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OPTICAL AND PHOTOCONDUCTIVE PROPERTIES OF CHEMICALLY DEPOSITED NANOCRYSTALLINE PbS THIN FILMS

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A nanocrystalline thin films of PbS with both thickness (400 and 600)nm have been prepared successfully by chemical bath deposition technique on glass and Si substrates. The structure and morphology of these films were studied by X-ray diffraction and atomic force microscope. It shows that the structure is polycrystalline and the average crystallite size has been measured. The optical parameters of the prepared films as absorption, transmittance, reflectance , optical energy gap, and absorption coefficient were found as affected by varying the thickness. The optical measurement showed that (PbS) films have an allowed direct energy gap (*Eg*) and that decreases with thickness increasing. The photoconductive measurement gives the positive photoconductive for PbS thin films.

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Keywords: PbS film, Chemical bath deposition, XRD, AFM, Optical properties

1. Introduction

In recent years, interest in the development of the semiconductor nanostructures materials has grown rapidly owing to their unique physical and chemical properties. This is due to their potential application in the area of solar cells, optoelectronic devices, photoconductors, sensor and infrared detector devices [1]. Their attractiveness arises from their low synthetic cost, their solution processing ability and the dependence of their optoelectronic properties as a function of size, shape, doping ,and surface chemistry. Therefore, many studies on shape controlled synthesis of semiconductor nanocrystals with different nanostructures have been reported. The study of optical properties of nanocrystalline solids have become the topic of great interest from the theoretical and experimental research point of view. It is known that nanocrystalline semiconductors exhibit the "quantum confinement effect'' ,and possess many superior properties as compared to bulk counterparts. As a consequence of quantum confinement, the continuum of states in the conduction and valance band are broken down into discrete states with an energy spacing relative to the band edge, which is approximately inversely proportional to the square of the particle radius [1], resulting in widening of the band gap as compared to the bulk, This is normally observed by a blue shift in the optical absorption spectra. The absorption edge of lead sulphide (PbS) exhibits a large blue shift when the size of the crystallite size is reduced to nanometer scale [2]. Consequently, the synthesis of PbS nanocrystals with different morphologies ,and the corresponding effects on material properties is of great importance in the search for novel applications in electroluminescent devices such as light emitting diodes. Lead sulphide have a direct energy gap, making them important for infrared applications.
At room temperature, its energy band gap is approximately 0.39–0.52 eV, it is changed by varying the shape and size from the bulk materials to nanocrystal structures [1-3]. Lead sulphide has been used in many application like sensors, solar cell, detector. For these reasons, many research groups have an increasing interest in the development and study of this material. Chemical deposition is the most appropriate and frequent way to prepare lead sulphide films. It has been found that the properties of chemically deposited PbS thin films depend on the growth conditions [2]. PbS nanocrystals are attractive for infrared applications because the energy of their first excitonic transition can be easily tuned from the visible to the infrared. The preparation of PbS has been

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explored by a number of methods including vacuum evaporation [4], liquid phase synthesis [5], chemical bath deposition (CBD) [6]. We have selected the CBD method owing to its many advantages such as low cost, large area production and simplicity in instrumental operation[7]. In this present study, we demonstrated simple CBD for making different PbS nanostructures films [8]. Thus In previous research, several researchers studied the technique of preparing lead sulphide films by chemical bath deposition. The aim of this paper is to preparation of PbS thin films and investigate the effect of thickness on the structure, morphology and optical properties of PbS nanoparticles prepared by the CBD method.

2. Experimental procedure

The lead sulfide films were deposited by the chemical bath deposition. Before the deposition, the glass substrate were very carefully cleaned using oxidant mixing ($K_2Cr_2O_7$:H_2SO_4), HNO_3, 1% EDTA, and successive rinsing with bi-distilled water. The cleaning of the substrate surface is very important to the quality and formation of the film. The deposition of PbS films were done in a solution prepared in a 100 ml beaker by the sequential addition of 5ml of 0.5M lead acetate, 5ml of 2M sodium hydroxide, 6ml of 1M thiourea and 2ml of 1M triethanolamine. The solution was diluted with deionized water to complete a total volume of 100ml. To obtain the films, the glass substrates were immersed into the solution, supported on the wall of the beaker and the beaker was put on the stirrer. The temperatures of the solution for growth were 20° C and kept constant for all deposition time. For this, the beaker with the reactive solution was immersed in water heating bath circulator, the PH was measured by PH meter and kept at 10, and here we analyze the samples obtained after 180min of deposition. The XRD phase patterns of the PbS deposited film of several thicknesses (0.4, 0.6μm) are established using Shimadzo X-ray difractometre model 6-2006. Microstructure surface topography was estimated using AFM by AA3000 Angstrom advanced lmtd. Optical absorption studies of the thin films in the wavelength range 200–800 nm were conducted using spectrophotometer (Model UV-160, (Shimadzu, Kyoto). Keithly Digital Electrometer 616, and D.C power supply, and Halogen lamp type philips 120W have been used for photoconductivity measurements.

3. Results and discussion

The structure properties of the PbS thin films of thickness (400, 600) nm have been studied by X-ray diffraction and AFM [7] as below, polycrystalline FCC cubic structure has been observed for the prepared films and it is corresponds with the standard JCPDS card no. (05-0592, a = 5.936 Å), as shown in Fig.(1), and the reflection surface (111), (200), (220), (311), (222) have been appeared, and this agree with Obaid et al. [8] ,and Choudhury et al. [9]. However, as the thickness was increased from 400 to 600 nm the extra peaks disappeared and the intensity of the peaks attributed to PbS films improved as shown in Fig.(1). This mean more crystallinity for the prepared films. The grain size of the films as a function of thickness was determined by using Scherer formula. It is clear from Table. (1) that the estimated average size increased with an increase in the thickness. The lattice constant is about 5.936 A which are consistent with the standard values. This lattice constant value is very similar to the bulk PbS indicating that films grow on the glass substrate without stresses at the interface. However, the increasing of thickness produces an increase in the grain size of PbS thin films, approximately 32 -44 nm for the thickness (400, 600) nm respectively, and this agrees with Abass et al. [3,10].

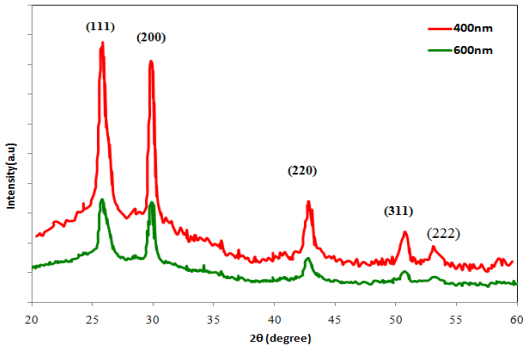

Fig. 1. The X-ray diffraction for PbS thin films at different thickness.

Table 1.X-ray diffraction data for PbS films for (200).

Thick.(nm)	d_{stand}(A°)	D (nm)	A (A°)	I/I_o
400	2.969	32	5.935	90
600	2.969	44	5.935	90

Atomic Force Microscope has been used for measuring the morphology of the prepared films. The 2D and 3 D AFM images in an area of 2x2 μm of the PbS films deposited at 20 C with different thicknesses, are shown in Fig. 2. It is observed that the formation of the films is regular, tightly composed and the adhesive of the material at the base is high.

No evidence of cracking observed, and it has larger number of grain size and is homogeneously distributed, which indicates the crystalline nature of the film. These results are in good agreement with XRD characteristics. The crystal morphology and molecular orientation change with thickness due to the change of molar concentration. The average grain size increases with thickness as in Table 2 from 91.12-108 nm, the grain density reduced indicating the smaller grains agglomerate together to form larger grains. Surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness Also the root-mean-square (rms) roughness of the film at different thickness is shown in Table 2 which increases with increasing thickness, which means the largest surface area, the best choice for solar cell making. From the application point of view, the higher efficiency devices are obtained from the film of greater roughness, and this is agreement with other literatures [8-10].

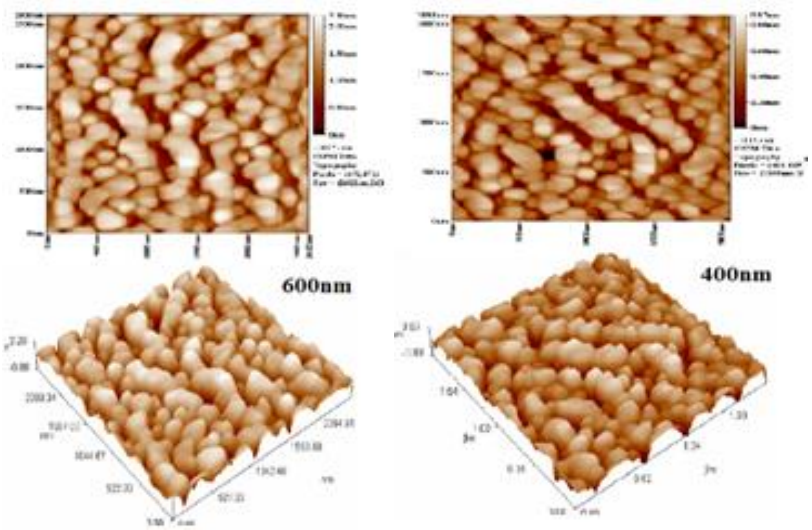

Fig. 2. Two and three-D AFM images of PbS thin films with different thickness.

Table 2.Grain size average, roughness, α and E_g of PbS thin films at different thickness.

Thickness (nm)	Roughness Average (nm)	Grain Size (nm)	α $cm^{-1}x10^4$	E_g(eV)
400	0.158	91.11	55	2.3
600	0.408	108	75	2.15

The UV-VIS absorption spectra of PbS thin films at different thickness is shown in Fig. 3 the study of optical absorption is important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is the band gap-the energy separation between the filled valence band and the empty conduction band. The optical absorption edge means that excitation of electrons through band gap from the valance band to the conduction band is allowed, leading to generation abrupt increase in the absorption at the wavelength corresponding to the band gap energy. The optical studies show that the absorbance of these film increases as thickness increases. High absorption in the VIS region has been observed. Also, It is observed that increasing of thickness shifts the peak of absorption spectrum to the red shift. The shift in the peak position films may be attributed to the crystallite of film structure by increasing the grain size which is confirmed by XRD results and AFM. Also, the spectrum of transmittance has been studied as in Fig. 3 it is obviously that its behavior is opposite to that of the absorbance spectrum. PbS may play an important role in photovoltaic devices due to high optical transmission . Similar behavior was observed by researchers [3], [9]. Also, the spectrum of reflectance are shown in Fig. 3.

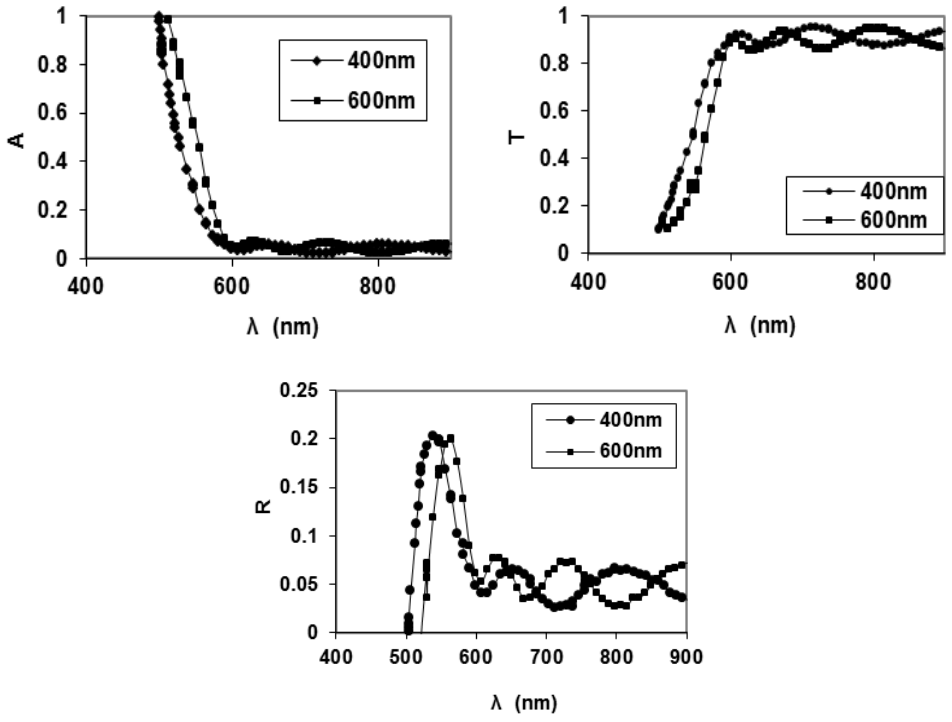

Fig. 3. The absorption, transmittance and reflectance spectrum PbS thin films at different thickness.

The absorption coefficient of direct band gap semiconductor is given by:

$$\alpha=B(h\nu-E_g)^{1/2}/h\nu \quad (5)$$

where α is the absorption coefficient which is calculated as in Table (2), B a constant, hν incident photon energy and E_g the band gap. The graphs between hν vs. $(\alpha h\nu)^2$ is plotted for different thickness and the intercepts of the extrapolated straight line at the $(\alpha h\nu)^2=0$ axis give the value of the E_g of the material as shown in Fig.4 and Table 2. The values of Eg so obtained vary from 2.3 to 2.15eV indicating increase of band gap with decrease of crystallite size. Such increase in band gap due to strong quantum confinement effects in PbS-Si nanostructure is also reported by[9].

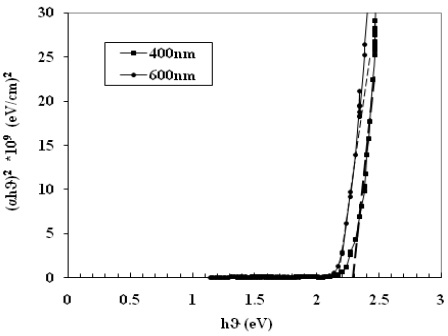

Fig. 4.The hν vs $(\alpha h\nu)^2$ for PbS thin films at different thickness.

The photoconductivity of the PbS films has been determined with two thicknesses of (300, 400 μm). The current voltage characteristics of these films were measured under dark and illumination condition at power intensity(50)mW/cm^2 as in the circuit in Fig(5).

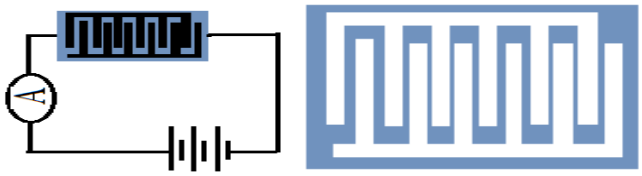

Fig.5. a) The Circuit diagram for I-V characteristics, b) Mask of electrode.

The relation between dark current, and the applied voltage for PbS films at two thicknesses (400,600) has been shown in Fig.(6). It is observed from this figure that by increasing voltage bias the dark current increases, the dark current was small at low voltage, whereas it has large values at high voltage. The increase in dark current is partially due to increase in the number of the free carriers, and decrease the potential barrier which increases the photoconductivity of the carriers. The value of dark current for films increase with increasing thickness This attributed to crystallization process and improvement the structure by increases the grain size. Also, the value of dark current is increased with thickness from 0.8 to 1.5 μA at 15V for (400,600).

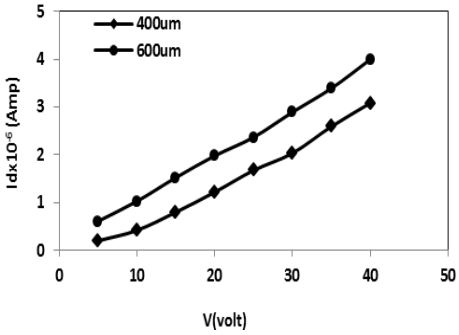

Fig.6. The relation between dark current and the applied voltage for PbS films at different thickness.

The relation between photocurrent and the applied voltage for PbS films at power intensity(50)mW/cm^2 with thickness of (300, 400)μm are shown in Fig.(7). The photocurrent increases with increasing thickness from 82 μA to 110 μA which mean positive photoconductivity, and this is in agreement with [11, 12]. Due to crystallite the films by increasing of thickness, the increasing in the grain size leads to reduce the mean free path of carriers and increases the photoconductivity. The photoconductive gain (G) is the ratio between the photocurrent to the dark current at the same bias voltage, and it's about (102.5-72.2) at 15V for thickness (300, 400)μm.

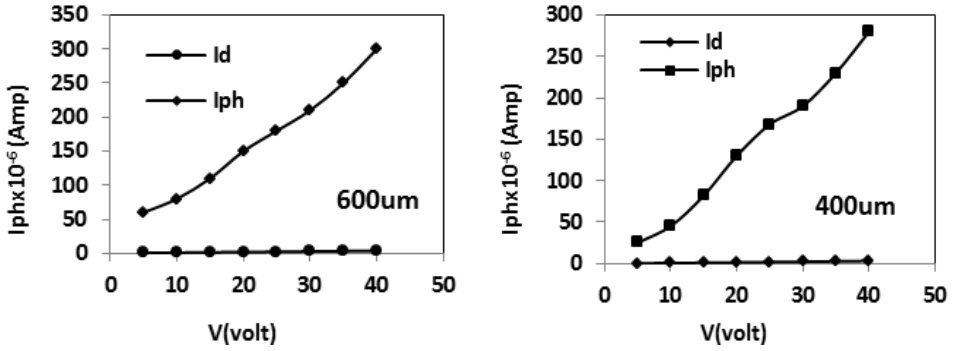

Fig.7 .The relation between photocurrent and the applied voltage for PbS films at at different thickness.

4. Conclusions

Lead sulfite Nanocrystalline thin film has been prepared successfully by chemical bath deposition method on glass substrate with two thicknesses. From XRD, the films are crystalline with cubic structure (111) and (200) direction. From AFM the morphology of these films have larger number of grain size and are homogeneously distributed, compact and uniform which indicates the crystalline nature of the film, the grain size ,and surface roughness of these films is increase with increasing of thickness, whereas, the energy gap decrease with crystallite size.

The band gap is strongly allowed and the absorbance of these film increases as thickness increases. It is observed that increasing of thickness shifts the peak of absorption spectrum to the red shift. The shift in the peak position films may be attributed to the crystallite of film structure by increasing the grain size which is confirmed by XRD results and AFM. The increases in positive photoconductivity have been observed in the prepared films.

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