Optical studies of chemically deposited PVA-capped PbS nanoparticle thin films

S. C. EZUGWU, F. I. EZEMA*, R. U. OSUJI[a], P. U. ASOGWA, B. A. EZEKOYE, A. B. C. EKWEALOR, C. CHIGBO[a], M. ANUSUYA[b], M. MAHABOOB BEEVI[b]
Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria
[a]*Enugu State University of Science and Technology, Enugu, Nigeria*
[b]*Trichy Engineering College, Trichy, Tamil Nadu, India*

PVA-capped PbS nanoparticle thin films were deposited by chemical bath deposition (CBD) method onto the glass substrate from an aqueous alkaline bath at room temperature. Lead nitrate and thiourea were used as Pb^{2+} and S^{2-} ions sources, respectively. The optical studies of the films were carried out by optical absorption measurements using a double beam Perkin-Elmer UV-VIS Lambda 35 spectrometer in the wavelength range of 200 – 1000 nm. The calculated direct allowed band gap energy lies in the range of 2.3 – 2.6 eV. The crystallite size measured by XRD studies was found to be 31.45 nm.

(Received April 06, 2009; accepted June 15; 2009)

Keywords: Optical properties, lead sulphide, thin films

1. Introduction

Solar energy is one of the most convenient non-conventional energy resources to be considered for the power requirements of the 21st century. The studies of semiconductor nanoparticles have shown that they exhibit novel optical properties. These unique properties led to the appearance of many new application areas, such as their use in solar cell, photodetectors, light-emitting diodes and switches [1].

Polymer capped inorganic thin film is the focus of many research groups [2 – 8]. For example, CdSe-polymer composites can be used to make blue light emitters [2]. Silver nanoparticles have been incorporated in the polyvinyl alcohol (PVA) matrix in order to improve its properties such as higher glass transition temperature and elastic modulus than only PVA [3]. Pattabi et al [5] prepared PVA capped CdS nanoparticles which showed better photoluminescence properties. Nanocrystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Extensive literature on size reduction effect is available [9 - 13]. Thin film deposition carried out within the pores of PVA is an effective means of modifying the sizes of the crystallites [9, 10, 14].

PbS is an important binary IV – VI semiconductor material with a narrow band gap (0.41eV) at room temperature. The band gap can be blue shifted from the near infrared to the visible region by forming nanocrystallites. In view of this, PbS nanoparticles have been successfully applied as IR detector, display devices, Pb^{2+} ion selective sensors, solar control coatings and electroluminescent devices such as LED [15 – 19]. Properties of nanostructured materials are different and often superior to those of conventional coarse-grained materials and also of amorphous alloys of the same configuration [20].

The CBD method for metal chalcogenide thin film preparation is attracting considerable attention, as it is relatively less expensive, simple and convenient for large area deposition. A variety of substrates such as insulators, semiconductors or metal can be used, since it is a low temperature process. The basic principle of CBD method has been already reported [21 – 24]

In the present investigation, nanocrystalline PbS thin films have been deposited using CBD method at room temperature, within the self-organized pores of polyvinyl alcohol. The structural, surface morphological and optical characterizations were carried out.

2. Experimental details

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following manner. First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA ($-C_2H_4O)_n$ (where n=1700), and stirred by a magnetic stirrer at 90°C for 1hour. The solution was aged until the temperature drops to room temperature. Analytical reagent grade lead nitrate and thiourea were used for the deposition of PbS thin films. The PbS films were grown on glass substrate from an alkaline bath. The films were prepared by dipping previously cleaned glass substrates in a mixture of solution of (0.1M) lead nitrate, (1.0M) thiourea, (1.0M) sodium hydroxide and PVA solution. The substrates were vertically immersed into the solution and supported on the walls of the beaker. The substrates were taken out of the beaker after 3hrs, rinsed with distilled water allowed to dry. The films were annealed in the oven at a temperature of between 150 and 350^0C

The samples were characterized with SEM, XRD and UV-VIS Spectrophotometer. Optical properties of chemical bath deposited PVA-capped PbS nanoparticle thin films were measured at room temperature by using a double beam Perkin-Elmer UV-VIS Lambda 35 spectrometer. Optical band-gaps were calculated from the absorption spectra. The XRD patterns for the samples annealed at 150^0C was recorded using D/max-2000 Rigaku powder X-ray diffractometer in the 2θ range 20^0 - 80^0 using CuK_α radiation of wavelength λ = 1.5408Å. The grain size of the film was viewed by using scanning electron microscopy (SEM) technique.

3. Results and discussion

3.1 Structure and surface morphology

X-ray diffraction (XRD) is an efficient tool for the structural analysis of crystalline materials. The XRD pattern for the sample annealed at 150^0C is shown in figure10.

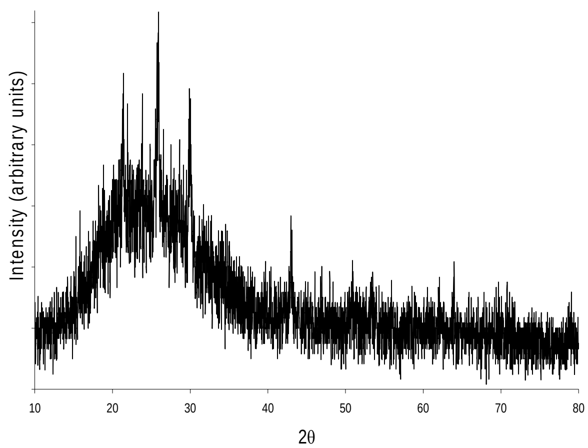

Fig.1. XRD result for PbS nanoparticle thin film.

The XRD pattern of the PbS thin film into the polymer matrix (Fig. 1) shows broadening of the peaks which indicates that PbS is nanocrystalline in nature into the amorphous polymer PVA matrix [8]. Prominent among the diffraction peaks are 2θ values of 25.92, 30.04, 43. 12 and 63.98^0. These were assigned to the diffraction lines produced by (111), (200), (220) and (400) planes of the face-centered-cubic (fcc) rock-salt structure of PbS [8].

The PbS thin films grain size (D) were determined by measuring the full width at half maximum (B) using the Scherrer formula $D = k\lambda/ \beta\cos\theta$, where k is a constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.54Å). Using Scherrer's formula grain size was found to be of the order of 31.45nm.

Scanning electron microscopy (SEM) (fig. 2) is a convenient method for studying thin films. The structure of the PbS film were almost homogeneous and without many cracks and covered the substrate well. The presence of over grown PbS particles were also observed.

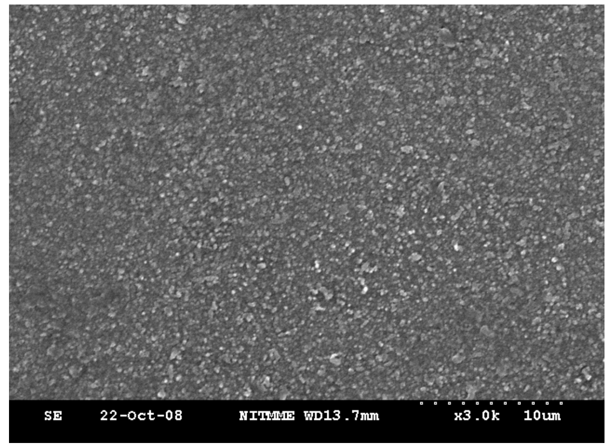

Fig. 2. SEM of PbS thin film.

3.2 Optical studies

3.2.1 Variation of the absorbance, transmittance and reflectance of the films with wavelength.

The optical absorption spectra of the films deposited onto glass substrate were studied in the range of wavelengths 200 – 1000nm. The variation of absorbance with wavelength for the samples annealed at different temperature and the as-grown are shown in fig. 3. The figure shows that the films have good absorption in the visible spectrum of solar radiation. The absorbance decreases almost linearly with wavelength from350nm up to 700nm.

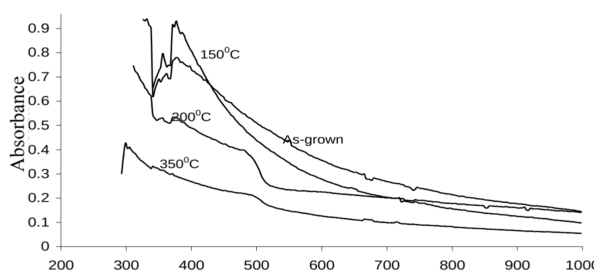

Fig. 3. Absorbance vs. wavelength for PbS nanoparticle thin films.

The spectral dependence of transmittance (T) as a function of wavelength for as-grown and annealed films of nanoparticle PbS thin films with different annealing temperature were also studied. Fig.4 shows that the transparency varies from 50 – 85% in the visible and NIR region of the solar spectrum.

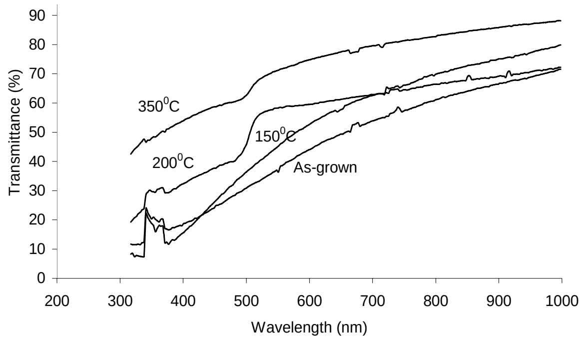

Fig. 4. Transmittance vs. wavelength for PbS nanoparticle thin films.

The figure shows that high temperature annealing has significant effect on the transmittance of the films. This can be seen from the high transmittance value displayed by the film annealed at 350^0C.

Fig. 5 shows the spectral reflectance against wavelength for nanoparticle PbS thin films deposited in this work. .With the exception of the film annealed at 350^0C, all the films show a reflectance of more than 15% in the VIS and NIR regions of the solar spectrum.

The thin films with high transmittance and low reflectance are good material for antireflection coatings of solar thermal devices. It has been shown that high transmittance and low reflectance properties of thin films in the visible region are the desired properties for their application in solar thermal control coatings [25]. The application of solar energy as a source of heat in chick breeding requires thin films with high absorbance in the VIS, high transmittance in the NIR with moderate reflectance.

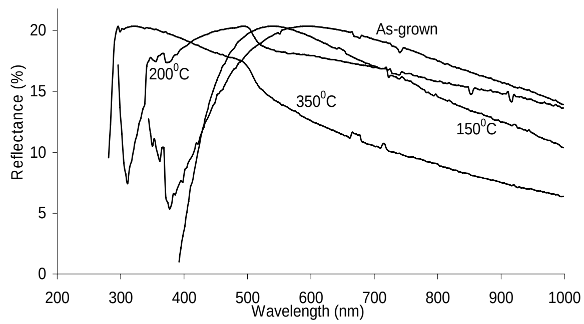

Fig. 5. Reflectance vs. wavelength nanoparticle PbS thin films.

The high transmittance in the NIR exhibited of this films therefore make them good materials for the construction of poultry roofs and walls. This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation. The strong absorbance of PbS nanoparticle thin films in the visible region also suggests that the films could be used for the fabrication of solar cells.

3.2.2 The absorption coefficient and optical energy gap

The details of the mathematical determination of the absorption coefficient (α) can be found in literature [11, 12] while the plots of absorption coefficient against photon energy is shown in Fig. 6.

These absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap, E_g. The E_g was calculated using the following relation [11-13]:

$$\alpha = A(h\nu - E_g)^n / h\nu,$$

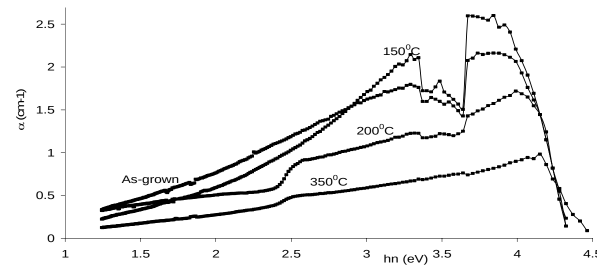

Fig. 6. The absorption coefficient nanoparticle PbS thin films.

Where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively. The usual difficulty in applying this concept to polycrystalline thin films with nanometer-scale crystalline grains is the size distribution of grains and consequent variation in the band gap due to quantum confinement effects. Thus the straight-line portion may not extend beyond a few tenths of an electronvolt, and hence value of the band gap could turn out to be very subjective [15].

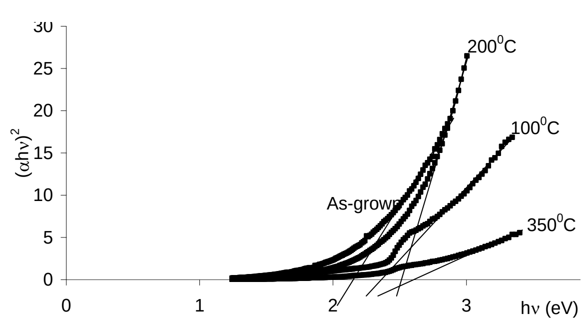

Fig. 7. $(\alpha h\nu)^2$ vs. hν for PbS nanoparticle thin film.

The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for n = ½. The calculated values of the direct energy band gap, from Fig. 7 lie in the range of 2.3 – 2.6eV. Annealing the sample in the oven lowers the value of coefficient of absorption of the films and thus increases the band gap energy. This may be a consequence of the decrease in crystallite size associated with high temperature annealing. The band gap energies obtained here are high compared with the room temperature value of 0.37 – 0.4eV [26]. However, they compare well with the values 2.4 – 2.8eV [28] and 1.6 – 2.44eV [9], reported elsewhere. The high band gap energy in relation to the room temperature bulk value has been attributed to quantum confinement effect of PbS nanocrystals. The properties of nanocrystalline materials change from their bulk properties because the sizes of the crystallite become comparable to the Bohr excitonic radius [28]. It has also been reported that thin film deposition carried out within the pores of a polymer matrice is an effective means of reducing the size of the crystallites [9, 10, 14]. This fact is thus responsible for the general high value of the band gap energy reported here. We thus infer that any process that increases the particle size of the crystallites tend to decrease the band gap energy of PbS thin films.

3.2.3 Other optical properties

The average values of other optical properties studied in this work are summarized in table 1. These values were obtained from Figs. 8, 9 10 and 11.

Table 1. Average optical properties for PbS nanoparticle thin film.

	n	k	ε_r	ε_i
As-grown	1.78	34.00	3.41	128.10
150^0C	1.64	29.29	2.99	99.33
200^0C	1.83	25.10	3.55	100.12
350^0C	1.66	13.39	2.88	48.06

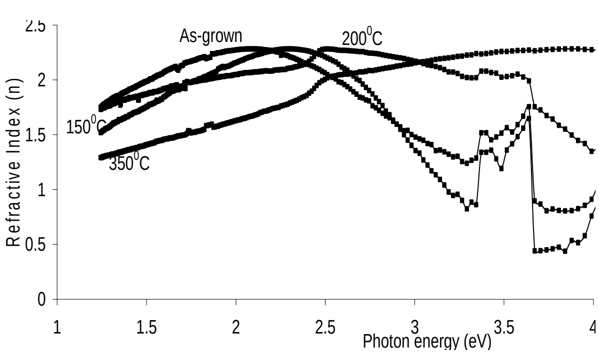

Fig. 8. Refractive index vs. photon energy for PbS nanoparticle thin film.

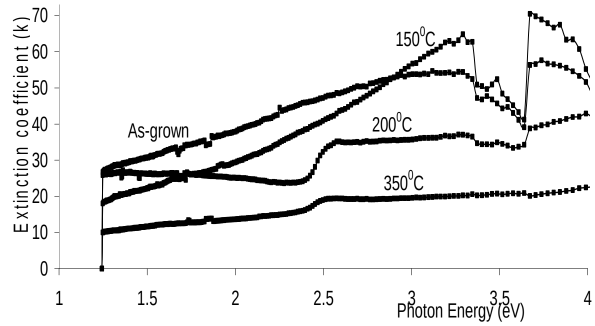

Fig. 9. Extinction coefficient vs. photon energy for PbS nanoparticle thin film.

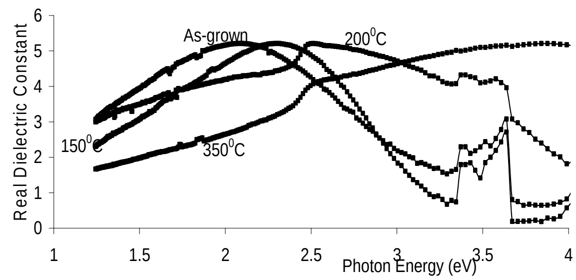

Fig.10. Real dielectric constant vs. photon energy for PbS nanoparticle thin film.

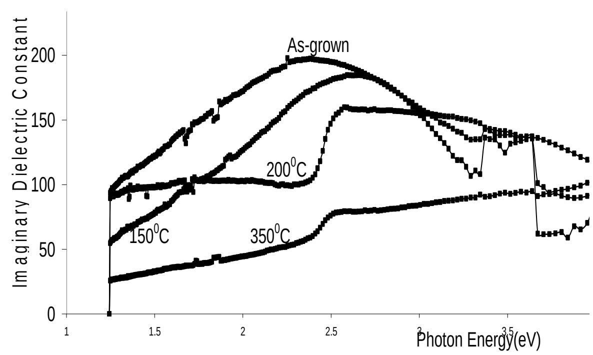

Fig. 11. Imaginary dielectric constant vs. photon energy for PbS nanoparticle thin film.

4. Conclusions

PbS nanoparticle thin films have been successfully deposited onto glass slide using chemical bath deposition technique. The optical studies showed that the films have good absorption in the visible spectrum of solar radiation. The absorbance decreased almost with wavelength from350nm up to 700nm.The properties of high absorbance in the VIS and wide band gap energy exhibited by the films make them suitable as window layers for solar cell application. XRD studies show that the PbS nanoparticle thin films prepared by CBD technique have face-centered-cubic (fcc) rock-salt structure. The crystallite size was found to be 31.45nm.

References

[1] H. Weller, Chem. Int. Edn. Engl. **32,** 41 (1993).
[2] X. Lu, L. Li, W. Zhang, C. Wang; Nanotechnology **16,** 2233 (2005).
[3] B. O. Dabbousi, M. G Bawendi, O. Omtduku, M. F. Rubne; Apll. Phys. Lett. **66,** 1316 (1996).
[4] Z. H. Mbele; Chem. Mater. **15,** 5019 (2003).
[5] M.Pattabi, B. S. Amm, K. Manzoor, Mater. Res. Bull.**42,** 828 (2007).
[6] K. Pato, E. Swatsitang, W. Jareonboon, S. Maensiri, V. Promarak; Optoelectron. Adv. Mater.-Rapid Comm. **1**, 287 (2007).
[7] R. Devi, P. Purkayastha, P. K. Kalita, B. K. Sarma; Bull. Mater. Sci., **30**(2), 223 (2007).
[8] S. Jana, R. Thapa, R. Maity, K. K. Chattopadhyay; Physica E (2008) doi; 10.1016/j Physe.2008.04.015
[9] P. K Ghosh, S. Jana, U. N Maity K. K Chaltopadhyay; Physica E **35,** 178 (2006).
[10] W. Lou, X. Wang, M. Chen, W. Liu, J. Hao; Nanotechnology **19,** 225607 (2008).
[11] J. P. Cheng, X. B. Zhang, Z. Q. Luo; Surface and coatings Tech.**202**, 4681 (2008).
[12] D. S. Dhawale, A. M. More, S. S. LAtthe, K. Y. R Ajpure, C. D. Lokhande; Applied Surface Science **254**, 3269 (2008).
[13] P. M. Rorvik, A. Almli, A.T . J. Helvoort, R. Holmestad, T. Tybell, T. Grande, M. Einarsrud; Nanotechnology **19**, 225605 (2008).
[14] R. S. Vaidyanathan; INTERFACE **16,** 2 (2007)
[15] E. Pentia, L. Pintilie, I. Matei, T. Boltia, E. Ozbay, J. Optoelectron. Adv. Mater **3**, 429 (2001).
[16] P. Yang, C. F. Song, M. K. Lu, X. Yin, G. J. Zhou, D. Xu, D. R. Yuan; Chem Phys. Lett. **345**, 429 (2001).
[17] H. Hirata, K. Higoshiyama; Bull. Chem. Soc. Jpn. **44**, 2420 (1971).
[18] P. K. Nair, M. T. S. Nair; J. Phys. D: Appl. Phys **23**, 150 (1990).
[19] A. Martucci, J. Fick, J. Schell, G. Battaglin, M. Guglielmi; J. Appl. Phys. **86**, 79 (1999).
[20] C. O. Lokhande, B. R. Sankapal, H. M. Pathan, M. Giersig, H. Tributch; Appl. Surf. Sci **181**, 277 (2001)
[21] F. I. Ezema, R. U. Osuji; J. of Appl. Sci **6**(8), 1827 (2006).
[22] F. I. Ezema, A. B. C. Ekwealor, R. U. Osuji; Turk J. Phys. **30**, 157 (2006).
[23] F. I. Ezema, M. N. Nnabuchi, R. U. Osuji; Trends in Applied Sci Research, **1**(5), 467 (2006).
[24] P. A. Ilenikhena; African Physical Review **2**, 0007 (2008).
[25] P. K. Nair, M. T. S. Nair, A. Femaardex, M. Ocampo; J. Phys. D. Appl. Phys. **22**, 829 (1989).
[26] J. I. Pankove; Optical Processes in Semiconductors. Prentice Hall Inc.: Eaglewood Cliff, NJ (1970).
[27] C. I. Oriaku, J. C. Osuwa; The Pacific J. Sci and Tech, **9**, 2 (2008).

*Corresponding author: fiezema@yahoo.com,