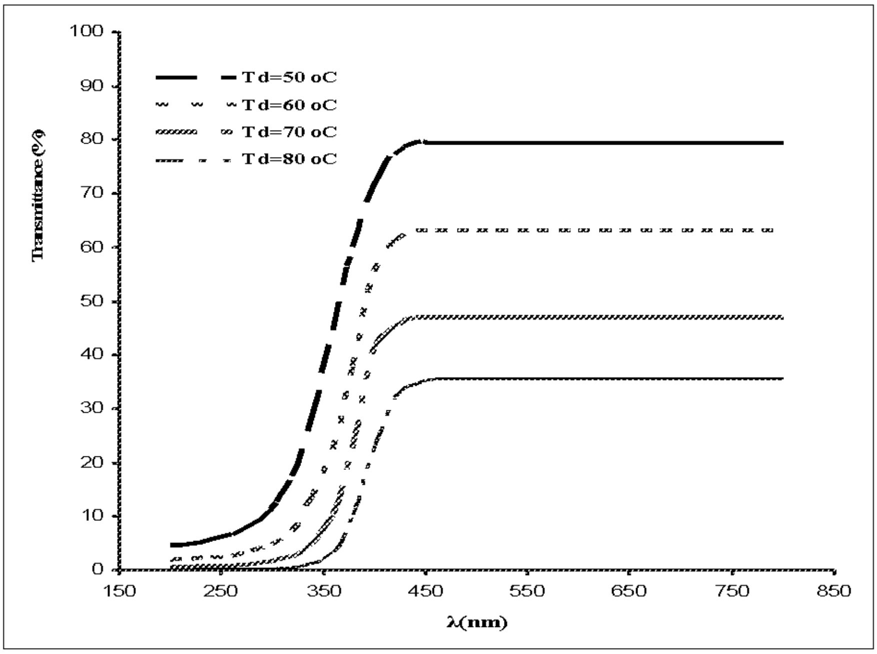

Figure (4):The optical transmission spectra as a function of wavelength of ZnS films at different bath temperatures .

The optical direct band gap Eg of the films can be estimated by extrapolation of the linear portion of $(\alpha h\nu)^2$ vs. hν plots using the Tauc relation [27]

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where α is the absorption coefficient, hν is the photon energy and A is the band edge constant. The corresponding plots are shown in Fig. 5. The band gap value decreases from 3.66 to 3.38 eV when the deposition temperatures decreases respectively from 50 ^{o}C to 80 ^{o}C. , this can be attributed to the effect of grain size and the crystal quality was improved [28] . The obtained values of band gap are agreed well with those reported recently [8,29,30].

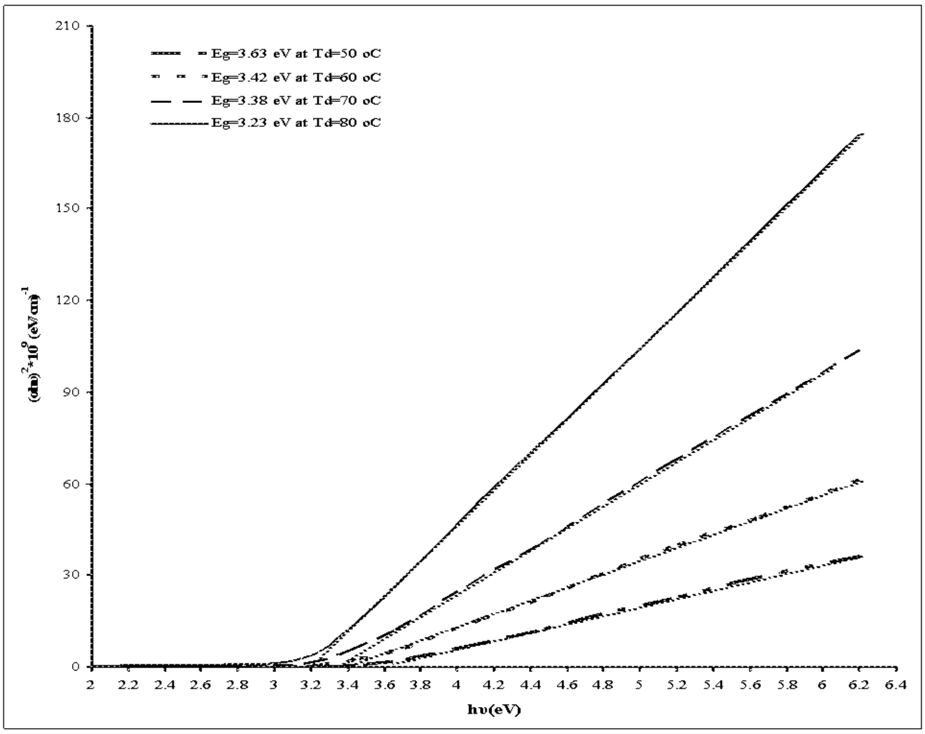

Figure (5): A plots of $(\alpha h\upsilon)^2$ versus (hυ) of ZnS films at different at different bath temperatures.

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Conclusions

The ZnS films are prepared by low cost chemical bath deposition technique with different bath temperature. The structural and optical studies were carried out. The XRD measurements indicate that the structure of the ZnS thin films is hexagonal structure. The crystallite size and band gap were found to change with the bath temperature. Band gap decreases with increase in crystallite size. The ZnS films are highly transmittance of more than 77% and decrease with the bath temperature. ZnS having wide band gap of 3.3-3.6 eV is a promising material to be used in photovoltaic devices, solar cells and detectors.

References

[1] Kurbatov D, Opanasyuk A, Kshnyakina S, Melnik V, Nesprava V, (2010). Rom. Jur. Phys., Vol. 55, p. 213–219.

[2] Kobayashi R, Sato N, M Ichimura,Arai E,(2003). J.opt. and adv. mater.,Vol. 5, p. 893 – 898.

[3] Yamamoto T, Kishimoto S, Iida S, (2001) . J. Phys. ,pp. 308–310.

[4] Karim A., Arle R.N., Mujeeb S,(2012). Research Expo International Multidisciplinary Research Journal, ,Vol.2,p.188-192..

[5] Kavanagh Y, Alam M.J, Cameron D.C, (2004). thin solid films,Vol.85,p.447–448.

[6] Contreras M.A, T. Nakada, Hongo M, Pudov A.O, Sites J.R, (2003). Proceedings 3rd World Conference of Photovoltaic Energy Conversion, Osaka, Japan, p. 570 .

[7] Ben Nasr T, Kamoun N,Kanzari M, Bennaceur R,(2006). thin solid films,Vol.500,p.4– 8.

[8] Kumar V,Sharma M.K,Gaur J,Sharm T.P,(2008). Chalcogenide Letters Vol.5, p.289– 295.

[9] Yildirim A.A,Kundakci M.A, Astam M. A,(2007).Mater.Sci .Semicond. Process ,Vol.10, p.281-286.

[10] Huang J.F, Zhu H, Cao L.Y, Wu J.P, He H.Y, (2008). Synth. Cryst.,Vol.37, p.862-865.

[11] Zhou L, Xue Y, Li J , (2009). environ. Sci. Vol.21,p. 76-79.

[12] Yazici A.N, Oztas M, Bedir M, (2003). Lumin,Vol.104,p. 115-122.

[13] Kashani H,(1996). thin solid films , Vol.288 ,p.50.

[14] Laughlin Mc, Sakeek M, Maguire H.F, Graham P, Molloy W.G, Morrow J, Laverty T, Anderson S, (1993). Appl. Phys. Lett. Vol.63, p.1865-1867.

[15] Brien P.O., McAleese J.,(1998). J. Mater. Chem. Vol.**8**, no.2309,p. 256.

[16] McKeever S.W.S., (1985).Thermo luminescence of Solids ,Cambridge: Cambridge University Press.

[17] McKeever S.W.S., Moscovitch M., Townsend P.D., (1995). Thermo luminescence Dosimetry Materials: Properties and Uses mAshford: Nuclear Technology Publications.

[18] Vij D.R., (1998).Luminescence of Solids ,New York: Plenum.

[19] Oladeji I.O, Chow L, (1999). thin solid films. Vol.339 , p.148-153.

[20] Eid A.H, Salim S.M, Sedik M.B, Omar H, Dahy T, Abou elkhair H.M,(2010). Appl. Sci. Research, Vol.6,p.777-784.

[21] Cullity B.D., (1978)Elements of X-ray Diffraction, Addison-Wesley, MenloPark.

[22] Sankapal B. R, Sartale S.D, Lokhane C.D, Ennaoui A, (2004). Sol. Energy Mater. & Solar Cells, Vol. 83,p. 447.

[23] Liu Q. Mao G,(2009).Surface Rev. and Letters, Vol. 16,p.895–899.
[24] Sanap V. B, Pawar B. H,(2011).Opto. and Biomedical Mater. Vol. ,p. 39-43.
[25] Beevi M.M, Anusuya M, Saravanan V,(2010). International Journal of Chemical Engineering and Applications, Vol. 1,p.151-154.
[26] Hai-Qing X,Yuan C,Wei-Qing H, Gui-Fang H, Ping P, Li P,Tai-Hong W, Yun Z, (2011).Chin. Phys. Lett. Vol. 28,p. 1-4.
[27] Noikaew B, Chinvetkitv A. P, Sripichai I, Chityuttakan C, (2008).Metals , Vol.18, p.49-52.
[28] Goudarzi A, Aval G. M, Sung Soo. P, Myeon-Cheon C, Reza S, Habib M. U, Avane A, Chang-Sik H, Chem. Mater. (2009), Vol.21, p. 2375–2385.
[29] Baishay U , Serka D, (2011). Indian J. Pure Appl. Phys, Vol.49, p.186-189.
[30] Borah J.P, Sarma K.C, (2008).Acta Physica Poloncia ,Vol. 114,p.713-719.

تحضير ودراسة خصائص الغشاء الرقيق ZnS بطريقة ترسيب الحمام الكيميائي

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الخلاصة

تم ترسيب أغشية رقيقة من مادة كبريتيد الزنك ZnS بطريقة ترسيب بالحمام الكيميائي، إذ استخدم ملح نترات الزنك$(Zn(NO_3)_2)$ كمصدر لايونات الزنك الموجبة (Zn^{2+}) والثايوريا$(SC(NH_2)_2)$ كمصدر لايونات الكبريت السالبة (S^{2-}) . وتم دراسة تأثير تركيز درجة حراة الترسيب على الخصائص التركيبية والبصرية. دراسة حيود الأشعة السينية(XRD) بينت ان الأغشية المرسبة لها تركيب متعدد التبلور ومن النوع السداسي وكذلك يزداد معدل الحجم الحبيبي من22 nm الى 45 nm مع زيادة درجة حرارة الترسيب.ومعدل النفاذية لأغشه كبريتيد الزنك ZnS في المدى المرئي من الطيف بين 40–70% مع فجوة طاقة مباشرة تقل من 3.66 eV إلى 3.38 eV مع زيادة درجة حرارة الترسيب.