ISSN 2347-3487

OPTICAL AND STRUCTURAL PROPERTIES OF PbCdS TERNARY THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION

Isaac Nkrumah, Francis K. Ampong, Bright Kwakye-Awuah, Tommy Ive
Department of Physics, Kwame Nkrumah University of Science and Technology,Kumasi, Ghana.
inkrumah.sci@knust.edu.gh
Department of Physics, Kwame Nkrumah University of Science and Technology,Kumasi, Ghana.
fkampong.cos@knust.edu.gh
Department of Physics, Kwame Nkrumah University of Science and Technology,Kumasi, Ghana.
bkwakye-awuah.cos@knust.edu.gh
Department of Microtechnology and Nanoscience, Chalmers University of Technology, Gotheburg,Sweden.
tommy.ive@chalmers.se

ABSTRACT

Thin films of PdCdS ternary compound have been successfully deposited using chemical baths containing cadmium acetate, lead acetate thiourea and ammonia. The films were characterised using a variety of techniques. X-ray diffraction analysis revealed that a number of prominent high intensity diffraction peaks originating from reflections of the tetragonal lead sulphide structure. Several smaller low intensity peaks related to reflections of the hexagonal structure of cadmium sulphide, were also observed. Scanning electron microscopy showed a compact layer with a surface composed of plate-like shaped nanocrystals of different dimensions with well defined boundaries. Energy dispersive X-ray spectroscopy confirmed the presence of lead cadmium and sulphide. The band gap determined from optical absorption spectroscopy was found to be 1.9 eV.

Indexing terms/Keywords

PbCdS; Chemical Bath Technique; EDAX; XRD and Band gap

Academic Discipline And Sub-Disciplines

Physics

SUBJECT CLASSIFICATION

Solid State Physics; Thin films

TYPE (METHOD/APPROACH)

Research and Experimental

Council for Innovative Research
Peer Review Research Publishing System
Journal: JOURNAL OF ADVANCES IN PHYSICS
Vol. 11, No. 1
www.cirjap.com, japeditor@gmail.com

ISSN 2347-3487

INTRODUCTION

The fabrication of binary and ternary semiconductor materials in varying sizes and shapes by means of chemical bath deposition (CBD) is currently one of the fastest growing areas of materials' research since this deposition method is straightforward, inexpensive and yields high quality materials that are interesting for applications in various optical and electronic devices [1]. Examples of semiconductor materials that have received much attention and that can be deposited by CBD are cadmium sulphide (CdS) and lead sulphide (PbS). These two semiconductor compounds are highly sensitive to light in the visible spectrum which have resulted in practical photovoltaic and luminescent applications based on both CdS and PbS. The study of the photoelectrochemical properties of thin films of CdS and PbS and their related compounds is therefore of significant technical and scientific importance [2].

CdS has a direct band gap of 2.42 eV, which falls in the visible spectrum at room temperature [3]. PbS with a narrow direct band gap of 0.41 eV at 300 K, is one of the most studied material among the group IV–VI semiconductor materials because of its potential applications in nonlinear optical devices [4]. It has also been widely used in many other fields such as Pb^{2+} ion exchange sensors, photography and solar absorbers [5]. PbS exhibits strong quantum size effects below excitonic Bohr radius of 18 nm and hence the energy band gap of its nanocrystals can be tuned to anywhere between 0.41 eV (bulk) to 4.00 eV [6]. In solar energy research, PbS thin films have been investigated for photothermal conversion applications, either independently on metallic substrates or in multilayer stacks of PbS-CdS-PbS, $(PbS)_{1-x}(CdS)_x$ composites [2]. PbS has also been recommended as an earth abundant sustainable material for affordable photovoltaic devices [7] .

Mixed thin film structures of PbS and CdS ($Pb_{1-x}Cd_xS$) have generated significant interest because they offer the advantage of tunable optical and opto-electronic properties of PbS, viz., its band gap, electrical conductivity, and structural properties [8, 9, 10]. Using $Pb_xCd_{1-x}S$, the near-infrared (NIR) component of solar spectrum can be utilized in energy harvesting.

CdS normally exists in a hexagonal (greenockite) or cubic (hawleyite) forms. At high pressures, CdS transforms to a NaCl (halite) structure [11]. PbS has a face centered cubic crystal structure [6]. There is a partial crystalline compatibility between CdS and PbS since both materials can exhibit cubic structures based on an fcc arrangement of atoms with similar lattice constants. This allows effective epitaxial growth on one common crystal surface.

Depositions of ternary $Cd_{1-x}Pb_xS$ thin films have been demonstrated by a variety of relatively simple and straight forward techniques, including chemical bath deposition (CBD) [12]. successive ionic layer adsorption and reaction [13], and sol–gel methods [14]. The motivation for this research is to develop cheap reproducible and relatively simple routes for large scale fabrication where low capital cost is important for successful commercialization of potential applications such as thin film photovoltaic technologies [15]. A method which may meet the above criteria is CBD [16, 17]. Metal chalcogenide thin films preparations by chemical deposition methods are currently attracting considerable attention as it is relatively inexpensive, simple and convenient for large area deposition. A variety of substrates such as insulators, semiconductors or metals can be used since these are low temperature processes which avoid the oxidation and corrosion of the substrates [18]. Properties such as film thickness, nanoparticle size and band gap can be controlled by varying the CBD growth parameters that include bath temperature, deposition time, concentration of reactants and bath pH

In this work, thin films of PbCdS have been deposited using CBD. The structure, morphology, composition and optical band gap of these thin films have been investigated.

MATERIALS AND METHODS

Substrate preparation

Silica glass slides were used as substrates for the deposition. The glass slides were degreased in nitric acid and subsequently cleaned in ethanol for about 30 minutes, then ultrasonically cleaned with distilled water and dried under ambient conditions before being used for the deposition.

Deposition of the thin films

The chemicals used were lead acetate dehydrate, $(Pb(CH_3COO)_2{\bullet}3H_2O)$, as the source of lead ions, cadmium acetate as the source of cadmium ions and thiourea $(CS(NH_2)_3)$ which provided sulphur ions. Ammonia (NH_3) was used as a complexing agent and to maintain the alkalinity of the chemical bath. In a typical experiment, 30 ml of 0.1 M lead acetate was poured into a beaker and the pH adjusted to 10.5 by adding a desired amount of ammonia. The beaker was then placed in water bath kept at a temperature of 40 ^oC. 30 ml each of 0.1 M thiourea and 0.1 M cadmium acetate were added to the solution which was continuously stirred using a magnetic stirrer. The pre-treated silica glass substrates were immersed vertically into the chemical bath and the temperature was raised to 70 ^oC for deposition. After two hours the glass slides were removed from the solution, rinsed ultrasonically with distilled water and dried under ambient conditions before film characterization. The deposited thin films appeared uniform, homogeneous, and well adherent to the naked eye.

ISSN 2347-3487

Characterization of the thin film

The crystallographic structure of the thin films were analyzed with an X'Pert PRO MRD four circle triple-axis diffractometer equipped with a $Cu_{k\alpha}$ source in the focus of a Ge(220) hybrid monochromater source for diffraction angles between 5 and 80 ^{0}. The elemental composition and surface morphology of the samples were determined using energy dispersive X-ray analysis (EDX) attached to a Ultra 55 FEG scanning electron microscope (SEM) operating with an accelerating voltage of 20 kV. Optical properties were measured at room temperature by using a Shimadzu UV/Vis mini-1240 Spectrophotometer within the wavelength range of 200 – 1100 nm.

RESULTS AND DISCUSSION

X-ray diffraction analysis

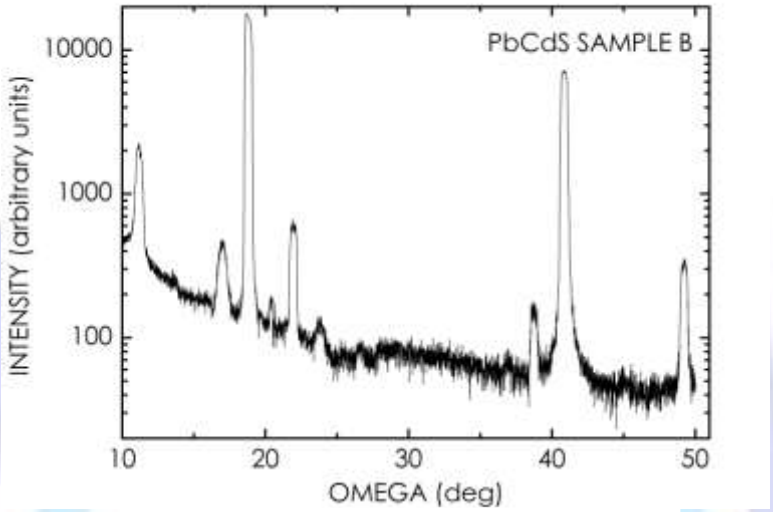

Figure 1: X-ray diffraction spectrum of the as-deposited PbCdS thin film

The x-ray diffraction spectrum of the PbCdS thin film is shown in figure 1. The peaks at 20.64, 41.58 and 48.65 ° originate from the (110), (113) and (004) reflections of the tetragonal lead sulphide (β-PbS_2) [ICDD 00-020-0596]. The smaller observed peaks, at 24.49, 26.58 and 28.40 °, are related to the (100), (002) and (101) reflections of the hexagonal structure of CdS [JCPDS 00-001-0780].

Elemental analysis and morphological studies

EDX analysis and a SEM micrograph of the PbCdS thin film are shown in figures 2 and 3.

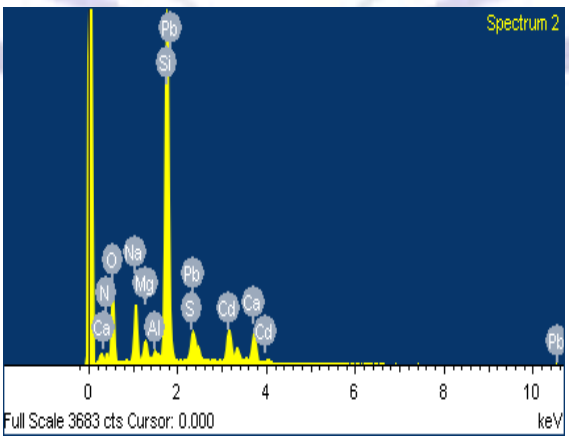

Figure 2: EDX spectrum of PbCdS thin film

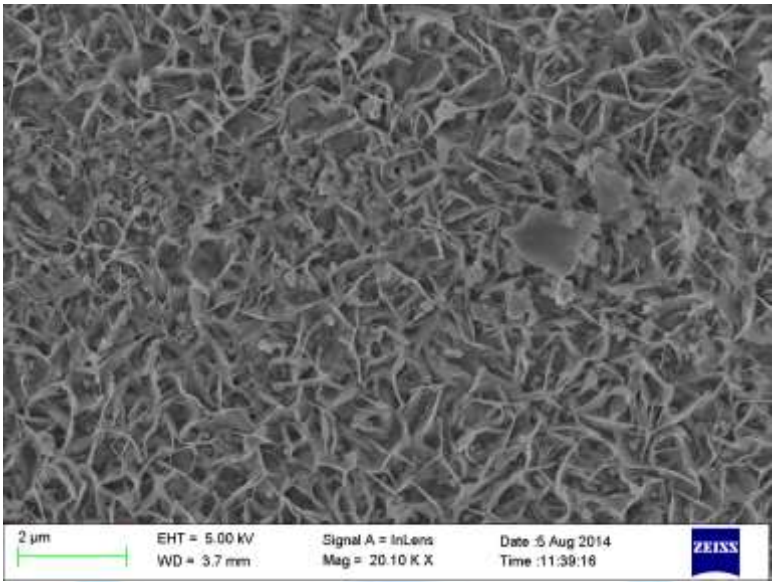

Figure 3a: SEM micrographs of the as-deposited PbCdS

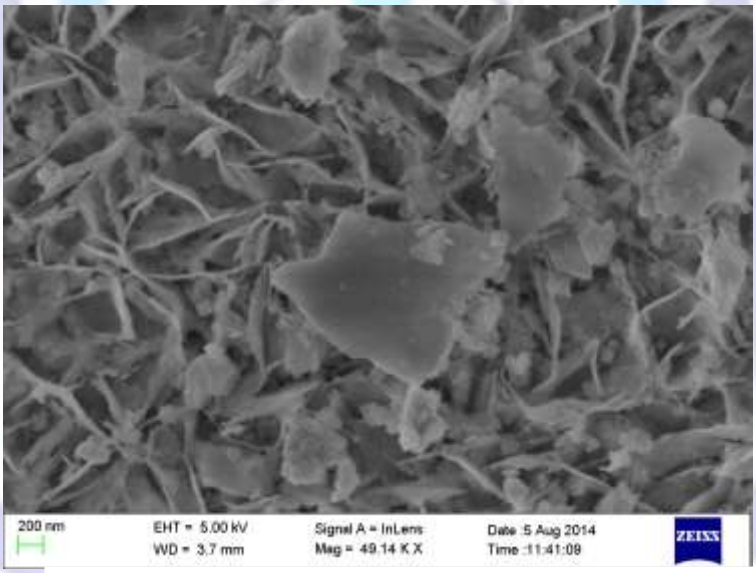

Figure 3b: SEM micrographs of the PbCdS thin film

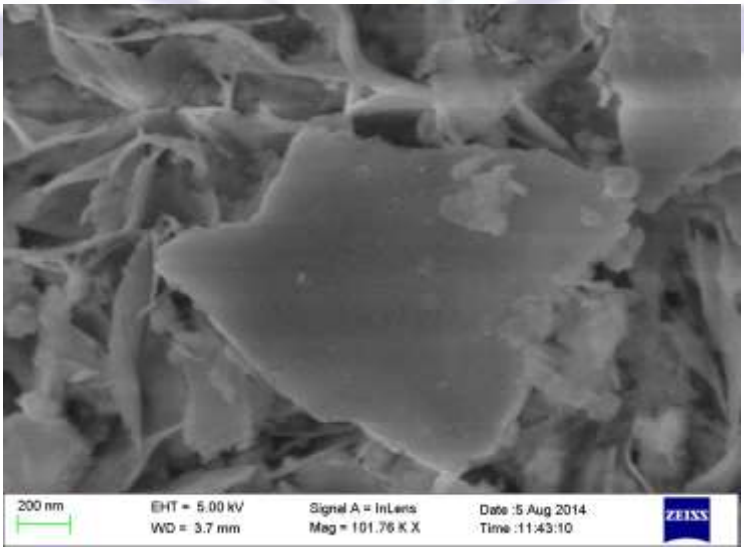

Figure 3c: SEM micrographs of PbCdS thin film

ISSN 2347-3487

Figures 3a, 3b and 3c show the SEM micrographs of the as-deposited PbCdS thin film taken at different magnifications. The micrographs show that the surface is composed of plate-like shaped nanocrystals of different dimensions with well defined edges, uniformly distributed over a smooth homogenous background without visible defects such as, cracks, peeling or pinholes.

Determination of the Optical Band gap

The energy band gap and transition type was determined from mathematical treatment of data obtained from measuring the optical absorbance versus the wavelength using the Stern (1963) relationship of near-edge absorption which is given as [19].

$$A = \frac{\left[K(h\nu - E_g)\right]^{\frac{n}{2}}}{h\nu}$$

where ν is the frequency, h is the Planck's constant, K is a constant while n carries the value of either 1 for direct transition or 4 for indirect transition. PbS and CdS are both direct band gap materials. Thus, we assume that their mixed compositions would also have a direct band gap and hence, n = 1. Figure 4 shows $(Ah\nu)^2$ as a function of $h\nu$. The energy band gap is obtained by fitting a line to the linear portion of the graph and extrapolating the fitted line to the point where it intersects the $h\nu$ axis as shown in Figure 4. The linear nature of the graph at high $h\nu$ indicates the presence of a direct transition.

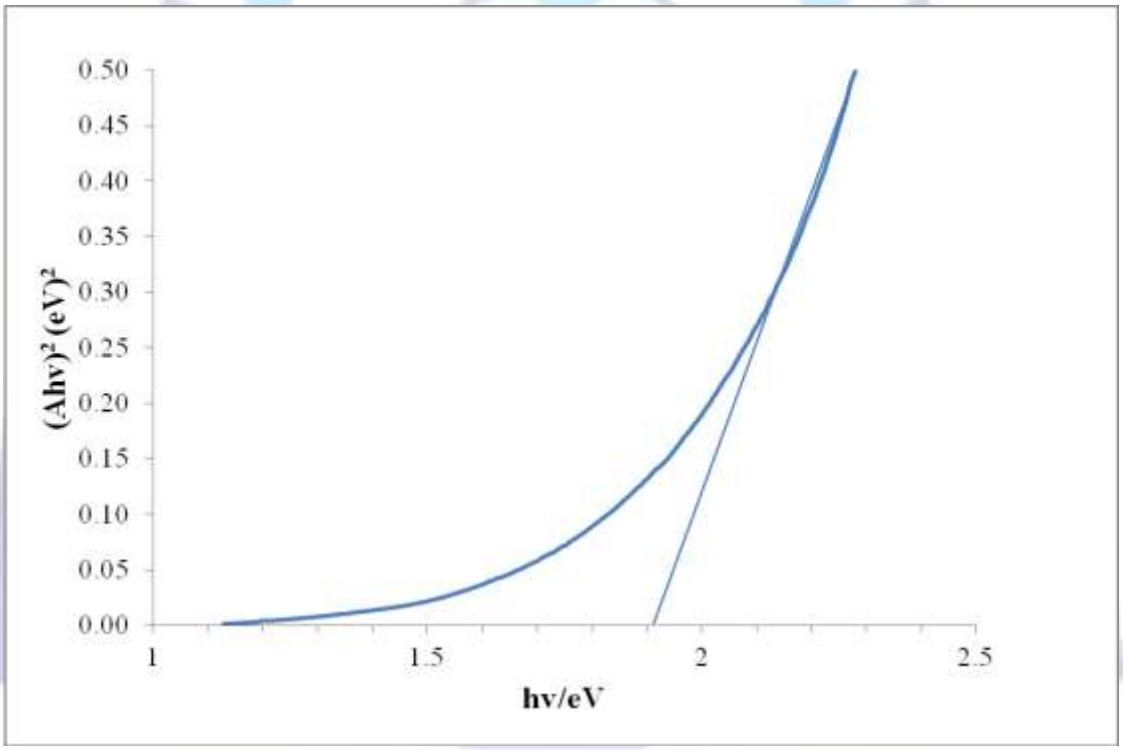

Figure 4: $(Ah\nu)^2$ plotted as a function of ($h\nu$) based on measurement data from the PbCdS thin film.

From Figure 4, the band gap of PbCdS thin film is found to be 1.9 eV, which is situated between the band gaps of PbS and CdS.

CONCLUSION

Well adherent, compact and homogenous thin films of PbCdS were successfully deposited on a silica glass substrate by the CBD technique. X-ray diffraction analysis revealed prominent diffraction peaks originating from the (110), (113) and (004) reflections of the tetragonal lead sulphide (β-PbS_2). Several smaller low-intensity diffraction peaks, related to the (100), (002) and (101) reflections of the hexagonal structure of CdS were also observed. The EDX analysis is consistent with the formation of ternary PbCdS material on the silica glass slide substrates. The SEM micrographs show that the surface is composed of plate-like shaped nanocrystals of different dimensions with well defined boundaries, uniformly distributed over a smooth homogenous background without visible defects such as, cracks, peeling or pinholes. The optical band gap of the thin film was found to be 1.9 eV, which is situated between the band gaps of PbS and CdS. In this

compound, the ideal band gap for solar energy conversion can be achieved if the percentages of the components are properly adjusted.

REFERENCES

[1] Barote, M. A. , Yadav, A. A. and Masumdar, E. U. 2001. Effect of deposition parameters on growth and characterization of chemically deposited Cd1-XPbXS thin films, Chalcogenide Letters 8(2), 129 – 138.

[2] Ampong, F. K., Nkrumah, I., Nkum, R. K. and Boakye, F. 2014. Investigating the structure, morphology and optical band gap of cadmium sulphide thin films grown by chemical bath deposition, International Journal of Technical Research and Application 2(6), 91-93.

[3] Choudhury, N. and Sarma, B. K. 2011. Structural analysis of chemically deposited nanocrystalline PbS films, Thin Solid Films 519, 2132-2134.

[4] Qadria, S. B., Singhb, A. and Yousuf, M. 2003. Structural stability of PbS films as a function of temperature, Thin Solid Films 431-432, 506-510.

[5] Hone, F. G., Ampong, F. K., Abza, T., Nkrumah, I., Nkum, R. K. and Boakye, F. 2014. Investigating the effect of deposition time on the morphology, structure and optical band gap of PbS thin films synthesisized by CBD technique, Elixir Thin Film Tech.76, 28432-28436.

[6] Deshmukh, L. P. and More, B. M. 1994. Preparation and properties of (CdS) x -(PbS)1 −x thin-film composites. Bulletin of Materials Science 17(5), 455-463.

[7] Wadia, C., Alivisatos, A. P. and Kammen, D.M. 2009. Materials availability expands the opportunity for large-Scale photovoltaics deployment, Environ. Sci. Technol. 43(6), 2072-2077.

[8] Thangavel, S., Ganesan, S., Chandramohan, S., Sudhagar, P., Soo, Y., Chang-Hee, H. 2010. Band gap engineering in PbS nanostructured thin films from near-infrared down to visible range by in situ Cd-doping, Journal of Alloys and Compounds 495, 234-237.

[9] Modaffer, A., Mousa, A. M. and Ponpon, J. P. 2009. Optical and optoelectronic properties of PbCdS ternary thin Films deposited by CBD, J. Semiconductor Tech. and Science 9(2), 1-6.

[10] Deshmukh, L. P., More, B. M., Rotti, C.B. and Shahani, G. S. 1996. Polycrystalline n-PbxCd1-xS mixed electrodes for photoelectrochemical (PEC) solar cell. Mat. Chem. & Phys. 45, 145-149.

[11] Ramasamy, K., Malik, M. A., Helliwell, M., Raftery, J. and O'Brien, P. 2011. Thio- and Dithio-Biuret Precursors for Zinc Sulfide, Cadmium Sulfide,and Zinc Cadmium Sulphide Thin Films, Chemical. Mater. 23, 1471–1481.

[12] Gadave, K.M., Jodgudri, S.A. and Lokhande, C.D. 1994. Chemical bath deposition of PbS from acidic bath, Thin Solid Films 245, 7-9.

[13] Puiso, J., Lindroos, S., Tamulevicius, S., Leskela, M. and Snitka, V. 2003. Growth of ultra thin PbS thin films From SILAR technique, Thin Solid Films 428, 223-226.

[14] Ray, S.C. , Karanjai, M.K. and Dashupta, D., 1998. Deposition and characterisation of Znx Cd1-x S thin films deposited by dip technique, Thin Solid Films 322, 117-122.

[15] Boyle, D. S., Robbe, O., Halliday, D. P., Heinrich, M. R., Bayer, A., O'Brien, P., Otway, D. J. and Potter, M .D.G. 2000. A novel method for the synthesis of the ternary thin film semiconductor cadmium zinc sulphide from acidic chemical baths, J. Mater. Chem. 10, 2439 – 2441.

[16] Lincot, D, Froment, M. and Cachet, H. 1999. Chemical deposition of chalcogenide thin films from solution, Advances in Electrochemical Science and Engineering 6, 165-235.

[17] Froment, M. and Lincot, D. 1995. Phase formation processes in solution at the atomic level: metal chalcogenide semiconductors. Electrochimica Acta 40, 1293-1303.

[18] Mane, R.S. and Lokhande, C.D. 2000. Chemical deposition for metal chalcogenide thin films, Materials Chemistry and Physics 65,1-31.

[19] Anuar, K., Tan, W. T., Jelas, Md., Ho, S. M. and Gwee, S. Y. 2010. Effects of Deposition Period on the Properties of FeS2 Thin Films by Chemical Bath Deposition Method, Thammasat Int. J. Sc. Tech.15(2), 64-69.