Structure and Optical Properties of Nano PbS Thin Film Deposited by Pulse Laser Deposition

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ABSTRACT

The present work the structure properties of nano Lead sulfide PbS thin films were studied. Thin samples were prepared by pulse laser deposition and deposited on glass substrate at 1064nm wavelength with 800mj laser energy. The structure properties of films were determined by X-ray diffraction studied the effect of variation of substrate temperature on these properties. The films are adherent to the substrate and well crystallized according to the centered cubic structure with the preferential orientation (111) and (200). The minimum value of grain size was 16.5 nm when the film deposited of at 70 ^{o}C substrate temperature. The optical investigation showed that, depending on the substrate temperature have direct allowed transitions in the range 1.55–2.45 eV.

Keywords: thin films, nanopartical, pulse laser deposition and lead sulfide

الخصائص التركيبية والبصرية لاغشية كبريتيد الرصاص النانوية المرسبة باستخدام الليزر

الخلاصة

في هذا البحث تم دراسة الخصائص التركيبية لاغشية كبريتيد الرصاص النانوية. تم تحضير تلك الاغشية باستخدام تقنية الترسيب بالليزر باستخدام ليزر ذو طول موجي يساوي 1064 نانومتر وبطاقة ليزر تساوي 800 ملي جول. تم دراسة حيود الاشعة السينية ودراسة تاثير تغير درجة حرارة القاعدة على الخصائص التركيبيةوقد لوحظ ان الغشاء المتكون من النوع المتعدد البلوري والطور السائد هو المستوي (111) و(200). ان اقل حجم حبيبي تم الحصول عليه كان 16.5 نانومتر عند درجة حرارة للقاعدة 70 درجة سيليزية. اما الخصائص البصرية تم دراستها ودراسة تاثير تغير درجة حرارة القاعدة عليها، فوجد امتلاكها انتقالات مباشرة ضمن المدى 1.55 الى 2.45 الكترون. فولت.

INTRODUCTION

Lead sulfide (PbS) is an important direct narrow gap semiconductor material with an approximate energy band gap of 0.4 eV at 300K and a relatively large excitation Bohr radius of 18 nm [1].

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The use of thin film polycrystalline semiconductors has attracted much interest in recent years, and has found many applications in various electronic devices. The main reason in this interest is the low costs production [2]. As result, this class of semiconductor materials is now occupying an outstanding situation in the basic research and solid state technology. In this category, the IV–VI compounds often named as lead salts have been considered as the most attractive semiconductors, because of their various applications in the infrared technology [3].

This material has also been used in many fields such as photography, Pb2+ ionselective sensors and solar absorption [4-6]. In addition, PbS has been utilized as photoresistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings [7]. These properties have been correlated with the growth conditions and the nature of substrates. For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition, spray pyrolysis, photoaccelerated chemical deposition, microwave heating and chemical bath deposition (CBD) [8-11].

Among the new and up to date techniques used for thin film deposition, pulsed laser ablation (PLA) is one of the most versatile methods to obtain layers of several materials that can be processed into a pellet target. One of the important features of this method is based on the possibility of maintaining the stoichiometry of the ablated target in the deposited layer [12- 14]. The target ablated by laser can create a highly energetic growth precursor, leading to non-equilibrium growth conditions. Therefore high quality films can be obtained at a fairly low substrate temperature. Furthermore, PLD is more flexible than other conventional techniques, and it is feasible to control the thickness of films. In the current work, we report the structural and optical properties of PbS thin films on glass substrate grown by PLD method at various substrate temperature.

Experimental details

The PLD method is performed with a Nd:YAG laser with wavelength 1064nm at repetition rate of 4 Hz. PbS films were deposited on glass substrates by ablating stoichiometric home-made targets. During the film deposition the laser energy was 800mj and ambient pressure were kept at 10^{-5} torr. In order to investigate the substrate temperature on the structural properties of PbS thin film, a series of samples were deposited using the substrate temperature of 50 ^{o}C, 60^{o}C, 80^{o}C and 90^{o}C. X-ray analysis (was performed by using a Bruker D8 Advance diffractometer using CuKα (λ = 1.54 Å) radiation.

We have determined the average crystallite sizes *L* by measuring full width at half β of the peaks and by using the Scherrer formula (eq. 1) [1,2], and the dislocation density δ can be calculated by using the fallowing relation (eq. 2) [3,14]:

$$L = \frac{0.9\,\lambda}{\beta\,cos\theta} \qquad \ldots(1)$$

$$\delta = \frac{1}{L^2} \;\left(\frac{lines}{cm^2}\right) \qquad \ldots(2)$$

Absorption and transmission spectra were measured at room temperature in the spectral range of 300–900 nm using VIS-NIR spectrophotometer DUC 3700instrument at ambient temperature

Results and discussion

The XRD patterns of the PbS thin films which was deposited at several growth temperature are shown in fig. 1, in the above condition. The crystallography of the film was characterized by three principal peaks corresponding to (111), (200) and (220) orientations. The width at half maximum of the (111) line was in the range 0.41–0.53 for all substrate temperature T_S deposition, the values are indicative of the good crystallinity. The narrow peaks show that the materiel has good crystallinity and oriented along the (220) direction which is perpendicular to the substrate and which intensity depends on T_S value. Table 1 displays the ratio values of the relative diffraction peaks intensities (I_{111}/I_{200}) for PbS films produced for various T_S. From the following table can note that an increase in the deposition T_S from 50 to 80 min is accompanied by an decrease in the I_{111}/I_{200} ratio. For T_S values varying between 50 and 60 ^oC, we notice that the peak (111) intensity is practically increased, whereas the intensity of (200) increases reaching its maximum for a growth time equal to 60 min. The intensity ratio I_{111}/I_{200} for thin films grown during 80^oC, were minimum value to 0.96.Fig.1 showing that the PbS samples grown by PLD have (200) preferred orientation with strong intensity and full width at half maximum. Which can be related to the larger number of both Pb2+ and S2− ions in the reaction solution at Ts equal to 60 ^oC. Similar results were obtained by other researcher [5, 9 and 13].

The peak of diffracted ray for Ts equal to 70^oC, the intensity of (111) and (200) decreases. In this case, the thin layers obtained are very rough. We tried to make thin layers of PbS for T_S more than 70 ^oC and noticed that the layer is detached from its substrate. The avarage grain size L of nanoparital thin films determined by measuring full width at half of the (200) peaks and by usin eq.1.

It was observed that the crystallite size reduces slightly for increased substrate temperature from (20.37 to 16.32 nm). The lattice constants range from 5.88 to 6.02 for the Ts increased from50 ^oC to 80 ^oC. The value of dislocation density vary from 0.24×10^{12} cm^2 to 0.31×10^{12} cm^2 by increaseing of the tempreature of substrate from50 ^oC to 80 ^oC.

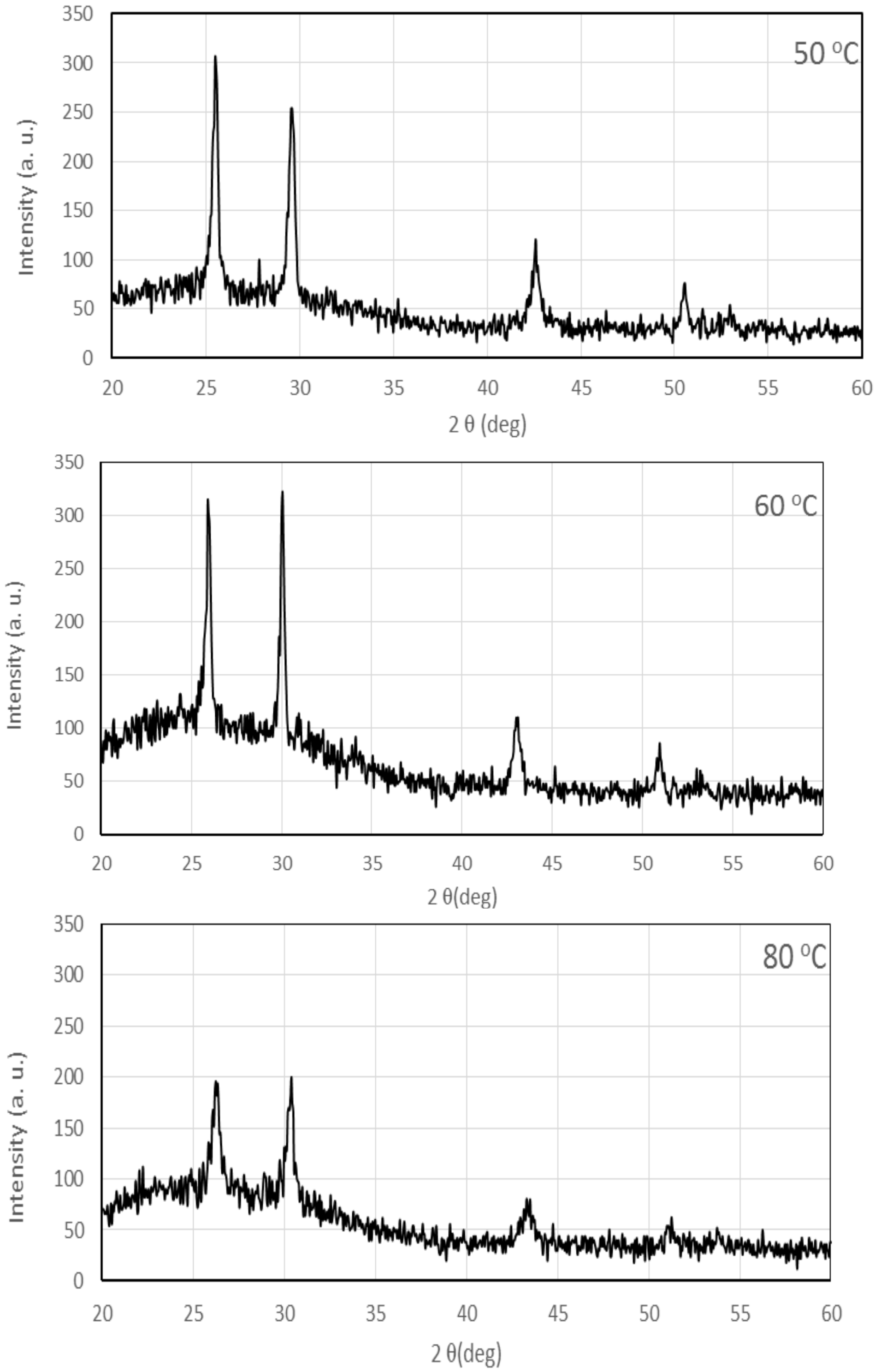

Figure (1) X-ray diffraction spectrum of PbS thin films for various substrate temperature.

Table (1) effect of substrate temperature on PbS properties.

(hkl)	FWHM (deg.)	Grain size (nm)	Lattice constant (Å)	Dislocation density (δ) x10^{12} (cm)^2
50 °C 111	0.4	20.37	6.0275	0.241
200	0.3	27.39	6.01	0.1333
220	0.2	42.64	5.93	0.055
311	0.5	17.57	5.969	0.3239
222	0.3	29.60	5.888	0.1142
60 °C 111	0.5	16.311	5.8543	0.3759
200	0.4	20.591	5.83	0.2359
220	0.2	42.703	5.93	0.0548
311	0.4	22.01	5.92	0.2064
222	0.3	29.6	5.888	0.1141
80 °C 111	0.5	16.32	5.8543	0.3754
200	0.4	20.59	5.85	0.236
220	0.2	42.71	5.65	0.0548
311	0.4	22.01	5.91	0.2064
222	0.3	29.61	5.88	0.1141

The optical transmission of PbS thin films which was deposited on glass substrates were determined optical spectra for a series of PbS films deposited for 50, 60, 80 and 90 °C from a PLD at λ=1064nm as shown in fig. 2 . The average transmittance of these films in the visible wavelength region wass calculated to be 57%, 67%, 46%, and 45%, respectively. This result is comparable to one which reported by researcher [22]. As it is clear from spectra, the films have a steep optical absorption feature, indicating good homogeneity in the shape and size of the nano-crystallines and low defect density near the band edge [7, 11].

The optical absorption coefficients (α) were calculated using the following equation [13]:

$$\alpha = \frac{2.303\,A}{t} \qquad ...(3)$$

where A is absorption and *t* is the film thickness. Fig. 3 shows the absorption coefficient as a function of wavelength. The absorption coefficients (α) were analyzed using the well-known relation for near edge optical absorption of semiconductors [6]:

$$\alpha h\nu = K(h\nu - E_g)^{\frac{n}{2}} \qquad ...(4)$$

where *K* is a constant, which is usually taken to be unit, *Eg* is the separation between valance and conduction bands of semiconductor (band gap energy), and *n* is a constant. *n* for direct band gap semiconductor materials is taken to be unit. Variation of $(\alpha h\nu)^2$ as a function of photon energy (h*v*) is plotted in the Fig. 4. As observable, $(\alpha h\nu)^2$ varies linearly with (h*v*) after a certain amount of photon energy, confirming the direct nature transition mode in the PbS films. The band gap energy is obtained by extrapolating the straight portion of the curve to zero absorption coefficients. In this work the band gap energy (*Eg*) was determined to be in the range of 2.54 2.67 eV for the PbS films with deposition at different substrate temperature varying from 50 to 90 ^{o}C. These values are rather larger than the literature value for

The bulk PbS (~0.4 eV) [19]. The result could be attributed to the quantum size effects as expected from the nanocrystalline nature of the PbS thin films [2, 4]. 6y

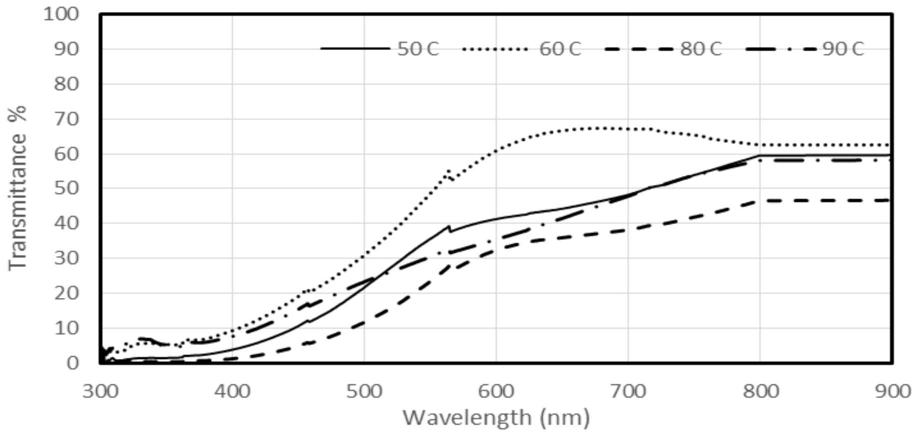

Figure (2) Transmission as function of wavelength for PbS films with different substrate temperature.

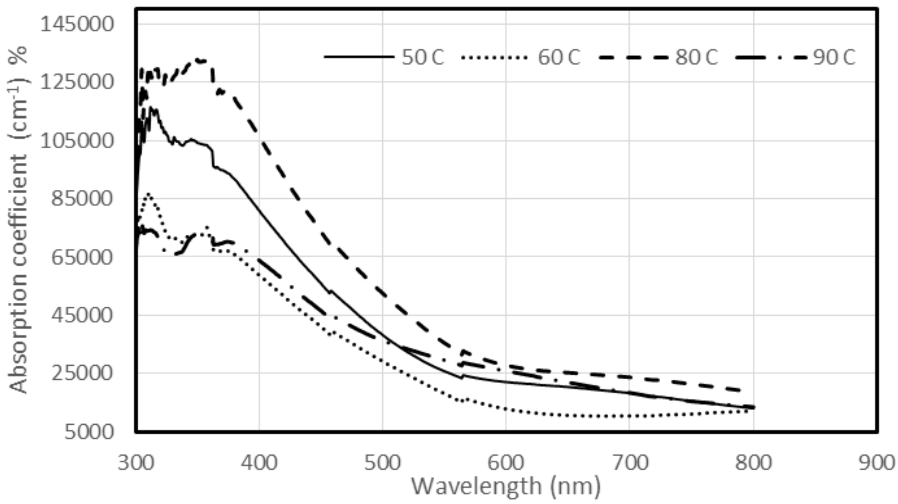

Figure (3) Absorption coefficient as function of wavelength for PbS films with different substrate temperature.

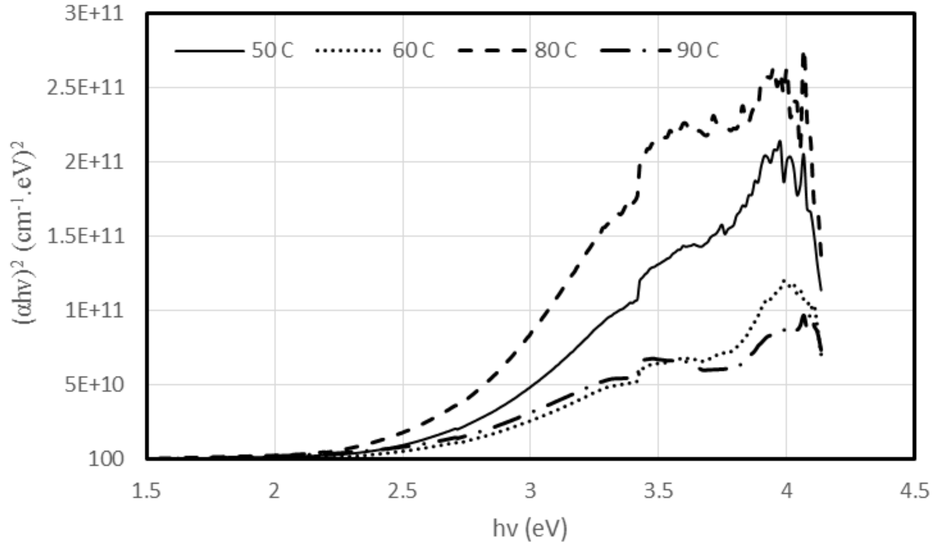

Figure (4) $(\alpha h\nu)^2$ verity as function of energy for PbS films with different substrate temperature.

CONCLUSION

We have successfully deposited the nano-crystalline PbS thin films onto glass substrates, from a pulse laser deposition. The XRD measurements indicate that the structure of the PbS thin films is cubic. In our experiment, based on the optical transmission measurements, the band gap energies are calculated to be between 2.54-2.67 eV for the PbS films with different substrate temperature. The possibility to vary the band gap of PbS in the range 0.41 – 2.7 eV is an important material property, which opens the way to a new class of applications.

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