Chalcogenide Letters Vol. 7, No. 1, February 2010, p. 95 - 100

STUDIES OF SOME ELECTRICAL AND PHOTOELECTRICAL PROPERTIES FOR PbS FILM OBTAINED BY SONOCHEMICAL METHODS

V. POPESCU[a*], N. JUMATE[b], G. L. POPESCU[a], M. MOLDOVAN[c], C. PREJMEREAN[c]

[a]*Department of Chemistry, Materials Science and Engineering Faculty, Technical University of Cluj-Napoca, 103-105 Muncii Avenue, 400641 Cluj-Napoca, Romania*
[b]*Department of Materials Science and Technology, Materials Science and Engineering Faculty, Technical University of Cluj-Napoca, 103-105 Muncii Avenue, 400641 Cluj-Napoca, Romania*
[c] *Institute of Research in Chemistry Raluca Ripan, Babeş-Bolyai University Cluj-Napoca, 30 Fantanele street, 500327 Cluj-Napoca, Romania*

The effect of ultrasounds and thermal treatments on the deposition of PbS films on glass substrates and the characteristics of formed films was studied. Ultrasounds increase the reaction rate leading to obtaining thicker films, with smaller electrical resistance. The photosensitivity decreases for the majority of samples obtained from ultrasonic baths, in comparison with those obtained for the control films obtained in the same conditions, without ultrasounds. Thermal treatments at 90 ^{o}C, applied to the films, leads to the increasing of electrical resistance and of photosensitivity respectively. The best results were obtained for the sample obtained by the deposition of two layers for 45 minutes from static baths.

(Received January 8, 2010; accepted January 29, 2010)

Keywords: Lead sulphide, Thin films, Chemical bath deposition, Sonochemical, Thermal treatment

1. Introduction

Photoconducting or thermo-reflecting PbS films could be obtained by Chemical Bath Deposition (CBD) [1-19] from alkaline baths containing Pb (II) salts and thiourea (TU) [2,3,6-9,12-17]. Generally, baths without agitation are used.

The reaction between Pb (II) and TU leading to the formation of PbS is an autocatalytic reaction [12-15], being characterized by an induction period.

In our paper the variation of electrical and photoelectrical properties of PbS films as a function of the deposition condition (static or ultrasonic (US) baths) was studied.

As an element of novelty is the obtaining of PbS films by CBD from ultrasonic baths, because there are no data in literature related to the obtaining of PbS films by sonochemical methods; although sonochemical methods were studied for the obtaining of lead sulphide nanoparticles [20-32] or microtubes [33].

* Corresponding author: violeta.popescu@chem.utcluj.ro

2. Experimental details

The PbS films were deposited on glass slides with dimensions of 75x25x1 mm, from baths containing $1.4 \cdot 10^{-2}$ M lead acetate, $5.7 \cdot 10^{-2}$ M thiourea and 0.158 M NaOH. The reagents were of analytical grade. The films consist in one or two PbS layers deposited at room temperature, at different deposition time.

After preparation, silver paste-based contacts were deposited for determining the electrical square resistance and the photo-sensitivities [15]. Later the films were subjected to a thermal treatment for 120 minutes, at 90^{o}C, in an electrical oven and then the properties were again measured.

The square (sheet) electrical resistance (R_{square}) was measured with a multimeter. This is a frequently used parameter and unanimously recognized by field specialists [34-37].

It is defined by the expression:

$$R_{sq} = \rho/h \qquad [k\Omega/square] \qquad (1)$$

where: ρ is the resistivity and h is the thickness of the film.

It could be observed that square resistance depends only on those two parameters. R_{square} vary inversely proportional to the thickness of the film.

The photosensitivity S has been determined at 25 ^{o}C.

$$S = \Delta R/R_{squareI.} = (R_{squareD} - R_{squareI.})/ R_{squareI} \qquad (2)$$

where: $R_{squareD}$ is the sheet electrical resistance in the dark; $R_{squareI}$ - the sheet electrical resistance measured under illumination with a tungsten lamp, under 100 W/m^2, as was described in a previous work [35].

2.1 The obtaining of the films in ultrasonic baths

Microscope glass slides degreased and rigorously cleaned were immersed in baths containing 50 ml of solution, with the concentration mentioned above, at room temperature.

The reaction vessels (Berzelius flasks) have been placed in an ultrasonic bath (Elma Sonic S 30 H, at a frequency of 37 kHz), and the deposition of the films took places under sonochemical agitation.

Table 1 presents the conditions for obtaining the samples selected for the study. The deposition time includes the induction period. The “control” samples were deposited in the absence of ultrasounds.

The induction period is influenced by ultrasounds. Ultrasounds determined an increase in the induction period from 12 minutes corresponding to static baths to 15 minutes for ultrasonic ones. That could be explained by the detachment of some of the nucleation centres from the surface of the substrate, favoured by ultrasonic agitation.

Sonochemical deposition of the film favoured the formation of uniform films even for short deposition time (24 minutes). By increasing deposition time, thicker uniform films were obtained both from static and ultrasonic baths.

Table 1. The conditions for obtaining of PbS films from static and ultrasonic baths

Sample no.	Solution	Layer number x deposition time [min]	Observations
1	Static bath	1x24	Shiny not uniform layer
2	Ultrasonic bath	1x24	Shiny uniform layer
3	Static bath	1x45	Shiny mirror-like uniform layer
4	Ultrasonic bath	1x45	Mirror-like uniform layer
5	Static bath	2x45	Shiny uniform layer
6	Ultrasonic bath	2x45	Mirror-like uniform layer

3. Results and discussion

3.1. Electrical and photoelectrical properties of PbS film

3.1.1. Electrical resistance

The electrical resistance of "as prepared" films were measured under darkness, after drying.

In Figure 1, the variation of electrical resistance as a function of the deposition time for PbS films obtained by chemical and sonochemical methods are presented.

For a total deposition time of 24 minutes, the ultrasounds determined a decrease in the electrical square resistance with 146 % in comparison with the "control" sample. This takes places due to the increasing of the reaction rate, with the increasing of the thickness of the film respectively.

The increase of deposition time to 45 minutes determined a decrease of electrical resistance both for films obtained in static and ultrasonic bath, due to the increase of film thickness.

The deposition of two layers of PbS determined the follow-up decrease of electrical resistance. The decrease of electrical resistance with 77 % for the film obtained in static bath takes places due to the autocatalytic effect of the first deposited layer. First, PbS particles deposited on the substrate have a catalytically role in the process of film formation. In the case of films obtained from ultrasonic baths the decrease of electrical resistance was 61 %. That could be due to the increase of the reaction rate that could be explained by the permanent refreshment of the solution on the surface of the PbS film as an effect of ultrasonic agitation.

In the case of the obtaining of PbS nanocrystals by chemical deposition, ultrasound irradiation induces the formation of particles of smaller size and higher surface area than those reported by other methods [22,38]. The effect arises from acoustic cavitation, i.e. the formation, growth and implosive collapse of baubles in a liquid. In our case (film formation) the mechanism of crystal growth was different since the formed PbS was attached to the substrate. Other determination has to be done in order to study the influence of the ultrasounds on the formation and the properties of the films.

3.1.2. The photosensitivity

In Figure 2, the variation of the photosensitivity of the films as a function of the deposition time and ultrasounds is presented. The photosensitivity of PbS films is influenced by many factors, such as: the film thickness, the electrical resistance, the structure, the morphology and the presence of impurities at the intergranular boundary or other characteristics [15, 39]. The films with high photosensitivity are thinner than those with smaller photosensitivity. It was also observed that the films obtained by the deposition of two layers have higher photosensitivity than the ones formed from a single layer.

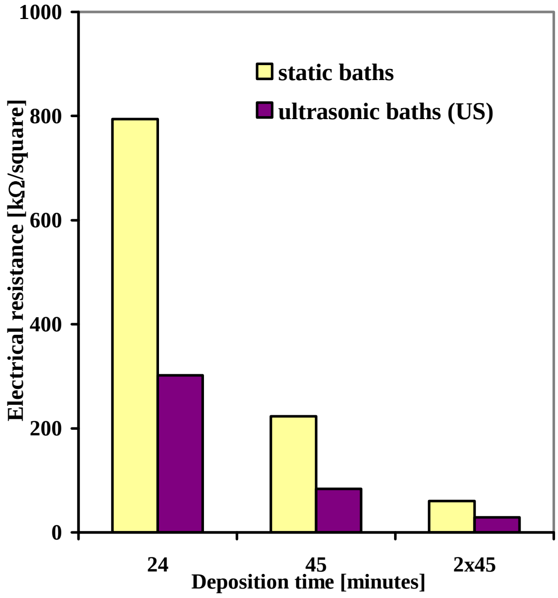

Fig. 1. The variation of dark electrical resistance as a function of the deposition time

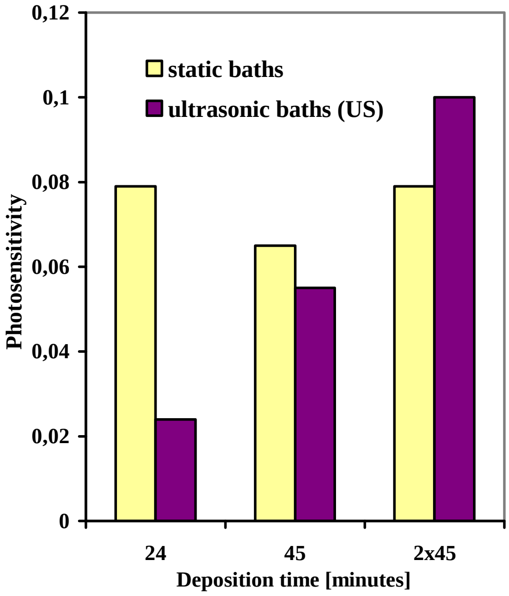

Fig. 2. The variation of photosensitivity as a function of the deposition time

In the case of the samples obtained by the deposition of one layer for 24 minutes, ultrasounds determined important decreases of photosensitivity (with 69 %).

The increase of the deposition time to 45 minutes led to the decrease of the photosensitivity (with 30 %). For this deposition time, ultrasounds determined a decrease of the photosensitivity.

The films obtained by the deposition of two layers of PbS, 45 minute each, led to the increase of photosensitivity by 21 %, in comparison with the films formed from a single layer. In this case ultrasounds determined a supplementary increase of film photosensitivity, respectively the deposition of two layers for 45 minutes from ultrasonic baths determined an increase of the photosensitivity with 82 %, in comparison with the photosensitivity of the films formed by the deposition of a single layer, for 45 minutes.

The decrease of photosensitivity of some of the films obtained by sonochemical method can be explained by the increase of the thickness of the films, and the decrease of electrical resistance respectively.

3.2. The influence of thermal treatment on the electrical resistance and on the photosensitivity

The obtained films were subjected to a thermal treatment at 90^{o}C for 120 minutes, in order to increase the photosensitivity of the film [17,35]. The electrical resistance of the films measured before and after the thermal treatment is presented in Figure 3. For all studied samples an increase of electrical resistance of the films took place due to desorption of water from the surface of the films and, to a certain extent, to the phenomenon of the oxidation that took places on the surface of the films [35]. The effect of thermal treatment was higher as much as the initial electrical resistance of the film was higher.

The photosensitivity of the films increased after the thermal treatment for all the samples (Figure 4). As we mentioned above, the films obtained from the deposition of two layers have higher photo-sensitivities.

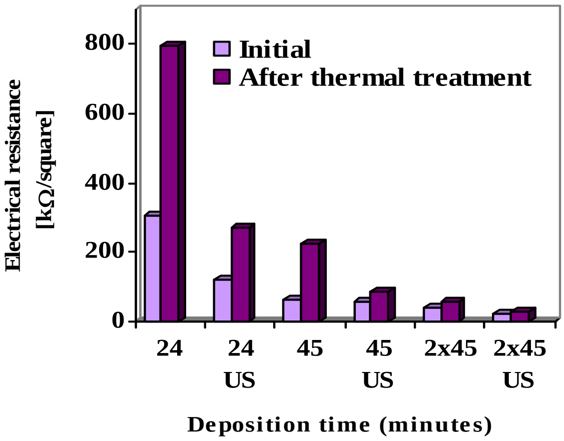

Fig. 3. The electrical resistances of PbS films before and after thermal treatment at 90°C

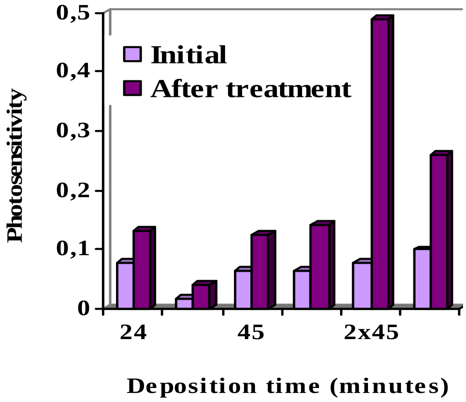

Fig. 4. The photosensitivity of PbS films before and after thermal treatment at 90°C

The best results were obtained for the sample obtained by the deposition of two layers for 45 minutes from static baths.

4. Conclusions

The films obtained in the presence of ultrasounds are thicker, respectively having smaller electrical resistances because ultrasounds accelerate the reaction of PbS formation. The deposition of two layers of PbS determined the follow-up decrease of electrical resistance due to the autocatalytic effect of the first deposited layer.

In the case of the samples obtained by the deposition of one layer for 24 minutes and 45 minutes respectively, ultrasounds determined a decrease of photosensitivity.

The deposition of two layers of PbS, led to the increase of photosensitivity, in comparison with the films formed from a single layer. Ultrasounds determined a supplementary increase of film photosensitivity for the films obtained by the deposition of two layers for 45 minutes.

An increase of electrical resistance and of photosensitivity of the films took place after thermal treatment for all samples.

The films obtained by the deposition of two layers have higher photo-sensitivities.

The best results were obtained for the sample obtained by the deposition of two layers for 45 minutes from static baths.

Because the increases of the photosensitivity were not significant, and took places only for the two-layered film, sonochemical methods can be applied for the obtained PbS films for other applications than the obtaining of photosensitive films, for example for thermo-reflecting films as ultrasounds allow the production of the films in shorter time than chemical bath deposition, leading to the increase of productivity.

References

[1] J.J. Valenzuela-Jáuregui, R. Ramírez-Bon, A. Mendoza-Galván, M. Sotelo-Lerma, Thin Solid Films, **441**(1-2), 104, (2003).

[2] A.A. Rempel, N.S. Kozhevnikova, A.J. G. Leenaers, S. Van Den Berghe, Journal of Crystal Growth, **280**(1-2), 300, (2005).

[3] L. Raniero, C.L. Ferreira, Materials Science Forum 455-456, 128, (2004).

[4] R.S. Parra, P.J. George, G.G. Sánchez, A.E.J. Gonzalez, L. Baños, P.K. Nair, Journal of Physics and Chemistry of Solids, **61**(5), 659, (2000).

[5] A. Osherov, V. Ezersky, Y. Golan, EPJ Applied Physics, **37**(1), 39, (2007).

[6] R.A. Orozco-Terán, M. Sotelo-Lerma, R. Ramirez-Bon, M.A. Quevedo-López, O. Mendoza-González, O. Zelava-Angel, Thin Solid Films, **343-344**(1-2), 587, (1999).
[7] F.C. Meldrum, J. Flath, W. Knoll, Journal of Materials Chemistry, **9**(3), 711, (1999).
[8] E.M. Larramendi, O. Calzadilla, A. González-Arias, E. Hernández, J. Ruiz-Garcia, Thin Solid Films, **389**(1-2), 301, (2001).
[9] M. Iype, S. Varghese, E.J. Mathew, C.S. Menon, Asian Journal of Chemistry, **14**(2), 927, (2002).
[10] K. M. Gadave, S.A. Jodgudri, C.D. Lokhande, Thin Solid Films, **245**(1-2), 7, (1994).
[11] F.A. Fernández-Lima, Y. González-Alfaro, E.M. Larramendi, H.D. Fonseca Filho, M.E.H. Maia da Costa, F.L. Freire Jr., et al. Materials Science and Engineering B: Solid-State Materials for Advanced Technology, **136**(2-3), 187, (2007).
[12] I. Pop, C. Naşcu, V. Vomir, V. Ionescu, Revue Roumaine de Chimie, **39**(1), 31 (1994).
[13] A. B. Lundin, G. A.Kitaev, Izv. Vuzmvo. Khim. i Khim. Technol., **10**, 408 (1967).
[14] A. B. Lundin, N. K. Bulatov, N. I. Darienko, L. B. Iakimova, Izv. Vuzmvo. Khim. i Khim. Technol., **19**, 1059, (1967).
[15] I. Pop, C. Naşcu, V. Ionescu, E. Indrea, I. Bratu, Thin Solid Films, **307**(1-2), 240 (1997).
[16] J. C. Osuwa, C. I. Oriaku, F. I. Ezema, Chalcogenide Letters, **6** (8), 385 (2009).
[17] V. Popescu, G. L. Popescu, M. Moldovan, C. Prejmerean**,** Chalcogenide Letters, **6** (9), 503 (2009).
[18] E. Pentia, L. Pintilie, I. Matei, T. Botila, E. Ozbaya, J. Optoelectron. Adv. Mat., **3,** 525 (2001).
[19] A. Popa, M. Lisca, V. Stancu, M. Buda, E. Pentia, T. Botila, J. Optoelectron. Adv. Mat., **8**, 43 (2006).
[20] R. Xie, D. Li, D. Yang, M. Jiang, M., Journal of Materials Science, **42**(4), 1376, (2007).
[21] H. Wang, J. Zhang, J. - Zhu, Journal of Crystal Growth, **246**(1-2), 161, (2002).
[22] Y. Zhao, X. Liao, J. -. Hong, J. - & Zhu, Materials Chemistry and Physics, **87**(1), 149, (2004).
[23] J. Zhu, S. Liu, O. Palchik, Y., Koltypin, A. Gedanken, Journal of Solid State Chemistry, **153**(2), 342, (2000).
[24] S.F. Wang, F. Gu, M. K. Lü, Langmuir, **22**(1), 398, (2006).
[25] S.M., Zhou, Y. S. Feng, L.D. Zhang, Journal of Materials Research, **18**(5), 1188, (2003).
[26] S.-. Zhou, X. -. Zhang, X. -., Meng, X. -., Fan, S.-. Lee, S. -. Wu, Journal of Solid State Chemistry, **178**(1), 399, (2005).
[27] S. Fen Wang, F. Gu, M.K. Lü, G. Jun Zhou, A. Yu Zhang, Journal of Crystal Growth, **289**(2), 621 006).
[28] Z. Xiu, S. Liu, J. Yu, F. Xu, W. Yu, G. Feng. Journal of Alloys and Compounds, **457**(1-2), L9, (2008).
[29] N. de la Rosa-Fox, V. Morales-Flórez, M. Piñero, L. Esquivias, Key Engineering Materials, **391**, 45, (2008)
[30] A. Aslani, A. Morsali, M. Zeller, Solid State Sciences, **10** (11), 1591, (2008)
[31] J. P. Park, S. K. Kim, J. Y. Park, S. Ahn, K. Min Ok, Ho-Y. Kwak, Il-W. Shim, Thin Solid Films **517**(24), 6663, (2009)
[32] H. Zhou, T. Fan, T. Han, X. Li, J. Ding, Di Zhang, Q. Guo, H. Ogawa, IOP Electronic Journals, Nanotechnology, **20** 085603 (10pp) doi: 10.1088/0957-4484/20/8/085603, (2009).
[33] W. Wang, Q. Li, M. Li, H. Lin, L. Hong, Journal of Crystal Growth, **299** (1), 17 (2007).
[34] V. Popescu, Revista de Chimie, **55**(10), 797 (2004).
[35] I. Pop, V. Ionescu (Popescu), C. Naşcu, V. Vomir, R. Grecu, E. Indrea, Thin Solid Films, **283**, 119, (1996).
[36] V. Popescu, H. I. Naşcu, Journal of Optoelectronics and Advanced Materials, **8**(5), 1874, (2006).
[37] I. Spînulescu, Thin layers physics and their applications - Fizica straturilor subţiri şi aplicaţii ale acestora, Scientific Publishing House, Bucharest**,** 365, (1975).
[38] K.S. Suslick (Ed.), Ultrasounds: Its Chemical, Physical and Biological Effects, VCH, New-York, 1988.
[39] C. Naşcu, V. Vomir, V. Ionescu, I. Pop, Rev. Roumaine Chim., **40**(2), 127 (1995).