

Effect Zinc Ion Concentration on Structural and Optical Properties of ZnS Thin Films Prepared by Chemical Bath Deposition Technique

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الخلاصة

في هذا لبحث تم تحضير أغشية كبريتيد الزنك ZnS بتقنية ترسيب بالحمام الكيماوي (CBD)، 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 ايونات الزنك عند 0.05M و 0.1M على الخصائص التركيبية والبصرية. أجريت المعاملة الحرارية للأغشية أجريت في الهواء بدرجة حرارة $(473 K^{\circ})$ ولمدة ساعتين. الخصائص التركيبية درست باستخدام تقنية حيود الأشعة السينية (XRD)، حيث بينت ان أغشية ZnS المرسبة على أرضيات زجاجية تمتلك تركيب مكعب (مشبك الخارصين) وكذلك يزداد معدل الحجم الحبيبي من 14 nm الى 22 nm مع زيادة تركيز ايونات الزنك في المحلول. الخصائص البصرية درست باستخدام أطياف النفاذية، حيث بينت إن أغشية كبريتيد الزنك لها نفاذيه عالية في المدى المرئي من الطيف وتصل إلى أكثر من 80%. أغشية كبريتيد الزنك تمتلك فجوة طاقة واسعة الطيف و تقل من 3.62 eV إلى 3.57eV مع زيادة تركيز ايونات الزنك في المحلول.

Abstract

In this work, ZnS films were prepared by chemical bath deposition technique where 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 cadmium ion concentration at 0.05 M and 0.1 M on the structural and optical properties is described. Annealing process is carried out in air at temperature 473K for 2h. The structural properties were studied by X-ray diffraction, where found that for ZnS films

deposited on glass substrates have cubic (zinc blende) structure and the grain size increases from 14 nm to 22 nm with increasing zinc ion concentration in solution. The optical properties were studied by transmission spectra where found that for ZnS films have highly transmittance in visible region of spectrum and reach to more than 80%. The ZnS films have wide band gap and decrease from 3.62 to 3.57 eV with increasing zinc ion concentration in solution.

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

1- 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 heterojunction photovoltaic solar cells; because the wide band decreases the window absorption losses 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]. Various techniques have been employed to prepare ZnS thin film including SILAR, electrodeposition, chemical bath deposition, spray pyrolysis, vacuum evaporation and pulsed laser deposition [9-14].

Chemical bath deposition (CBD) is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions[15-18]. It is widely used for the deposition of different metal chalcogenide thin films, it results good deposits on suitable substrates by the controlled precipitation of the compounds from the solution. This method offers many advantages over other well-known methods of vapor phase synthetic routes. It could allow us to easily control the growth factors, such as, film thickness, deposition rate and crystalline quality by varying the solution pH, temperature and bath concentration [19]. In this method, we need not use high voltage equipments, moreover it works at room temperature and hence, it is inexpensive. The only need for this deposition is an aqueous solution made up of few common chemicals and a substrate on which the film is deposited. Often it suffers lack of reproducibility comparing with other chemical processes; however, by the proper and careful optimization of the growth parameters, one can have reasonable reproducibility. The principle of direct deposition of film via CBD method is based on gradual release of metal ion from super saturation solution. A chelating agent is usually used to limit the hydrolysis of the metal ion and impart some

stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. It is well known that there are distinct mechanism or models leading to the formation of CBD films, notably:(a) adsorption and coagulation of colloids performed solution by homogeneous reaction (as usually called cluster-by-cluster process), and (b) ion –by-ion condensation at the surface of the substrate by heterogeneous reaction. In practice, both processes may occur and/or interact in the grown films. The predominance of one mechanism over another is controlled by the extent of heterogeneous and homogeneous nucleations. Key parameter include the degree of super saturation of solution and the catalytic activity of the surface of the substrate [20].

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

2- 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(NO₃)₂.6H₂O] in two various molarity of 0.05M and 0.1M as a source of zinc ions(Zn⁺²) and 0.1M thiourea [SC(NH₂)₂] as a source of sulphide ions (S⁻²). Ammonia solution (NH₄OH) 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 bath temperature was kept at 60°C for 5h and under unstirred condition. A lower bath temperature could retard the ZnS deposition rate, however, a higher temperature would produce a higher evaporation of chemical bath to make an uncontrollable deposition rate. The glass substrate was held by Teflon holder when they were immersed vertically in the chemical bath. After 5h, the glass slides were removed from the beaker and were cleaned with distilled water to remove the white, loosely adherent powders precipitates in the solution during deposition. The obtained films were white, uniform and with a consistent with previous reports [18]. The residual powder formed in the reaction bath was collected, washed with water and dried in air at 473K for 2h.

Film thickness is important parameter in the study of film properties. For thickness measurement, gravimetric weight difference method with the relation $t=\Delta m/(\rho \times A)$ where, Δm is the mass of the film deposition on the substrate in gram; A the area of the deposited film in cm² and ρ the density of the deposited material (ZnS=4.089 g/cm³) in bulk form[21].The maximum thickness for ZnS thin film was 428 nm.

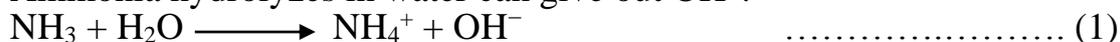
The X-ray diffraction(XRD) analysis was carried out using X-ray 6000(Shimadzu) diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.541 \text{ \AA}$) at 40 kV and 30 mA. The optical transmission spectra were investigated by UV-Visible Spectrophotometer (Cintra 5) GBC-Astrural).

3- Results and discussion

Reaction Mechanism

The CBD is based on the formation of the solid 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 [20]. The reaction mechanism for the formation of ZnS could be understood as follows.

Ammonia hydrolyzes in water can give out OH^- :



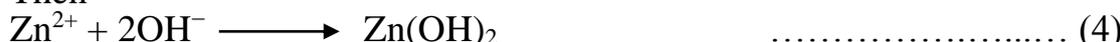
The source of Zn^{2+} :



Zn^{2+} and NH_3 form a complex species of cadmium $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (to slowly release Zn^{2+}):



Then



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



Zinc sulfide is formed:

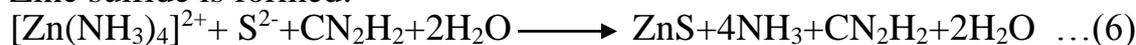
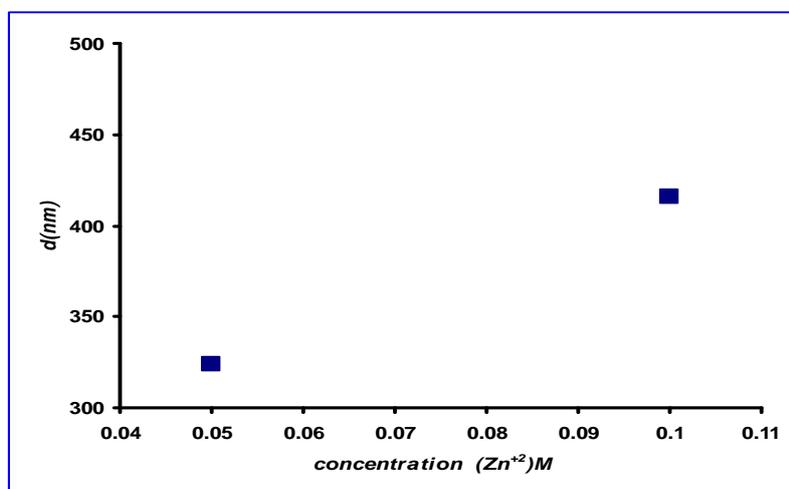


Fig. (1) shows the growth is strongly influenced by the molarity of zinc nitrate. The deposition rate increases with increasing zinc ion concentration, the terminal thickness increases with increasing zinc ion concentration from 324 nm to 416 nm. The increase in deposition rate refers that in any chemical reaction the reaction rate is proportional to the concentration of the reacting species.



X-Ray Diffraction terminal thickness of ZnS films as a function molarity.

Fig. 2(a and b) shows X-ray diffractograms of ZnS thin films deposited on glass substrate, and were deposited at various zinc ion concentrations (zinc nitrate molarity) for constants bath temperature of (60C°) and pH of (11) at fixed deposition time of 5h and annealing at 473 K for time of annealed is 2h. Fig. 1(a) show XRD pattern of ZnS film at 0.05M, can be observed appearing peaks at $2\theta = 28.93^\circ, 48.5$ and 58.49° which correspond to diffraction from (111), (220) and (222) crystalline planes respectively, where the peak refer to the cubic ZnS phase. Fig. 1(b) show XRD of ZnS film at 0.1M film which was reveals the diffraction peaks $2\theta = 29.54^\circ, 49.13^\circ$ and 58.89° corresponding to diffraction from (111), (220) and (222) planes respectively. All the above mention planes refer to the polycrystalline ZnS with cubic phase. The diffraction intensity increases with increasing the (Zn^{2+}) molarity due to film thickness increasing and this implies a larger number of Bragg plane. These values of 2θ and its crystal planes are comparable with standard data from ZnS matches well (JCPDS No.05 -0566), While comparing the X-ray diffraction pattern of 0.05M and 0.1M of CdO, it is obvious that, Bragg's peaks became more intense for higher molarity indicating a clear improvement in crystallinity. This behavior appreciably a constant procedure for all films were prepared by CBD as reported in literatures [7,18,22,23].

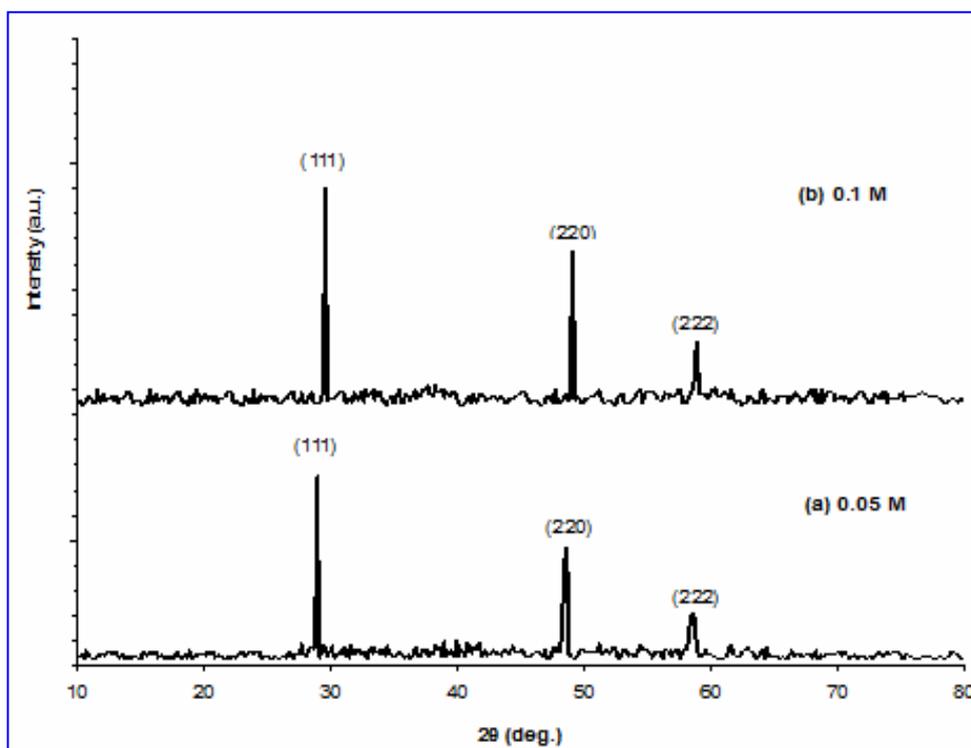


Figure (2): The X-ray diffraction patterns of the zinc ions concentration (a) 0.05 M and (b) 0.1M.

The average grain size of ZnS film was calculated from the following Scherrer's equation for the (111) direction [24].:

$$d = \frac{0.9\lambda}{\beta \cos \theta} \dots\dots\dots (7)$$

where λ is the X-ray wavelength, β is the full-width at half-maximum (FWHM) of the peak, and θ is the reflection angle. The grain size was increased from 14nm to 22nm with molarity increasing from 0.05M to 0.1M [25]. And the diffraction peaks become more intense and sharper which indicated that the grains become larger and the crystal quality was improved. The noticeable difference in grain size between the 0.05M film and the 0.1M films may be attributed to the fact that there are two different deposition processes in CBD that compete with each other; cluster by cluster deposition and ion by ion deposition[7].

Optical Properties

Fig.3 shows the effect of the zinc ion concentration(0.05 and 0.1)M on the transmission spectra in for the range 300 – 800 nm. The average transmittance of the ZnS films in the visible region was found to be with a transmittance of more than 80% when the wavelength is above 400 nm. We have found film transmission decreases with increasing zinc ion concentration, because of Zn⁺² ion concentration increasing causes an increase of grain size as a result of increasing the film thickness. This behavior appreciably a constant procedure for all films were prepared by CBD as reported in literatures [26,27].

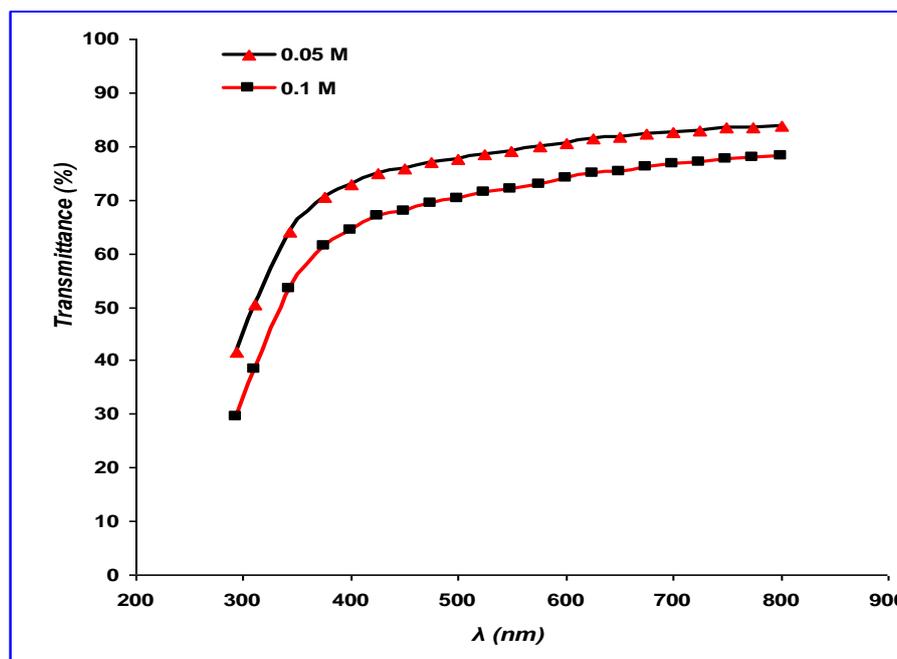


Figure (3): The optical transmission spectra as a function of wavelength of ZnS films at different zinc ion concentration.

Fig.4 shows effect the zinc ion concentration (0.05 and 0.1)M on direct band gap of ZnS film, where the band gap value is estimated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy. The linear nature of the plots indicates the existence of direct transitions. The values of direct optical band gap have found to be 3.6 eV and 3.5 eV for 0.05M and 0.1M ZnS films. The optical band gap of CdO film prepared with 0.05M is larger than that for 0.1M, 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 [8,29,30,31].

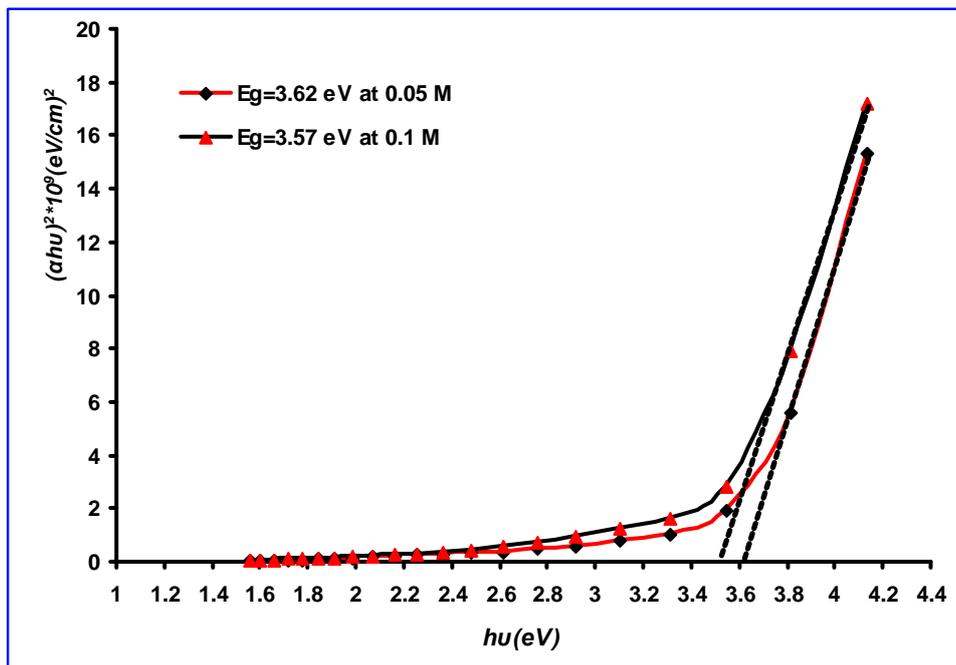


Figure (4): A plots of $(\alpha h\nu)^2$ versus $(h\nu)$ of ZnS films at different zinc ion concentration.

4- Conclusions

The ZnS films are prepared by low cost chemical bath deposition technique with different zinc ion concentration. The present method is simple, economic and easily reproducible for Zinc Sulphide. The XRD measurements indicate that the structure of the ZnS thin films is cubic(zinc blend) for both molarties, Bragg's peaks became more intense for higher molarity indicating a clear improvement in crystallinity. The average grain size increase with increasing Zn^{+2} ions concentration. The ZnS films are highly transmittance of more than 80% and decrease with increasing Zn^{+2} ions concentration. The band gap of ZnS thin films decrease with increasing zinc ion concentration. ZnS having wide band gap of 3.57-3.62 eV is a promising material to be used in photovoltaic devices, solar cells and detectors.

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