

The Influence of Substrate Temperature on the Structural , Morphology and Optical Properties of ZnS Thin Films Prepared by Pulsed Laser Deposition

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Abstract

Effects of substrate temperature on the microstructure, morphology, and optical properties of ZnS thin films were investigated. ZnS films were deposited on glass substrates by pulsed laser deposition at different substrate temperatures using a pulsed 532 nm Nd:YAG laser is presented . The structure and morphology of the film were studied by X-ray diffraction and atomic force microscopy, the average surface grain size and RMS surface roughness of the films increases with increasing substrate temperature. Optical properties of the films were determined from the transmittance data using Swanepoel model, Transmittances of film were measured by spectrophotometer. Additionally, the increase of the substrate temperatures increase the pores and the transmittance in the films, it was observed that the energy band gap is increased from 3.4 eV to 3.6 eV of the films are decreased with the increase of substrate temperature . Moreover , considerable improvement in blue response of the films was noticed with increasing substrate temperature .

تأثير درجة حرارة الأساس على الخصائص التركيبية ، طبوغرافية، والبصرية لأغشية كبريتيد
الخاصين النقية باستعمال تقنية الترسيب بالليزر النبضي

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الخلاصة

درس في هذا البحث تأثير درجة حرارة الأساس على الخواص التركيبية ، الطبوغرافية والبصرية لأغشية كبريتيد الخاصين الرقيقة ، رسبت أغشية ZnS على أرضيات من الزجاج باستعمال تقنية الترسيب بالليزر النبضي وبدرجات حرارة مختلفة وكان الليزر المستعمل Nd:YAG بطول موجي 532 nm . درس تركيب و سطح الغشاء باستعمال تقنية حيود الأشعة السينية ومجهر القوى الذرية ، وبينت بان معدل الحجم الحبيبي والخشونة للسطح تزداد بزيادة درجة حرارة الأساس . حددت الخواص البصرية للأغشية من خلال بيانات النفاذية وكانت من النوع سوانابول، قيست النفاذية باستعمال المطياف . بالإضافة ، انه عند زيادة درجة حرارة الأساس تزداد المسامية والنفاذية للغشاء . أما فجوة الطاقة البصرية تزداد من 3.4-3.6 eV بزيادة درجة حرارة الأساس ، علاوة على ذلك ، لوحظ تحسن كبير في الاستجابة الزرقاء للغشاء عند زيادة درجة حرارة الأساس .

1. Introduction

Studies of sulphide films are quite important because of their possible technological applications. Among the various sulphides, zinc sulphide (ZnS) is promising one. It is a II–VI compound, both in bulk and thin film forms, that is receiving ever-increasing attention owing to its potential uses in a wide variety of applications. ZnS is a direct wide band gap (3.65 eV) II–VI compound semiconductor material. It can thus be used for the fabrication of optoelectronic devices such as blue light-emitting diodes, electro-optic modulators and the n-window layer of solar cell, ZnS can be used as reflectors and dielectric filters because of its high refractive index and high transmittance in visible range. ZnS can be used for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electro optic modulator, optical coating, heterojunction solar cells, and photoconductor [1,2,3,4]. and Various techniques have been employed to prepare ZnS thin films, such as chemical bath deposition and ,pulsed laser deposition ,spray pyrolysis , and so on. In this work the pulsed laser deposition process was used to fabricate films [5].and pulsed laser deposition (PLD) have been employed to prepare ZnS films. Among them, PLD is a recognized method, best known for its low substrate-heating requirement, fast deposition rate, and simple setup[6].



Figure (1): Pulsed laser deposition

Additionally, The observed changes in the optical properties of ZnS films are attributed to the phase transition between

zinc-blende and wurtzite of the ZnS matrix due to different growth temperatures.

This view is further substantiated by structural studies using x-ray diffractometry XRD[6]. ZnS crystallizes either in the cubic zinc blende (ZB) structure (traditional called α ZnS) or the hexagonal wurtzite (W) structure (traditional called β -ZnS [7]. Experimental results show that the as-deposited ZnS film exhibiting cubic structure, The average surface grain size and root mean square surface roughness increase with the increase of substrate temperatures. Therefore, the effects of substrate temperature on the properties ZnS films should be well understood from a fundamental as well as from an applied point view. In this paper, the effects of substrate on the structure and optical properties of ZnS films deposited by pulsed laser deposition were investigated [8,9,10].

2. Experimental procedure

2.1 Film preparation

High purity (99.9%) ZnS powder was used as a source for deposition of ZnS films on glass substrates[2] , Additionally, Crystalline ZnS films were deposited on cleaned coring glass substrates using 10 Hz, 7 ns, Nd:YAG laser at 532 nm ..The laser beam was focused on high purity ZnS target using (3 cm) positive lens . Laser fluence of (0.7 J/cm²) as used for in the ablation. The glass substrates were placed at 5 cm distance from ZnS target. The chamber was kept at vacuum pressure of 10⁻¹ mbar. The ZnS target was ablated from 100 to 300 pulses (10–20 min) to get single layer thin films. During the deposition the substrate temperatures (T_s) were kept at 200 °C , 300 °C and 400 °C [8,11.12] .

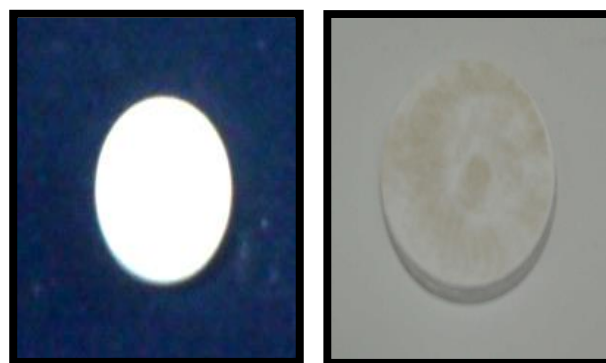


Fig.(2-a): ZnS target before being ablated by the laser.

Fig.(2-b): ZnS target after being ablated by the laser.

2.2 Film characterization

The structure of the grown films was determined by X-Ray diffraction (XRD) measurements (Philips PW 1050, $\lambda=0.1542$ nm) using Cu- α source. Film transmission measurement is performed at spectral range 300–800 nm using UV–VIS–PV-8800 (PerkinElemerCompany)spectrophotometer. The surface morphology was examined by atomic force microscopy (AFM-Digital Instruments NanoScope) working in tapping mode [8,13,14].

3. Result and Discussion

3.1. Structural Properties

Figure 3.a shows the XRD pattern of the ZnS films deposited on glass substrate at 200 °C under an oxygen pressure of 0.1 mbar. The film is polycrystalline in nature and the diffracted peaks located at $2\theta = 38.6^\circ$, $2\theta = 44.82^\circ$ and $2\theta = 65.16^\circ$ are observed, which correspond to (102), (110),(104) of ZnS phase, no other diffracted peaks are found in spectrum. The mean grain size (d) of the film, using the Scherrer’s equation, $G = 0.9 \lambda / B \cos\theta_B$, where λ the wavelength of X-ray radiation, B the full-width at half-maximum, and θ_B is the diffraction angle. However, when the substrate temperature increased to 300 °C peaks located at $2\theta = 38.58^\circ$, $2\theta = 44.84^\circ$ and $2\theta = 65.12^\circ$ as shown in Fig. 3.b, which correspond 102), (110) and (104) planes of ZnS structure, Fig.3.c present the pattern at 400 °C which is the most stable structure of the membrane phase of ZnS and (102) and (110) at $2\theta=38.6^\circ$ and $2\theta=44.84^\circ$ respectively, in addition (104) at $2\theta=65.14^\circ$ at substrate temperatures 400 °C.

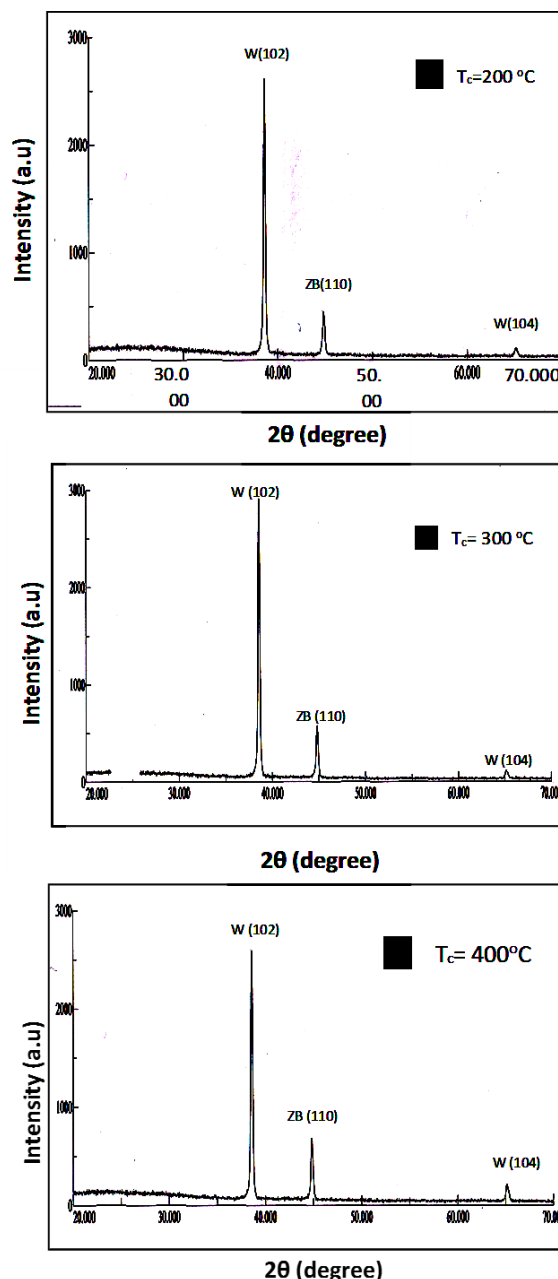


Figure 3: The XRD of ZnS Thin Films: (a) 200 °C, (b) 300 °C, (c) 400 °C.

Table 1: The XRD Patterns of ZnS Thin Films Deposited at Different substrate temperatures

Grain size (nm)	FWHM°	(hkl)	2θ (degree)	substrate temperatures (°C)
33.7	0.249	W(102)	38.6	200
31	0.277	ZB(110)	44.82	
28.3	0.332	W(104)	65.16	
40.8	0.206	W(102)	38.58	300
37.5	0.229	ZB(110)	44.84	
34.8	0.27	W(104)	65.12	
45.9	0.183	W(102)	38.6	400
38.1	0.225	ZB(110)	44.84	
35.5	0.265	W(104)	65.14	

3.2. Surface morphology

The evolution of surface morphology of ZnS films at substrate temperatures 200, 300, and 400 °C, are presented in Fig. 4, RMS surface roughness increases slowly (3, 3.24, 3.58 nm) when the substrate temperature increases. Also, the average grain size films increases with increasing substrate temperature, which is result of the movement of the atoms or molecules on film surface as the substrate temperature is increase.

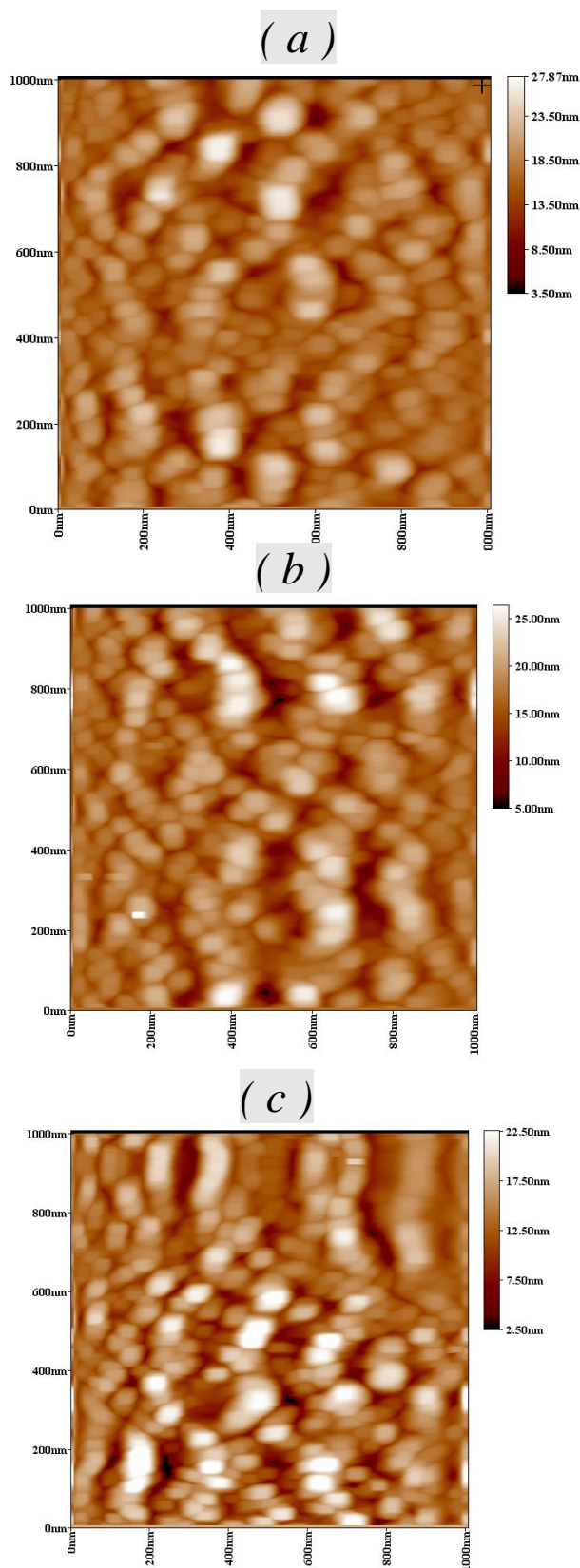


Fig. 4: Surface morphology of the ZnS film at different substrate temperature (a)200 , (b) 300 ,(c)

3.3. Optical properties

Fig.5. shows transmittance spectra as a function of the wavelength of the change over between (300-800) nm of the ZnS film

grown at (200,300,400) °C with pressure = 0.1 mbar and fluencies energy 0.7 J/cm² .

The average transmittance of ZnS films in the visible wavelength region is calculated to be 71%,78%,89% and, respectively. the interference peaks shift to shorter wavelengths and amplitude of the spectra decreases with increasing substrates temperature , Where we note that transmittance spectra for film at 200 °C is less than the transmittance at 300 °C substrate temperature while Where we note that transmittance spectra for film at 300 °C is less than the transmittance at 400 °C substrate temperature .Optical properties of the films were determined from the transmittance data using Swanepoel model.

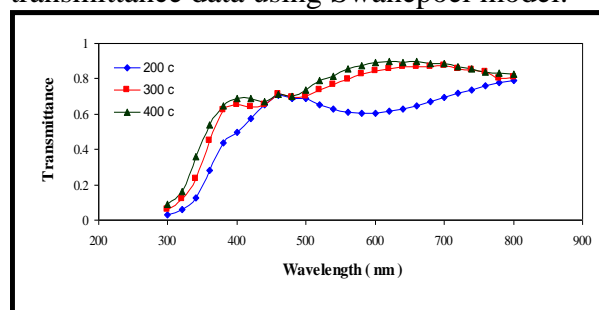


Fig.4: Transmittances of the ZnS films at different substrates temperatures at the wavelength from 300 to 800 nm .

The plots of $(\alpha h\nu)^2$ versus $(h\nu)$ shown in Fig. 5 are linear indicating the presence of direct transition. The energy gap of films at different temperatures are calculated from Fig. 5 and found to be 3.4 and 3.5 eV for 200 °C and 300 oC respectively. And The energy gap 3.6 eV of films at 400 °C substrates temperature . Direct band gap energy of these samples was measured to be in the range of 3.4-3.6 eV in Fig. 5.

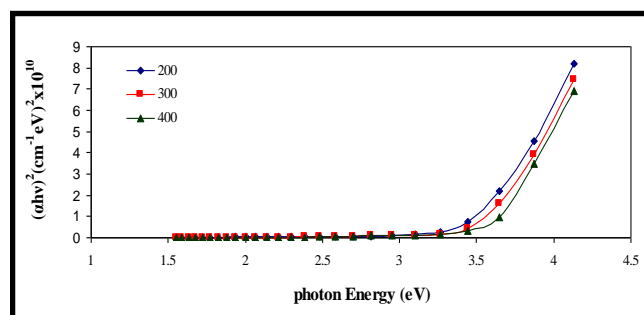


Fig. 5: Plots of $(\alpha h\nu)^2$ verses photon energy $(h\nu)$ of the ZnS thin films prepared at different substrate temperature.

References

- [1] Xiaochun ,Fachun , Yongzhong , Zhigao & Rong , " Journal of Proc.of Spin (Fujian Normal University)", Vol. 6722, 67222L, (2007).
- [2] M. Ashraf, S.M.J. Akhtar, Z. Ali and A. Qayyum," Optics Laboratories", , Vol 45, pp. 5, (2011).
- [3] P.P. Hankare,P.A. Chate,D.J. Sathe and A.A. Patil," Journal of Applied Surface Science "Vol. 256, pp. 81–84 ,(2009).
- [4] B. Ray, "II-VI Compounds", 1st edition, printed in Great Britain by Neill and Co. Ltd. of Edinburgh, (1969).
- [5] M.A. Hernandez-Fenollosa,M.C. Lopez,V. Donderis,M. Gonzalez,B.Mari and J.R. Ramos-Barrado , " Journal of Thin Solid Films", Vol.516, pp.1622–1625, 2008.
- [6] K. M. Yeung , W. S. Tsang, C. L. Mak & K. H. Wong , “ Journal of Applied Physics”, Vol 92, No 7 ,(2002).
- [7] K.Matras-Postolek," University of Applied Sciences Department of Chemical Engineering Steinfurt/Muenster ", (2009).
- [8] M .Jawad ,R.Ismail,K.Yahea," Journal of Mater Sci. Mater Electron ",Vol.22, pp.1244–1247,(2011).
- [9] V.Gayou , B. Salazar-Hernandez , M. Constantino, E. Rosendo Andre,T. Diaz ,R. Delgado Macuil , M. Rojas Lopez," journal homepage ", Vol. 84 , pp.1191–1194, (2010).
- [10] C.Yang, Y.Liu, H.Sun, D.Guo, X.Li,W. Li, B. Liu and X.Zhang,"Pressure-induced transition temperature reduction in ZnS nanoparticles," Nanotechnology, vol. 19,pp. 095704-1-095704-5,(2008).
- [11] N. Hasan, A.Haider,M. Al-Amar," European Journal of Scientific Research", Vol.69 ,No.4, pp. 520-526 , (2012).
- [12] G.Nabiyouni1, R. Sahraei2, M. Toghiani1, M.Majles and K.Hedayati ," Journal of Rev.Adv.Mater.Sci " , Vol.27,pp. 52-57,(2011).
- [13] J. Cheng, D.B. Fan, H. Wang, B.W. Liu, Y.C.Zhang and H. Yan," Journal of Semicond. Sci.Technol ",Vol.18 , (2003).
- [14] V.KUMAR, M.K.SHARMA, J. GAUR, T. P.SHARMA," Journal of Chalcogenide Letters", Vol. 5, No. 11, pp. 289 – 295, (2008).