CHEMICALLY PREPARED NANOCRYSTALLINE PbS THIN FILMS

E. Pentia, L. Pintilie, I. Matei, T. Botila, E. Ozbay[a]

National Institute of Materials Physics, Bucharest, Magurele P.O.Box MG-7, R-76900, Romania
[a]Department of Physics, Bilkent University, Ankara 06533, Turkey

PbS nanocrystalline thin films were prepared by Chemical Bath Deposition (CBD) technique. A comparative study between "standard" and "nanocrystalline" PbS thin films was performed. We denoted "standard" the PbS film with a good photosensitivity for to use as IR detector. This film was deposited after 1 hour from chemical bath containing reducing agent and Bi ions as doping element. The "nanocrystalline" film was obtained at shorter reaction time (after 17 minutes) from reducing bath without doping element. The other parameters: concentration of the reactants, pH, temperature were kept constant for the all depositions. The morphological properties of the films were determined by SEM analysis. Also, the electrical and photoelectrical behaviors were investigated for the both types of PbS films. The "nanocrystalline" film had a very high electrical resistance (10^{10} -$10^{11} \Omega/$) compared with the "standard" film (10^5-$10^6 \Omega/$). Both types of films proved to be sensitive to the surrounding atmosphere, air or vacuum. Thermally Stimulated Current (TSC) measurement had shown the presence of trap concentration in the both cases, probably due to the large amount of disordered regions.

1. Introduction

A variety of physical properties of nanoparticles semiconductors have been reported in the literature [1-5]. Many authors have predicted for nanoparticle semiconductors enhanced nonliniarities resulting from quantum confinement effects [6-8]. The materials application that has attracted considerable attention relates to nonlinear optics 9,10]. Most studied nanocrystalline semiconductors belong to the II-VI and IV-VI groups as they are relatively easy to synthesize and are generally prepared as particles or in thin film form. In the last years, several methods to synthesize PbS nanoparticles, semiconductor from IV-VI group, were studied such as grown in a glass, glass-ceramic, polymer matrix respectively [11-13]. PbS is a semiconductor with band gap about 0.41 eV at room temperature and 0.29 eV at liquid-N_2 temperature. For PbS, the size effect can be observed for a crystallite as large as 180Å, which contains over 10^5 atoms [4].

Chemical Bath Deposition (CBD) is a very comfortable method for deposition polycrystalline PbS thin films with a good photoconductive properties. By CBD method, the dimensions of the crystallites can be varied controlling deposition parameters: reaction time, temperature, pH, and presence of impurities in the solution. Most of the works on nanosize semiconductor particles reported so far have been restricted to optical absorption. The absorption edge has been found to be blue shifted as the particle size reduced. Only o few studies of electrical and photoelectrical properties of these kind of materials have been presented in the literature.

This article presents some comparative preliminary results between two types of PbS films "standard" and "nanocrystalline", prepared by CBD method. The morphology of the films was investigated by scanning electron microscopy (SEM). Also, we have investigated the electrical and photoelectrical properties of the films.

2. Experimental

Two sets of PbS samples were prepared: "standard" and "nanocrystalline" thin films. The PbS film deposition was performed on glass substrates by CBD method. The substrates were very carefully cleaned using oxidant mixing ($K_2Cr_2O_7$: H_2SO_4; 1:10), HNO_3, 1% EDTA and successive rinsing with bidistilled water. The cleaning state of the substrate surface is very important for the quality of the film formation. The substrates were introduced vertically in the chemical bath.

The deposition bath contained an aqueous solution, consisting of: $Pb(NO_3)_2$ 0.06M, thiourea $SC(NH_2)_2$ 0.24M, NaOH 0.6M and reducing agent (hydroxylamine hydrochloride, $NH_2OH \cdot HCl$ 0.1M). The concentration of the reagents, pH (12.7) and temperature (24^0C) were kept constant for all depositions.

In the alkaline medium, the thiourea decomposed and released S^{2-} ions, which precipitate Pb^{2+} ions from the solution:

$$SC(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \rightarrow H_2O + S^{2-}$$
$$Pb^{2+} + S^{2-} \rightarrow PbS$$
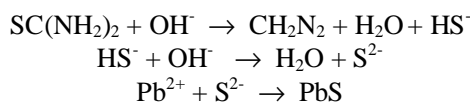
Hydroxylamine hydrochloride seems to accelerate the chemical deposition reaction so that acceleration causes a decrease in the size of the crystallites.

For "standard" film the precipitation took place in the presence of Bi ions ($Bi(NO_3)_2$ $2.06 \cdot 10^{-4}$M). It is known that PbS film with a good photoconductivity had an average grain size of 300nm [14,15]. Optimum proportion between hydroxylamine hydrochloride and Bi as doping element allowed us to obtain quality films with average grain size of 250-300nm. The films prepared by above mentioned procedure had very good photoconductivity and can be used in IR detection.

To impede the growth of crystallites, the "nanocrystalline" film was deposited without doping, at shorter reaction time (17 minutes). Our previous studies shown that a small amount of Bi ions in the deposition bath lead to the enhance of the grain size [16]. This was reason that in case of "nanocrystalline" film preparation we have eliminated the doping element from deposition bath.

For the electrical and photoelectrical measurements gold electrodes in a coplanar configuration, were evaporated in vacuum on the surface of the PbS for both type of films. The distance between electrodes was 6 mm. After that the samples were annealed at 80^0C for several (24-30) hours to improve the sensitivity of the films and stabilize the parameters.

The set-up presented in Fig.1 was used to perform the photoconductive measurements. The radiation source was a SYLVANIA lamp (30 W electrical power). The collimated radiation beam passed through a Carl Zeiss monochromator, with LiF prism, and falls on the surface of the PbS film. For photoconductivity measurements on " standard" PbS films, the incident light was modulated with an ITHACO 383A type mechanical chopper. The measurements were performed at 200Hz. The photosignal was taken from a load resistance (see Fig. 1) and measured with a UNIPAN 233 nanovolmeter. Because of the high dark resistance and a small photosignal the photoconducive measurements on "nanocrystaline" films were performed without light modulation.
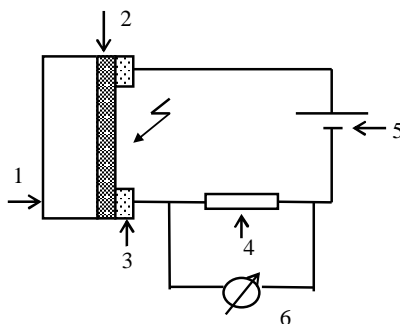

Fig. 1. The experimental setup for the photoconductive measurement. 1) glass substrate; 2) PbS film; 3) gold electrodes; 4) load resistance; 5) current source; 6) amplifier.

For TSC measurements, the samples were irradiated with light (5mW/cm^2 optical power) for 5 minutes at liquid–nitrogen (N$_2$) temperature. During the heating, with constant rate (0.1 K/s), a constant potential (25V) was applied between the coplanar electrodes situated on the PbS film surface. The current was measured with a KEITHLEY 6517 electrometer.

3. Results and discussion

A very adherent film with gray-black color and metallic aspect was obtained in case of the "standard" film. SEM photographs (Fig. 2) of the "standard" PbS film reveal existence of a continuous compact polycrystalline film with grain size around 250-300nm. The thickness of the film is about 300nm and was determined by interpherometric method.
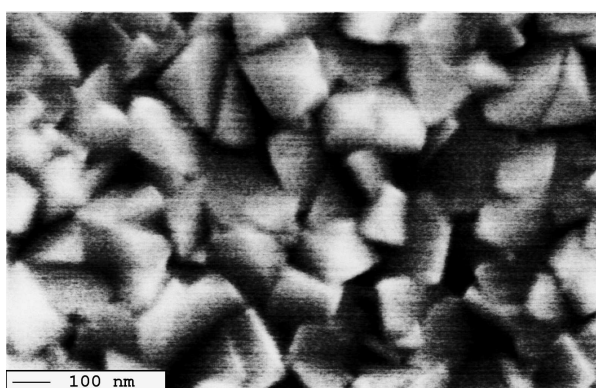

Fig. 2. SEM photograph of "standard" PbS film deposited on glass.

The SEM photo of the "nanocrystallite" film (Fig. 3) showed a continuous layer with grain size around 50nm and less. This film is also very adherent on the glass substrate and had a brown color.
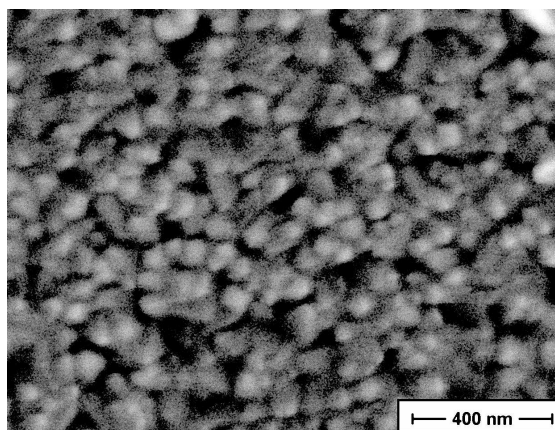

Fig. 3. SEM photograph of PbS "nanocrystalline" film deposited on glass.

The dark resistance of the "nanocrystalline" film had a high value, 10^{10}-$10^{11}\Omega/$, comparing with "standard" films when dark resistance not exceeded 1-2 $10^6\Omega/$.
Correlating these values with SEM photo, we can claim that the high resistance of the "nanocrystalline" film is due to the small crystallite sizes. Change in crystallite size will mainly affect the mobility of the carriers and so change the resistance [17].
Both the "nanocrystalline" and "standard" PbS films presented p-type conductivity, determined by "hot probe" method. Spectral distribution measurements of photoconductive signal revealed a shift of the maximum sensitivity towards shorter wavelenghts for "nanocrystalline" PbS

film. (Fig. 4 b). Thus, "standard" film presented one maximum of sensitivity at 2.55μm and another at 2,2 μm, while "nanocrystalline" films show maximum at 1.8 and 0.8μm (Fig. 4a and b).

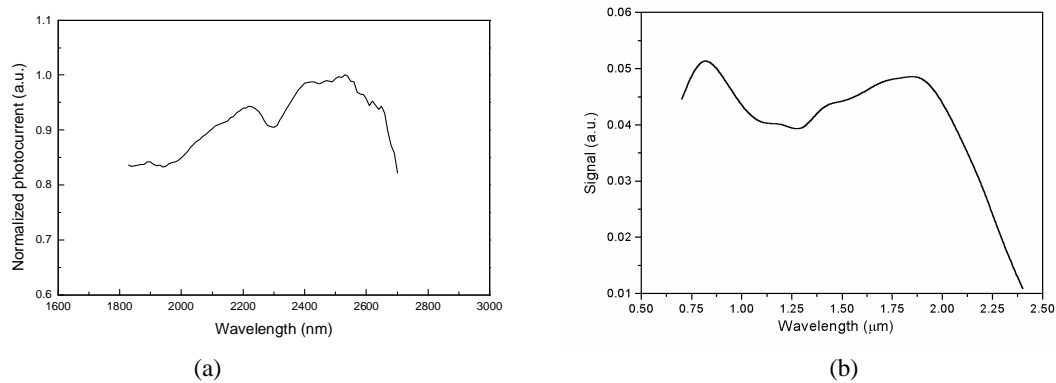(a)   (b)

Fig. 4. Spectral distribution of photoconductive signal normalized to the incident power for PbS films: (a) "standard" film measured in modulated light; (b) "nanocrystalline film measured in permanent light.
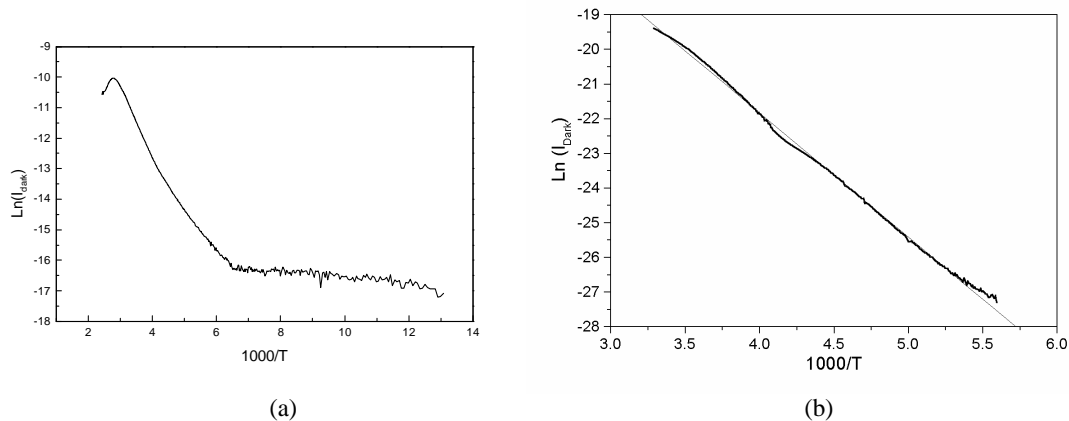

(a)   (b)

Fig. 5. Dark current vs temperature for (a) "standard" and (b) "nanocrystalline" PbS films.

The thermally activation energy E_a for both type of films was determined from the slope of dark current curve vs temperature (Fig. 5 a and b). This energy, for "standard" film, was estimated to be about 0.196 eV and for "nanocrystalline" film 0.3 eV. Considering that E_a represent ½ from band gap energy E_g, it can evaluated that $E_g = 0.4eV$ for "standard" film and $E_g = 0.6$ eV for "nanocrystalline" film.

Thermally Stimulated Current (TSC) is a method used to obtain information about the energy level in the band gap, associated with the various defects in semiconductors. Fig. 6 a and b are presenting the TSC curves for " standard and "nanocrystalline" films. Two levels are observed for "standard" sample. The activation energy of the first level was estimated to be about 0.16 eV and second 0.19 eV using the empirical formula, for activation energy of trapping level, $E_a = nkT_m$ (k is the Boltzmann constant, T_m is the peak temperature and n = 19 is assumed). In the "nanocrystalline" film are observed three peaks in the TSC current but two of them appeared at a higher temperatures. The activation energy estimated for these two levels were 0.36 eV and 0.45 eV. We are noted that the band gap of PbS is 0.41 eV at room temperature. Comparing the second activation energy of trap level (0.45 eV) of "nanocrystalline" film with band gap energy of PbS, it can be supposed that for this film the band gap energy was larger that of "standard" film, in accordance with value obtained from dark current vs temperature measurement.

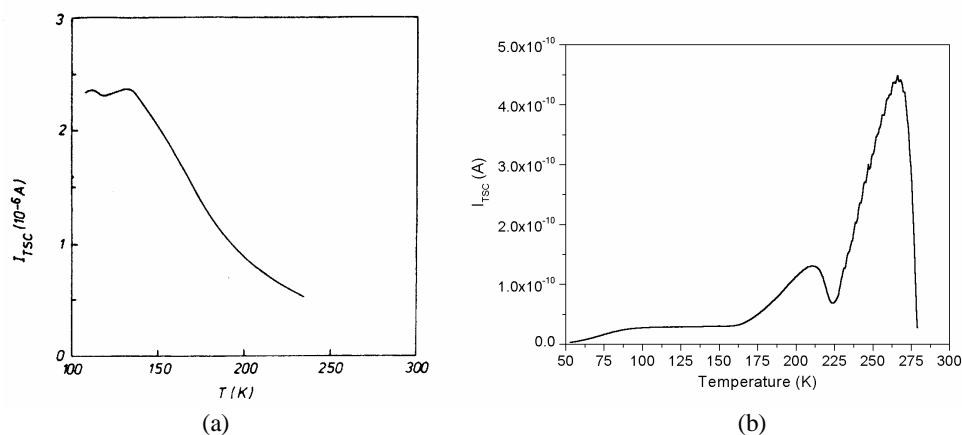(a)   (b)
Fig. 6. TSC curves for a) "standard" PbS film b) nanocrystalline PbS films.

4. Conclusion

Several conclusions can be drawn on the basis of the experimental data. The CBD method can be used for the preparation of nanocrystalline PbS films. Comparative studies on the electrical and photoelectrical properties of "standard" and "nanocrystalline" film have shown important differences between them. Our results suggest that the shift of the maximum of photosensitivity to shorter wavelengths and the larger value of E_g can be ascribed to nanoparticles size effect.

References

[1] A. L. Efros, L. Efros, Fiz. Tekh. Poluprovodn., **16**, 1209 (1982).
[2] M. L. Steigerwald, L. E. Brus, Annu. Rev. Mater. Sci. **19**, 471 (1989).
[3] Y. Wang, N. Harron, W. Mahler, A. Suna, J. Opt. Soc. Am. **B 6**, 808 (1989).
[4] Y. Wang, N. Herron, J. Phys. Chem., **95**, 525 (1991).
[5] D. Chakravorty, A. K. Giri, Chemistry of Advanced Materials, edited by C. N. R. Rao (Blackwell Sci. Publications, Oxford), 217 (1992).
[6] P. H. Roussingnol, D. Ricard, C. H. R. Flytzanis, Appl. Phys. **B51**, 437 (1990).
[7] H. Minti, M. Eyal, R. Reisfeld, G. Berkovic, Chem. Phys. Lett. **183**, 277 (1991).
[8] K. Fukumi, A. Chayahara, K. Kadono, T. Sakaguchi, Y. Horino, M. Miya, J. Hayakawa, M. Satou, Japn. J. Appl. Phys. **30**, L742 (1991).
[9] R. Vogel, P. Hoyer, H. Weller, J. Phys. Chem. **98**, 3184 (1994).
[10] R. Konenkamp, R. Henninger, P. Hoyer, J. Phys. Chem. **97**, 7328 (1993).
[11] M. Mukherjee, A. Datta, D. Chakravorty, Appl. Phys. Lett. **64**, 1159 (1994).
[12] P. Hoyer, R. R. Konenkamp, Appl. Phys. Lett. **66**, 349 (1995).
[13] M. Mukherjee, A. Datta, D. Chakravorty, J. Mater. Res. **12**, 2507 (1997).
[14] G. P. Kothiyal, B. Ghosh, R. Y. Deshpande, J. Phys. *(D)* **13**, 869 (1980).
[15] T. Botila, E. Pentia, M. L. Ciurea, P. Pausescu, C. Sirbu, Proc. Annual Conf.Sem.Proc (Romania) p. 51 (1985).
[16] E. Pentia, Ph. D. Thesis, I.F.A. Bucharest, Romania, 2000.
[17] N. F. Mott, Contemp. Phys, **10**, 125 (1969).