Optical properties of lead sulfide films obtained by chemical bath deposition from static and ultrasonic baths

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Lead sulphide is a narrow band semiconductor (0.41 eV at 300 K), studied for applications related to NIR radiation detection, infrared solar cells or sensors. PbS films, consisting in one and two layers, have been obtained from solutions containing lead acetate and thiourea in alkaline environment from static and ultrasonic baths. The effect of ultrasounds and the number of deposited layers on the formation and on the optical properties of the PbS has been studied. Both films consisting in one or two layers were thinner when the deposition took place under ultrasonic agitation when the films were formed from the same number of layers and the ultrasounds were applied only 10 minutes at the beginning of the reaction. Ultrasounds lead to the detachment of the particles from the substrate, reducing the deposition rate. Optical properties were measured for UV-VIS wave lengths and the band gaps have been calculated

1. Introduction

Lead sulphide is a narrow band semiconductor (energy band gap is 0.4 eV for direct transitions, at 300 K), studied for applications related to NIR radiation detection, infrared solar cells or sensors.

Lead sulphide films can be obtained by Chemical Bath Deposition (CBD) [1-24] from alkaline baths containing Pb (II) salts and a sulphur compound such as thiourea (TU). A series of substances that forms in the reaction conditions complexes that decompose with a small reaction rate must be added to the bath, leading to the formation of the film. The main advantage of CBD is the possibility of using simple and inexpensive laboratory equipments allowing the deposition of films on diverse substrates with planar or complex shapes.

If lead nitrate and TU are used as reagents for the film, the chemical reactions which can be considered between precursors are as follows [21,22]:

$$Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaNO_3$$
$$Pb(OH)_2 + 4NaOH \rightarrow Na_4Pb(OH)_6$$
$$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO_2^- + 3OH^- + H_2O$$
$$HPbO_2^- + SH^- \rightarrow PbS + 2OH^-$$
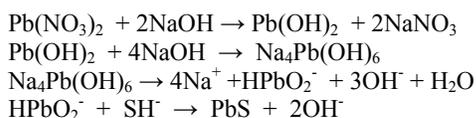
The reaction between Pb (II) and TU leading to the formation of PbS is an autocatalytic reaction [12-15], being characterized by an induction (initiation) period [21]. Initiation involves the nucleation in which a layer of $Pb(OH)_2$, formed on the glass substrate, is chemically converted into PbS by the reaction with S^{2-} ions available in the bath from the hydrolysis of thiourea [22]. The intermediate layer of $Pb(OH)_2$ play an essential role in the formation and adhesion [23] of the film on the substrate. If the glass substrate is introduced in the deposition bath after initiation period no films are formed.

Due to the large Bohr radius of the exciton in the bulk (about 180 Å), reduction of particle size in the range of 8-28 Å, determine a strong quantum confinement [25].

Due to quantum confinement, the energy band gap of PbS films obtained by CBD vary in a wide range as a function of crystallite's sizes. The values of energy band gaps of PbS films depends mainly on the size of the particles from the films. In the case of thin films particles sizes depends on the deposition conditions such as: precursors concentration, deposition time, bath temperature, concentration of surface active agents or complexing compounds. When lead acetate was used as Pb^{2+} source, in the presence of NH_3, the obtained band gaps ranged between 1.9 to 2.6 eV, depending on lead salt concentration [26].

In the case of polyvinyl alcohol (PVA) capped nanocrystalline PbS obtained by CBD [27] the values of direct band gap energy were 2.4–2.81 eV, while the values for indirect transitions the values were 1.24–1.61 eV.

The paper presents the optical properties of PbS films as a function of the deposition conditions (static or ultrasonic baths) and as a function of the number of the deposited layers.

A previous study [20] presented the influence of ultrasounds on electrical and photoelectrical properties of PbS films deposited by CBD. As far as we know there are no data in literature related to PbS films obtaining by sonochemical methods; although sonochemical methods were studied to obtain lead sulphide nanoparticles [27-41] or microtubes [42].

2. Experimental

A series of samples of PbS films were deposited on glass slides with dimensions of 75x25x1 mm, from baths

containing $1.4 \cdot 10^{-2}$ M lead nitrate, $3 \cdot 10^{-2}$ M thiourea and 0.3 M NaOH, using reagents of analytical grade whiteout any purification. The films consist in one or two PbS layers deposited at 30 ^{o}C, for 30-45 minutes.

The substrates were rigorously cleaned with commercial detergent using a cotton swab and after rinsing a treatment with nitric acid was applied.

In a 150 ml beaker, the deposition solution has been prepared adding in 75 ml water and the appropriate amount of lead nitrate solution, under vigorous stirring. In the next step a solution containing NaOH was added dropsied. A white precipitate appears and the precipitate dissolved when the total amount of NaOH solution was added. Then, a solution containing TU was added to the clear solution containing lead nitrate and sodium hydroxide, followed by the addition of water until a total volume of 100 ml solution was obtained. The final solution was homogenized and then was divided in two 50 ml Berzelius beakers. Two microscopic glass slides were introduced in each beaker. One of the beakers was placed in a thermostatic bath at 30 ^{o}C, and the other one in an ultrasonic bath (Elma Sonic S 30 H). In the first bath, the deposition took place without mixing the solution, while in the second one the deposition took places under sonochemical conditions. The deposition took places for 45 minutes both in the static and ultrasonic bath. After 45 minutes the glass plates were removed from the Berzelius flasks, washed with running and distilled water and a second layer of PbS was deposited from a freshly prepared bath in the same conditions.

The obtained films were thick, opaque with a rough surface being covered with PbS powder. The films deposited in the ultrasonic bath tend to peel of from the glass slide surface. One of the reasons related to high thickness of the films was the temperature increasing in the ultrasonic bath due to the ultrasonic agitation. In those conditions, the deposition took places at a higher temperature in the ultrasonic bath, the temperature increase leading to the further increasing of the reaction rate.

In the next experiments we reduced the ultrasonication time from 45 minutes/layer to 10 minutes /layer, applying the ultrasonication only in the induction period. We also reduced the total deposition time/layer from 45 minutes to 30 minutes including the induction period. In the final we obtained 4 smooth shiny mirrors like samples of PbS (Table 1).

After the film deposition, the films were washed with running water and then with distilled water.

The films were then drayed in an oven for 30 minutes at 60 ^{o}C, in order to avoid any transformation of the films and than the films were measured and weighted for thickness determination applying the micro-weighting method. For this purpose, a precision balance (Precisa XT220A) with 0.0001 g standard deviation has been used. It was assumed that the film has a bulk density of PbS (7.569 gr/cm^3). The thickness of each grown film was calculated from the known mass of the deposit, surface area and its density [43,44].

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

Sample name	Layer no. x dep. time [min]	Thickness [μm]	PbS depos. [g]
PbS 1	1x30 no mixing	0.51	0.0054
PbS 2	2x30 no mixing	0.96	0.0102
PbS 1 US	1x30 -10 min. US	0.20	0.0022
PbS 2 US	2x30 – 2x10 min. US	0.58	0.0062

Under a visual observation the obtained films seems to be uniform. Examining the thickness of the films from table 1, one can see that in the case of the film obtained in the static baths, the thickness was higher than in the case of the films obtained under ultrasonication. As we state in [20,23], in the first stage of the deposition reaction, a series of complexes of lead with hydroxide and thiourea are formed, including lead hydroxide. The formed complexes were absorbed at the substrate surface, leading to the formation of adherent films. These intermediate layers have an important role for the films adhesion. Under ultrasonic agitation, the intermediate compound that forms in the initiation stage was removed from the surface of the glass slides, leading to the formation of thinner films than in the case of the films obtained from static baths.

In a previous study we showed that ultrasounds applied for all deposition time, leads to the formation of thicker films than in the case of the films obtained from static baths [20]. The composition of solution and the conditions for the deposition were different.

Optical transmittance, specular and diffuse reflectance of the obtained films were determined using a UV-VIS spectrophotometer Lambda 35 (Perkin Elmer), provided with solid sample holders and an integrated sphere. For optical transmittance we used a clean substrate for reference. Aluminium mirror and spectralon references were used for specular and diffuse reflectance measurements.

One layer from a side of the glass side was removed using a solution of hydrochloric acid before optical properties were measured.

3. Results and discussion

Optical transmittance and specular reflectance after removing the PbS from one side of the glass slide are presented in fig. 1.

The obtained films are very shiny, having a mirror like appearance, with a high specular reflectance; in this situation the transmission is very small, for all samples. The transmission increases with the increasing of wavelength, almost linear in NIR region of the spectrum.

One can see that the ultrasounds have a small influence on the transmittance of the films, leading to a slight decreasing of transmittance. In the case of one layered film the difference was 2.5 %, for 1100 nm, while for the films formed from two layers, the difference was even smaller (0.3 % at 1100 nm). The films containing two layers have a transmittance close to zero, for all

visible wavelengths, while the films formed from one layer have a higher transmittance.
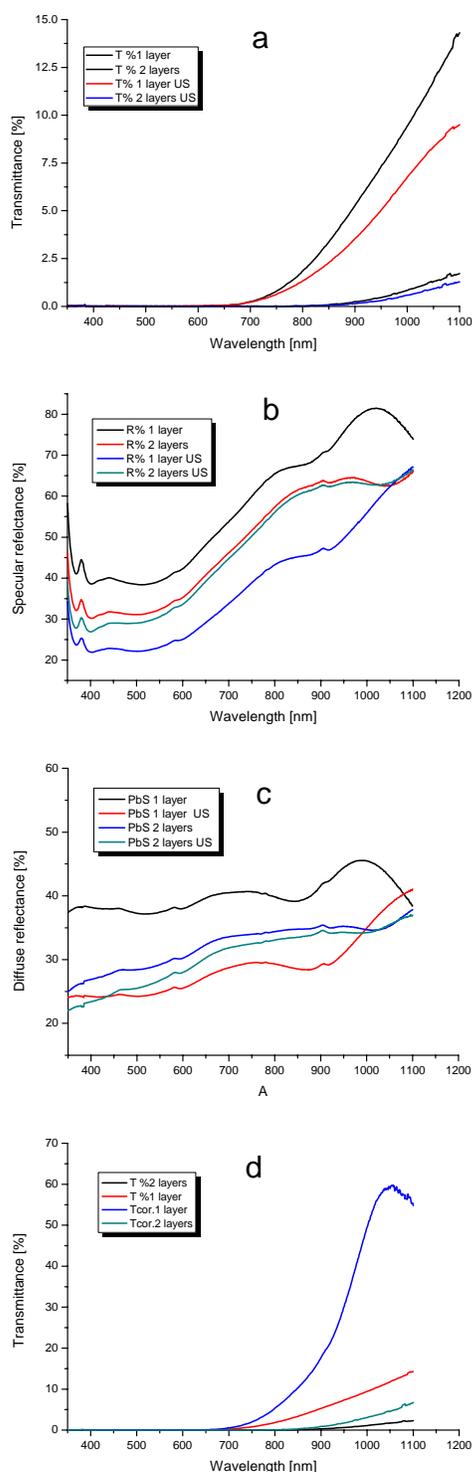
Fig. 1. VIS transmission (a), specular reflection (b) diffuse reflection (c) and corrected transmission (e) spectra of PbS films

If two layers have been deposited, the film obtained in ultrasonic bath was thinner than the one obtained from the static bath. This unexpected behaviour can be explained by the displacement of PbS particles from the surface of the film during the 10 minutes ultrasonication in the first 10 minutes of film formation (the induction period).

Because there is no correlation between the calculated film thickness, the quantity of deposited PbS on the surface of glass slides and the transmittance of the films, one can conclude that the morphology of the films has been strongly influenced by the ultrasounds; leading to an increased absorption of radiation even if, according to our measurements, the film thickness was smaller when ultrasonication during induction period was applied. Probable, the ultrasounds promoted the formation of smaller, much denser germination centres on the substrate, leading to the formation of films with a very good continuity at microscopic level. Further investigations are necessary in order to explain this behaviour.

The ultrasounds influenced the process of the formation of the film conducting to very different specular and diffuse reflectance for the samples formed from one deposited layer. The film with the highest specular reflectance is the one obtained by depositing one layer from static bath (up to 80 %), while the film obtained from ultrasonic baths has the smallest reflectance. Depositing two layers, the influence of the ultrasounds on the reflectance of the films was very small. The reflectance of the films formed by the two layers deposition is intermediate between the specular reflectance of the two films formed from one layer.

Diffuse reflectance has also the highest values for the sample PbS 1 and the smallest values for PbS 1 US, while the differences of diffuse reflectance for samples formed from two layers was small. Ultrasounds leads to the formation of films with smaller diffuse reflectance than the films obtained from static baths.

Based on the optical properties one can determine the band gaps of the semiconducting films.

There are a series of graphical methods for optical band gap determination, starting from the calculation of absorption coefficient (α).

The absorption coefficient was calculated using the following equation [16]:

$$\alpha = \frac{1}{d} \cdot \ln \frac{1}{T} \qquad (1)$$

where d is the thickness of the film and T is the transmittance.

The dependence of the α as a function of photon energy is presented in fig. 2 a. The value of α increases with photon energy increasing in the region, where α is smaller than the band gap, *Eg*.
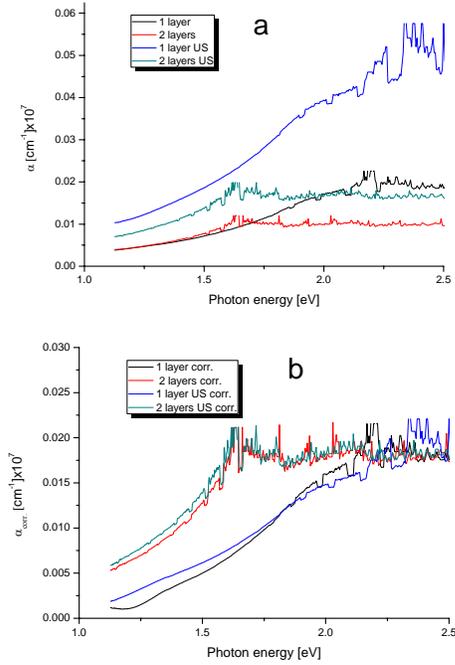
Fig. 2. The dependence of α as a function of photon energy. a. from the measured transmittance. b. from corrected transmittance

decreasing of the band gaps was observed both, for films formed from one and two layers. Depositing two layers, the band gap decreased from 1.57 (PbS 1) to 1.43(PbS 1 US) and from 1.50 (PbS 1 US) to 1.41 (PbS 2 US). Ultrasounds lead to the band gaps decreasing.
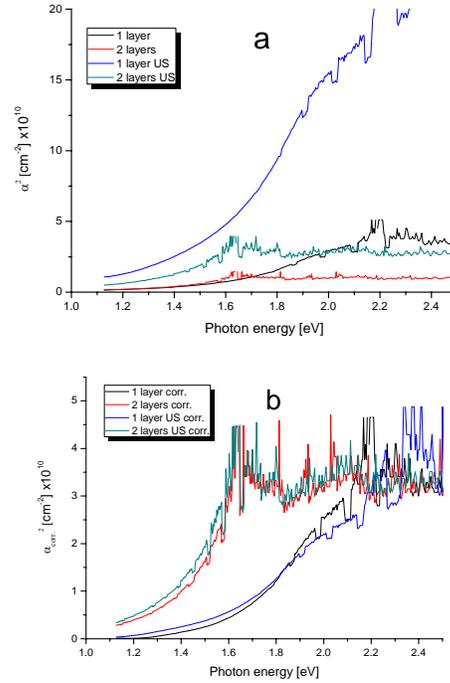
Fig. 3. The plot of α^2 versus photon energy. a. from measured transmittance. b. from corrected transmittance

The highest values for α were obtained for the film formed from one layer, deposited from ultrasonic bath (PbS 1 US), followed by the sample PbS 2 US.

Smaller values were obtained for the films deposited from static bath. The smallest vales were obtained for the sample consisting on two layers deposited from the static bath.

According to Sadovnikov et al [47], the long tails observed in the absorption spectra of PbS films near the absorption band edge are basically due to the dispersion of nanoparticles in size in the films, or, in other words, due to deviations in the nanoparticle dimensions from their average dimension.

A plot of α^2 versus photon energy, *hν*, gives a straight line (not presented), which extrapolates at $\alpha^2 = 0$ to the band-gap value, *E*g [43] (fig. 3 a).

One can see from figure 3 and table 2, that the band gap for sample PbS 1 is around 1.57 eV, and the one for PbS 1 US is about 1.50 eV, leading to the conclusion that ultrasounds have influenced the crystallite size of the film. The increasing of crystallite size leads to the decreasing of the band gap. Comparing the band gap for the films formed from one and two layers, respectively, an obvious

The optical band gap energy of the films can be also determined from the following equation.

$$\alpha h\nu = A(h\nu - Eg)^n \qquad (2)$$

where hν is the incident photon energy, A is a constant and Eg is the gap energy between the conduction and valance band of the film. The $(h\nu)^{1/n}$ vs. hν plot for n = 1/2, indicates the presence of direct band gap in the film, while n=2 indicate the indirect band gap. The optical band gap energy can be determined by extrapolating the curve to the energy axis for zero absorption coefficients (figures 4 and 5 [24,47].

Table 2. The energy band gaps (Eg) obtained using different methods.

Sample Info.	Eg $\alpha^2=f$ (eV)	Eg $\alpha_{corr}^2=f$ (eV)	Indirect Eg $(\alpha h\nu)^{1/2}=f(h\nu)$	Indirect Eg $(\alpha_{corr}h\nu)^{1/2}=f(h\nu)$	Direct Eg $(\alpha h\nu)^2=f(h\nu)$	Direct Eg $(\alpha_{corr}h\nu)^2=f(h\nu)$
	[eV]	[eV]	[eV]	[eV]	[eV]	[eV]
PbS 1	1.57	1.55	1.03	1.04	1.60	1,67
PbS 1 US	1.43	1.42	0.71	0.76	1.29	1.64
PbS 2	1.50	1.50	0.91	0.93	1.49	1.38
PbS 2US	1.41	1.41	0.82	0.78	1.37	1.36
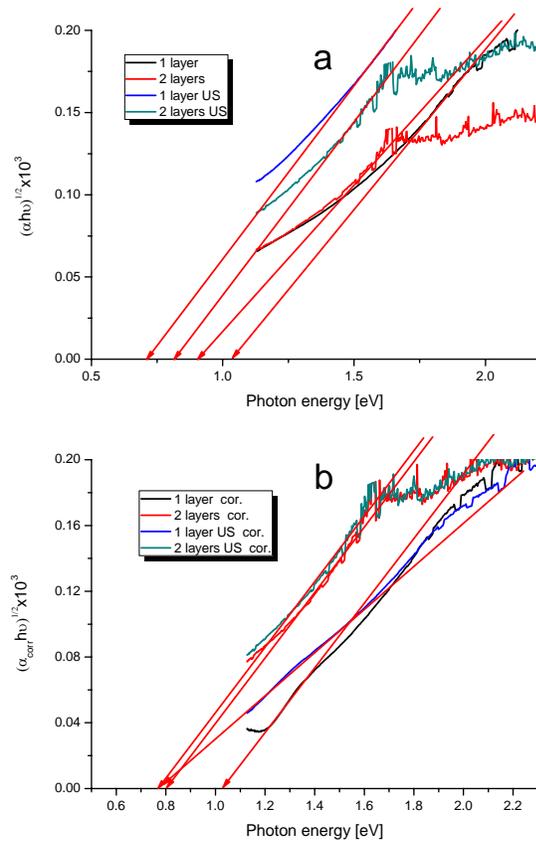
Fig. 4. The determination of the indirect energy band gap. a. from measured transmittance. b. from corrected transmittance

Fig. 5. The determination of the direct energy band gap. a. from measured transmittance. b. from corrected transmittance

Indirect band gap vary between 0.71 to 1.03 eV.

Because the reflectance has an important contribution to the optical properties of the film, in order to evaluate the influence of the reflection loss on the energy band gaps of the films, we determined the corrected optical transmittance taking into account the specular reflectance using the following relation [45, 48]:

$$T_{cor. \lambda}(\%)= \frac{100 \cdot T_{\lambda}(\%)}{100 - R_{\lambda}(\%)} \qquad (3)$$

One can see that the corrected transmissions for wavelengths higher than 700-800 nm (fig. 1. d) are higher than transmission measured without correction (fig. 1.a).

Absorption coefficient has been also calculated taking into account the corrected transmittance:

$$\alpha_{corr.} = \frac{1}{d} \cdot \ln \frac{1}{T_{corr.}} = \frac{1}{d} \cdot \ln \frac{1-R}{T} \qquad (4)$$

The variation of the α_{corr} as a function of photon energy is presented in fig. 2 b. One can observe that the values obtained for the corrected absorption coefficient, taking into account the reflectance of the films, is smaller than the values obtained without correction. More than that, applying the corrections, the shape of the curves has been improved and the values for the absorption coefficient for sample obtained from one layer from static bath was close to the values obtained from ultrasonic bath for one layered film.

When α^2 was calculated using corrected transmittance the shape of the plots of α^2 versus photon energy has been changed, the curves looking very similar for the samples obtained from one layer and two layers, respectively (fig. 3 b), but the values obtained for Eg were very close, or even equal to those obtained using uncorrected α^2 (table 2).

If the indirect energy band gap was determined using corrected values (fig. 4 b), a small difference between the values obtained without correction has been noticed, while the difference obtained for direct band gap was higher. One can conclude that the errors related to reflection lost in the determination of direct band gaps were higher for the thinnest film (PbS 1 US) (1.64 instead 1.29 eV).

For all samples, a blue shift of Eg has been observed leading to the conclusion that we obtained nanostructured films. The response of PbS shifted from NIR (corresponding to bulk PbS) toward visible wavelengths.

Considering the influence of ultrasounds on the values of band gaps one can conclude that US had a small influence on Eg (direct band gap was smaller for samples obtained from ultrasonic baths).

If the films were obtained from two layers, the band gap decreased from around 1.6 to 1.3 eV.

4. Conclusions

The study related to the influence of ultrasounds on the optical properties of lead sulphide films leads to the following conclusions:

- When ultrasounds were applied for 45 minutes (all deposition time/layer) the obtained films were thicker than those obtained from static baths, and tend to peel of the substrate.

- If ultrasounds were applied only in the initiation time, for 10 minutes /layer, the obtained films were thinner than those obtained from static bath.

- Ultrasounds lead to a small decrease of band gaps of the films, probable due to a grain sizes increasing.

- When corrected transmission has been used, for the calculation of absorption coefficient we obtained curves with similar shapes for samples obtained by depositing one layer in static and ultrasonic baths, comparing to α obtained using the uncorrected α; whose dependence on wavelength differ a lot for the samples consisting in one layer.

- If the values of the band baps have been calculated taking into account the absorption losses due to the reflection, a clear difference has been observed and a better correlation with theory.

- The number of deposited layers influenced the values of the band gap. If the film consisted on two layers the band gaps was smaller.

- Ultrasounds can leads to the increasing or decreasing of the reaction rate, as a function on the application time and duration. We suppose that one can establish the conditions of ultrasonication in order to reduce the reaction time and to improve the efficiency of deposition. A series of studies are necessary in order to correlate the concentration of the precursors, the temperature and the duration of ultrasonication.

Further investigations are necessary in order to correlate the optical properties with the structure and the morphology of the films.

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