Structural and optical properties of nanocrystalline ZnS thin films prepared by chemical bath deposition technique

Jamal. F. Mohammad, Hamed. S. Al-jumaili

University of Anbar, College of education for pure Sciences, Physics Department

Abstract

Nanocrystalline ZnS films grown on glass substrates by chemical bath deposition technique (CBD) using the mixed aqueous solution of zinc chloride, thiourea and ammonia at 80 °C and pH=10 for different deposition time. The characterization of thin films was carried out for the structural and optical properties using X-ray diffraction and UV-VIS spectrophotometer. A UV-VIS optical spectroscopy study was carried out to determine the optical band gap of the nanocrystalline ZnS thin film and it found to be higher (3.8 eV) compared with respect to the bulk value. In present work effects of deposition time on the structural and optical properties of CdS nanocrystalline thin films were studies.

Keywords: ZnS thin film, Nanostructured material, Chemical Bath Deposition.

الخصائص التركيبية والبصرية لأغشية كبريتيد الخارصين (ZnS) النانوية المحضرة بتقنية الترسيب بالحمام الكيميائي

جمال فاضل محمد ، حامد صالح الجميلي

جامعة الانبار – كلية التربية للعلوم الصرفة – قسم الفيزياء

الخلاصة

تم تحضير أغشية كبريتيد الخارصين ذو التركيب النانوي بتقنية الترسيب بالحمام الكيميائي على أرضيات زجاجية ، وباستخدام كلوريد الخارصين، الثايوريا والأمونيا وعند درجة حرارة 80 °C وعند قيمة للأس الهيدروجيني (PH=10) ولزمن ترسيب متغير. خصائص الغشاء تم دراستها من خلال دراسة الخصائص التركيبية والبصرية باستخدام تقنية حيود

الأشعة السينية وتقنية دراسة الطيف البصري للمنطقة الطيفية المرئية وفوق البنفسجية، حيث تم تحديد قيمة فجوة الطاقة البصرية للغشاء النانوي ووجد إنها ذات قيمة أعلى من 3.8 eV مقارنة بقيمة فجوة الطاقة البصرية للحالة المحسوسة. في هذا البحث تم دراسة تأثير زمن الترسيب على الخصائص التركيبية والبصرية لأغشية كبريتيد الخارصين النانوية.

الكلمات المفتاحية: أغشية ، ZnS ، مواد نانوية التركيب, تقنية الحمام الكيميائي.

Introduction

In recent years nanocrystalline ZnS attracted much attention because the properties in nano form differ significantly from those of their bulk counter parts. Therefore much effort has been made to control the size, morphology and crystallinity of ZnS thin film. There has been growing interest in developing techniques for preparing semiconductor nano particles and films[1]. ZnS is an important semiconductor compound of the II–VI group with excellent physical properties and large direct band gap between 3.4 to 3.70 eV (bulk, corresponding to wavelength of 337 nm) at 300 K (depending upon composition) makes it transparent to practically all wavelengths of the solar spectrum and 40 meV as exciton binding energy[2-6]. ZnS a wide direct band gap semiconductor with high refractive index (n=2.35), is a promising material for appropriate antireflection coating (ARC) on silicon solar cells[7]. Semiconductor nanoparticles exhibit size-dependent electronic band gap energies, melting temperatures, solid -solid phase transition temperatures and pressures [8]. It is a promising material for optoelectronic device applications such as blue light emitting diodes, electroluminescent devices and photovoltaic cells [9]. Several techniques such as thermal evaporation, molecular beam epitaxy, metal-organic vapor phase epitaxy, chemical vapor deposition, spray pyrolysis, and chemical bath deposition (CBD) have been used to produce ZnS thin films[10]. CBD is one of the most convenient, reliable, simplest, inexpensive methods and useful for large area industrial applications as well as preparation of thin films at close to room temperature [11]. In the present work we study the effect of deposition time on the structural and optical properties of ZnS thin films.

Experimental

Preparation of nanocrystalline ZnS thin films

Microscope glass slides with the size of (1×25×75 mm) were used as substrates. Before deposition, the substrates were degreased with chromic acid solution, washed with deionized water and finally dried in air. Nanocrystalline ZnS thin films have been deposited on glass substrates by CBD technique using zinc chloride ($ZnCl_2$) as Cd^{2+} ion source and thiourea $Cs(NH_2)_2$ as S^{-2} ion source and a suitable complexing agent. All the solutions were prepared in deionised water. For preparation of nanocrystalline ZnS thin films. First, 20 ml (0.1M) of $ZnCl_2$ was taken in a beaker After stirring for several minutes. By continues stirring, 3 ml of hydrazine added drop by drop. It is observed that as soon as the color become milky, after few seconds ammonia solution was added slowly to form the complex and the solution became clear and homogenous. By using PH meter, the pH maintain at pH=10. Then under continuous stirring, 20 ml (0.1M) of $Cs(NH_2)_2$ solution was introduced. Using temperature controller, the bath temperature was raised from room temperature to a maximum of 75± 2 °C and the deposition time was taken to be (1,1.5 and 2 hr.) The clean slide was immersed vertically in a solution beaker with the help of substrate holder. After the end of deposition time, the deposited ZnS film was taken out with white color, then washed with deionized water ultrasonically to remove the loosely adhered ZnS particles on the film and finally dried in air.

Reaction mechanism for the deposition of ZnS films

The deposition mechanism is largely the same for all such materials, but the exact mechanism is not clear enough. A soluble salt of the required metal is dissolved in an aqueous solution, to release cations. The non-metallic element is provided by a suitable source compound, which decomposes in the presence of hydroxide ions, releasing the anions. The anions and cations then react to form the required compound. So before the deposition, the precursor solution which contains the zinc and sulfide ions should be obtained. The sources of zinc ions can be some soluble zinc salts such zinc sulphate ($ZnSO_4$), zinc chloride ($ZnCl_2$), zinc nitrite

$Zn(NO_3)_2$ [7]. Film formation occurs when high surface energy particles reach the substrate (or any other surface) before they precipitate. the sulphide ions are generated through the decomposition of thiourea ($SC(NH_2)_2$) in aqueous solution, according to the following reactions [12]:

$$CS(NH_2)_2 + OH^- \rightarrow SH^- + CH_2N_2 + H_2O \quad \text{.....(1)}$$

$$HS^- + OH^- \Leftrightarrow S^{2-} + H_2O \quad \text{.... .....(2)}$$

which lead to the release of sulphide ions. For the case of zinc complexed with ammonia (zinc tetra amine) firstly there is a dissociation of the complex to release Zn^{2+} ions:

$$Zn(NH_3)_4^{2+} + S^{2-} \Leftrightarrow Zn^{2+} + 4NH_3 \quad \text{.....(3)}$$

At the same time the sulphide ion is formed;

$$CS(NH_2)_2 + 2OH^- \Leftrightarrow S^{2-} + H_2CN_2 + 2H_2O \quad \text{.....(4)}$$

The ionic reaction of S^{2-} and Zn^{2+} forms the ZnS molecule.

$$Zn^{2+} + S^{2-} \rightarrow ZnS \quad \text{.....(5)}$$

If the ion product $[Zn^{2+}][S^{2-}]$ exceeds the solubility product Ksp of ZnS, then, neglecting kinetic problems of nucleation, ZnS will be formed as a solid phase. Since the reaction is normally carried out in alkaline solution, a complex is then needed to keep the metal ion in the solution and to prevent the hydroxide from precipitating.

Optimization of Time of Deposition

For optimization of time of deposition, concentration of $ZnCl_2$ (0.1 M), concentration of thiourea (0.1 M), volume of hydrazine monohydrate (3 ml^3), PH (10) and bath temperature (80 °C) were kept constant. Figure (1) shows variation of ZnS film thickness with different deposition time (0.5, 1, 1.5, 2 and 2.5 hour). Below (0.5 hr.) deposition time, there has no continuous film on the substrate. In the quasi-linear region the rate of deposition is high due

to high concentrations of Zn^{2+} and S^{2-} and the film thickness can be controlled easily by time of deposition. The film thickness increases with the increase in time of deposition approximately up to (2 hour) deposition time and then increases very slowly. This mean, the rate of film growth gradually decreases.

The thickness of the film reaches to (125 nm) after (2 hr) of deposition time. The obtained film were homogenous , good adhesion on to the glass substrate and white in colour.

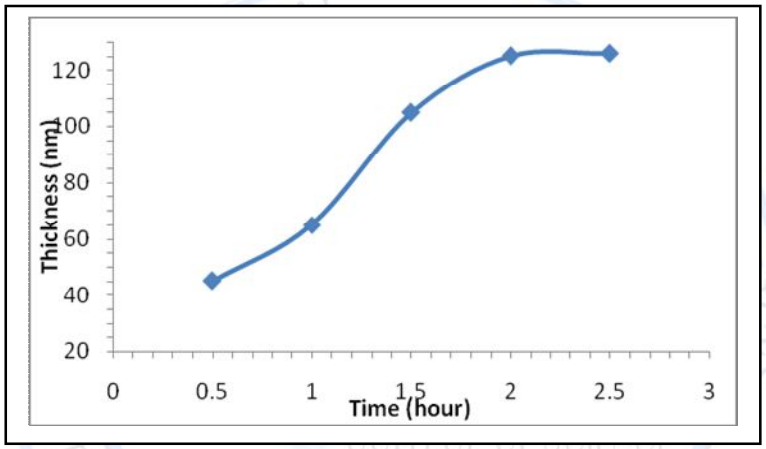


Figure 1: shows variation of ZnS film thickness with different deposition time

Results and discussion

Structural studies

Figure 2 shows the XRD patterns of ZnS nanocrystalline thin films deposited on slide glass substrates at different deposition time. It can be seen from x-ray diffraction for ZnS nanocrystalline thin film deposited at 60 minute (time deposition) has not revealed diffraction peak (amorphous structure). A similar behavior was reported by several workers [8,13]. But with the 1.5 hour deposition time show a small diffraction peak situated at $2\theta = 28.6°$ reflection from (111) plane, indicating the formation of ZnS nanocrystalline thin film. With increase deposition time up to 2 hour, the prominent peak at $2\theta = 28.69°$ and the intensity

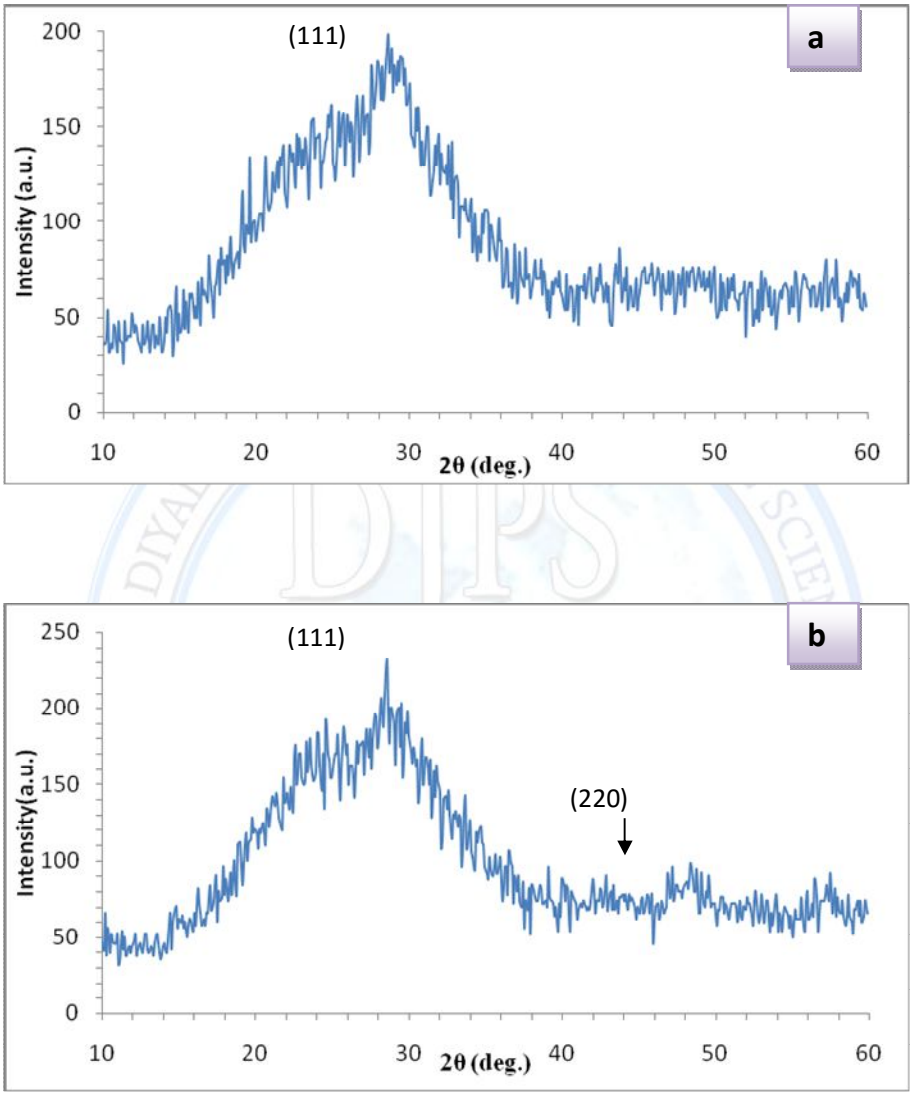
slightly increase due to increase in the film thickness. Also small peak appear at $2\theta = 47°$ which belong to ZnS thin film structure. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal of very small size. From (111) peak, the grain size of the nanocrystalline films is estimated using the Debye-Scherrer formula[14];

$$D_{hkl} = k\lambda / \beta \cos\theta \qquad \text{……..(6)}$$

where K is a constant taken to be 0.94, β is the broadening of diffraction line measured at full width of half maximum intensity (rad.) and λ_{av}= 1.5406 A is the wavelength of CuKα radiation. The grain sizes were found to be 3 nm. The crystalline information from the X-ray diffractogram of the films with (1, 1.5 and 2 hr.) deposition time are shown in table (1).

Table 1 : X-ray results of the deposited ZnS films with (1, 1.5 and 2 hr.).

Experiment no.	Deposition time (hr.)	ASTM			Observed values		
		2θ (deg.)	d (Å)	Hkl	2θ (deg.)	d (Å)	Grain size (nm)
1	1	28.53	3.1263	(111)	28.65	3.1128	……
2	1.5				28.67	3.0894	……
3	2				28.69	3.1085	3


a
(111)
Intensity (a.u.)
2θ (deg.)
b
(111)
(220)
Intensity(a.u.)
2θ (deg.)

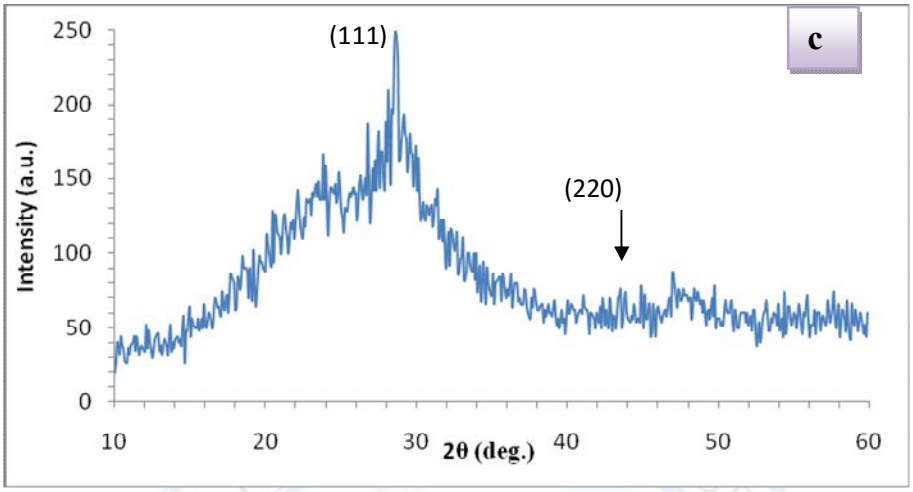


Fig. 2: The X-ray diffraction pattern of as-deposited ZnS on glass substrate at (80 °C) temperature for different deposition time: (a)(t=1), (b) (t=1.5) and (c) t=2 hour.

Optical properties

Transmittance

The optical properties of ZnS nanocrystalline thin films are determined from absorbance measurements in the range of (300-1100) nm. at normal incidence. Figure (3) shows the transmittance spectra of nanocrystalline ZnS thin films deposited at different time.

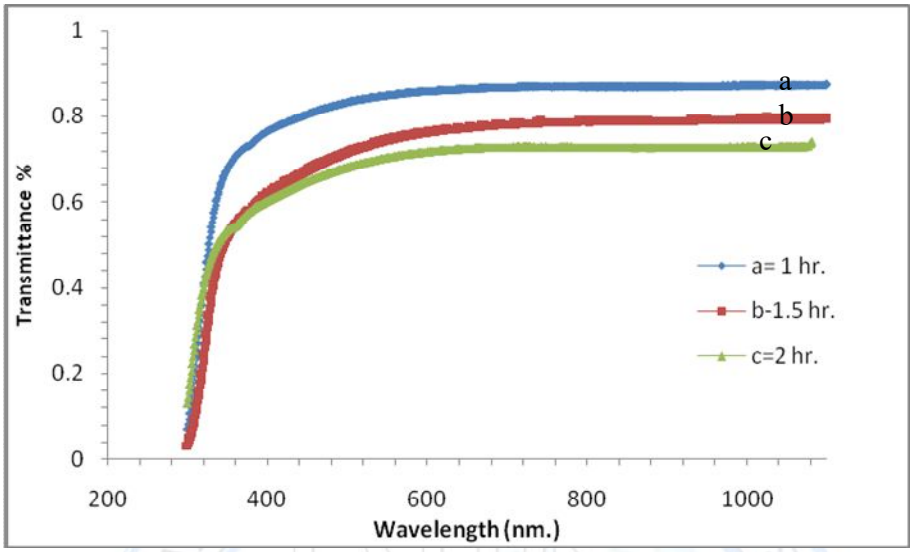


Figure 3: Transmittance spectra of nanocrystalline ZnS thin films versus wavelength deposited at different time: (a) (t =1), (b)(t =1.5) and (c)(t=2 hr.).

The increase in deposition time from 1 hour to 2 hour results in an increase ZnS thickness which is directly observed from the decreasing of optical transmission spectra. The transmittances of the films in the visible region was (65-73 %). Also we observe steep optical absorption feature, which indicates a relatively better crystallinity and lower defects density near the band edge. This feature make these films a good material for optoelectronic devices.

Absorption coefficient and optical band gap

Absorption coefficient associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation [8]:

$$\alpha = 2.3026\ A/t \quad \ldots\ldots\ldots\ldots\ldots(7)$$

Figure (4) shows varying of the absorption coefficient (α) with wavelength for ZnS nanocrystalline thin films with various deposition times (1, 1.5 and 2 hr.). In this figure it can be observed that absorption spectra are blue shifted in all cases (compared with the bulk) due

to the quantum confiment effect (decreases in grain size and grain). The fundamental absorption, which corresponds to the transition from valence band to conduction band, can be used to determine the band gap of the material. The relation between (α) and the incident photon energy (hν) can be written as [1]

$$(\alpha h\nu) = k\,(h\nu - E_g)^n \quad \ldots\ldots\ldots\ldots (8)$$

where k is Boltzmann's constant, the best linear fit was obtained for (n = 1/2). Figure (5) shows varying of the optical band gap of nanocrystalline ZnS thin films versus photon energy at different deposition time in the range (1-2 hr.). The intercept on the horizontal axis, when straight portion of the graph is extrapolated to the point (α = 0) gives the band gap energy E_g. The band gap energy were found to depend on the deposition time. The band gap decreased as the deposition time increased (or as crystallite size increased). The results of variation optical band gap with deposition time are summarized in table (2). The optical band gap obtained using the absorption spectra are greater than the bulk band gap (3.7 eV) and this indicates the formation of nanoparticles.

Table (2): Variation optical band gap of ZnS thin films with deposition time.

Experiment no.	pH	Temperature (°C)	Concentration of $ZnCl_2$ and $CS(NH_2)_2$	Deposition time (hr.)	Eg (eV)
1	10	80	0.1	1	3.99
2	10	80	0.1	1.5	3.88
3	10	80	0.1	2	3.78

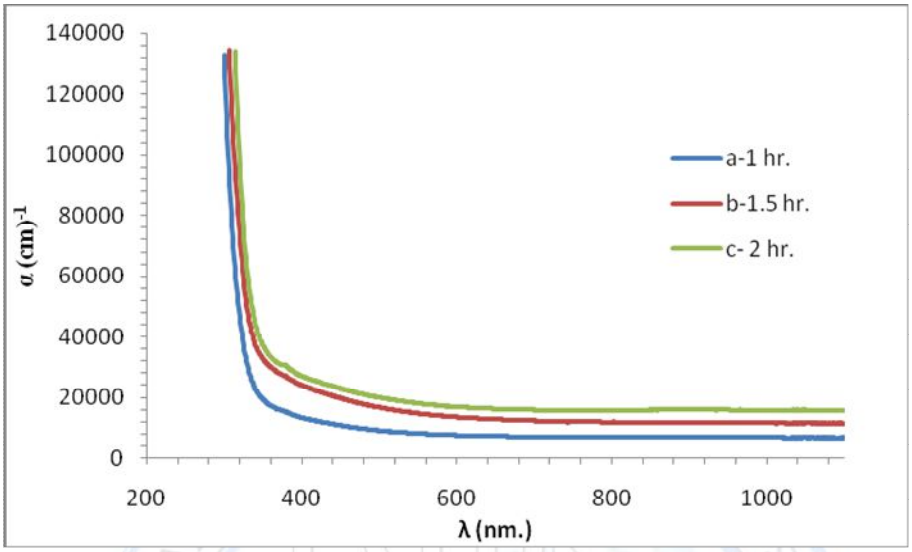


Figure 4: Absorption coefficient of nanocrystalline ZnS thin films versus wavelength at different deposition times:(a)(t =1), (b) (t =1.5) and (c) (t=2 hr.).

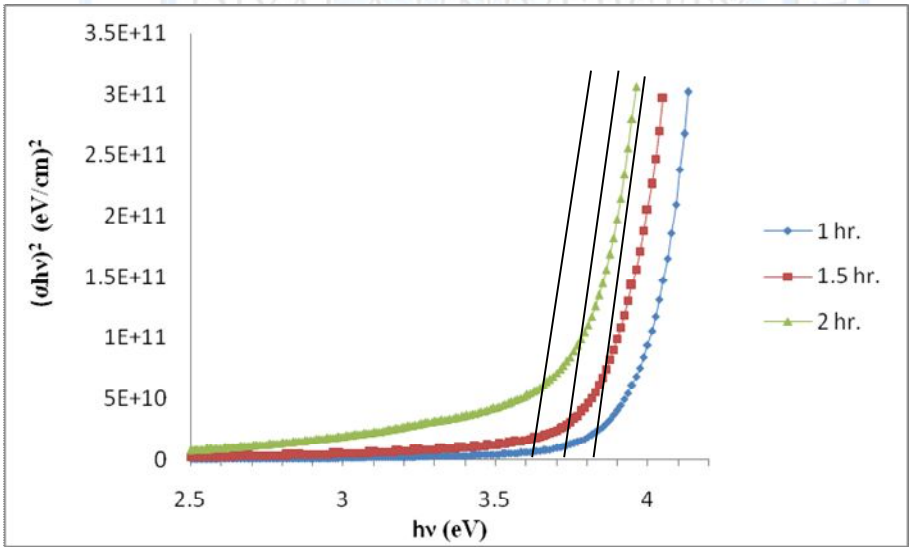


Figure 5: Optical band gap of nanocrystalline ZnS thin filmsversus photon energy at different deposition time:(a) (t =1), (b) (t =1.5) and (c)(t=2 hr.).

Refractive index

The variation of the refractive index with the wavelength (300-1100 nm.) for different deposition time are shown in figure (6).

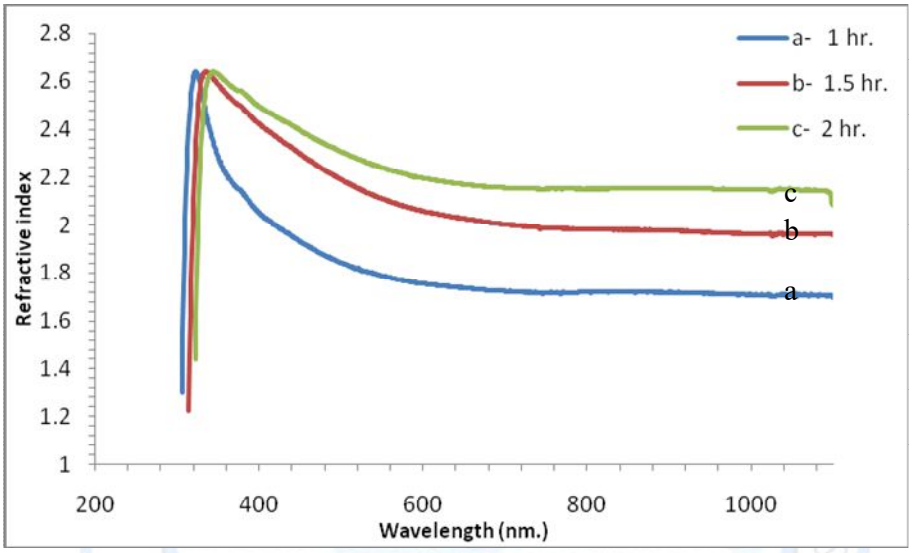


Figure 6: Refractive index of nanocrystalline ZnS thin films versus wavelength at different deposition times:(a) (t =1), (b) (t =1.5) and (c) (t=2 hr.).

From the reflectance and transmittance spectra, the refractive index was determined as a function of wavelength using simple approximations relation [19];

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K^2\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where R is the reflectance for any intermediate energy photons recorded by spectrophotometer. Where $k = \alpha\lambda/4\pi$ is the extinction coefficient. The refractive index found to increase by increasing deposition time in the range from 1 to 2 hour, this may be as a result the increase in the film thickness i. e. this may be due to the change in nanocrystallite size of ZnS films. The calculated value of the refractive index in the visible region (550 nm) at deposition time 92 hr.) is(2.23).

Conclusion

Nanocrystalline ZnS thin film was successfully deposited onto glass substrates by chemical bath deposition technique at varies deposition time. The x-ray diffraction spectrum shows that Nanocrystalline ZnS thin film is polycrystalline with a cubic structure. The deposited films has good adherent to the substrates with various thickness . The band gap energy was decreased as the deposition time increase from (1-2 hour). Therefore, we think that (time=2 hour, pH=10 and T= 80 ℃) optimum bath conditions to use nanocrystalline ZnS thin film in optoelectronic device such as window layer in solar cells.

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