

## THE INFLUENCE OF CADMIUM SALT ANION ON THE GROWTH MECHANISM AND ON THE PHYSICAL PROPERTIES OF CdS THIN FILMS

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Cadmium sulphide films were prepared by Chemical Bath Deposition (CBD) technique from  $\text{CdCl}_2$ ,  $\text{CdSO}_4$ ,  $\text{Cd}(\text{CH}_3\text{COO})_2$  respectively, as cadmium precursor salts, and thiourea in ammoniacal medium. In this paper we study the changes in the morphology and properties of the films prepared from different cadmium salts, although the starting reaction parameters as concentration of the reactants, pH (denoted as  $\text{pH}_i$ ), temperature, and time of reaction for all precursor cadmium salts are identical. It is proposed that, during the deposition process, depending upon the anion type of cadmium salt the pH of reaction mixture decrease with different rates. The  $\text{pH}_i$  decreases in the deposition bath could allow the change of the layers growth mechanism and therefore the change in the morphology and properties of the films. Above a certain value of starting pH ( $\text{pH}_i > 12.5$ ), the pH decrease did not affect the growth mechanism and properties of the layers. The structure and morphology of the films were investigated by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray diffraction (XRD). Also the optical, electrical and photoelectrical characteristics of the layers and their dependence on films morphology were presented. These studies have allowed us to establish the optimum conditions for fabrication of quality CdS films using  $\text{CdCl}_2$ ,  $\text{CdSO}_4$ , or  $\text{Cd}(\text{CH}_3\text{COO})_2$  as cadmium precursor salts.

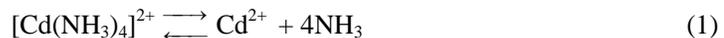
*Keywords:* CdS thin films, Chemical Bath Deposition, Growth mechanism

### 1. Introduction

CdS under thin film form is well known as an opto-electronic material for solar cells, photo-detectors, and other optoelectronic devices [1-5].

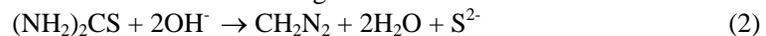
The chemical bath deposition (CBD) is a low-cost technique and appears to be well suited for the manufacture of thin CdS films. The deposition bath contains the cadmium salt and thiourea solution in ammoniacal medium. The presence of ammonia solution in the reaction mixture serves the purpose of providing the  $\text{OH}^-$  ions required for the hydrolysis of thiourea that gives  $\text{S}^{2-}$  and of controlling the amount of  $\text{Cd}^{2+}$  ions in the bath through the creation of the tetraammine complex. The method consists in a slow generation of the  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  ions by decomposition of  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  complex ions and thiourea hydrolysis in alkaline medium, followed by CdS synthesis. The chemical reactions leading to the layer formation may be represented as:

1) the tetraammine complex ion decomposition:



-the instability constant of  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ :  $K_i = 7.56 \cdot 10^{-8}$

2) the hydrolysis of thiourea in alkaline solution with  $\text{S}^{2-}$  ions generation:



This reaction consumes hydroxide ions tending to decrease the starting pH value of the reaction mixture.

3) the CdS synthesis:



When the ionic product of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  exceeds the solubility product of  $\text{CdS}^{16}$  ( $K_s = 1.4 \cdot 10^{-29}$ ) one obtains  $\text{CdS}$  precipitate either in the bulk of the solution, with the formation of colloids, or at the surface of the substrate immersed in the solution, leading to the formation of the layer.

The kinetics studies [5-9] of CBD technique have established the interdependencies among reaction parameters (pH, concentration of the various reactants, temperature), layer growth mechanisms and layer structure. The layer deposition process can be subdivided into three periods [6-8]: 1) induction period, with nucleation center formation, 2) the layer growth period by "ion by ion" mechanism, 3) the layer growth period by "cluster by cluster" mechanism.

The "ion by ion" layer growth takes place by successive ions adsorption on the substrate, followed by chemical reaction between adsorbed species, resulting a very adherent specularly reflecting layer. This process is enhanced by a hydrophilic surface that preferentially adsorbs  $\text{OH}^-$  ions from aqueous alkaline solutions, resulting in formation of  $\text{Cd}(\text{OH})_2$  nuclei on the substrate [9,11]. The  $\text{Cd}(\text{OH})_2$  is gradually transformed in  $\text{CdS}$ .

In the CBD process there are involved both the heterogen precipitation reaction on the substrate surface and homogeneous precipitation reaction in the bulk solution respectively [7,8]. As a result of the homogeneous precipitation reaction in the bulk solution,  $\text{CdS}$  colloidal or cluster aggregates are produced. Some of the clusters adhere on the substrate over the specularly reflecting layer and form porous less adherent overlayer, as a result of a "cluster by cluster" growth mechanism. It is proved that this latter layer includes electrolyte from the deposition bath [6-8,12]. The "cluster by cluster" growth mechanism is characteristic either to a long time reaction or to a fast  $\text{S}^{2-}$  and  $\text{Cd}^{2+}$  ions generation. The non-adherent clusters are deposited on the bottom of the reaction beaker as precipitate.

Relative to the influence of anion of cadmium salt on layer growth kinetics it was established [8,12] that the deposition rate decreases with the cadmium salt anion type changing in the following sequence:  $\text{Cl}^- > \text{CH}_3\text{COO}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{I}^-$ .

We observed that the  $\text{CdS}$  layers prepared from different cadmium salts in the same preparation conditions lead to the layers with different morphology and properties [13].

This work intends to establish the influence of the anions of cadmium salt on the layer growing mechanism and on its properties, taking into account the pH changing in the reaction bath during deposition process.

## 2. Experimental

Four sets of samples were prepared from reaction mixtures with starting pH (denoted  $\text{pH}_i$ ) 10, 11, 12, and  $> 12.5$ , for each cadmium salts used as  $\text{Cd}^{2+}$  ions precursor:  $\text{CdCl}_2$ ,  $\text{Cd}(\text{CH}_3\text{COO})_2$  and  $\text{CdSO}_4$ . The  $\text{pH}_i$  value of the reaction mixture have been controlled with "Mettler Toledo" pH-meter and adjusted with various volumes of 25 %  $\text{NH}_4\text{OH}$ .

All the reaction parameters as: the concentration and the volumes (except ammonia used for pH adjustment) of the reactants, the temperature, the reaction time for all the experiments were identical.

The samples preparation has been performed in a closed reactor beaker to avoid ammonia evaporation. The reaction beaker has been placed in a thermostat to keep a constant temperature during preparation. The  $\text{CdS}$  layers were deposited onto glass substrates of  $10 \times 6 \times 0.5 \text{ mm}^3$  which have been chemically cleaned, then rinsed with bidistilled water and dried.

The starting concentration of the reactants were: cadmium salt solutions 0.1M, thiourea 1M and  $\text{NH}_4\text{OH}$  25%. The  $\text{NH}_4\text{OH}$  solution was added first to the cadmium salt solution to form the cadmium-ammonia complexes followed by addition of the thiourea solution. After pH adjustment of the reaction mixture, the glass substrates were immersed vertically in the beaker. This was placed in the thermostat at  $70^\circ\text{C}$  for half an hour and afterwards the substrates were taken out, washed with distilled water and dried.

We marked following observations about layer formation at different  $\text{pH}_i$  from different cadmium salts:

- (a) For  $\text{pH}_i = 10$  only layers from the mixture containing  $\text{Cd}(\text{CH}_3\text{COO})_2$  have been deposited. The deposited layers were porous and have not a good adherence. No layer has been observed on the substrate when  $\text{CdCl}_2$  and  $\text{CdSO}_4$  were used as cadmium precursors.
- (b) For  $\text{pH}_i = 11$  the layers were deposited only from the mixtures containing  $\text{CdCl}_2$  and  $\text{Cd}(\text{CH}_3\text{COOH})_2$ , respectively. No layer was deposited from the mixture containing  $\text{CdSO}_4$ . The layers grown from cadmium acetate are adherent and specularly reflecting, whereas the layers grown from  $\text{CdCl}_2$  are adherent but more porous.
- (c) For  $\text{pH}_i = 12$  the layers were deposited from all three precursor salts, but with different qualities of the films. The layers prepared from acetate are adherent and specularly reflecting, while from  $\text{CdCl}_2$  are adherent and porous. The layers deposited from  $\text{CdSO}_4$  were roughly and had poor adherence.
- (d) All the layers prepared at  $\text{pH}_i > 12.5$  from all three cadmium precursors salts were adherent with specularly reflecting aspect.

### 3. Results and discussion

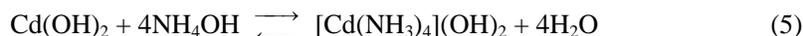
To explain the differences among the layers obtained in our experiments we must consider the chemical aspects of the deposition process.

The preparation by CBD method, developed in alkaline solution, requires thiourea hydrolysis reaction (eq.2). In the case of CdS preparation,  $\text{NH}_4\text{OH}$  acts as base and complexing agent for cadmium ions. The formation of the complex ions gets through the  $\text{Cd}(\text{OH})_2$  precipitation:



where:  $\text{A} = \text{Cl}^-$ ;  $\text{CH}_3\text{COO}^-$  and  $2\text{A} = \text{SO}_4^{2-}$

The white  $\text{Cd}(\text{OH})_2$  precipitate is soluble in ammonia excess with formation of complex ion  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ .



The precipitation [14,15] of  $\text{Cd}(\text{OH})_2$  starts at  $\text{pH} \sim 8$  and its dissolution in ammonia excess at  $\text{pH} \sim 11$ .

According to eq.(4) the reaction between cadmium salt and ammonia produces ammonium salts:  $\text{NH}_4\text{Cl}$  when uses  $\text{CdCl}_2$  as precursor,  $\text{CH}_3\text{COONH}_4$ , when uses  $\text{Cd}(\text{CH}_3\text{COO})_2$  and  $(\text{NH}_4)_2\text{SO}_4$  when uses  $\text{Cd}(\text{SO}_4)_2$ . The presence of ammonium salts and ammonium hydroxide in the reaction solution leads to the alkaline buffer formation. The pH value of the alkaline buffer can be obtained by following relation [15, 17]:

$$\text{pH} = -\lg P_{\text{H}_2\text{O}} - \lg c_s + \lg K_b + \lg c_b \quad (6)$$

where:  $P_{\text{H}_2\text{O}}$  - ion product constant of water,  $c_b$  - base concentration,  $c_s$  - salt concentration, and  $K_b$  - dissociation constant of base.

In agreement with equation (6), pH value of alkaline buffer solution depends on the temperature (as  $P_{\text{H}_2\text{O}}$  depend of temperature), and salt and base concentrations ratio. If salt concentration  $c_s$  increases or base concentration  $c_b$  decreases the pH of buffer decreases.

These remarks about buffer formation in the deposition solution explain our experimental results.

*a. The pH changes in the reaction mixture when precursor cadmium salt are  $\text{CdCl}_2$  or  $\text{CdSO}_4$*

Two aspects must be considered to describe the preparation of the CdS layers from  $\text{CdCl}_2$  and  $\text{CdSO}_4$ ; the different behaviour of  $\text{CdCl}_2$  and  $\text{CdSO}_4$  solution and the decrease of pH during deposition processes.

In contrast with  $\text{CdSO}_4$ ,  $\text{CdCl}_2$  form selfcomplexes by dissolution in water<sup>15</sup>:



with instability constant for  $[\text{CdCl}_4]^{2-}$ ,  $K_i = 9 \cdot 10^{-3}$ .

Due to the presence of  $[\text{CdCl}_4]^{2-}$  complex, the concentrations of  $\text{Cd}^{2+}$  and  $\text{Cl}^-$  ions are small or at short reaction time and will gradually increase by  $[\text{CdCl}_4]^{2-}$  decomposition with the formation of  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  and  $\text{NH}_4\text{Cl}$  according to eq. (1) and (2).

The  $\text{CdSO}_4$  solution does not form selfcomplexes, that is at a short reaction time the available  $\text{Cd}^{2+}$  and  $\text{SO}_4^{2-}$  ions according to eq. (1) and (2) rapidly form  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  and  $\text{NH}_4\text{SO}_4$ .

As a result of ammonium salts accumulation in the deposition solution, the buffer systems  $\text{NH}_4\text{OH} - \text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH} - \text{NH}_4\text{SO}_4$ , are formed. Their pH value depends on salt and base concentration ratio.

The analysis of sample preparation for each cadmium precursor is carried out in terms of  $\text{pH}_i$  value and pH modification during deposition process:

a)  $\text{pH}_i = 10$

The starting mixture contains small quantities of  $\text{Cd}(\text{OH})_2$  particles (eq.1), because the total dissolution of  $\text{Cd}(\text{OH})_2$  takes place at  $\text{pH} \sim 11$ .

During deposition process, the mixture pH decreases as a result of  $\text{OH}^-$  consumption for thiourea decomposition and accumulation of ammonium salts in deposition solution (see eq.2 and 4). In these conditions the  $\text{Cd}(\text{OH})_2$  particles give rise to the formation of more nucleation centres, involving a homogeneous  $\text{CdS}$  precipitation in the bulk solution. In conclusion no layers on the substrates are obtained from  $\text{CdSO}_4$  and  $\text{CdCl}_2$  mixtures at  $\text{pH}_i = 10$ .

b)  $\text{pH}_i = 11$

The starting mixture is clear for both cadmium salts. How seen above, the more rapid increase of ammonium salt and  $\text{Cd}^{2+}$  ion concentrations for  $\text{CdSO}_4$  mixture (compared with  $\text{CdCl}_2$  mixture) leads to a more rapid decrease of pH. Even at a short reaction time, in case of the mixture containing  $\text{CdSO}_4$  the pH rapidly decreases below 11 and  $\text{Cd}(\text{OH})_2$  precipitation starts in the bulk solution leading to homogeneous precipitation. No layers on the substrates are obtained.

For mixture containing  $\text{CdCl}_2$ , at a short reaction time, solution contains small  $\text{Cd}^{2+}$  and  $\text{Cl}^-$  ion concentrations and conditions for "ion by ion" growth mechanism are achieved. The  $\text{pH}_i$  did not considerably decrease and very thin  $\text{CdS}$  films precipitates on glass substrate. The obtained films are adherent and specularly reflecting. During reaction time, as result of slower pH decrease, in the bulk deposition solution the  $\text{Cd}(\text{OH})_2$  colloidal particles are formed followed by their conversion into  $\text{CdS}$ . This process leads to the change of the growth mechanism. Part of colloids created in the bulk solution diffuses to the substrate and forms the porous  $\text{CdS}$  layer by growth mechanism called "cluster by cluster" [6,7]. Large part of colloids is deposited to the bottom of the reaction bath. Finally, the  $\text{CdS}$  films obtained from  $\text{CdCl}_2$  are formed by two superimposed layers: an inner adherent, very thin, layer grown by "ion by ion" mechanism and an outer rough and less adherent layer grown by "cluster by cluster" mechanism (duplex layer structure).

c)  $\text{pH}_i = 12$

The duplex layer structures were obtained in these conditions for both precursor cadmium salts. The above discussion about pH change in the chemical deposition bath is valid with the remark that the adherent inner layer grown by "ion by ion" mechanism is very thin and the rough, outer layer is less adherent for  $\text{CdSO}_4$  bath.

d)  $\text{pH}_i > 12.5$

The starting mixtures were clear for all cadmium precursor salts with cadmium ions in complex form. The growth mechanism was only "ion by ion" during the deposition reaction. During reaction, the pH decrease did not allow the change of growth mechanism. The obtained layers were adherent and specularly reflecting for both salts.

*b. The pH change in the reaction mixture when the  $\text{Cd}(\text{CH}_3\text{COO})_2$  is the precursor cadmium salt*

Using as starting salt  $\text{Cd}(\text{CH}_3\text{COO})_2$ , the  $\text{CH}_3\text{COONH}_4$  is formed in the mixture in accordance with eq.(1).

The  $\text{NH}_4\text{OH} - \text{CH}_3\text{COONH}_4$  system did not form a buffer. By hydrolysis of  $\text{CH}_3\text{COONH}_4$  a weak acid ( $\text{CH}_3\text{COOH}$  with  $K_a = 1.75 \cdot 10^{-5}$ ) and a weak base ( $\text{NH}_4\text{OH}$  with  $K_b = 1.79 \cdot 10^{-5}$ ) are formed. The very close value of dissociation constant for acid and base confer to the solution neutral pH. [15]

This means that the starting pH value is not changed with  $\text{CH}_3\text{COONH}_4$  accumulation in the deposition bath. The pH value decreases gradually only due to  $\text{OH}^-$  consume by thiourea hydrolysis.

Consequently, the duplex layer structures were formed at  $\text{pH}_i = 10$ , and the specularly reflecting adherent layers at  $\text{pH}_i \geq 11$ .

*c. Morphology and structure of the layers*

For morphology and structure studies two sets of samples were investigated:

a) samples prepared at  $\text{pH}_i \cong 12$ , as a minimum  $\text{pH}_i$  for layer formation from  $\text{CdSO}_4$ ; they have been noted as Fa (from bath with  $\text{Cd}(\text{CH}_3\text{COO})_2$ ), Fc (from bath with  $\text{CdCl}_2$ ), and Fs (from bath with  $\text{CdSO}_4$ ),

b) samples prepared at  $\text{pH}_i \geq 12.5$ , as the  $\text{pH}_i$  value for adherent, specularly reflecting layers precipitation from all cadmium salts used. They have been noted as Fa' (from bath with  $\text{Cd}(\text{CH}_3\text{COO})_2$ ), Fc' (from bath with  $\text{CdCl}_2$ ), and Fs' (from bath with  $\text{CdSO}_4$ ). The  $\text{pH}_i$  value for each set of samples are presented in Table 1

Table 1. The  $\text{pH}_i$  values for the CdS samples deposited from different cadmium salts as cadmium precursors and used for physical properties analysis.

Samples	Cadmium precursor salt	$\text{pH}_i$
Fa	$\text{Cd}(\text{CH}_3\text{COO})_2$	12.04
Fc	$\text{CdCl}_2$	12.02
Fs	$\text{CdSO}_4$	12.03
Fa'	$\text{Cd}(\text{CH}_3\text{COO})_2$	12.50
Fc'	$\text{CdCl}_2$	12.70
Fs'	$\text{CdSO}_4$	12.95

The SEM studies were performed with a PHILIPS 515 electron microscope and the X-ray diffraction with an HZG4A diffractometer.

SEM photographs of the Fa samples reveal the continuous, homogeneous, layer with nanometer crystallites size (Fig. 1a). The dominance of the hexagonal phase (80%) was confirmed by XRD-analysis on Fa layers (Fig. 2). These layers deposited at  $\text{pH}_i \cong 12$  were grown by "ion by ion" mechanism.

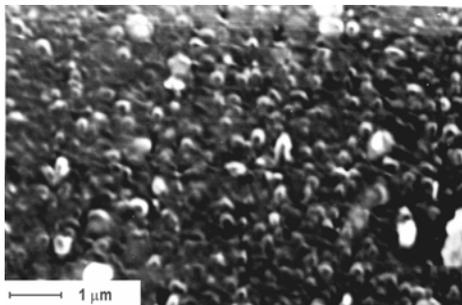


Fig. 1a. SEM photograph of the Fa sample (prepared from cadmium acetate at  $\text{pH}_i \cong 12$ ). The magnification is 10,000.

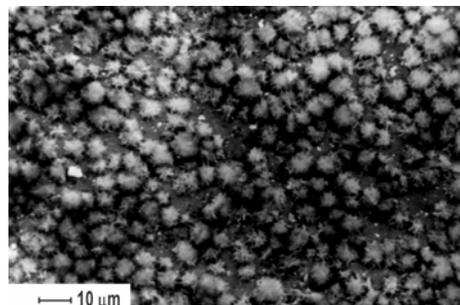


Fig. 1b. SEM photograph of the Fc sample (prepared from cadmium chloride at  $\text{pH}_i \cong 12$ ). The magnification is 500.

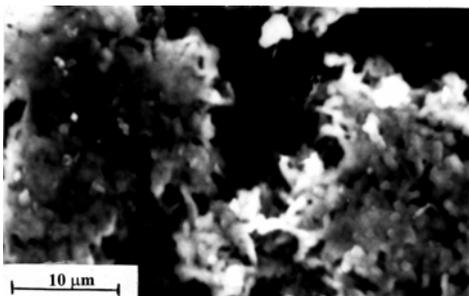


Fig. 1c. SEM photograph of the Fs sample (prepared from cadmium sulphate at  $\text{pH}_i \cong 12$ ). The magnification is 2,500.

The SEM photos on Fc and Fs samples (Fig. 1b and Fig. 1c), show that the morphology of the CdS deposited from  $\text{CdCl}_2$  and  $\text{CdSO}_4$  is different from the morphology of the films deposited from  $\text{Cd}(\text{CH}_3\text{COO})_2$ , in consequence of change of the growth mechanism. These layers present duplex layer structure: 1) a very thin and adherent layer, formed by very small (nanometric size) crystallites grown by “ion by ion” mechanism; 2) a thicker and porous layer, formed by larger crystallites grown by “cluster by cluster” mechanism.

X-ray diffraction performed on Fc and Fs samples has put into evidence the existence of a mixture of cubic and hexagonal phases (Fig. 2). Moreover, X-ray spectrum of the Fs layers, with large crystallites in the outer layer, shows the existence of the  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  (noted X in Fig. 2) remained from the deposition solution.

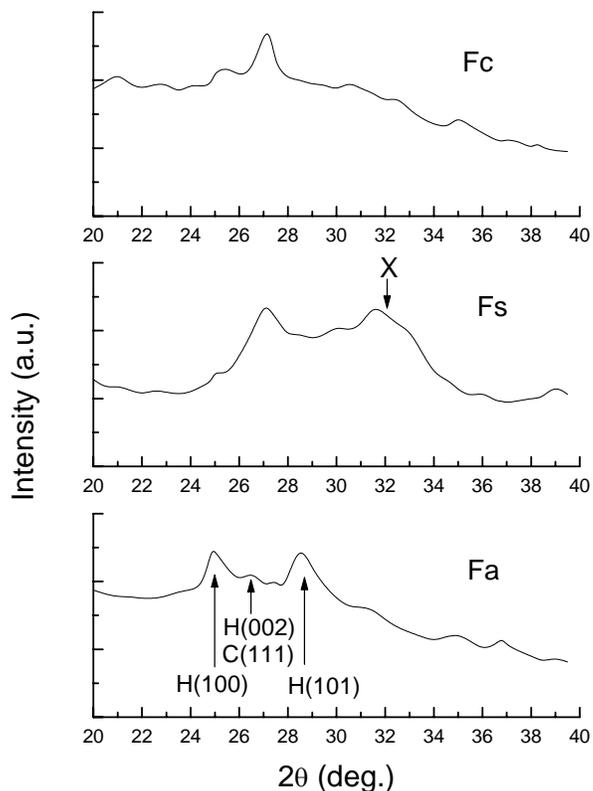


Fig. 2. XRD pattern for CdS films deposited from: cadmium chloride (Fc); cadmium acetate (Fa); cadmium sulphate (Fs). The cross indicates the peak attributed to  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ .

The layers obtained for  $\text{pH}_i > 12.5$  have been grown only by “ion by ion” mechanism. The layers show a compact and specularly reflecting aspect for all the samples. The AFM (ATOMIC FORCE MICROSCOPY) studies on Fa', Fc', Fs' layers (Fig. 3 a, b, c) show some differences between average dimension of crystallites: for Fa' 80 nm, Fc' 100nm, Fs' 160 nm respectively. Roughness analysis on  $5 \times 5 \mu\text{m}^2$  surface exhibit: 12.4 nm for Fa', 13.9nm for Fc' and 17 nm for Fs' layers respectively.

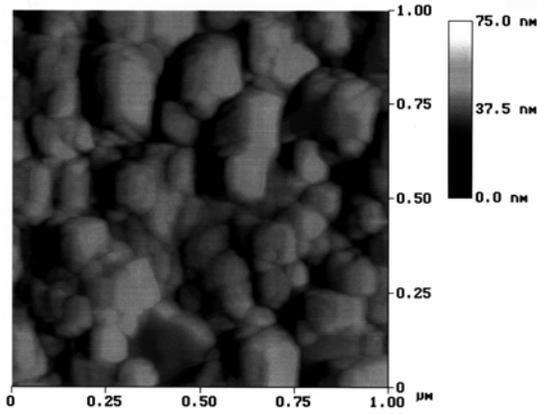


Fig. 3a. AFM image of Fa' film deposited from cadmium acetate at  $\text{pH}_i > 12.5$ .

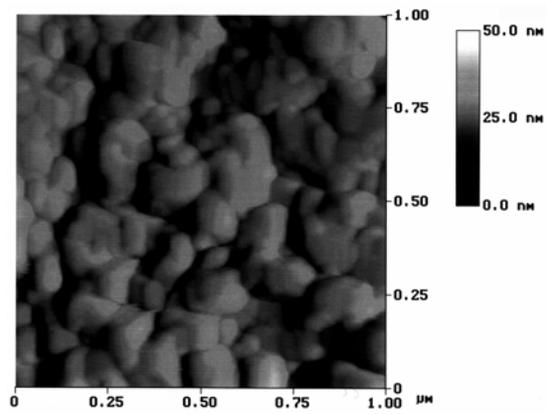


Fig.3b. AFM image of Fc' film deposited from cadmium chloride at  $\text{pH}_i > 12.5$ .

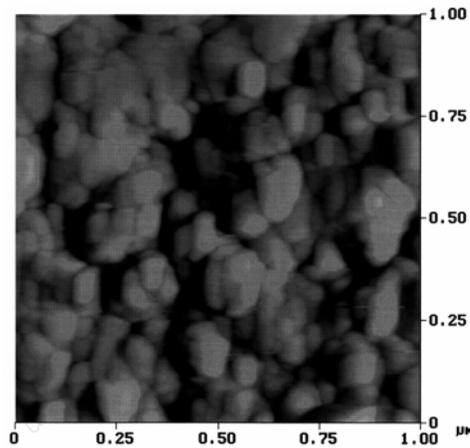


Fig. 3c. AFM image of Fs' film deposited from cadmium sulphate at  $\text{pH}_i > 12.5$ .

*d. Optical characterisation*

The optical transmission measurements were performed with a UV/VIS/NIR PERKIN ELMER spectrophotometer. Fig. 4 shows the transmission curves of Fa, Fc, Fs, layers. A poor optical transmission can be observed for Fc layers at wavelengths larger than those corresponding to the absorption edge, due to the overgrown crystallites. The optical transmission of Fs layers is rather weak, up to 40%, while the best transmission is obtained for the Fa layers.

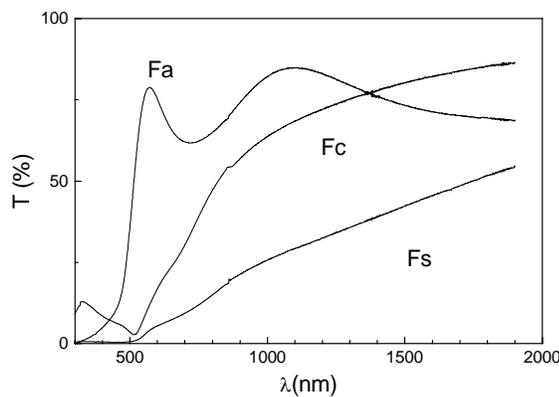


Fig. 4. Optical transmission spectra of CdS films deposited from: cadmium acetate (Fa); cadmium chloride (Fc); cadmium sulphate (Fs) at  $\text{pH}_i \cong 12$ .

The improvement of optical transmission was observed for Fa', Fc', Fs' layers (Fig. 5), due to the absence of the overgrown crystallites and due to the structural similitude between the samples.

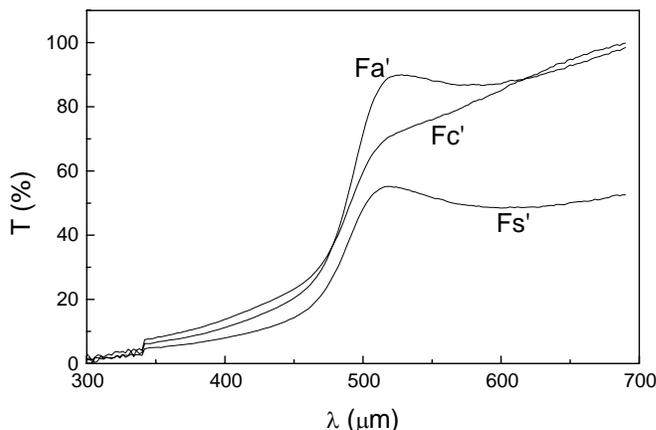


Fig. 5. Optical transmission spectra of CdS films deposited from: cadmium acetate (Fa'); cadmium chloride (Fc'); cadmium sulphide (Fs').

#### e. Electrical and photoelectrical characterisation

For electrical and photoconductive measurements silver printed electrodes were used, with the sensitive area of  $1 \times 6 \text{ mm}^2$  between electrodes.

The current flowing through the CdS layer was measured with a KEITHLEY 642 electrometer or with a KEITHLEY 2000 multimeter. The voltage applied on the film was supplied by a KEITHLEY 241 power source. The irradiation was performed with SYLVANIA lamp and the intensity of the incident light on the samples was 3000 lx. All the measurements were performed at 300<sup>0</sup> K. The small conductivity of CdS layers ( $\sigma = 10^{-6} - 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ ) indicates that these layers are almost intrinsic<sup>10,18</sup>. The low value of the dark conductivity is a consequence of the fact that the CdS layers deposited by CBD are nearly stoichiometric<sup>19,20</sup>. It is expected that in such situation the concentration of photogenerated carriers is much higher than the concentration of thermal equilibrium carriers. If we compare the  $I_{\text{light}} / I_{\text{dark}}$  ratio (Table 2) for the two groups of samples (prepared at  $\text{pH}_i \sim 12$  and  $\text{pH}_i > 12.5$ ) we observe that for the layers grown by “ion by ion” mechanism the ratio is constant and has a large value, while for the layers grown mainly by mechanism “cluster by cluster”, the ratio has a lower and inconstant value. For the samples prepared at  $\text{pH}_i \sim 12$ , during the deposition time, both the growth mechanism and the structure of the layers are changed depending on the used cadmium salt. Consequently, the photoconductive properties of the layers are different. The Fa layers grown by “ion by ion” mechanism had a high  $I_{\text{light}} / I_{\text{dark}}$  ratio while Fc and Fs layers with a duplex layer structure and overgrown crystallites had low  $I_{\text{light}} / I_{\text{dark}}$  ratio.

Table 2. The value of the  $I_{\text{light}}/I_{\text{dark}}$  ratio for the CdS films deposited from different cadmium salts.

Samples	Fa	Fc	Fs	Fa'	Fc'	Fs'
$I_{\text{light}} / I_{\text{dark}}$	$10^6$	$10^4$	$10^2$	$10^6$	$10^6$	$10^6$

## 4. Conclusions

The experimental data on CdS films deposited from different cadmium salts leads us to the conclusion when selecting the deposition parameters we must take into account the anion type of the cadmium salt. Depending upon the anion type of the cadmium salt, even at a short reaction time, the  $\text{pH}_i$  value could become lower, allowing to the change in the growth mechanism of the layer and therefore the change in the morphology and properties of the films.

The morphology and the structure studies show differences among the films prepared at  $\text{pH}_i \leq 12$  from  $\text{CdCl}_2$ ,  $\text{CdSO}_4$ , and  $\text{Cd}(\text{CH}_3\text{COO})_2$  respectively, although the starting reaction parameters for all three deposition mixtures were identical. The crystallites size and the layers structure depend on the anion type of the cadmium salt. The optical, electrical and photoelectrical measurements had revealed a strong dependence of physical properties of the layers on the crystallites size and on the layers structure, that is on the growth mechanism.

Above a certain  $\text{pH}_i$  value the growth mechanism of the layers and their properties are independent of cadmium salt anion.

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