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NANOMETRIC CdS FILMS OBTAINED BY SPRAY PYROLYSIS. II. OPTICAL PROPERTIES

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ABSTRACT. The paper presents the results concerning optical properties of nanometric CdS (20-80 nm) films obtained by spray pyrolysis on glass substrate from aqueous solution containing $CdCl_2$, thiourea and ether sulfate 12-14 (ES). Transmission and absorption spectra in Vis range wavelength were presented. Near-IR reflection was also determined. The film thickness was determined microgravimetrically and spectrometrically. The vis transmittance varies between 45-60% and the NIR reflectance is 15-32%. The obtained results lead to the conclusion that CdS nanostructured films could be applied as solar control coatings.

Introduction. CdS thin films are well known because of the applications in achievement of solar cells. Metal sulphides such as lead sulphides [1], cooper sulphides [2-4] and cadmium sulphides [5], have good solar control properties, because of those good transmission for visible range radiation (λ=400-700 nm) higher than 10-80 % and near IR reflection of 20-45%. Those properties limit the unwanted increasing of temperature inside the building and cars, providing good lighting properties. Yellow CdS films has one more advantage in the esthetical looks. The visible transmittance is higher than stainless steel, Ni or Au layers [6].

Thin CdS films were obtained successfully on different substrates by spray pyrolysis [7-9] using cadmium salts and thiourea., at 120-450°C. Chemical bath deposition was also a successfully method for nanostructured film preparation [10-12].

Temperature is an important parameter, which influence the properties of the film. Even if CdS films were obtained at temperatures smaller than 200°, optical properties were not good enough [13]. The purity of the film was low, because of the secondary products of reaction trapped into the film. Complexes formed between Cd salts and thiourea were not completely decomposed. Film deposition does not take places at constant temperature. Because of the temperature gradients the grain growth is limited to sizes below 1 μm [14].

In order to increase the film purity, the films were subjected to thermal treatment [15]. Photoelectrical properties were improved, but optical properties vary insignificantly.

We obtained adherent, optically clear, homogenous, thermoreflective CdS nanostructured films from solutions containing $CdCl_2$, thiourea in the presence of ether sulfate 12-14 (ES) as surfactant, by spray pyrolysis deposition [16].

The aim of this paper is to present optical properties of CdS obtained films.

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Experimental details. The experimental set-up for spray pyrolysis deposition used by us also for CuS [2] and PbS [1] was described elsewhere. On the heated substrate at 300-500°C the solution containing $CdCl_2$, thiourea (TU) and ether sulfate 12-14 (ES) is sprayed. Dry air was used as carrier gas. A multi-layered film was deposited. The flow rate of the solution varies between 40-70 ml/sec.

The thickness of the film was determined spectrophotometrically with a photocolorimeter FEK-M [16]. The transmittance and absorbance using neutral and/or blue filter respectively were determined with a photocolorimeter FEK-M.

The VIS transmission and absorption spectra have been recorded with a SPECORD UV-VIS spectrometer and those of the NIR reflection with a UR-20 Carl Zeiss Jena spectrophotometer. NIR extension of UR-20 spectrophotometer was made by a calibration with known standards, using the LiF prisma.

Results and discussion. The obtained films are light yellows, having a good adherence to the glass substrate.

The thickness and the optical properties of the films depend on many factors such as: reagent concentration, substrate temperature, number of deposited layers, distance between spraying nozzle and substrate and the solution flow rate [16].

Optical properties, for CdS monolayers films, deposited from aqueous solution containing equimolar $CdCl_2$ and thiourea (air flow rate - 66.66 ml/sec, substrate temperature - 450^0C, the distance from substrate to the spraying nozzle 25 cm) are presented in table 1.

Table 1

Optical properties of CdS monolayers films deposited by spray pyrolysis from aqueous solution containing equimolar 0.1 M $CdCl_2$ and thiourea; (T [%] –transmittance)

Sample	Deposition time [seconds]	T [%]		Thickness [nm]	Observations
		Neutral filter	Blue filter		
1	10	59.8	56.20	39	Yellow adherent, optically clear film, uniform thickness
2	15	58.1	54.5	48.5	Relatively optically clear uniform film
3	20	51.6	48.8	61.0	Yellow adherent, transparent, optically clear film, with spots
4	25	50.0	47	63.0	Ununiform film with spots

For increasing the uniformity of the film, 3 layers were deposited in the presence of (ES) from equimolar solution varying the concentration of the solutions (table 2). The deposition time for each layer was 10 seconds, airflow rate - 66.66 ml/sec, substrate temperature - 450^0C. Visible transmittance for samples presented in table 2 are presented in fig. 1.

Nanostructured CdS films presented in fig. 1 have a good transmission for wavelength bigger than 550 nm.

Visible transmission spectra for another series of samples obtained from solution with different concentration of reagents were recorded and presented in Fig. 2. Obtaining conditions for films are presented in table 3.

Table 2

Condition for CdS films formation by spray pyrolysis from aqueous solution containing $CdCl_2$ and thiourea in the presence of ES $3 \cdot 10^{-3}$ %

Sample	Solution composition $CdCl_2$:TU	h [nm]	Observations
5	0.1:0.1	54	Adherent, relatively optically clear film
6	0.05:0.05	35	Adherent, optically clear film
7	0.025:0.025	24	Transparent optically clear film
8	0.01:0.01	15	Optically clear film

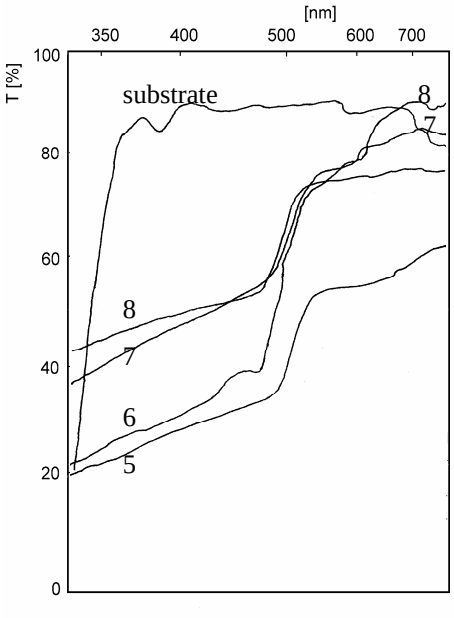

Fig. 1. Visible transmission spectra of glass slides as thick as 1 mm, coated with CdS films deposited from equimolar ratio solution containing $CdCl_2$, thiourea and ES.

From Fig.2. can be seen that in the range (350-700 nm) the transmittance of the films are increasing, starting from very low values (T<10 %), and having a maximum between 550 and 700 nm value. The thickest films have the lowest transmittance. Between 500-700 nm the transmittance varies from 65% for sample 11 (72 nm) to 92% for sample 9 (34 nm).

Table 3

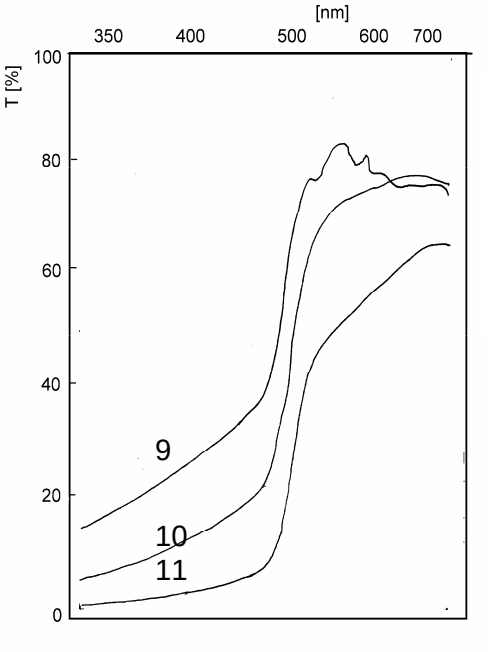

Fig. 2. Visible transmission spectra of glass slides as thick as 1 mm, coated with CdS films different thickness

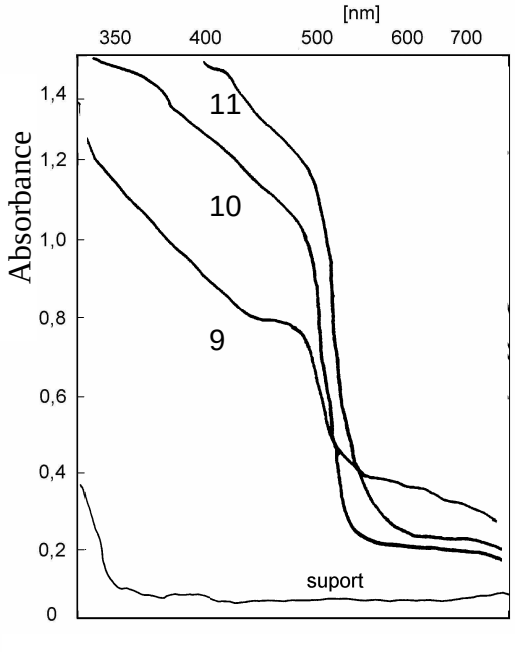

Fig. 3. Absorption spectra of glass slides as thick as 1 mm, coated with CdS films different thickness

Condition for CdS films formation by spray pyrolysis from aqueous solution containing $CdCl_2$ and thiourea, as well as thickness h (air flow rate - 66.66 ml/sec, substrate temperature - 450^0C, 3 layers were deposited each layer for 10 seconds)

Sample	Solution composition	h [nm]
9	0.025 M $CdCl_2$; 0.1 M thiourea; $3x10^{-3}$ % ES	34
10	0.05 M $CdCl_2$; 0.1 M thiourea; $3x10^{-3}$ % ES	62
11	0.075 M $CdCl_2$; 0.1 M thiourea; $3x10^{-3}$ % ES	72

For the same samples (presented in Fig.2) the absorption spectra were recorded (Fig.3.). Absorption decreases linearly in the range 330-500 nm, than a suddenly decrees take places for about 500 nm. This behaviour made possible the spectrophotometrical method for thickness determination.

For samples presented in Fig.3. NIR reflection spectra have been recorded (Fig. 4). All the samples present a maximum for reflectance at approximately 1.2 μm. CdS nanostructured films deposited by spray pyrolysis have maximum NIR reflectance of about 30%. Those properties provide good solar control properties.

Fig. 4. Near IR reflection spectra for Cd S films deposited by spray pyrolysis

Conclusions. CdS nanometric films as thick as 34-72 nm, having the visible transmittance between 45-80 % and the near –IR reflectance of about 15-32 % were obtained by spray pyrolysis. The deposition conditions influence the thickness and the optical properties. Controlling the film thickness film with known optical properties could be preparated. The obtained results lead to the conclusion that CdS nanostructured films have solar control properties.

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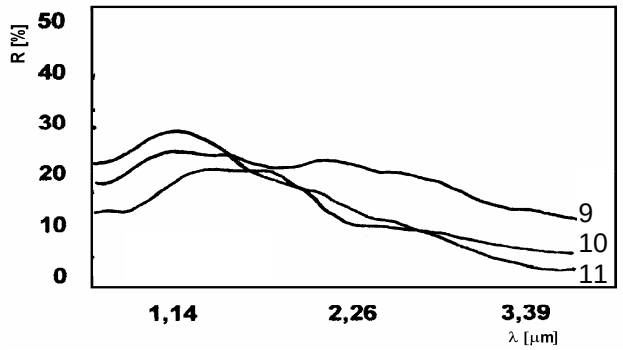

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