Knowledge of Research
Section A : Physical Science

DOI:10.7598/kor2015.141
ISSN: 2394-4234

ANGEL SUSAN CHERIAN*,
J. V. EMIL, M. C. THOMSON,
C. V. RASHIDA and S. MALU

Department of Physics,
Marthoma College,
Thiruvalla, Kerala, India

angelsusanc@yahoo.com

Received 18 March 2015
Accepted 28 March 2015

PbS Thin Films Using Cost Effective Chemical Method and Enhancement in its Conductance†

Abstract: In the present work the PbS thin films were coated on a glass substrate using chemical bath deposition (CBD) technique which is a scalable technique that can be employed for large area devices. PbS is a direct narrow gap semiconductor which has also been used as photo resistance, diode lasers, humidity and temperature sensors, decorative coatings and solar control coatings. At room temperature, its energy band gap is approximately 0.37–0.4 eV. The reactive substances used to obtained the PbS layers were $(Pb(NO_3)_2)$, (NaOH), $(SC(NH_2)_2)$ and H_2O for different concentrations at constant room temperature. The structure was determined by X-ray diffraction studies. The thickness of these films was controlled to around 200 nm on changing the concentrations of lead nitrate and thiourea of the reaction solution. When the concentration of lead nitrate is varied from 0.15 o 0.19 M, the resistance decreased considerably which can even be measurable using multimeter. This shows that the films are not resistive. The film was found to be of *p*-type by hot probe method.

Keywords: Thin film, Semiconductor, PbS, Chemical bath deposition

Introduction

Thin film technology is pervasive in many applications, including microelectronics, optics, magnetic, hard resistant coating, micro-mechanics *etc*. Progress in each of these areas depends upon the ability to selectively and controllably deposit thin films – thickness ranging from tens of angstroms to micrometers – with specified physical properties. With rapid technology advances in the preparation of films with controlled reproducible and well defined structures, thin film are expected to play an important role in the studies of a variety of solid state phenomenon of basic and practical interest[1]. The properties of a large variety of new and exotic materials obtained by thin film techniques will undoubtedly draw considerable attention in future.

The present work deals with the preparation of lead sulphide (PbS) thin film on a glass substrate using the chemical bath deposition (CBD) technique. CBD is a chemical process in which a liquid solution containing precursors is prepared and a substrate is exposed the solution. Over the course of seconds or minutes (depending on the reagents and their concentrations), the precursors react to produce a solid material that grows, atom by atom, on all the surfaces exposed to the bath. This technique also offers the advantage of being able to deposit films on different kinds, shapes and sizes of substrates[2]. This method of deposition, compared to other thin film deposition methods, is often

†Presented to the National Seminar on Optics and Optoelectronic Devices at Catholicate College, Kerala, India

noted for its low cost and for the simple apparatus required to perform the deposition. The CBD method is one of the cheapest methods to deposit thin films and nanomaterials, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition. This method is based on successive adsorption and reaction of species on the substrate surface from aqueous solutions. By CBD method pinhole-free thin films have been grown easily since the basic building blocks are ions instead of atoms[3].

PbS is an important direct narrow gap semiconductor material with an approximate energy band gap of 0.4 eV at 300 K[4]. This makes PbS very suitable for infrared detection application[5]. This material has also been used in many fields such as photography[6], Pb^{2+} ion-selective sensors[7] and solar absorption[8]. In addition, PbS has been utilized as photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings[9-10].Many researchers have reported properties of chemically deposited PbS thin films[10–14].

Experimental

The reactive substances used to obtain the PbS layers were ($Pb(NO_3)_2$), (NaOH), ($SC(NH_2)_2$) and H_2O for different concentrations at constant room temperature. The concentration of lead nitrate was kept fixed at 0.175 M, thiourea at 0.1 M and NaOH at 0.55 M. All of these were measured in measuring jars and individually made up to 10 mL in the corresponding measuring jars in the case of lead nitrate and thiourea and then added to 30 mL of NaOH to make the final solution to 50 mL. But a characteristic blackish solution of PbS was not formed. White suspension was formed which may be due to the presence of lead oxide or lead nitrate. Now the order of mixing was changed. First the complexing agent, NaOH was added to lead nitrate and after some time thiourea was added. First a white precipated solution was formed which turned into a blackish colour after some time which indicates the presence of PbS. NaOH fixes the alkalinity of lead nitrate solution. The reaction of lead nitrate and NaOH resulted in the production of $HPbO_2^-$ ions. Then thiourea was added which resulted in the formation of PbS. Water was added only after mixing the reactants. Thus it became clear that order of precursor mixing is very important in the formation of good PbS thin films. The substrate used is a rectangular piece of glass of dimensions 4cm × 1cm × 0.1cm. It was cleaned first by dipping in chromic acid and washed in pure water and rubbed thoroughly with cotton waste. It was then cleaned using distilled water and then dried. This glass substrate was dipped in the above prepared solution and it was examined that an adherent film was seen to be deposited on the substrate only after 50-60 minutes without any heat treatment. Then the concentration of lead nitrate was changed from 0.15 M to 0.19 M and examined the properties of the PbS films.

Results and Discussion

To study the role of lead nitrate on PbS thin films, the concentration of NaOH was fixed at 0.55 M and that of at thiourea 0.1 M and the concentration of lead nitrate was varied from 0.15 to 0.19 M (Table 1). Structural characterisation were done using x ray diffraction technique and electrical properties using multimeter.

Table 1. Concentration of thiourea and lead nitrate solutions used in different samples

S.No	Molarity of NaOH, M	Molarity of Thiourea, M	Molarity of Lead nitrate M
A	0.55	0.1	0.15
B	0.55	0.1	0.16
C	0.55	0.1	0.17
D	0.55	0.1	0.18
E	0.55	0.1	0.19

Figure 1 and Figure 2 indicates the XRD pattern of samples A and E. The (h k l) values of the observed peaks are compared with the works of Seghaier *et al.*[15]. This proved From XRD plots, we can infer that crystallinity decreased when $Pb(NO_3)_2$ concentration increased. While the $Pb(NO_3)_2$ exceeds 0.17M, the thickness of PbS layer decreases. The result seems to confirm that the nucleation rate is mainly regulated by the concentration of Pb^{2+} ions in solution, which results in the development of PbS complex[15]. For samples with high $Pb(NO_3)_2$ molarity, PbS films formed are removed from its substrate then, so the solution becomes depleted of ions, resulting in a lower rate of deposition and less crystalline PbS thin films.

Sheet resistance of PbS thin films was measured using two probe multimeter and obtained result is given in Table 2. From hot probe method it was understood that the films were *p*-type.

Table 2. Sheet resistance of PbS thin films

Sample	A	B	C	D	E
Resistance(M**Ω**)	0.46	0.41	0.38	0.32	0.2

From this table, we can understand that as the concentration of lead nitrate was increased, the sheet resistance decreased and this may be due to the slight decrease in PbS layer thickness.

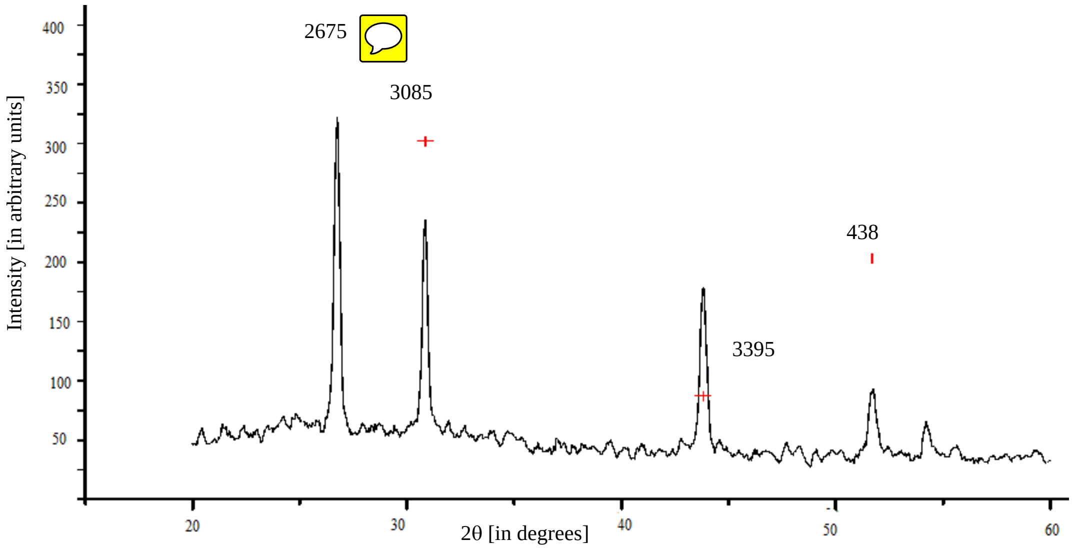

Figure 1. XRD pattern of samples A

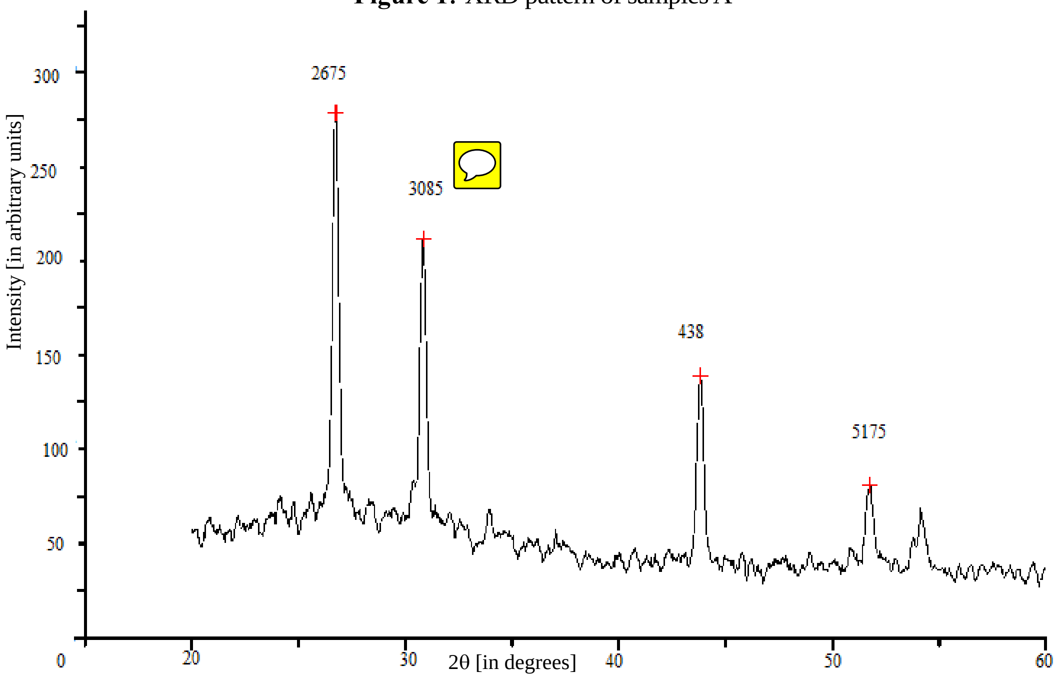

Figure 2. XRD pattern of samples E

Conclusion

It was found that CBD is a cost effective method for the formation of thin films. Our method does not involve heating or stirring. The order of adding the reactants of the precursor solution is important to deposit PbS layers on substrate. The films formed are conductive and crystalline in nature. The molarity of lead nitrate also play a great role in controlling the resistance of films.

Acknowledgement

The first author would like to acknowledge the faculty, non-teaching staff and M.Sc. Students (2012-14) of department of physics, Marthoma College, Tiruvalla, Kerala, India.

References

1. Goswami, "Thin film fundamentals", New Age International, New Delhi, 1996; ISBN:81-224-0858-3
2. Eya D O, *Pacific J Sci Technol.*, 2006, **7(1)**, 114.
3. Ubale A U, Junghare A R, Wadibhasme N A, Daryapurkar A S, Mankar R B and Sangawar V S, *Turk J Phys*., 2007, **31**, 279-286.
4. Machol J L, Wise F W, Patel R C and Tanner D B, *Phys Rev B*, 1993, **48(4),** 2819-2822.
5. Gadenne P, Yagil Y and Deutscher G, *J Appl Phys*., 1989, **66,** 3019.
6. Nair P K, Gomezdaza O and Nair M T S, *Adv Mater Opt Electron*., 1992, **1**, 139-145.
7. Hirata H and Higashiyama K, *Bull Chem Soc Jpn*., 1971, **44(9)**, 2420-2423; DOI:10.1246/bcsj.44.2420
8. Chaudhuri T K and Chatterjes S, *Proceed Int Conference Thermoelectronics*, 1992, **11**, 40-46.
9. Nair P K, Garcia V M, Hernandez A B and Nair M T S, *J Phys D: Appl Phys*., 1991, **24(8),** 1466–1472; DOI:10.1088/0022-3727/24/8/036
10. Ileana Pop, Cristina Nascu, Violeta Ionescu, Indrea E and Bratu I, *Thin Solid Films,* 1997, **307(1-2),** 240–244; DOI:10.1016/S0040-6090(97)00304-0
11. Larramendi E M, Calzadilla O, Gonzalez-Arias A, Hernandez E and Ruiz-Garcia J, *Thin Solid Films*, 2001, **389(1-2),** 301-306; DOI:10.1016/S0040-6090(01)00815-X
12. Pentia E, Pintilie L, Tivarus C, Pintilie I and Botila T, *Mater Sci Eng B*, 2001, **80(1-3)**, 23-26; DOI:10.1016/S0921-5107(00)00578-X
13. Rakesh K Joshi, Aloke Kanjilal and Sehgal H K, *Appl Surf Sci*., 2004, **221(1-4)**, 43-47; DOI:10.1016/S0169-4332(03)00955-3
14. Valenzuela-Jauregui J J, Ramirez-Bon R, Mendoza-Galvan A and Sotelo-Lerma M, *Thin Solid Films*, 2003, **441**, 104–110; DOI:10.1016/S0040-6090(03)00908-8
15. Seghaier S, Kamoun N, Brini R and Amara A B, *Mater Chem Phy*., 2006, **97**, 71–80; DOI:10.1016/j.matchemphys.2005.07.061