Synthesis and Study of the Structural and Electrical Conductivity for Nanocrystalline PBS Thin Films

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Received on: 1/11/2012 & Accepted on: 4/4/2013

ABSTRACT

Structural and electrical properties of prepared nanocrystalline lead sulfide thin films were studied which deposited on glass substrates by chemical bath deposition (CBD) techniques. The films were obtained in a reaction bath at times of (15, 30, 45,60and90) min. The X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements confirmed that the thin films grown by this technique had good crystalline cubic structures and homogeneous surfaces. The dc electrical conductivity found in the range of 10^{-6} -10^{-5} $(\Omega.cm)^{-1}$.

Keywords: Nano PbS, CBD method, XRD, AFM, Electrical Conductivity.

تحضير ودراسة التركيب والتوصيلية الكهربائية لأغشية كبريتيد الرصاص النانوية

الخلاصة

درست الخصائص التركيبية والكهربائية لأغشية كبريتيد الرصاص النانوية المحضرة باستخدام تقنية الترسيب بالحمام الكيمياوي على قواعد زجاجية.تم الحصول على الاغشية بغمرها بحمام التفاعل بازمان مختلفة (15,30,45,60,90)دقيقة .بين فحص حيود الاشعة السينية ومجهر القوى الذرية ان الاغشية تتميز بتركيب بلوري مكعب منتظم و سطح متجانس.تم حساب التوصيلية الكهربائية للاغشية النانوية ووجد بانها تتراوح مابين 10^{-6} 10 الى. 10^{-5} $(\Omega.cm)^{-1}$.

INTRODUCTION

A variety of physical properties of nanoparticles semiconductors have been reported in the literature [1]. Many authors have predicted for nanoparticle semiconductors enhanced nonlinearities resulting from quantum confinement effects .The materials application that has attracted considerable attention relates to

https://doi.org/10.30684/etj.31.6B.3
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nonlinear optics. Most studied nanocrystalline semiconductors belong to the II-VI and IV-VI groups as they are relatively easy to synthesize and are generally prepared as particles or in thin film form [2] . PbS is a semiconductor with band gap about 0.41 eV at room temperature and 0.29 eV at liquid-N_2 temperature. For PbS, the size effect can be observed for a crystallite as large as 180Å, which contains over 105 atoms [3]. Chemical bath deposition (CBD) is a very comfortable method for deposition polycrystalline PbS thin films with a good photoconductive properties. By CBD method, the dimensions of the crystallites can be varied controlling deposition parameters: reaction time, temperature, pH, and presence of impurities in the solution. Most of the works on nano size semiconductor particles reported so far have been restricted to optical absorption [4]. The absorption edge has been found to be blue shifted as the particle size reduced [5]. This paper, We present the synthesis of nanocrystalline PbS thin films using CBD method. Preparative parameters such as deposition time were optimized to obtain good quality of PbS thin films on glass. The size dependent properties of films were studied by X-ray diffraction, AFM, and electric conductivity measurements.

EXPERIMENTAL DETAILS

The deposition of PbS films was done in a reactive solution prepared in a 100 ml beaker by the sequential addition of 5 ml of 0.25 M lead acetate, 5 ml of 1M KOH, 6 ml of 0.5M thiourea and 1 ml of 0.1M triethanolamine. The solution was added with deionized water to complete a total volume of 100 ml. The films were deposited on glass slide substrates. The substrates were immersed into the solution vertically. The substrates were subsequently retired from the beaker at different times: 15, 30, 45, 60, and 90 min. After deposition of the films , substrates were taken out and thoroughly washed in doubly distilled water and then dried in air. The resultant films were homogeneous, well adhered to the substrate, and secularly reflecting with a varying color depending on the deposition time. Film thickness was measured by optical interferometer method, using He-Ne laser and the thickness (d) were determined using the formula[6]:

$$d = \frac{\Delta x}{x} . \frac{\lambda}{2} \qquad \text{... (1)}$$

Where Δx is the distance between two fringes, x is the fringe width and λ is the wavelength of He-Ne laser light (0.632 μm). The thickness of films varies with in the range (90 to162) nm. Structural characteristics of the films were determined by using X-ray diffraction system (Philips–PW1840) at room temperature with Cukα radiation and 0.15405 nm wavelength. The two-dimensional images of the surface samples were obtained by using atomic force microscopy (AFM) a scanning prop microscopy (CSPM-5000) instrument. The electrical resistivity of the deposited films was determined by equation [7]:-

$$\rho = R \frac{bd}{l} \qquad \text{… (2)}$$

Where ρ, is the electrical resistivity of the film and l, b and d are the distance between two centers of electrodes , width of electrode and thickness of the film

respectively. Resistance change of thin film with temperature is achieved, and putting the samples under vacuum to prevent oxidation of the films. K type thermocouple was used to measure the temperature via digital meter of the type (Digit-sense). Sample resistivity measured with Keithley (602) electrometer as a function of temperature. The electrical conductivity of nano PbS films was measured in the 313-321 K temperature range using dc two- point probe method and its temperature dependence can be expressed by usual Arrheneous equation as [8]:

$$\rho = \rho_{\circ} \exp (Ea / K_B) \qquad \ldots (3)$$

Where ρ is the resistivity at temperature (T), where ρ_o is the resistivity at room temperature, K_B is the Boltzmann´s constant and E_a is the activation energy.

RESULTS AND DISCUSSION

XRD Analysis

Structural identification of PbS films was carried out with x-ray diffraction in the range of angle 2θ between (10 to 60). Figure (1) shows the XRD patterns for PbS thin films, which were nanocrystalline in nature. All PbS films have cubic structure as confirmed by standard ASTM data. The well defined (111), (200), (220), (311), (113) and (222) peaks were observed in the XRD patterns. The average crystalline size (G.S) of nano PbS in the film was determined from the (200) by using Scherrer formula [9]:

$$GS = \frac{A\lambda}{\Delta\theta \cos\theta} \qquad \ldots (4)$$

Where A is a constant taken to be 0.94[9], λ is the wavelength of X-ray used which is Cukα radiation, and Δθ is full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane . The value of the crystallite size (G.S) as shown in Table.1 varies with in the range (4.9 to 11.3) nm. The value of G.S as determined by Scherrer s formula which gives the size of the crystallites in a direction perpendicular to the respective planes, FWHM of whose diffraction profile is taken for calculation of G.S, is found to be different in different directions for all the crystallites the size is small in a direction perpendicular to (200) plane [10].

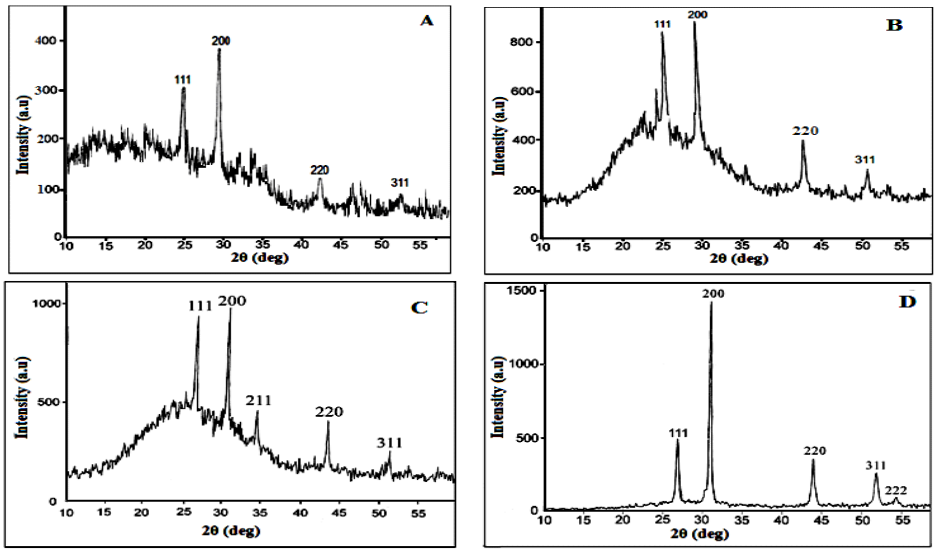

Figure (1) X-ray patterns of nano PbS thin films for different time: (A) 15min (B) 30min (C) 45min (D) 60min.

Table (1) Structural parameters of nano PbS thin films for different time.

t(min)	d(nm)	hkl	a $_{XRD}$ (nm)	d (nm)	G.S (nm)
15	**90**	**200**	**0.5952**	**90**	**4.9**
30	**129**	**200**	**0.5937**	**129**	**6.4**
45	**140**	**200**	**0.5922**	**150**	**9.2**
60	**152**	**200**	**0.5778**	**162**	**11.3**

The lattice constant (a) is calculated from the relation [11]:

$$d=a/(h^2+k^2+l^2)^{1/2} \qquad ...(5)$$

Where h, k ,l are Miller indices, d is the inter-planer spacing. From Figure (2a,b), it is clear that the PbS films show a decreasing of lattice constant with time(a_o=0.5936 nm).The decreasing of the lattice constant is more floral due to the enhanced of the degree of crystallity of films and indicating that films grow on the glass substrate without stresses at the interface. However, increasing time deposition produce an increase in the grain size of the PbS films from approximately 4.9 to 11.3 nm for the films deposited at 15 to 90 min, respectively.

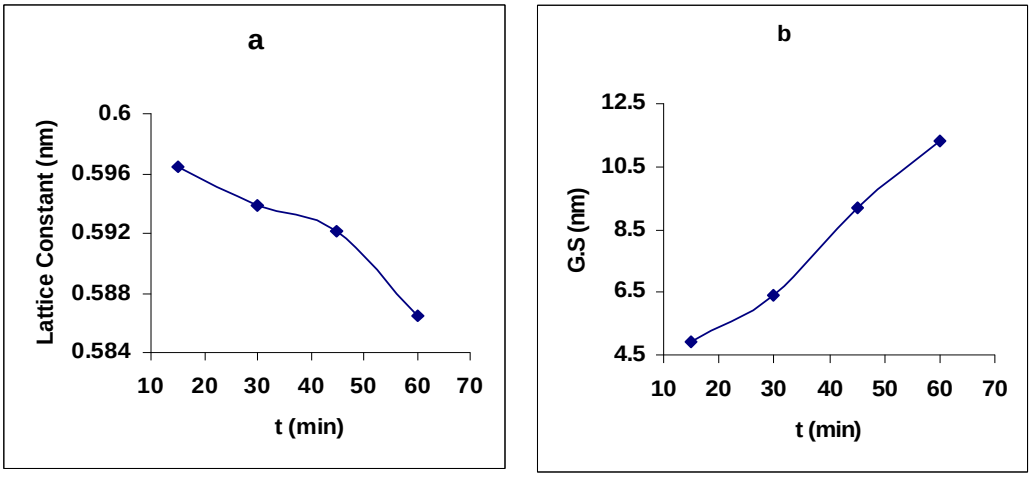

Figure (2a,b) Variation of (a) lattice constant (b) grain size with deposition time for nano PbS films .

Atomic Force Microscopy (AFM) Analysis

The surface images of the PbS films deposited at different time , obtained by AFM, are shown in Figure(3). It can be observed that the surface of the films is very compact. The films are constituted by round shaped rectangular pyramids packed together with a regular size distribution. A lot of empty spaces can be seen between these pyramids. The average size of the clusters increased with time. The larger pyramids in the surface of the films exhibit clearly an aggregate structure, that is, they are composed of small crystallites or grains. The changes in the structural and surface morphology properties of the PbS films produced by the deposition time can be related to the larger number of both Pb^{2+} and S^{2-} ions in the reaction solution at higher time. The release of metal ions by the complexing agent is a thermal activated process and the double hidrolisation of thiourea to produce S^{2-} ions is also more effective at higher temperatures [12].Our results show that both processes can take place in a reaction solution at time as 15min.

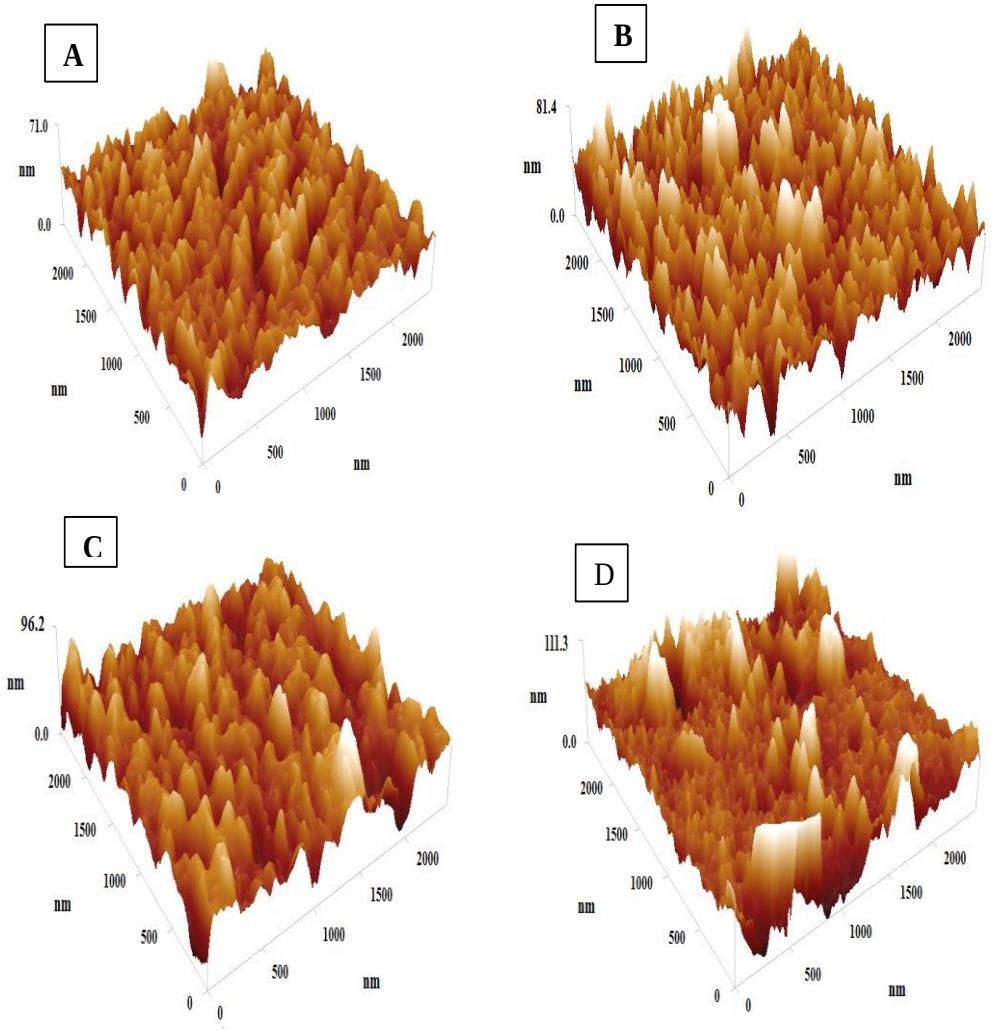

Figure (3) AFM image of nano PbS for different time:(A)15 min (B)30 min(C)45 min (D)60 min at (T=30°C, pH=11.6, MPb=0.25M and MSc=0. 5M).

ELECTRICAL PROPERTIES ANALYSIS

Figure (4) reveals the variation of lnσ versa $10^3/T$ as a function of deposition time for nano PbS films. The dark electrical conductivity of as–deposited PbS films is in the range 10^{-6} –10^{-5} $(\Omega.cm)^{-1}$. We can notice from this figure that the conductivity of PbS films increased with increasing deposition time which is due to the increasing in the grain sizes [13].

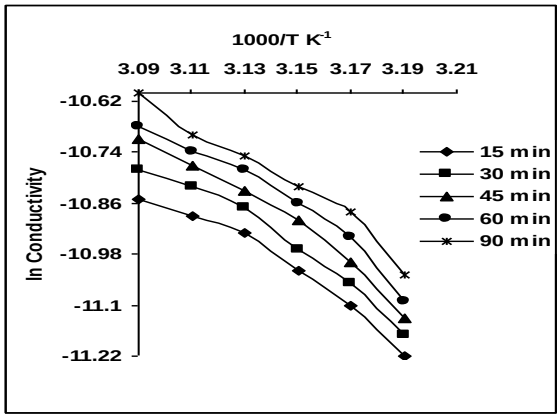

Figure (4) lnσ against (1000/T) for nano PbS films at Different Deposition time.

In almost all deposited films showed two different regions corresponding to two activation energies as shown in Figure (4). The activation energies of an electrical conduction have been determined in both low and high temperature regions [14].

CONCLUSIONS

Nanostructured PbS thin films were prepared by a simple chemical bath deposition method. The results of XRD study shows nanocrystalline structure with cubic phase (galena) and AFM show that the deposited PbS film consists of nano-sized grains. The grain size increases with increasing deposition time. The deposits are dark chocolate in color with conductivity of range 10^{-6} -10^{-5} $(\Omega.cm)^{-1}$.

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