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Structural and Optical Properties of Nanocrystalline Pbs Thin Films Prepared by Chemical Bath Deposition Method

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ABSTRACT

Nanocrystalline PbS thin films were prepared by chemical bath deposition (CBD) method by varying synthesis temperatures. The influence of the synthesis temperature on the structure and optical properties of PbS nanostructures were investigated. The X-ray diffraction (XRD) pattern of the PbS nanostructures correspond to the various planes of a single phase cubic PbS. It was observed that the decrease in the synthesis temperature resulted into extra diffraction peaks which may be due to the presence of the impurity phases. The morphological properties of the films are observed by scanning electron microscopy (SEM) characterization. UV-Visible spectroscopy is done to measure the absorption and transparent properties of all the prepared systems. The optical band gap of all the prepared systems is also calculated and correlated with the structural properties.

1. Introduction

Thin films of organic compound semiconductors are taking vital roles in advanced technologies of society. To drastically improve the performance of thin films based devices, it is necessary to realize a precise control of the films structure at an atomic level in the films processing. Semiconductor nanocrystals display a wealth of size-dependent physical and chemical properties, including quantum confinement effect, shape dependent electronic structure and control over assembly through modification of surface functionalization. Photovoltaic devices are easily recognized potential applications of nanocrystals due, in part, to their photoactivity, solution process ability and low cost of production

In recent years, the development of the semiconductor nanostructured materials has grown very rapidly [1]. This is due to their wide application in the area of solar cells, optoelectronic devices, photoconductors, sensor and infrared detector devices [2]. The Pb chalcogenide family of nanocrystals in actively investigated for nanocrystals solar cell applications because they have large exciton Bohr radii (18 nm), in the limit where the nanocrystals are only a tenth or so the bulk exciton diameter, electrons and holes can be tunnel through a thin organic surface coating, and therefore strong electronic coupling between particles facilities transport of charge between nanocrystals. Consequently, the synthesis of PbS nanocrystals with different morphologies and the corresponding effects on material properties is of great importance in the field of light emitting diodes, infrared-related applications. We have selected the CBD method owing to its many advantages such as low cost, large area production and capable of yielding good quality thin films. The aim of this paper is to investigate the effect of synthesis temperature and molar concentration of lead acetate on the structure, morphology and optical properties of PbS nanoparticles prepared by CBD method.

2. Experimental Details

Nanocrystalline PbS thin films were deposited on glass substrates by CBD method. The substrates were very carefully cleaned using an oxidant mixture (K2Cr2O7: H2SO4 -1:10, HNO3, 1% EDTA) and were then thoroughly rinsed with distilled water before deposition. The cleaning of the substrate is of crucial importance for the quality of the film formation.

The deposition bath contains a mixture of matrix solution and thiourea. The chemical bath solution was prepared as follows: 60 ml of lead acetate, thiourea, sodium hydroxide and along with 2% of PVA solution. The amount of solutions of lead acetate, thiourea and PVA was held constant at ratio of 1:1:1. Each mixture was continuous stirred for 10 minutes by varying the synthesizing temperature at 60, 70, 80 and 900C respectively. The pH of the solution was maintained at around 10.5 by slowly adding NaOH solution drop by drop. The substrates were kept in the solution for 26 h for deposition of PbS through following reactions in the solutions:

$Pb(CH3COO)2.3H2O \rightarrow Pb2{+}{+}2CH3COO{-}{+}3H2O$ …….(1)

$Pb2{+}{+}4NH3 \rightarrow Pb(NH3)42{+}$ ...…..(2)

$SC(NH2)2+2OH^{-} \rightarrow S2{-}{+}CH2N2+2H2O$ ...…...(3)

$Pb(NH3)42{+}{+}SC(NH2)2+2OH \rightarrow PbS+4NH3+CH2N2+2H2O$….(4)

After deposition of the films, substrate were taken out and thoroughly washed in doubly distilled water and then dried in air. Structural characteristics of the films were determined by X-ray diffraction (XRD) method using Philips X-pert pro diffractometer (PW 1830) at room temperature with CuK radiation. Grain size of the films were also determined by scanning electron microscopy (SEM) at different magnifications. Optical absorption spectra of the samples were taken with the help of a UV spectrophotometer.

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3. Results and discussions

(a). Structural Characterization

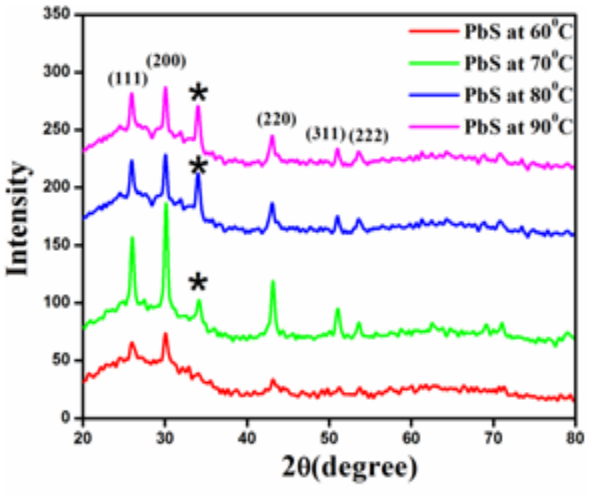

Fig. 1

Fig 1(a) shows X-ray diffraction patterns of PbS synthesized at different bath temperature as indicated (60, 70, 80 and 90^{0}C). All XRD patterns show four intense peaks at around 2θ=25.99, 30.11, 43.09 and 51.03^0. All these peaks corresponding to the cubic phase of PbS which matched with the standard JCPDS card no. (05-0592). An extra peak at 2θ=34.06 can be observed for all the samples except PbS prepared at 60^{0}C infact even the regular peaks are not clear in this samples and it may be due to the lack of reacting temperature. As the bath temperature increases all the peaks becomes prominent.

Table 1. System, crystallite size, lattice volume and band gap.

System	Crystallite Size(A^0)	Lattice volume(A^0)^3	Band gap(eV)
PbS at 60^{0}C	6.42	147.20	2.71
PbS at 70^{0}C	5.07		2.76
PbS at 80^{0}C	4.09		2.69
PbS at 90^{0}C	3.86		2.65

The arisen of this extra peak may be due to the unreacted lead acetate oxide hydrate. This improved intensity with sharper peaks indicates a higher crystallinity of the material. The crystallite size of the PbS increased as the bathing temperature increases. This may be due to the coalescence between neighboring islands during compacted deposition and atomic mass transport. The bathing temperature has not affected lattice volume as it remains same for all. The size of the unit cell remained same whereas the collection of ordered unit cell increases as the crystallite size increaes with the increase in bathing temperature. The increase in temperature allows different clusters to combine and form a nucleation centre.

Fig 2(a), (b), (c) show surface morphologies of PbS synthesized at various temperature. All the samples were taken at 20 KeV with a 0.05 nm field of view. Karami et al [2] have reported that by increasing the synthesizing temperature there was no influence on particle size and morphology. But we observed that particle size increased slightly with the increase in synthesized temperature. With the increase in synthesized temperature, the particle becomes unsymmetrical. From the micrograph it is observed that grain sizes are not much of uniformity.

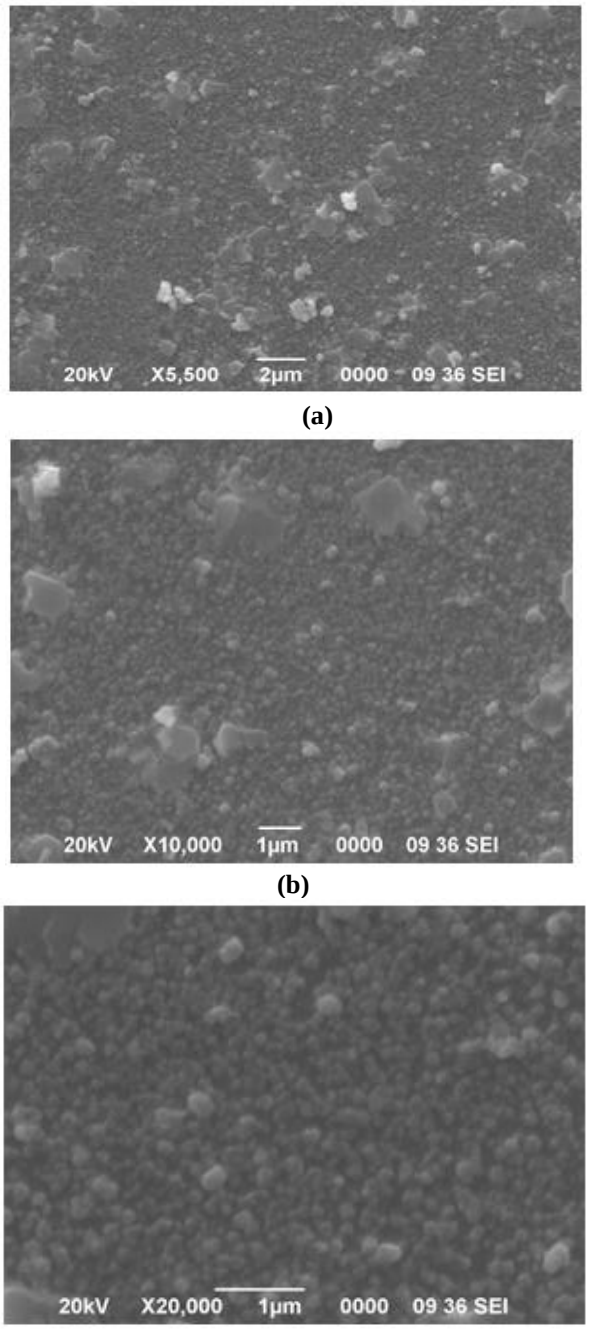

Figure 2. The SEM micrograph of PbS synthesized at the various temperatures but at constant molar concentration of lead acetate: (A) 70^{0}C (B) 80^{0}C and (C) 90^{0}C.

(b). Optical characterization

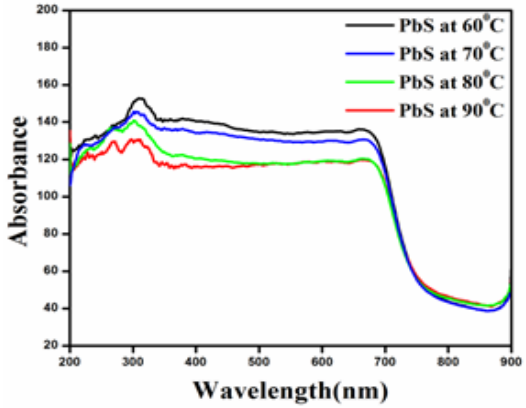

Fig 3. Absorbance Vs wavelength for all the systems.

Fig. 3 shows that all the systems have almost same pattern of absorbance in the given wavelength region. PbS is known to have high absorbance and hence low transmittance in the visible region and we have observed this as well. The absorbance of the system decreases with the increase in bathing temperature. The increase in crystallite size and increase in height of the XRD peaks confirms better crystalline nature as the bathing temperature increases. The better crystallinity of the material implies a defect free system. A less defective system tend to be more transparent and hence absorb less. Therefore, improvement in crystallinity of PbS with the increase in bathing temperature leads to decrease in absorbance. Band gap of all the system is calculated using Tauc's plot and values are shown in table 1. The band gap values are found to decrease with the increase in bathing temperature. This can be linked to the fact that increase in crystallite size leads to decrease in band gap value. The trend of decrease in band gap with the increase in crystallite size is in accordance with the quantum confinement law.

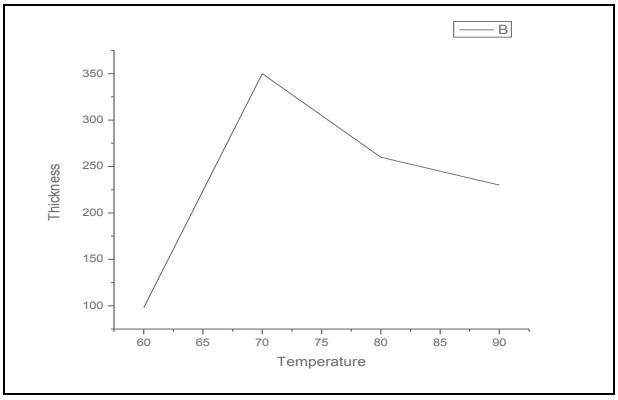

Fig 4. Temperature Vs Thickness graph.

Figure 4 shows the variation of bath temperature Vs film thickness. It is seen that initially film thickness increases as the bath temperature increases and obtains maximum value at 70^0C . Finally thickness decreases as the temperature increases.

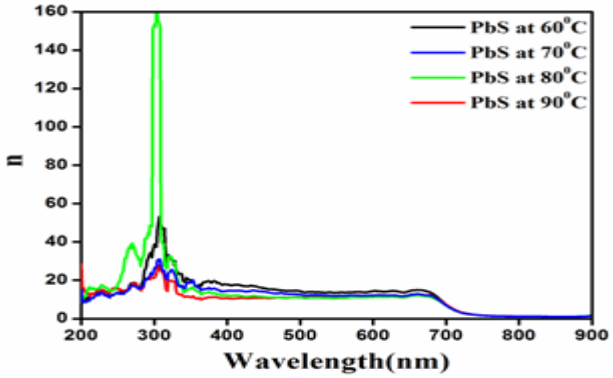

Fig 5. Refractive index Vs Wavelength of all the systems.

The refractive index (n) of all the systems are calculated using the following equation and

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K^2\right]^{1/2}$$

Where R and K are the reflectance and extinction coefficient respectively.

The refractive index of the materials as shown in Fig.5 follows the same pattern as that of absorbance in the visible range.

The value of refractive index decreases as the bathing temperature increases which means light suffers lesser retardation as the bathing temperature increased. Overall, all the system shows very little change in refractive index value in visible range of wavelength.

Conclusions

Nanocrystalline PbS thin films with constant molar concentration of the solutions have been prepared and synthesized. We have observed that the size of the PbS nanocrystals in the deposited film is affected by the temperature of the bath solutions. The optical study shows that the absorbance of the system decreases as the bathing temperature increases. We also calculated band gap value and found it to be decreasing with the increase in bathing temperature. The refractive index value is also calculated and found that all the systems shows very little change in the visible range of wavelength.

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