IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861, PP 07-10
www.iosrjournals.org

Optical and Electrical Characterization of Nanocrystalline ($Pb_{1-X}bi$) S Thin Films Deposited at Room Temprature

Rajesh Kumar and R. Das
Department of Applied Physics, Bhilai Institute of Technology, Durg (C.G.) 491001 India

Abstract: *In this paper, nanocrystalline ($Pb_{1-x}Bi_x$)S thin films were successfully deposited on suitably cleaned glass substrate at constant room temperature, using the chemical bath deposition technique. The deposited films were further annealed at 400^0 C in air. The optical characterization of the films was done by optical absorption and transmission spectra in the range 400-1100 nm using UV spectrophotometer. The band gap of the films was found to be in the range 1.6-2.2 eV for x = 0 to 0.05. The room temperature electrical resistivity of the synthesized films was measured by photoconductivity measurement unit. On increasing Bi doping concentration, electrical conductivity decreases.*

Keywords: *Band Gap, Chemical Synthesis, Electrical Resistivity, Optical Properties, Thin Films*

I. INTRODUCTION

The synthesis and characterization of semiconductor nanoparticles is an exciting field of research for future applications in optoelectronics [1, 2]. Nanostructured materials and in particular semiconductor nanostructures and thin films may be exploited for their novel electronic and optical properties. These structures are of great interest since they have potential applications in future quantum and photoinic devices [3]. Lead chalcogenides have been the subject of considerable research due to their technological importance in crystalline and polycrystalline forms. PbS is an attractive semiconductor material that exhibits strong size quantization effects due to the high dielectric constant and the small effective mass of electron and holes, suggesting that its band gap energy can be easily manipulated from the bulk value (0.41 eV) to a few electron volts by the changes in the material's size [4-6]. This material has also been used in many fields such as infrared photography, diode laser, humidity and temperature sensors, and decorative and solar control coatings among other applications [7-11]. Novel materials are needed for thin film solar cells apart from the most extensively studied material CdTe and $CuInSe_2$. PbS thin films have excellent solar control characteristics [12]. Nanocrystalline PbS materials are novel materials, and their properties are different and often superior to those of conventional coarse-grained materials. The absorption edge has been found to be blue shifted as particle size reduced. [13]. Also polycrystalline PbS thin films show good photoconductive properties [14]. Many methods have been developed to synthesize Pbs thin films, including vaccum deposition [15], electrochemical deposition [16], chemical bath deposition (CBD) [17], pulsed laser deposition [18], and, spray pyrolysis [19]. Among those deposition techniques, chemical bath deposition (CBD) is the convenient and frequently used deposition technique to grow good quality thin films. On account of the various applications of these films, an attempt has been made to deposit nanocrystalline ($Pb_{1-x}Bi_x$)S thin film using the CBD method and to investigate the optical and electrical properties of these films.

II. EXPERIMENTAL DETAILS

Nanocrystalline ($Pb_{1-x}Bi_x$)S thin films were deposited on properly cleaned glass substrates by chemical bath deposition (CBD) technique. The previously cleaned substrates were introduced vertically in a chemical bath containing an aqueous solution consisting of: 0.06M lead nitrate, 0.24M thiourea, 0.6 M Sodium hydroxide and a reducing agent 0.1M hydroxylamine hydrochloride and 2.06 x 10^{-4} M Bismuth Nitrate (All AR grade 99.9% pure). The solution was prepared in triple distilled water and pH value of the mixture was 12.56. All the depositions were made at constant room temperature. After deposition the films were annealed in air at 400^0C in furnace for 1hr. The film thicknesses were determined by gravimetric method. The optical characterization was done from absorption and transmission spectra of the films using a Chemito, double beam UV-VIS spectrophotometer (SPECTRASCAN-UV-2600) at wavelengths ranging from 400-1100 nm. Electrical conductivity measurements were done using digital nanometer (DNM-121) and a high voltage power supply by fabricating carbon electrodes.

III. RESULTS AND DISCUSSION

Optical characterization

The optical absorbance and transmittance spectra of different as-deposited and annealed nanocrystalline ($Pb_{1-x}Bi_x$)S thin films deposited on amorphous glass substrates prepared at room temperature are displayed in Fig.1 and 2 respectively . During scanning process, a blank glass slide was placed in one of the beam direction and another glass with the deposited film was in the other beam's direction. Thus, the absorption and transmission spectra displayed by the spectrophotometer were as a result of the films deposited on the glass slides. The transmittance of the light increases with increased concentration of Bi, while at lower wavelength region the transmission was nearly zero. The absorption coefficient of the films can be deduce by transmission spectra using the relation $\alpha = -lnT/t$ where t is the thickness of the films [20]. The absorption coefficient is greater than 10^5 cm^{-1}, suggesting that films have direct band gap. The optical data were analyzed from the following classical relation (Tauc relation) [21]

$$(\alpha hv) = A(hv - E_g)^{n/2}$$

where, hv is the photon energy, E_g is the band gap energy, A and n are constant. A is related to the effective masses associated with the valence and conduction bands. For allowed direct transitions, the value of n is equal to 1 and for forbidden direct transition n is equal to 3. For indirect allowed transitions n is equal to 4 and for indirect forbidden transition n is equal to 6. It is known that, PbS has a direct band gap; therefore the constant n is equal to 1 (for an allowed direct transition). The variation of $(\alpha hv)^2$ with hv for different films is a straight line which confirms the direct transition. The optical band gap (Eg) was determined by extrapolating the straight region of the plot of $(\alpha hv)^2$ versus the photo energy [not shown here] .The band gap of as-deposited and annealed nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films are shown in Table 1. The band gap of the as-deposited films was found to be in the range of 1.6-1.55 eV which very high as compared to the bulk PbS (0.4 eV). This may be due to quantum confinement effect in nanocrystalline thin films. Also it is observed that, the band gap of the films reduce with increasing Bi doping content in PbS. This decrease of band gap is consistent with dependence on crystallite size. After annealing at high temperature, the band gap of the films further increases. This may be due to change in crystallinity with annealing.

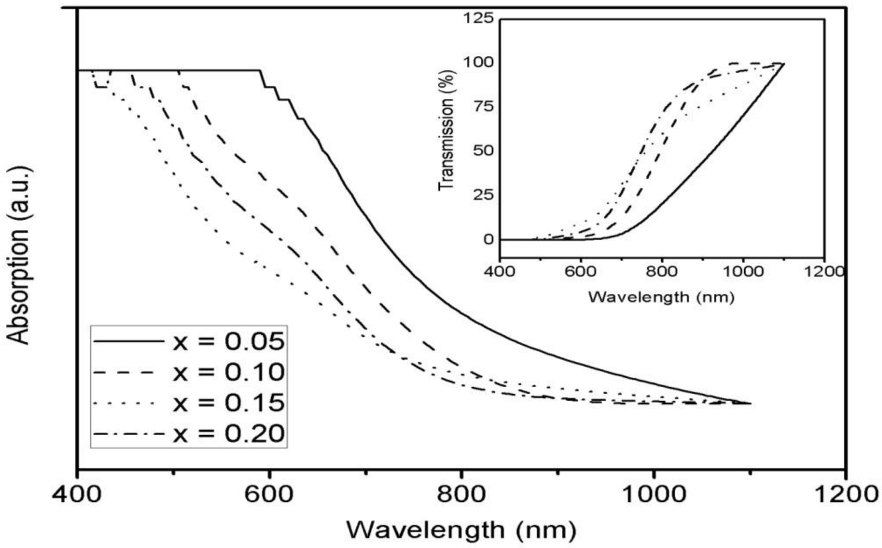

Fig. 1: Optical absorption and transmission spectra of different as-deposited nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films.

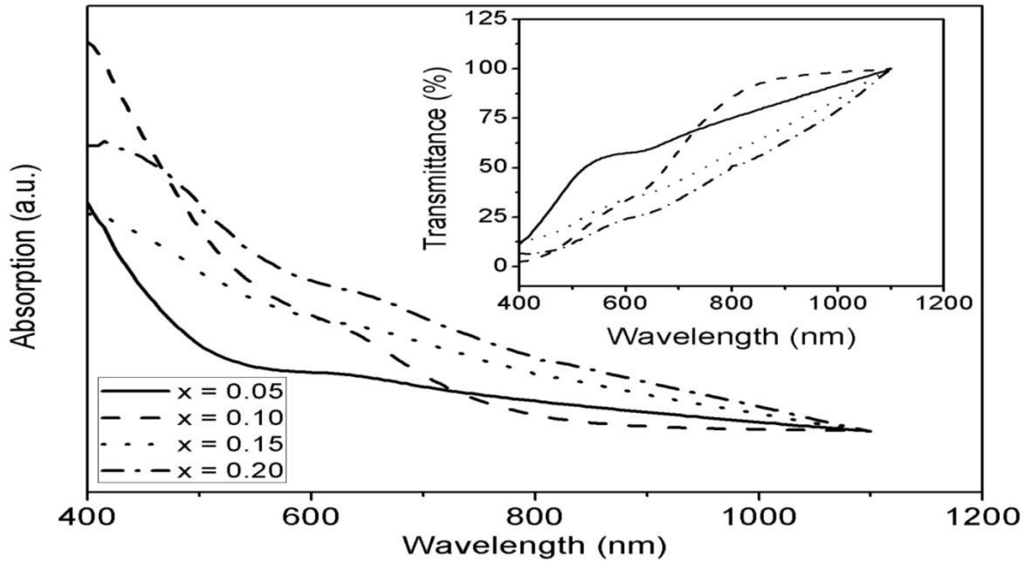

Fig. 2: Optical absorption and transmission spectra of different annealed nanocrystalline ($(Pb_{1-x}Bi_x)S$) thin films.

Table-1 Energy band gaps of different as-deposited and annealed nanocrystalline ($(Pb_{1-x}Bi_x)S$) thin films

S. No.	x	Band Gap (eV)	
		As-deposited Films	Annealed Films
1.	0.05	1.68	2.18
2.	0.10	1.65	2.14
3.	0.15	1.61	2.08
4.	0.20	1.55	1.98

Electrical characterization

The electrical resistivity of the films were determined by I-V characteristics curves using carbon electrodes and their values were calculated using the relation, $\rho = RA/l$ where R is the resistance of the films and is measured by the slope of the I-V characteristic curves, A is the area of the film under investigation and L is the spacing between electrodes. Fig. 3 shows the I-V characteristics of different nanocrystalline ($(Pb_{1-x}Bi_x)S$) thin films. The resistivity of the films was found to be in the range 1.1 x 10^6 to 2.4 x 10^6 Ω cm.

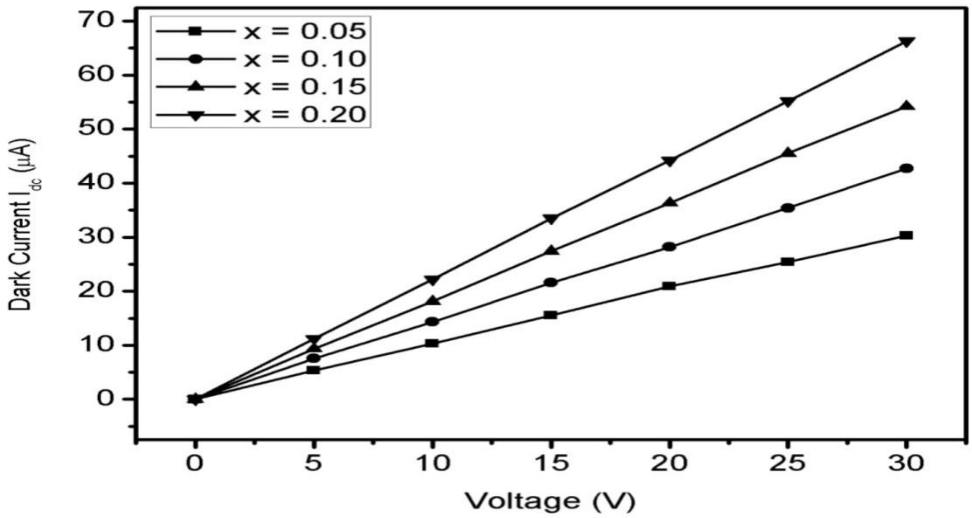

Fig. 3: Variations of dark currents with voltages for different as-deposited nanocrystalline ($(Pb_{1-x}Bi_x)S$) thin films.

IV. CONCLUSIONS

In this work, nanocrystalline ($Pb_{1-x}Bi_x$)S thin films were deposited on cleaned glass substrate by chemical bath deposition technique. The experimental characterization indicates that Bi doping and annealing play an important role in optical properties of the films. The optical properties show a significant change in band gap value with doping. The band gap of the films was calculated in the range 1.6 eV – 2.1 eV, which is higher than bulk Pbs (0.4 eV), which decreases on increasing Bi doping concentration in pure PbS. The blue shifting of the absorption edge is the clear confirmation of quantum confinement. The band gaps of the films lie in the visible range, so these films can be used in solar cell applications. The electrical resistivity of the films decreases with doping. These results indicate that there is a strong relation between the doping concentration and optical and electrical properties of the films.

V. ACKNOWLEDGEMENTS

The authors are grateful to BIT, Durg management for providing all financial support.

REFERENCES

[1] R.K. Joshi, A. Kanjilal, and H.K. Sehgal, Size dependence of optical properties in solution grown $Pb_{1-x}Fe_xS$ nanoparticle films, Nanotechnology, 14, 2003, 809.
[2] A. Martucci, J. Fick, Serge-Emile LeBlanc, M. LoCascio, and A. Hache, Optical Properties of PbS Quantum Dot Doped Sol-Gel Films, J. Non-Crys. Solids, 345-346, 2004, 639.
[3] D. Riabinina, F. Rosei, and M. Chaker, Structural properties of Ge nanostructured films synthesized by laser ablation, J. Eng. Nanosci 1(1), 2005, 83-89.
[4] Y. Wang, W. Suna, W. Mahler, and R. Kasowski, PbS in polymers. From molecules to bulk solids, J. Chem. Phys. 87, 1987, 7315-7322.
[5] Y. Wang, and N. Herron, Nanometer-Sized Semiconductor Clusters: Materials Synthesis, Quantum Size Effects, and Photophysical Properties, J. Phys. Chem. 95, 1991, 525-532.
[6] F.W. Wise, Lead salt quantum dots: the limit of strong quantum confinement, Acc. Chem. Res. 33, 2000, 773-780.
[7] C. Nascu, V. Vomir, I. Pop, V. Ionescu, and R. Grecu, The study of lead sulphide films. VI. Influence of oxidants on the chemically deposited PbS thin films , Mater. Sci. Eng. B. 841, 1996, 235-240.
[8] J.L. Machol, F.W. Wise, R.C. Patel, and D.B. Tanner, Vibronic quantum beats in PbS microcrystallites Phys. Rev. B. 48, 1993, 2819-2822.
[9] B.B. Nayak, and H.N. Acharya, Characterization of chemically deposited $Pb_{1-x}Cd_xS$ films by scanning electron microscopy, J. Mater. Sci. Lett. 4, 1985 651-652.
[10] B. Thangaraju, and P. Kaliannan, Polycrystalline lead tin chalcogenide thin film grown by spray pyrolysis, Cryst. Res. Technol. 35(1), 2000, 71-75.
[11] P.K. Nair, V. M. Garcia, A.B. Hernandez, and M.T.S. Nair, Photoaccelerated chemical deposition of PbS thin films: novel applications in decorative coatings and imaging techniques J. Phys. D: Appl. Phys. 24, 1991, 1466.
[12] P.K. Nair, M.T.S. Nair, A. Fernandez, and M. Ocampo, Prospects of chemically deposited metal chalcogenide thin films for solar control applications, J. Phys. D: Appl. Phys. 22, 1989, 829.
[13] I. Pop, C. Nascu, V. Ionescu, E. Indrea, and I. Bratu, Structural and optical properties of PbS thin films obtained by chemical deposition, Thin Solid Films, 307, 1997, 240-244.
[14] N. Choudhary, and B.K. Sharma, Structural characterization of nanocrystalline PbS thin films synthesized by CBD method, Ind. J. Pure Applied phys. 46, 2008, 261-265.
[15] N.I. Fainer, M.L. Kosinova, Yu. M. Rumyantsev, E.G. Salman, F.A. Kuznetsov, Growth of PbS and CdS thin films by low-pressure chemical vapour deposition using dithiocarbamates, Thin Solid Films, 280, 1996, 16-19.
[16] A. Mondal, and N. Mukherjee, Cubic PbS thin films on TCO glass substrate by galvanic technique, Mater. Lett. 60, 2006, 2672-2674.
[17] R. Das and Rajesh Kumar, Preparation of nanocrystalline PbS thin films and effect of Sn doping and annealing on their structural and optical properties, Materials Research Bulletin 47, 2012, 239-246
[18] J. Vaitkus, V. Kazlauskiene, J. Miskinis, and J. Sinius, PbS Thin Film Formation on Terrace-Step Surface by Pulsed Laser Deposition, Mater. Res. Bull. 33, 1998, 711-716.
[19] B. Thangaraju, and P. Kaliannan, Spray pyrolytically deposited PbS thin films, Semicond. Sci. Technol. 15, 2000, 849.
[20] J.I. Pankove, Optical processes in Semiconductors (Prentice-Hall Inc., New Jersey, 1971).
[21] R.R. Philip, and B. Pradeep, Structural analysis and optical and electrical characterization of the ordered defect compound $CuIn_5Se_8$, Semicond. Sci. Technol. 18, 2003, 768.