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OPTICAL PROPERTIES OF CdS-Cu_xS THIN FILMS DEPOSITED ON GLASS SUBSTRATE BY SPRAY PYROLYSIS

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Multi-layered, firmly adherent, optically clear CdS/Cu_xS films were deposited by spray pyrolysis on glass substrate. The glass/CdS/Cu_xS system was investigated. Firstly, CdS films were deposited using a solution containing $CdCl_2$ and thiourea. For Cu_xS films deposition the solution used consisted on $CuCl_2$ and thiourea. Multilayered films were also deposited. Mixed films of copper and cadmium sulfides were also deposited from solutions containing both copper and cadmium salts and thiourea on heated glass substrates, by spray pyrolysis. Visible transmission spectra were recorded for CdS/Cu_xS films. The film characteristics depend on the concentration and the molar ratio of cadmium and copper salts. These thin layers may be applied in solar control coatings, leading to important energy saving for air conditioning devices used for cars or other closed spaces.

Keywords: Mixed films, Thin films, Cadmium sulfide, Copper sulfide, Spray pyrolysis, VIS transmission, NIR reflection

1. Introduction

Thermo-reflecting thin-films used for solar control should have a transmittance ranged between 10 and 30% for the visible part of light radiation, *i.e.* in the range 400 – 700 nm (VIS), and a near infrared reflection (NIR, 0.7-2.5 μm) between 15 and 50 % [1-8].

Metallic sulphides thin-films with termo-reflecting properties can be obtained by chemical route and the most frequently used method according to literature is the chemical bath deposition (CBD) [1-7] followed by spray pyrolysis [10 – 14] and by other physical methods.

In a previous work, thermo-reflecting thin layers of PbS, CdS, Cu_xS and Au were obtained [9-15]. CuS thin films with the thickness in the range 15-62 nm, - deposited by spray pyrolysis – exhibit a VIS transmission of about 30 – 80% and, simultaneously, a NIR reflection of about 15-25% [13,14]. CdS films deposited in the same way with thickness from 39 to 63 nm presented a transmission of about 50 – 59.8 %, for neutral filter and a NIR reflection from 5 to 30 % [11].

In the present paper are reported the results of a study concerning the preparation of mixed CdS-Cu_xS thin layers by spray pyrolysis as well as their optical properties.

2. Experimental

Mixed sulphides thin films were deposited on heated glass substrate by spray pyrolysis from solutions containing cadmium and copper salts, thiourea (TU). In some particular cases, surfactants (polyethyleneglycole – PEG or ethersulphate), were used for higher uniformity of the films [12-14]. CdS-Cu_xS thin films were successfully deposited both as multi-layers (glass|CdS|CuS) and as mixed films. For multi-layers, on the heated glass substrate a layer of CdS was deposited first, and then on the surface of the deposited CdS a layer of CuS was deposited. For mixed CdS+CuS layers, solutions containing both Cd and Cu and a sulphur compound were used. The concentration of reagents and the number of deposited layers have been varied. In a preliminary stage of this work, the optimum flow-rate of spraying solution, the flow-rate of air and the distance between substrate and spraying nozzle have been determined. Furthermore, for these films the transmission in white light were measured by using a FEK-M photo-colorimeter, for $\lambda = 600$ nm – neutral filter - and for $\lambda = 540$ nm – green filter. The VIS transmission spectra were recorded with SPECORD UV-VIS and the reflection spectra with a UR-20 spectrophotometer (Carl-Zeiss, Jena) using usual standards and LiF prism.

3. Results and discussion

3.1. Preparation of cadmium and copper mixed sulphides

In order to obtain mixed cadmium and copper sulphides by spray pyrolysis, solutions containing both cadmium and copper salts, thiourea, as source of sulphur, and PEG as surfactant, were used. The reactions that take place during the deposition process were previously reported [10, 13, 14].

For obtaining (Cd-Cu)S mixed films, spray pyrolysis deposition on heated glass slides was used, maintaining a constant temperature of 400°C. The reaction between cadmium and copper salts with thiourea took place instantly on the heated glass surface. The flow rate of the solution was maintained in the range 20 – 24 ml/minute.

The deposition solution contains cadmium and copper chlorides and their molar ratio was varied between 1:1 and 4:1. The concentrations of cadmium chloride (5×10^{-2}M) and of thiourea (0.25M) were kept constant but the copper chloride concentration vas variable in the range $1.25 \times 10^{-2} - 5 \times 10^{-2}$ M. The PEG surfactant concentration was maintained at 0.1%. From this solution, two consecutive sulphide layers were deposited, the deposition time being 10 s for each layer. In table 1, the conditions for obtaining these layers are given together with the transmission T%, in white light (neutral filter) and in green light (green filter).

Table 1. Composition of the solutions used for deposition of mixed cadmium and copper sulphides by spray pyrolysis and transmission in films measured after deposition

Sample no.	Concentration				T neutral filter [%]	T green filter [%]	Qualitative remarks
	$CuCl_2x10^2$ [M/L]	$CdCl_2x10^2$ [M/L]	TU [M/L]	PEG [%]			
1	5	5	0.25	-	48	44.2	Optical clear film, yellow-brownish in transmission, yellow-purplish metallic in reflection
2	5	5	0.25	0.1	62	59.8	Macroscopic appearance of the film alike that of film no.1.
3	2.5	5	0.25	0.1	55.8	51	Optical clear film, yellow-brownish
4	1.25	5	0.25	0.1	54.2	49.2	Uniform, optical clear film, yellow-brownish clearer than the precedents.

3.2 Optical properties of thin films

All mixed (Cd-Cu)S thin films presented in table 1 are optically clear, with un appearance similar to that of CdS films. The presence of CuS changed the shade of the film, this exhibiting a brownish tint, with a particular aesthetic aspect. The VIS transmission of the film, measured with a neutral filter ranged in the interval 48 – 62 %, being intermediate between the transmission of pure CuS and CdS layers.

On the other hand, an influence of surfactant presence in the spraying solution may be noticed. Thus, sample 2, deposited in the presence of PEG, in the same conditions as sample 1 and looking very similar, exhibits a higher transmission both for neutral and green filter. It is well known that the surfactant presence in the solution leads to the obtaining of lower grain size for particles in the film. This fact has an evident influence on the optical properties of thin films obtained.

VIS transmission spectra of (Cd-Cu)S thin films, with the compensation of substrate effect, were recorded (fig. 1). As seen from fig. 1 the transmission of (Cd-Cu)S layers was intermediate between the transmissions of individual CdS and CuS layers. Since the transmission for wavelengths higher than 500 nm is greater than 60 % for all samples, this film is potentially useful for obtaining thermo-reflecting layers.

By selecting proper deposition conditions, thin films with different optical properties are obtained.

The NIR reflection spectrum only for the most uniform sample (sample 4) was recorded. Different aspects of the reflection spectra are noticeable. A flat peak for wavelengths higher than 0.2 μm appears, as compared to the reflection spectra of pure CdS or Cu_xC. The reflectance diminishes abruptly for wavelengths lower than 2.8 μm (fig. 2).

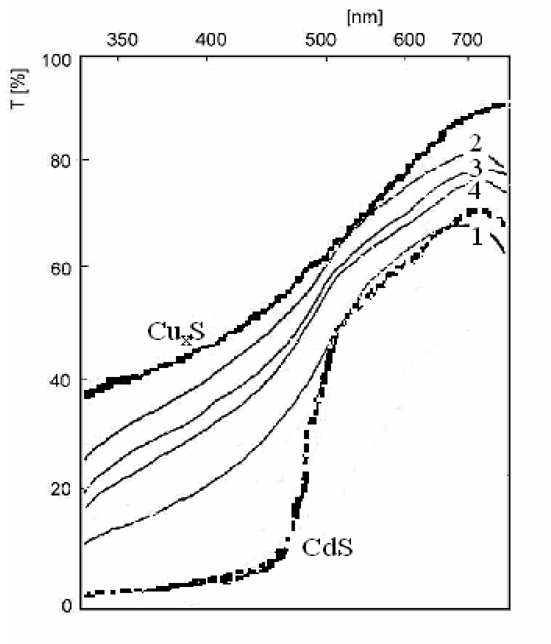

Fig. 1. Optical visible transmission spectra for CdS-Cu_xS mixed films (samples from table 1)

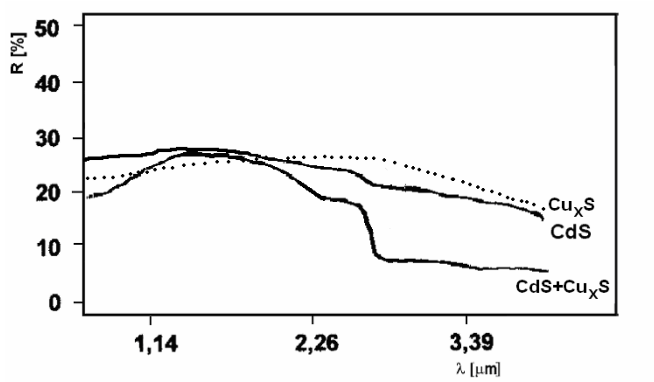

Fig. 2. NIR reflection spectra of some a mixed film of CdS and Cu_xS compared with pure CdS and Cu_xS films

3.2. Deposition of multilayer films (sandwich type films)

In the preparation of both multilayer thin films and the mixed films, as presented above, our goal was to improve the optical characteristics of these films as compared to each individual sulphide. The optimum deposition conditions for every sulphide were published elsewhere [9-14].

Thin films of CdS were deposited from equimolar cadmium chloride and thiourea 0.1M solutions. The range of concentration for solutions used in obtaining CuS thin films fall between $8.3 \times 10^{-2} - 1.67 \times 10^{-2}$ M for $CuCl_2$ and between $8.3 \times 10^{-2} - 8.3 \times 10^{-1}$M for thiourea. Cetyl-pyridinium bromide (CPB) - $C_{21}H_{38}NBr$ (cationic surfactant), and polyethyleneglicole (PEG-600) were used as surfactants.

Multilayer films with the structure glass |CdS|Cu_xS have been deposited. This type of layers consists of 1-3 layers of CdS and layers of Cu_xS. Optically clear sandwich type layers with a brown-yellow colour in transmission and in the same time purplish in reflection with a VIS transmission in the boundary of 35 – 58 % have been obtained.

When higher concentration was used for the precursor solutions, 0.167 M $CuCl_2$, 0.83 M thiourea and equimolar 0.1 M $CdCl_2$ – thiourea respectively, by applying 3 layers of each sulphide type, distinct color nuances on the two sides of glass slides could be obtained. For instance a pair of colours was purplish-yellow and metallic grey. In the later case the transmission was 24 – 26.5 % for visible light.

The preparation conditions and certain optical characteristics for CdS/Cu_xS multi-layers films are shown in table 2. From these data the conclusion that may be drawn is that the optimum condition for obtaining an optical clear CdS/Cu_xS thin film with a transmission of about 45 % and a purplish-metallic reflection, almost identical on both sides are: consecutive deposition of three CdS layers for 10 seconds each, from a solution with the composition: 0.1M $CdCl_2$, 0.1M thiourea, 0.1 % PEG-600 at 450°C followed by deposition of three Cu_xS layers from other solution: 1.67×10^{-2}M $CuCl_2$, 8.3×10^{-2}M thiourea and 1.67×10^{-2}% CPB.

Optically clear thin films with a transmission of 24 – 58 % and a brown-orange aspect in transmission but other different nuances in reflection on both sides (purplish-yellow and metallic grey) have been obtained in the conditions described above.

3.3. VIS transmission of multilayer films

In fig. 3 VIS transmission spectra for the representative sample of CuS/CdS are shown. The transmission for wavelengths higher than 500 nm is smaller than 60 % for samples 7 and 8.

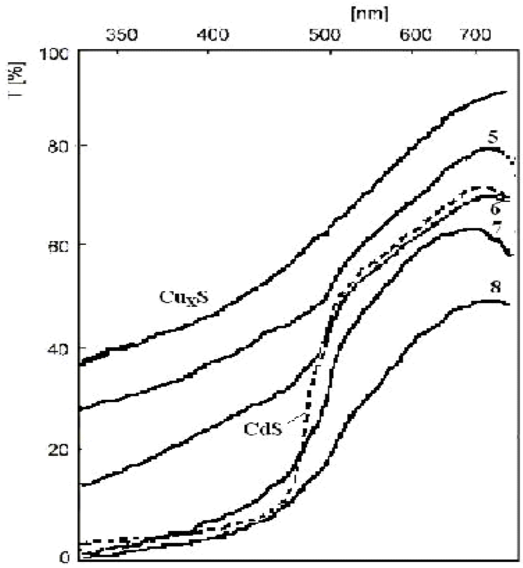

Fig. 3. Optical visible transmission spectra for multilayered Cu_xS/CdS films (samples from table 2)

The Cu_xS film presented in fig. 3 was obtained by the deposition of 3 layers from a solution containing 0.01 M $CuCl_2$, 0.01 M TU, 10^{-2} % CPB [12]. For comparison the spectra of a CdS film is also presented. The three-layered CdS film was obtained from a solution containing 0.075 M $CdCl_2$, 0.1 M thiourea; 3×10^{-3} % ether sulphate [11].

It may be seen that the spectra for samples 7 and 8 has a shape rather similar to that of CdS films but presents a lower transmission, for wavelengths over 480 nm. The outstanding aesthetic appearance is an important quality for their potential application on glass panels used in modern architecture and in manufacturing of glasses for automotive industry. We believe also that practical application of this films may be extended in manufacturing of photovoltaic cells [16– 19].

By varying the deposition conditions, thin films with different properties could be obtained and thus, by selecting the deposition parameters, the optical properties of the film can be controlled.

Table 2. The condition for obtaining sandwich type CdS/Cu_xS multi-layers films and their optical properties

Sample no.	Solution composition	Temp [°C]	Deposi-tion time	Layers no.	T [%]		Observations
					green [%]	neutral [%]	
5	0.1 M $CdCl_2$; 0.1 M TU $1.67x10^{-2}$ M $CuCl_2$; $8.3x10^{-2}$ M TU; 1.67 $x10^{-2}$ % CPB	450 350	5 3x10	1 3	52.5	58	Relatively uniform film optically clear, yellow – brownish in transmission. Purplish grey with metallic glare in reflection.
6	0.1 M $CdCl_2$; 0.1 M TU, 0.1 % PEG $1.67x10^{-2}$ M $CuCl_2$; $8.3x10^{-2}$ M TU; 3x $x10^{-2}$ % CPB	450 350	3x10 3x10	3 3	41	44.8	Uniform film optically clear, yellow – brownish in transmission. Specular purplish with metallic glare in reflection.
7	0.1 M $CdCl_2$; 0.1 M TU, 0.1 % PEG $1.67x10^{-1}$ M $CuCl_2$; $8.3x10^{-1}$ M TU; 1.67 $x10^{-2}$ % CPB	450 350	10 10	2x1	32	35.5	Uniform film optically clear, yellow – brownish in transmission. Specular purplish – orange in reflection
8	.1 M $CdCl_2$; 0.1 M TU, 0.1 % PEG $1.67x10^{-1}$ M $CuCl_2$; $8.3x10^{-1}$ M TU; 1.67 $x10^{-2}$ % CPB	450 350	3x10 3x10	3 3	20.5	26.5	Relatively uniform film optically clear, orange. In reflection the face containing CdS film is yellow with purplish shades, The other one metallic – grey diffuse. Purplish grey with metallic glare in reflection.

4. Conclusions

The optimal conditions for preparing mixed and multilayer cadmium and copper sulphide thin films by spray pyrolysis were established.

The mixed CdS-CuS thin films obtained in this paper present a good VIS transmission (26 – 52 %). By varying the composition of the deposition solutions and the number of applied layers, thin films with outstanding aesthetic appearance and various optical properties could be obtained. These thin layers may be applied in solar control coatings, leading to the achievement of important energy saving for air conditioning devices used for cars or other closed spaces.

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