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NANOSTRUCTURED CdS FILMS OBTAINED BY SPRAY PYROLYSIS. I. THE INFLUENCE OF DEPOSITION PARAMETERS ON THE FILM QUALITY

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ABSTRACT. A study regarding conditions for spray pyrolysis deposition of CdS nanostructured films on glass substrates, using aqueous solution containing $CdCl_2$, thiourea and surfactants, is presented. Dry air was used as carrier gas. Deposition parameters such as: substrate temperature, solution composition, gas and solution flow rates, deposition time, layer number, and distance between spraying nozzle and substrate were studied. The optimal conditions for obtaining compact, adherent, and optically clear, with good esthetical looking, thermoreflecting films were established. The film thickness was in the range 20-80 nm. The mechanism of CdS film deposition on glass substrates take places by thermal decomposition of the complexes $[Cd(H_2O)(SCN_2H_4)]Cl_2$ and $[Cd(SCN_2H_4)_2]Cl_2$. These films can be applied for solar control coatings.

Introduction. Progress in development, characterisation, and utilisation of advanced materials has been spectacular [1]. The preparation of nanostructured materials, by physical or chemical methods, [2] has become an important branch of advanced materials.

A reduction in particle size to the nanometer scale results in quantum size effects, at dimensions comparable to the length of the de Broglie electron.

Band-gape engineering by size and dimension quantization is important since it leads to mechanical, chemical, electrical, optical, magnetic, electro-optical properties, which are substantially different from those, observed for bulk material [1].

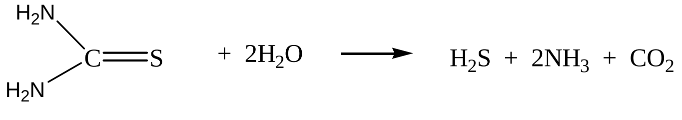
The study of metallic sulfide films deposited on transparent substrates was stimulated by their possible application to the manufacture of solar control coatings. Optical properties of PbS thin films chemical bath deposited have been studied comparatively with those of thin Au and Ni layers [3]. VIS transmission and near-IR reflection are comparable with those of metallic films. CuS [4] and PbS [5] films deposited on glass by spray pyrolysis are also suitable, for solar control coatings.

Spray pyrolysis was successfully used for CdS deposition on different substrates [6,7,8], on different conditions.

The studies of reaction between cadmium salts and thiourea, with forming of CdS films by this method were performed by IR spectroscopy [9-12].

Two possible mechanism for CdS film formation were proposed: hydrolytic [13] and by thermal decomposition of Cd (II)·thiourea complexes [10].

Hydrolysis mechanism could be explained after Bursuc at al by the following reactions [13]:



(1)

$$CdCl_2 + H_2S \longrightarrow CdS + 2HCl \qquad (2)$$

and after Semenov et al [10]:

The second proposed mechanism consists of thermal decomposition of complexes:$[Cd(SCN_2H_4)_2]Cl_2$; $CdCl_2 \cdot [Cd(SCN_2H_4)]Cl_2$ and $Cd(H_2O)(SCN_2H_4)]Cl_2$ [11].

By fast heating at a temperature higher than 210°C, $[Cd(SCN_2H_4)_2]Cl_2$ decomposes after the following reaction:

$$[Cd(SCN_2H_4)_2]Cl_2 \xrightarrow{3O_2} CdS + 2NH_4Cl + 2CO_2 + SO_2 + N_2 \quad (5)$$

The aim of this paper is to establish the best condition for spray pyrolysis

$$(H_2N)_2C{=}S \xrightarrow{+\ 2H_2O} H_2S\uparrow + H_2CN_2 \xrightarrow[80^o]{+\ 2H_2O} (NH)_2CO \quad (3)$$

$$Cd^{2+} + S^{2-} \longrightarrow CdS \quad (4)$$

deposition of 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. The later dramatically influences the film quality, limiting the grain growth. For the first time CdS nanostructured films were obtained in the presence of surfactant.

Experimental. The experimental set-up for spray pyrolysis deposition used by us also for CuS [4] and PbS [5], nanometric films consists of a reaction chamber foreseen to its lower part with a plate heated by electrical resistance. On the plate, the substrate is placed. Substrate temperature is measured with a thermocouple. Above the substrate at variable distances (10-30 cm) the glass-spraying nozzle is fixed. The solution is sprayed (from a reservoir) by means of the carrier gas, incidently to the substrate. Standard commercial glass slides, (75x25x1mm^3), were used as substrates. The spraying solution consists of an aqueous solution of 0,01–0,1 M $CdCl_2$ and 0,01–0,1 M thiourea and ES. The reagents were analytical grade, except ES which is a technical anionic surfactant (made by "Intreprinderea de Detergenți" Timişoara Romania). The substrate temperature was 200-500^{o}C, the gas (dry air used as carrier gas) flow rate 40-70 ml/s. The spraying time vary between 10-30 seconds and the layer number between 1-5. The thickness of the film was determined by microweighting and spectrophotometrically with a photocolorimeter FEK-M (USSR).

Results and discussion. The quality of the films depends on many factors such as: substrate temperature, distance between spraying nozzle and substrate, deposition time, number of deposited layers, reagent concentration, and the liquid flow rate. After some preliminary studies regarding deposition condition, working with aqueous solution containing $Cd(CH_3COO)_2$ or $CdCl_2$ in the presence of thiourea, in the same conditions of concentration, $CdCl_2$ was selected as cadmium salt taking into consideration the uniformity of obtained film.

Using spraying solutions containing, 0,1 M $CdCl_2$ and 0,1M thiourea, ***the influence of the deposition time*** on the thickness and the quality of the obtained film was studied. The thickness of the film increases linearly with the deposition time (fig. 1). Increasing the deposition time to 30 seconds the quality of the film worsen. The film presents spots and thickness variation. During the deposition process, the substrate temperature decreases, the reaction isn’t complete. Secondary reaction products are trapped in to the film.

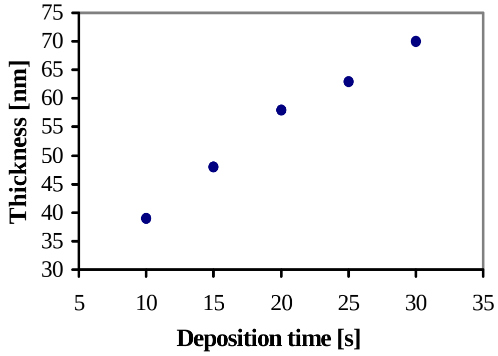


Fig. 1. Influence of the deposition time on the thickness of the film

The thickness of the films has been determined through the spectrometrical method using an FEK-M spectrometer with blue filter. The calibration curve (fig.2) has been obtained on samples with known thickness, microgravimetrically determined. For thickness determination the following relationship have been established: $h=k\cdot A$ [nm] where $k = 10^2$ is a constant, and A is the absorbance.

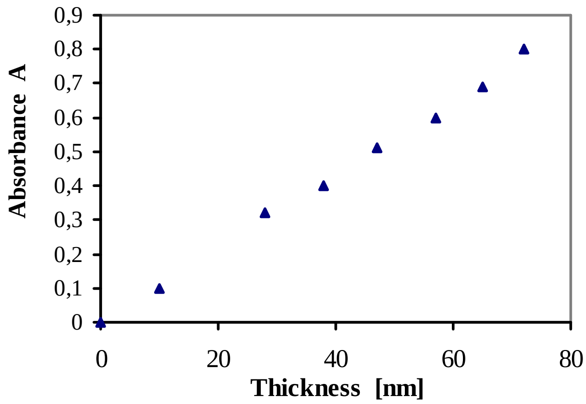


Fig 2. Calibration curve on the spectrophotometric determination of CdS nanometric film

Deposition ***temperature*** influence was studied for the range 150-500°C. The best results (the most uniform films) were obtained at 450°C.

The influence of the reagent concentration was studied using solutions containing $CdCl_2$, and thiourea in equimolar ratio in the range 0,01 - 0,1 M and $3x10^{-3}$ % ES 12-14. Three layers were deposited, 10 seconds for each layer, solution-spraying flow rate 20 ml/s, the distance nozzle-substrate 20 cm and substrate temperature 450^0C. Yellow, uniform, adherent, optically clear films, which thickness was between 15-54 nm were obtained.

Variation of film thickness as a function of the concentration of the spraying solution is presented in fig.3 and 4. For equimolar ratio of reagents when $[Cd(SCN_2H_4)_2]Cl_2$ are formed (fig.3) a linear increases of the film thickness with the reagent concentration take places.

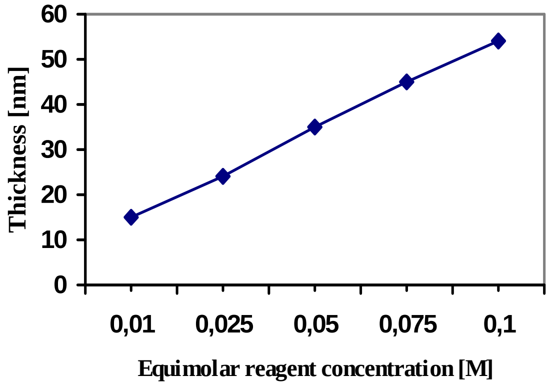


Fig. 3. Variation of CdS film thickness as a function of equimolar reagent concentration

For equimolar reagent concentration the best results were obtained for solution concentration less than 0,025 M $CdCl_2$ and thiourea. The films are uniform and perfectly clear when the thickness is less than 54 nm. All of the films was good optical properties. Using diluted solutions the deposition of more than 3 layers were necessary.

Varying thiourea concentration, at constant content of $CdCl_2$ (0,025 M) the conditions for $Cd(SCN_2H_4)_2]Cl_2$ complex formation was created (fig. 4. Curve 1). By spraying aqueous solutions on heated substrate, in the first stage, the deposition of a thin solid film of this complex take places [10,14]. In the second stage, complexes decompose with the formation of CdS film (relationship 5). The CdS film thickness increases linearly with the increasing of thiourea concentration.

Keeping thiourea concentration constant (0,1 M) and varying $CdCl_2$ concentration (fig. 4. Curve 2), film thickness increases till thiourea concentration reach 0,05 M, (thiourea: $CdCl_2$ 2:1 molar ratio) when formation of $[Cd(SCN_2H_4)_2]Cl_2$ complex take places, and than when that ratio Cd(II):thiourea decreases the thickness remain unchanged. That means the reaction rate remains constant because the concentration of the complexes is constant.

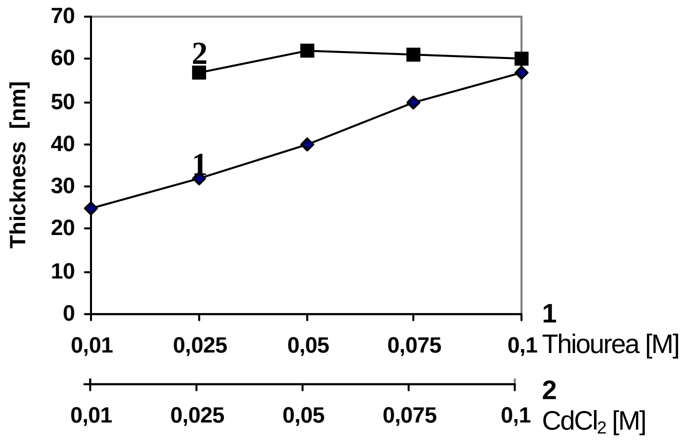


Fig. 4. Variation of CdS film thickness as a function of reagent concentration

For obtaining optically clear, uniform films with proper thickness multi-layered (2-5 layer) films were deposited from equimolar ratio $CdCl_2$-thiourea 0,025 M solutions, when $[Cd(H_2O)(SCN_2H_4)]Cl_2$ is the intermediate reaction product. Good uniform films were obtained also with solutions containing 0,05 M $CdCl_2$, 0,1 M thiourea from $[Cd(SCN_2H_4)_2]Cl_2$. The best results were obtained for 3 layered film.

Conclusions. A study regarding conditions for spray pyrolysis deposition of CdS nanostructured films on glass substrates using aqueous solution containing $CdCl_2$, thiourea and ES as surfactant was presented. The thickness of the film increases linearly with the deposition time in the range 10-30 s. A relationship between absorbance value and thickness has been established. Regarding deposition temperature, the most uniform films were obtained at 450°C. Solution concentration influences the film formation and the quality of the film. The best results were obtained for solution containing less than 0,025 M $CdCl_2$ and thiourea in equimolar ratio, in the presence of $3\cdot10^{-3}$ ES, when solution-spraying rate was 20 ml/min, the distance nozzle-substrate 20 cm. Uniform optically clear multi-layered films were obtained also using solutions containing 0,05 M $CdCl_2$, 0,1 M thiourea in the presence of ES. In the both cases the films are uniform and perfectly clear, when the thickness is less than 54 nm. All of the obtained films have good optical properties. Using diluted solutions the deposition of more than 3 layers were necessary. The film thickness was in the range 20-80 nm. These films can be applied to the manufacture of solar control coatings.

The mechanism of CdS film deposition on glass substrates take places by thermal decomposition of the complexes $[Cd(H_2O)(SCN_2H_4)]Cl_2$ and $[Cd(SCN_2H_4)_2]Cl_2$.

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