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CdS NANOMETRIC LAYERS GROWN ON SnO_2 COATED GLASS SUBSTRATES FOR PHOTOVOLTAIC DEVICES

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CdS layer thickness decreases at high substrate temperatures due to the fact that a part of $CdCl_2/(NH_2)_2$ CS aqueous solution evaporates without reaching the substrate surface. CdS layers deposited at the substrate temperature from 250^{o}C to 450^{o}C are growing with a deficit of sulfur. CdS layers with better stoichiometry were grown in the conditions when in the solutions, used for CdS layers growing, there is an excess of thiourea ($CdCl_2$/ TU =1:2). The high charge carrier concentration of $10^{20}cm^{-3}$ in CdS layers grown on glass substrates coated with SnO_2 layer is related to Sn doping of the layers from SnO_2 layer.

INTRODUCTION

The chemical pulverization method was initially used for the fabrication of transparent oxide layers. This method was intensively used by R.R.Chamberlain for the fabrication of sulphide and selenide thin films [1] and it has gained a wide development due to R. Bube [2] and other works [3-6].

The most complete analysis on the chemical pulverization method was carried out by K.Chopra [6].

The main advantages of the chemical pulverization method are:

- The possibility of fabrication of a large variety of $A^{II}B^{VI}$ compound thin layers;
- The deposition is carried out at atmospheric pressure, which simplifies the technological process;
- The process of high quality layers fabrication is of lower cost and less toxic comparable with other methods;
- The use of lower temperatures for pyrolysis (including the pyrolysis of chlorides is within a temperature interval between 300^{o}C to 500^{o}C;
- The possibility of layer deposition on a large area surfaces.

These advantages make the chemical pulverization be a perspective method in nanotechnologies for the growth of a new generation of thin films suitable for use in optoelectronics, photonics and creation of anticorrosive layers. Indeed, the thin film growth represents a process of layer by layer deposition of atoms, ions and molecules. Therefore, depending on the obtained film thickness, the chemical pulverization can be used not only in thin films deposition but also in the formation of nanostructures and nanostructural layers.

TECHNOLOGY OF CDS LAYERS FABRICATION

The paper contains the results of the studies of the influence of deposition technological conditions on CdS layer parameters made by CdS pulverization on glass substrates coated by SnO_2. The use of such substrates is determined by the fact that SnO_2 layer can be used as an ohmic front contact to the "window" CdS layer of a solar cell. At the deposition of CdS layers are used the aqueous $CdCl_2$ and $(NH_2)_2CS$ solutions with a molarity of 0,1M. The used $CdCl_2$ and $(NH_2)_2CS$ give the possibility to obtain CdS layers according to the reaction:

$$CdCl_2 + (NH_2)_2CS + H_2O \rightarrow CdS + 2NH_4Cl + CO_2$$

The analogous reactions take place when using a series of other salts such as Cd:$CdNO_3$, $CdSO_4$ etc.

At the fabrication of CdS layers a unit for ITO thin film deposition described in [7] was used. The main components of this unit are: pulverization system, electric furnace, substrates holder, a system for substrate

introducing into the furnace and the control system. The unit allows to obtain CdS layers of large area up to 80 cm^2. The furnace temperature is maintained constant with an accuracy of $\pm 0,5^oC$. CdS layers were grown in an argon ambiance at the pressure through pulverizing device of 40 kPa. The glass plackets coated with a SnO_2 layer were used as the substrates. The plackets were degreased in the toluene, isopropyl alcohol, etched in a solution of methanol +5%Br during 10 min., then dried in isopropyl alcohol and placed in the deposition chamber (electric furnace). Further the furnace temperature was raised to the needed level, the pulverizing device was connected to the transport gas system, the $CdCl_2$ and $(NH_2)_2CS$ solution was poured into the pulverizing device and the deposition process followed. For a solution volume of 15 ml., regardless of the $CdCl_2/(NH_2)_2$ CS ratio, the deposition time was 5 min.

THE LAYER COMPOSITION AND SURFACE MORPHOLOGY

The surface morphology of different CdS layer thickness deposited on SnO_2 coated glass substrates was studied using a scanning electron microscope (SEM). The surface morphology of CdS layer deposited at the temperature of 350^oC is given in Fig.1. These CdS layers consist of chaotically distributed oval granules.

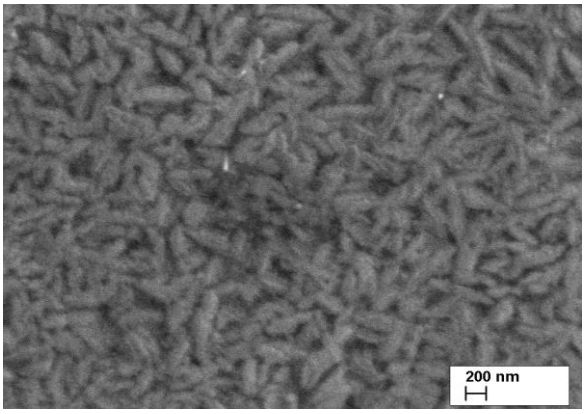


Fig. 1. Surface morphology of CdS layer deposited at 350^oC.

The surface morphology pattern of a CdS layer deposited at 450^oC is given in Fig.2.

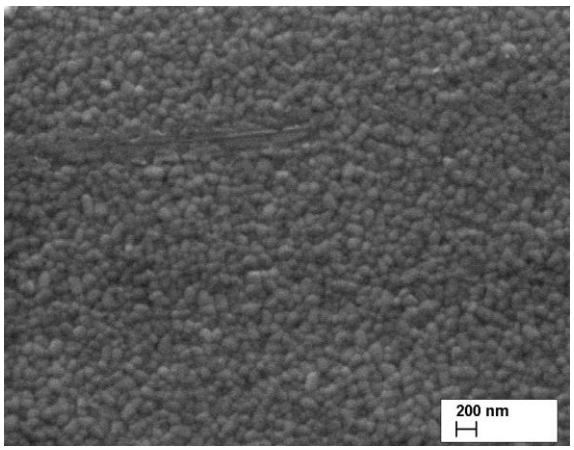


Fig. 2. Surface morphology of CdS layer deposited at 450^oC.

As one can see from Fig. 2, the growth figure dimensions are decreasing as the deposition temperature increases from 350^oC to 450^oC and their form is changing. The cross sections of these CdS layers, studied also using SEM, are of column form (Fig.3).

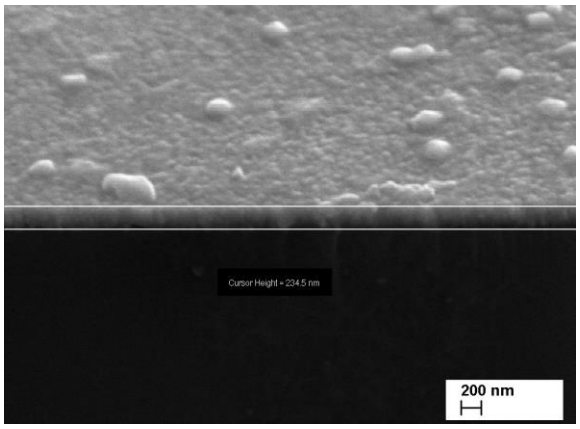


Fig. 3. Cross section image of a CdS layer grown at the temperature of 450^oC.

CdS layer thickness decreases when the deposition temperature increases regardless of the $CdCl_2/(NH_2)_2$ CS aqueous solution ratio (Fig.4). This can be explained by the fact that for the given argon flow value, at the temperature increase, a part of the solution is evaporating before reaching the substrate surface.

The sulfur and cadmium contribution on weight and atomic concentration was determined by EDX (energy dispersion of X-rays) measurements on the base of stoichiometry of 1:1, which is equal to the ratio between Cd and S for single crystal CdS used as etalon.

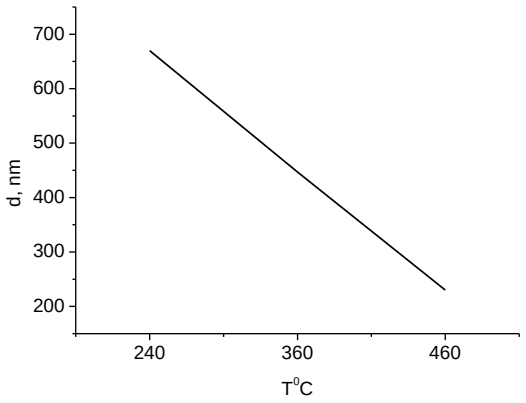


Fig.4. CdS layer thickness dependence on deposition temperature.

The atomic concentration of sulfur and cadmium in the CdS layers grown at different substrate temperatures is given in Table 1.

The layers are characterized by a sulfur deficit comparable to cadmium. Sulfur and cadmium percentage in the studied layers decreases when the deposition temperature increase. Such elements as Cl, Sn and Si were found to exist in the studied layers.

Table 1. Elements concentration in CdS layers, at.%

Deposition temperature,°C	S	Cl	Cd	Sn	Si	Total
250	45,1	3,01	31,05	0,84	-	100
350	44,93	4	50,69	0,33	0,05	100
400	41,4	6,18	48,5	3,63	0,29	100
450	41,2	1,38	48,43	8,34	0,64	100

The tin and silicon atoms concentration in CdS layers increases when the deposition temperature increases and, practically, the layers grown at temperatures higher than 400°C, depending on Sn and Si quantity represent the solid solutions of cadmium sulfide with these elements.

In the Table 2 we can see the distribution of elements which are contained in CdS layers grown at the substrate temperatures from 250°C to 450°C depending on their specific weight.

Table 2. Elements contribution in CdS layers, weight %

Deposition temperature,°C	S	Cl	Cd	Sn	Si	Total
250	19,57	1,44	77,65	1,34	-	100
350	19,68	1,94	77,84	0,53	0,02	100
400	17.9	2,96	73,51	5,52	0,11	100
450	16.91	0,63	69,68	12,55	0,23	100

The sulfur and cadmium weight contribution as well as their atomic concentration decrease when the deposition temperature increase. The weight difference between sulfur and cadmium in the layers is rather high and is due to the atomic weight of cadmium and sulfur which have the values of 127g/mol., and 32g/mol., accordingly.

The atomic composition of CdS layers grown at the temperature of 450°C for different $CdCl_2/(NH_2)_2CS$ aqueous solution ratio was studied. As one can see from the Table 3, thiourea percentage increase in the solution leads to the increase of sulfur and cadmium atomic percentage in the layer, while the silicon and tin percentage is decreasing.

Table 3. Elements concentration in CdS layers, at.%

$CdCl_2$/ TU ratio	Si	S	Cd	Sn
2 : 1	2,22	25,96	31,4	39,77
1 : 1	0,93	35,59	43,01	20,47
1 : 2	0,65	41,2	48,43	8,34

The weight contribution of the elements found in the studied CdS layers depending on $CdCl_2/(NH_2)_2$ CS aqueous solution ratio depends on the deposition temperature analogically with the atomic composition of these elements.

ELECTRO-PHYSICAL PARAMETERS OF CDS LAYERS

The electro-physical parameters of CdS layers were measured using an unit for electrical and thermo-electrical parameter testing in the magnetic field with the magnetic induction of 0,5T and a steady electric current. The charge carrier concentration in CdS layer dependencing on the deposition temperature is given in Fig.5. As one can see from Fig. 5, the substrate temperature increase from 250^{o}C to 450^{o}C during the layer growth leads to the increase of charge carrier concentration by two times, which could be related to Sn doping of the layers from SnO_2 previously deposited onto the glass substrates.

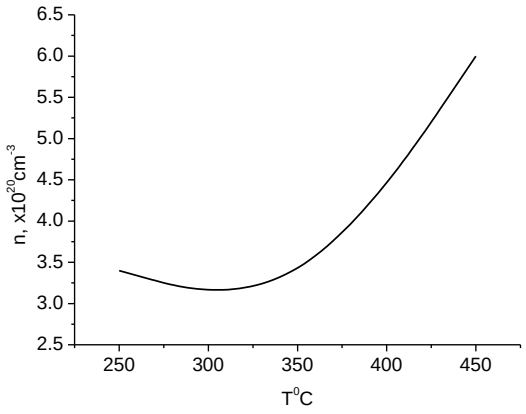


Fig.5. Charge carrier concentration in CdS layers deposited at different substrate temperatures T_s

The charge carrier concentration in CdS layers deposited on glass substrates coated with SnO_2 layer is of the order of magnitude of $10^{20}cm^{-3}$, which considerably differs from the charge carrier concentration of CdS layers deposited directly on glass substrates without SnO_2 layer, which is of $10^{17}cm^{-3}$.

The charge carrier mobility in CdS layers deposited at different substrate temperatures is given in Fig.6.

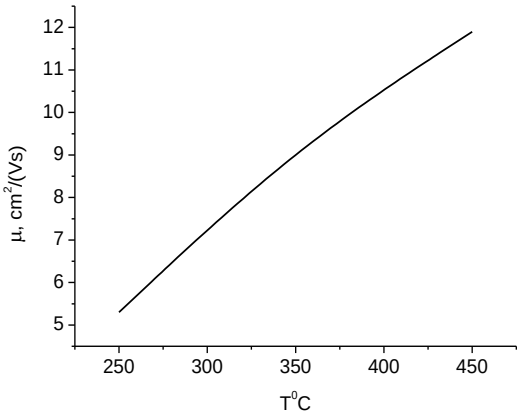


Fig.6. Charge carrier mobility in CdS layers grown at different substrate temperatures T_s.

One can see a slight charge carrier mobility increase in the layers obtained at higher substrate temperature, which is due , probably, to the decrease of potential barrier value between the layer granules at higher temperatures.

CONCLUSIONS

The thickness of CdS layers decreases at high substrate temperatures due to the fact that a part of $CdCl_2/(NH_2)_2$ CS aqueous solution evaporate, without reaching the substrate surface. CdS layers deposited at the substrate temperature from 250^{o}C to 450^{o}C grow with a deficit of sulfur. CdS layers with better stoichiometry were grown in the conditions when in the solutions used for CdS layers there is an excess of thiourea ($CdCl_2$/ TU=1:2). The high charge carrier concentration of $10^{20}cm^{-3}$ in CdS layers grown

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STRATURILE NANOMETRICE CdS FORMATE PE SUBSTRATURILE DE STICLĂ ACOPERITE CU SnO_2 PENTRU DISPOZITIVELE FOTOVOLTAICE

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Grosimea stratului de CdS se diminuiază la temperaturi ridicate ale substratului, datorită faptului că o parte din soluţia apoasă $CdCl_2/(NH_2)_2CS$ se evaporă fără a atinge suprafaţa substratului. Straturile CdS depuse la temperatura substratului de la 250°C la 450°C sînt în creştere cu un deficit de sulf. Straturi CdS cu o stoichiometrie mai bună au fost obţinute în condiţiile în care în soluţiile, utilizate pentru depunerea straturilor CdS, există exces de tiouree ($CdCl_2$/ TU = 1:2). Concentraţia înaltă de transport de 10^{20} cm^{-3} în straturile CdS depuse pe substraturi de sticlă, acoperite cu un strat de SnO_2, este legată de dopajul straturilor cu Sn din stratul SnO_2.

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