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Optical properties of PbS-CdS multilayers and mixed (CdS+PbS) thin films deposited on glass substrate by spray pyrolysis

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Two kinds of films containing both PbS and CdS were obtained by spray pyrolysis. The first one, sandwich type, consisting on 2-6 layers, was obtained trough the successive deposition of CdS at 450 ^oC, and PbS at 400-425 ^oC, from solutions containing either $Pb(Ac)_2$ or $CdCl_2$ and thiourea. The second one, mixed (CdS+PbS) was obtained from solutions containing both Cd and Pb salts, having a molar ratio Cd:Pb from 5:1 to 1:5.3, and thiourea, depositing 1-5 layers, at 300-350 °C. The transmission for sandwich type was of 15.5-23.8 % for neutral light, and 20 - 23 % for green light, respectively, as a function of the deposition conditions. For mixed (CdS+PbS) films the transmission for neutral light was of 6-45 %. For all layers the deposition time was 10 seconds, and the flow rate of the solution 20-25 ml/minute. VIS transmission spectra were recorded for the obtained films. The transmission was intermediate between that obtained for PbS or CdS films deposited separately. The color parameters in the CIELAB color space have been calculated based on the obtained spectral data. For two of CdS+PbS layers NIR reflection spectra were also recorded. NIR reflection is lower than the reflection of PbS or CdS deposited separately. The film characteristics depend on the concentration and the molar ratio of cadmium and lead salts and on the number of deposited layers.

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Keywords: Cadmium sulfide, Lead sulfide, Thin films, Optical properties, Spray pyrolysis

1. Introduction

Due to their optical, electrical and photoelectrical properties, PbS and CdS thin films have a large spectrum of applications in optoelectronics, chemistry (as temperature [1], gas or humidity [2] sensors or catalysts) or as solar control coatings etc. The films used for thermo-reflecting windows must have an optical transmission for visible wavelengths of 10-50 %, a VIS reflection <10% and NIR reflection as large as possible [2-10].

In our previous papers we have presented a series of studies related to the preparation and characterization of thermo-reflecting PbS [11], CdS [12-15], CuS [15,16] and Au [17,18] thin films. From the studied films, Au has the maximum NIR reflection [19], followed by PbS. PbS films, have a NIR reflection of 10- 45 % [11], and an optical transmittance for visible spectrum of 10-50 %. CdS thin films have a very good optical transmittance for visible spectrum (45-60 %), but their NIR reflection was smaller than 32 % [13]. We started the present work with the assumption that films of both these sulfides would have improved optical properties.

Thin metallic sulfide films can be obtained by chemical bath deposition (CBD) [3-9,20], spray pyrolysis (SP) [11-16] and by physical and electrochemical methods [21-22].

Some authors [23-24] reported a CBD technique for deposition PbS-CdS bilayers films on glass substrates. The obtained films were characterized trough XRD, SEM and optical absorption measurements.

The aim of this paper is to establish the conditions for deposition, of multilayered (sandwich type) CdS/PbS/CdS/PbS and mixed (CdS+PbS) thin films, by spray pyrolysis on heated glass substrates.

2. Experimental

Sandwich type films of CdS and PbS were successively deposited on heated glass slides from solutions containing cadmium and lead salts respectively, thiourea (TU), and surfactants, such as polyethylene glycol (PEG) and ethersulfate (ES) [14-16]. The optimal parameters for obtaining optical clear PbS [11] and CdS [10] films were reported elsewhere.

The mixed (PbS+CdS) films were deposited from solutions containing both Cd and Pb salts and thiourea at 300 – 350 ^oC.

The transmission of the films for neutral filter (glass slide) and green filter was determined with a FEK-M spectrophotometer. VIS transmission spectra have been recorded with a spectrophotometer SPECORD UV-VIS and NIR reflection spectra with a Carl Zeiss Jena UR-20 spectrophotometer, calibrated with known standards, using a LiF prism. Based on the obtained spectral data, the color parameters in the CIE 1976 L*a*b* color space (CIELAB) have been calculated (observer: 10°, illuminant: D65) (Fig. 1).

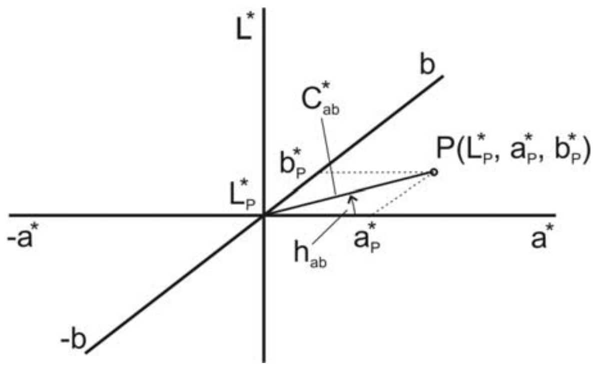

*Fig. 1. The CIE L*a*b* color space (CIELAB).*

The CIE 1976 L*a*b* color space (CIELAB) is the most widely used method for measuring and ordering object color [26]. In the CIE L*a*b* uniform color space, the color coordinates are:
L - the lightness* coordinate with 0 to 100.
*a** - the red/green coordinate, with +a* indicating red, and -a* indicating green.
*b** - the yellow/blue coordinate, with +b* indicating yellow, and -b* indicating blue.
C* and h* coordinates are computed from the a* and b* coordinates: *C* - the chroma* coordinate, the perpendicular distance from the lightness axis (more distance being more chroma), *h* - the hue angle*, expressed in degrees, with 0° being a location on the +a* axis, then continuing to 90° for the +b* axis, 180° for -a*, 270° for -b*, and back to 360° = 0°.

3. Results and discussions

3.1. Multilayered films CdS/PbS

3.1.1. Obtaining of the films

The optimal temperature, established previously, for the deposition of CdS films is 450 °C and respectively 350-400 °C for PbS films [12]. The first layer deposited on the glass substrate was CdS. During deposition the temperature decreased at the optimal value for formation PbS layers. Table 1 presents the conditions for obtaining CdS/PbS multilayered films and the transmissions for neutral and green filter respectively.

As a function of the deposition condition, the optical transmittance for obtained films was of 15.5-23.8 % for neutral filter and 19.5-23 % for green filter.

The superposition of CdS and PbS films having different colors leads to the obtaining of different shades of colors in reflection on the two sides of the glass slides (see table 1).

Using diluted solutions (sample no. 5 and 6), in order to obtain continuous films, it was necessary to deposit three layers. We measured the transmission for green filter, because human eyes are the most sensitive for this wavelength.

3.1.2. Optical properties

For a selection of samples, presented in Table 1 optical transmission spectra for visible wavelengths have been recorded (Fig. 2). VIS transmission spectra of CdS/PbS films, for wavelengths of 380-700 nm revealed a better transmission than the one of PbS for λ of 550-700 nm, and smaller transmission for λ of 380-500 nm. All studied films have smaller transmission and improved colors than CdS deposited alone.

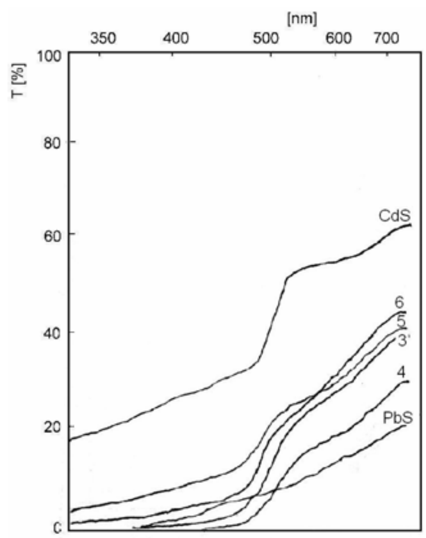

Fig. 2. Visible transmission spectra for multilayered CdS/PbS films.

For CdS-PbS samples, the calculated color parameters are shown in Fig. 3, and Fig. 4.

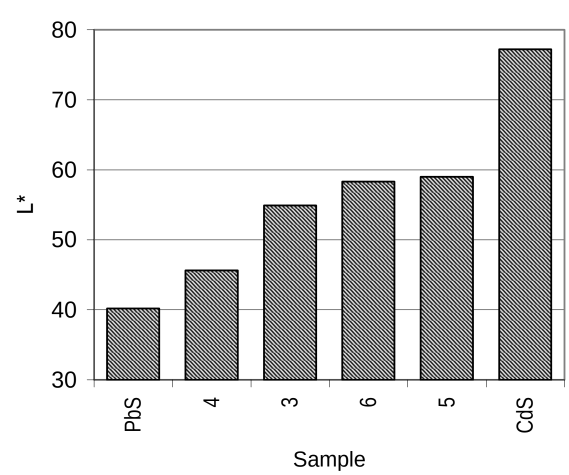

Fig. 3. The CIELAB lightness for multilayered CdS/PbS films.

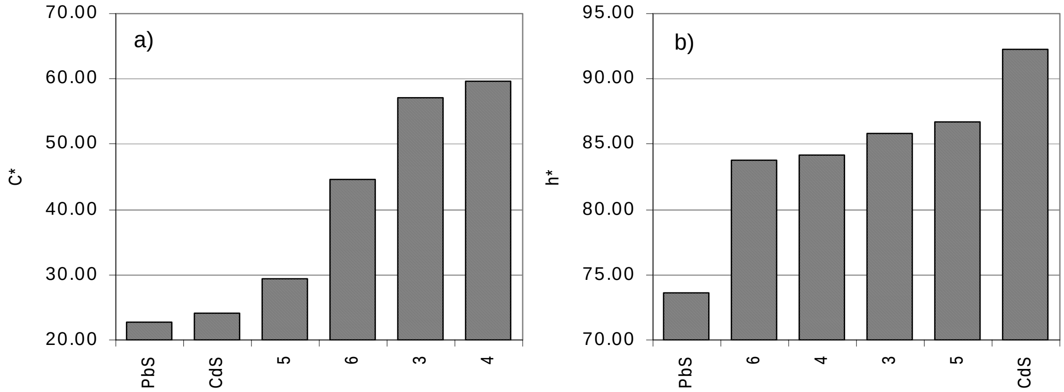

Fig. 4. The CIELAB chroma (a) and hue angle (b) for multilayered CdS/PbS films .

Table 1. The condition for obtaining multilayered PbS and CdS films and their optical properties.

Observations	On face I, specular reflectance with yellowish shade. On Face II diffuse reflectance grey-metallic	In transparency pale yellow. The appearance almost identical with sample 1	Much uniform film. On face I specular reflectance with yellow-orange shade. On Face II specular reflectance grey-metallic	The quality and appearance identically with sample 3	They have not formed distinct layers of CdS and respectively PbS. On face I specular reflectance with yellow-grey. On Face II feeble diffuse purple reflectance	Film similar to sample 5
T [%] neutral [%]	21	20	20.1	19.5	23	20.3
T [%] green [%]	15.5	17	21.5	18.8	23	23.8
Layers no.	1 1	2×1	1 1	2×1	3 3	3
Distance nozzle-substrate [cm]	20-25 20-25	20-25 20-25	20-25 20-25	20-25 20-25	20-25 20-25	20-25 20-25
Deposition time [sec]	10 10	10	10 10	10 10	3×10 3×10	3×10 3×10
Solution flow rate [ml/min]	30 30	30	20 20	20 20	30 30	30 30
Temp. [°C]	450 400	450 400	450 425	450 425	450 400	450 400
Solution composition	0.1 M $CdCl_2$; 0.1 M TU 0.01 M $Pb(NO_3)_2$; 0.1M TU	0.1 M $CdCl_2$; 0.1 M TU 0.01 M $Pb(NO_3)_2$; M TU	0.1 M $CdCl_2$; 0.1 M TU 0.01 M $Pb(NO_3)_2$; 0.1M TU	0.1 M $CdCl_2$; 0.1 M TU 0.02 M $Pb(NO_3)_2$; 0.1M TU	0.05 M $CdCl_2$; 0.05 M TU;0.1%PEG 0.01 M $Pb(NO_3)_2$; 0.1M TU	0.05 M $CdCl_2$; 0.05 M TU; 0.1 PEG 0.01 M $Pb(NO_3)_2$; 0.1M TU
Sample no.	1	2	3	4	5	6

The hue and lightness values for multilayered CdS/PbS films present small variations between the values for CdS and PbS. The chroma values are smaller for CdS and PbS (<25), as for the rest of the samples the value is higher (30-60).

These films have a decorative, distinct appearance and could be applied as thermo reflecting coatings for architectural windows used in warm climates and also for auto-vehicle windshields.

3.2. Mixed films of CdS-PbS

3.2.1. The preparation of the films

In order to prepare the mixed sulfide films (CdS+PbS), solutions containing both cadmium and lead salts together with thiourea were used. Ether sulphate was added (3×10^{-3} %) in order to improve the uniformity of the obtained films. Solution concentrations, molar ratio Cd/Pb, layers number, substrate temperature, and some optical properties (transmissions for neutral filter and optical density) are presented in table 2.

Table 2. The preparation conditions of mixed PbS-CdS films.

Sample no.	Concentration			Layer number	T neutral filter [%]	D_{opt}	Temp. [°C]	Molar ratio Cd/Pb
	Cd Acetate [M/l]x10^2	Pb Acetate [M/l]x10^2	Thiourea [M/l]x10^2					
7	7.50	1.50	10.0	1	25.7	0.76	300	5:1
8	7.50	1.50	10.0	1	22.5	0.81	300	5:1
9	0.75	3.75	5.0	1	24.5	0.76	300	1:5
10	0.75	3.75	5.0	2	13.0	1.00	300	1:5
11	0.35	1.85	2.5	4	6	1.38	300	1:5.3
12	0.35	1.85	1.75	5	4.5	1.55	300	1:5
13	0.18	0.90	1.75	4	9.4	1.25	300	1:5
14	0.18	0.90	1.75	5	9.3	1.20	300	1:5
15	0.18	0.90	1.75	5	6.8	1.35	300	1:5
16	0.18	0.90	1.75	5	23.5	0.78	300	1:5
17	0.18	0.90	2.50	5	14.6	0.68	300	1:5
18	0.50	0.50	1.00	3	10.5	0.72	350	1:1
19	1.00	0.50	1.50	5	24	0.62	350	2:1
20	1.00	0.24	1.20	5	45	0.38	350	4:1

Films with optical properties of PbS films were obtained by the use of lead acetate solutions with concentration ranging between 1.5×10^{-2} M and 3.75×10^{-2} M, even if only one layer was deposited, whatever was the concentration of Cd(II). The optical transmittance for neutral filter varies between 4.5 to 45 % as a function of solution concentration and of the number of deposited layers. Varying the concentration of the salts, films with various colors, from yellow-grey to almost black grey, could be obtained.

The samples 7 – 10, having a dark grey color, with metallic glance were heterogeneous, looking alike PbS. The samples 11 – 15 having the same colors were more homogeneous. For obtaining these films (samples 11- 15) the concentration of solutions was reduced when depositing thinner layers. In order to obtain continuous films, the number of deposited layers was increased from 1-2 to 4-5.

The color of samples 17 – 18, is marked by the presence of CdS. Thus, sample 17 had a brown-grey color, sample 18 had a yellow-brownish color shade, and the sample 20 was yellow, the specific color for CdS. The transmission for neutral filter of obtained films vary between 6 %, for sample 11 obtained by the deposition of 4 layers, from a solution containing $0.35\cdot10^{-2}$ M Cd acetate and $1.85\cdot10^{-2}$ Pb acetate (Cd:Pb=1:5,3), to 45 %, for sample 20, obtained by the deposition of 5 layers, from a solution containing $1\cdot10^{-2}$ M Cd acetate and $0.24\cdot10^{-2}$ lead acetate (Cd:Pb=4:1).

The films obtained at 300°C had a weak adherence and were inhomogeneous. Increasing the temperature to 350°, the homogeneity and the adherence of the films were improved.

3.2.2. Optical properties

The optical transmission spectra of a series of samples are presented in fig 5. As shown in fig. 5. it can be observed that increasing Cd(II) and decreasing Pb(II) concentration the optical transmittance increased too, and the peaks of maximum transmission displaced to lower wavelengths. The shape of mixed sulfide spectra resemble with those of PbS films [11].

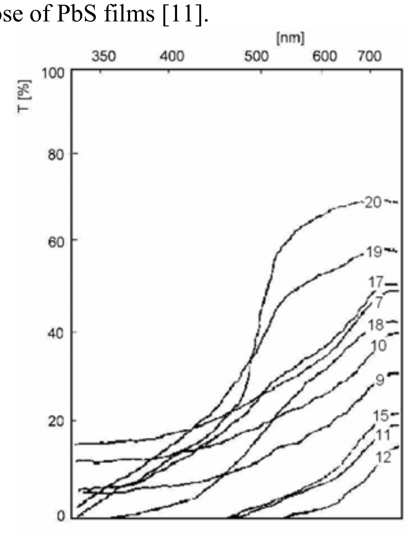

Fig. 5. Visible transmission spectra for CdS-PbS mixed films.

For CdS and PbS mixed films, the calculated color parameters are shown in Figs. 6 and 7.

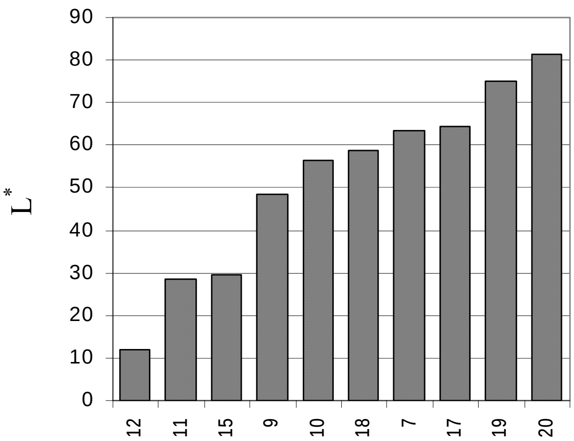

Fig. 6. The CIELAB lightness for CdS-PbS mixed films.

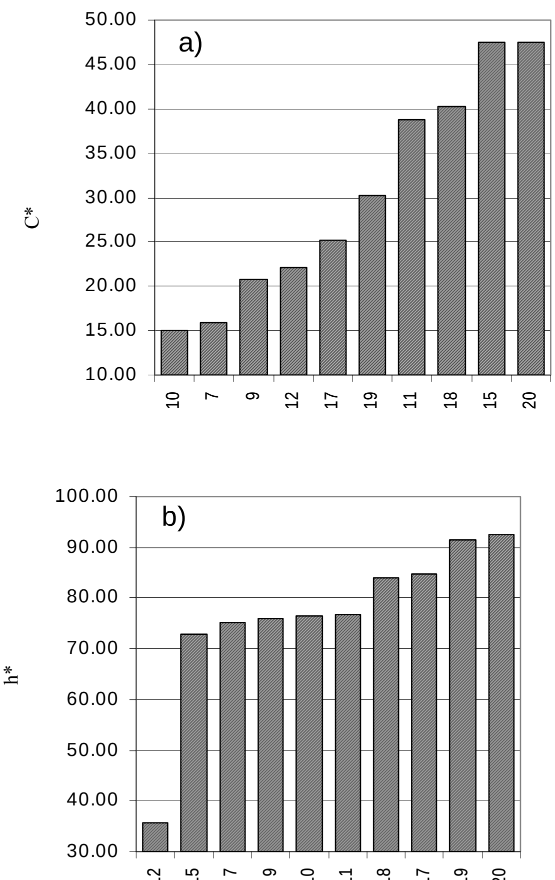

Fig. 7. The CIELAB chroma (a) and hue angle (b) for CdS-PbS mixed films.

The chroma and the lightness (Figs. 6 and 7) vary in wide limits depending on the layers number and Cd:Pb molar ratio. For example, sample no. 12, consisting on 5 deposited layers and a relatively high Pb concentration (Cd:Pb ratio 1:5), has a small lightness and saturation, with the hue angle (*h**) much different comparing with the other samples. High Cd:Pb ratio (4:1) when Pb concentration is small leads to the obtaining of a film with high lightness (81.22), yellow hue (*h**=92.6) with high saturation (C=47.55). Excepting sample 12, films hues do not differ much; hue angle is between 70 and 93°.

For two of the most representative samples of mixed Pb and Cd sulfides, the NIR reflection spectra have been recorded (Fig. 8), together with the spectra for pure CdS and PbS films. The obtaining conditions for pure CdS and PbS are presented in Table 3.

Table 3. The conditions for obtaining pure PbS and CdS films.

Sample number	Concentration M/lx10			Layer number	Color
	Cd Chloride	Pb Acetate	Thiourea		
PbS	-	0.1000	0.100	6	Grey-black with metallic glance
CdS	1	-	1	3	Clear yellow

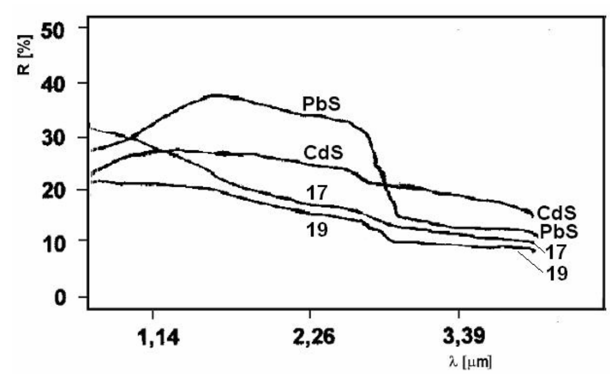

Fig. 8. NIR reflection spectra of some mixed films of CdS and PbS (samples 17 and 19) comparing with pure PbS and CdS films.

The molar ratio Cd acetate : Pb are very different, for the two studied samples, for instance in the case of sample 17 the molar ratio Cd/Pb is 1:5, and in the case of sample 19 it is 2:1.

The CdS film presents a maximum reflection of 27 % for wavelengths from 1.8 to 2.1 μm. The PbS film presents a maximum reflection of 39 %, for λ≈2 μm. PbS's reflection is higher than the reflection of the other samples for λ of 1.15-3.01 μm.

The spectrum of sample 19 (Cd:Pb 1:5) presents a maximum of 20% and it decreased almost linearly with the increasing of wavelengths while the one of sample 17 (Cd:Pb 2:1) presents a maximum of 30% for wavelengths of 0.76-1.14 μm. The reflection decreases almost linearly for wavelength higher than 1.14 μm (sample 17).

The increase of the concentration of lead (sample 19), determined important changes in the NIR reflection spectrum, in comparison with the spectra of sample 17 (Cd:Pb 2:1). The film with the higher content of lead has the maximum reflection 10 % higher then the film in which prevail CdS.

From the studied films, PbS has the best thermo-reflecting properties for the NIR domain, followed by the CdS film.

The decreasing of NIR reflection for samples 17 and 19, could be explained by the presence in the film of lead and cadmium complexes, which have not been decomposed yet. In order to increase the reflection, a thermal treatment, is necessary. During thermal treatment complexes that were embedded in the film decompose and the crystallinity of the films increases.

According to Podder et al. [25], the transmission of the films is mainly depending on the composition and the thickness of the films.

From the data presented in the table 2, it can be observed that the mixed sulfides films transmission for the neutral filter is of 6-45 %, as a function on deposition condition and the number of deposited layers. We can notice that even if the transmission for neutral light have very close values (24.6% for sample 17 and 24.0 % for sample 19), they have different reflection spectra. That can be explained by the difference of the compositions. As mentioned above, the films containing more PbS has a higher NIR reflection.

4. Conclusions

Two kinds of films containing both PbS and CdS were obtained by spray pyrolysis. The first one (sandwich type) was obtained by the successive deposition of CdS and PbS, from solutions containing either $Pb(Ac)_2$ or $CdCl_2$. The second ones (mixed CdS+PbS) were deposited from solutions containing both Cd and Pb salts.

The transmission for multilayered (sandwich type) CdS/PbS/CdS/PbS films was of 15.5 -23.8 % for neutral light, or 20 - 23 % for green light respectively, as a function of the deposition conditions.

VIS transmission spectra of CdS/PbS films, for wavelengths of 380-700 nm revealed a better transmission than the one of PbS for λ of 550-700 nm, and smaller transmission for λ of 380-500 nm. All studied films have smaller transmission than CdS deposited alone.

By varying the concentration and molar ratio of lead and cadmium salts, mixed PbS+CdS sulfides films could be obtained in a various scale of colors, from yellow (the specific color of CdS films), brown-yellow, brown, gray, to dark gray with metallic gloss (the specific color of PbS films). The composition and the molar ratio of Cd:Pb ranged in a wide scale, from 5:1 to 1:5.3.

In the case of mixed sulphide films, Pb and respectively Cd concentrations and their ratio influenced both the lightness and chroma of the films. The lightness reduced with the increasing of de number of deposited layers.

Films with desired transmission for VIS spectrum can be obtained as result of altering the solution concentration and deposition conditions.

The obtained PbS+CdS sulfides had a good optical transmission (around 24 %) and reflection until 30 % for NIR wavelength, optical properties that made them appropriate for applications as thermo-reflecting films for solar control coatings in architectural and motorcars constructions. The optical transmission for micrometric neutral filter varies between 4 – 45 %. The obtained films characteristics depend on the concentration and the molar ratio of cadmium and lead salts and on the number of deposited layers.

The use of cadmium sulfide gives films with better optical transmission than that of PbS films.

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