

Electrophysical Properties of Nanometric CdS Layers Deposited by Pulverization Method

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Abstract — The objective of this paper is establishing of the optimum conditions for CdS layers deposition by pulverization method on glass substrates coated with a previously deposited tampon SnO₂ layer, studies of their electrical and luminescence properties in dependence on the deposition temperature in an argon flux and on the annealing in a hydrogen flux. CdS layers were grown from aqueous solutions of cadmium chloride (CdCl₂) and thiourea (NH₂)₂ CS with the molarity of 0,1M by pulverization method in the temperature range of (250...450)°C. CdS layers were grown on glass substrates covered with a previously deposited SnO₂ layer. Electrophysical properties and photoluminescence of these layers were studied. For the layers deposited at 450°C a slight decrease of charge carrier concentration is observed with the increase of treatment temperature up to 450°C. The photoluminescence spectrum consists of a large band in the energy interval from 1,6 eV to 2,6 eV. A photoluminescence peak with the energy of 1,95 eV is observed, which is shifting with CdS layer growth temperature increase and it reach the value of 2,5 eV for the layers grown at the temperature of 450°C.

Index Terms — CdS layers, morfology, electrical and photoluminescence properties.

I. INTRODUCTION

The chemical pulverization method was firstly used at the fabrication of transparent conductive oxides fabrication. Later this method was used by Chamberlin R.R [1] for the fabrication of sulfide and selenide films and it gain a wide development, more complex and qualitative in the works of Chopra K.L. [2]. In the technology of semiconductor thin films an apart place is taken by a group of different metal and compound sulfides which possess of electrical, photoelectrical and luminescent properties having an usable value. Based on such compounds a series of semiconductor devices were made such as: sensors, detectors, energy converters, photo-resistors [3]. They also are of perspective in the fabrication of solar cells and solar batteries [4-8].

An important advantage of sulfides thin layer fabrication by chemical pulverization consists of the fact that this method is of low cost and is accesible at the cadmium sulfide deposition with the properties which could be controlled by changing the technological regime of corresponding layers fabrication. The perspective of this method installation consists of simplicity semiconductor compounds layers fabrication and layers of their solid solutions, of the doping with active impurities and heterojunctions fabrication in a single technological cycle [4]. This method provides the realization of a low material expending technological method of different sulfides layers deposition with the unique properties and gives the possibility to extend the range of these layers installation. Depending on the thickness of the grown layers, the chemical pulverization method can be used not only in the fabrication technology of thin layers but also for the formation nano-layers and nano-dimensional structures. These advantages make the chemical pulverization to be of a perspective one in nanotechnologies in the realization of new generations of thin layers, devices based on it designed for

optoelectronics, photonics, chemical sensors and for deposition of anticorrosive layers.

The studies carried out in the direction [9] indentified the conditions needed for the fabrication of pure sulfides and their solid solution layers as well as for the fabrication of heterojunction based on such layers. This requiers specific approach in the study of CdS layers growth on SnO₂ coated glass substrates by pulverization method in an argon flow combined with the variation of the pulverized mixture composition and substrate temperature.

Particularly, in any certain case, depending on the device to be realized, new additional studies are needed related to the structural defects of layers, their electrical and photoelectrical properties and to the strategy for the control of these properties.

II. EXPERIMENTAL DETAILS

The technological conditions of CdS layers deposition by chemical pulverization method on a glass substrates coated with a previously deposited tampon SnO₂ layer are given below. Using of such substrates is caused, particularly, by the fact that SnO₂ layer can serve as a transparent ohmic contact at the elaboration of photovoltaic devices, when CdS layer is used as an optical window [10-12]. The CdS layers deposition by pulverization has a series of advantages: do not require high performance units; assures a minimum material losses at the large area layer deposition; excludes the necessity of toxic gases using. For CdS layers deposition an aqueous solutions of CdCl₂ and (NH₂)₂ CS with the concentration of 0,1M were used.

At CdS layers fabrication an unit for ITO (Indium Tin Oxide) deposition presented in [13] was used. The main components of this unit are :the pulverization system, an electric furnace, the substrates holder, the system of substrates introduction into the furnace and the control system. The unit allows to obtain CdS layers

with an area of up to 80 cm². The furnace temperature was maintained constant with an accuracy of ± 0,5° C. CdS layers were grown in an argon atmosphere at the pressure in the pulverization unit was of 40 kPa. Glass plates coated with a SnO₂ layer were used as substrates. Before CdS layer deposition the substrates were degreased in toluene, isopropyl alcohol etched in methanol+ 5%Br during 10 min, dried in the isopropyl alcohol vapors and placed into deposition chamber (electric furnace). Then the furnace temperature was increased to the needed for the deposition, the pulverizing unit was connected to the gas transporting system, the CdCl₂ and (NH₂)₂ CS solution was poured into pulverizing unit funnel and the deposition process began. For a solution volume of 15ml, regardless of the CdCl₂:(NH₂)₂ CS ratio, the deposition time was of 5 min.

The thicknesses of CdS layers were studied by scanning electron microscope (SEM).

The electro-physical parameters of CdS layers with the thickness under (150...750)nm were measured by using an universal automatic unit for studies of electric and thermoelectric parameters in magnetic field of 0,5T at constant current. Electrical conductivity, charge carriers concentration and mobility in the layers grown and annealed at different temperatures in a hydrogen flow were determined.

For luminescence spectra studies a MDR-23 spectrometer was used. The photoluminescence excitation was carried out by a laser beam (λ=0,337μm) of a power and duration pulse of 3 kW and 10 ns, accordingly. The luminescence radiation signal was recorded by a ФЭУ-51 photomultiplier and a standard system of synchronized detection at 77K

III. CdS LAYERS ELECTROPHYSICAL PROPERTIES AND PHOTOLUMINESCENCE

The charge carrier concentration in CdS layer in dependence of deposition temperature is given in Fig.5. As one can see from Fig. 1. the substrate temperature increase from 250°C to 450°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 SnO₂ previously deposited onto the glass substrates. The charge carrier concentration in CdS layers deposited on glass substrates coated with SnO₂ layer is of the order of magnitude of 10²⁰cm⁻³, which considerably differ from the charge carrier concentration of CdS layers deposited directly on glass substrates without SnO₂ layer, which is of 10¹⁷cm⁻³.

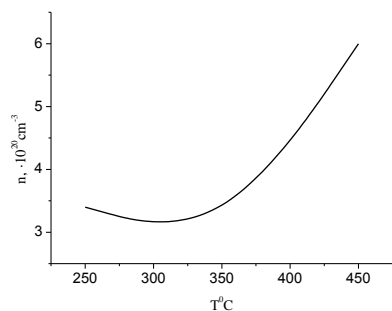


Fig. 1. Charge carrier concentration in CdS layers

deposited at different substrate temperatures T_s

The charge carrier mobility in CdS layers deposited at different substrate temperatures is given in Fig. 2.

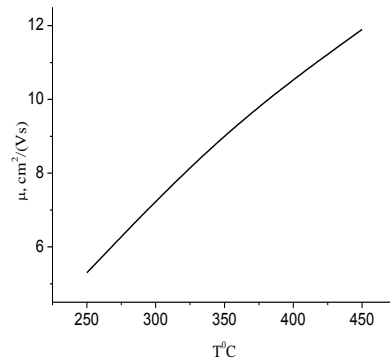


Fig. 2. Charge carrier mobility dependence on substrate temperatures T_s in CdS layers

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.

The charge carriers concentration in CdS layers deposited at different temperatures and annealed in a hydrogen flow in a temperature range of 250...450°C is shown in Fig. 3. As one can see the charge carrier concentration in CdS layer deposited at 450°C has a tendency of decreasing with the increase of the annealing temperature from 250°C to 450°C.

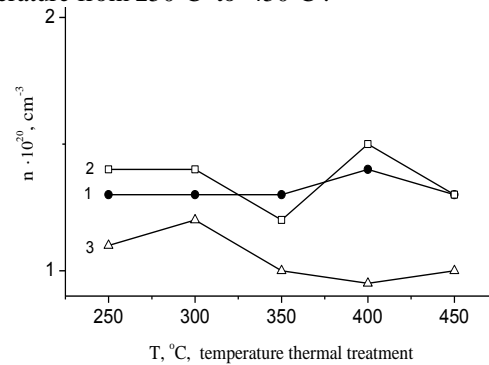


Fig. 3. Charge carrier concentration dependence on the annealing temperature in CdS layers. The deposition temperature in °C: 1-250°C; 2-350°C; 3-450°C

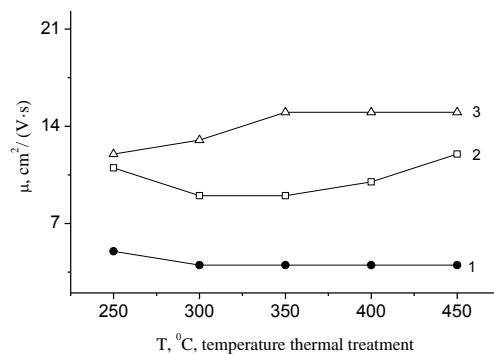


Fig. 4. Charge carrier mobility dependence on the annealing temperature in CdS layers. The deposition temperature in °C: 1-250°C; 2-350°C; 3-450°C

The charge carrier mobility dependence on the annealing temperature in a hydrogen flow in the temperature range 250°C ...450°C in CdS layers deposited at the temperatures 250°C; 350°C; 450°C for CdCl₂ to thiourea ratio of 1:2 is shown in Fig. 4. For all annealing temperatures the charge carrier mobility varies insignificantly but it is doubled with the growth temperature increase from 250°C to 450°C.

The charge carrier concentration in CdS layers grown at 450°C for different CdCl₂:TU ratio and then annealed at different temperatures was studied. As one can see from Fig. 5. the lowest charge carrier concentration is in the layers grown at 450°C for CdCl₂:TU ratio of 1:2.

The consideration of electrical conductivity, charge carrier concentration and mobility dependence on the annealing temperature leads to a conclusion about to a crystalline restructuring of the layers at the annealing. The studies of the electro-physical properties of CdS layers had shown that the best parameters have CdS layers grown and annealed at the temperature ~450°C.

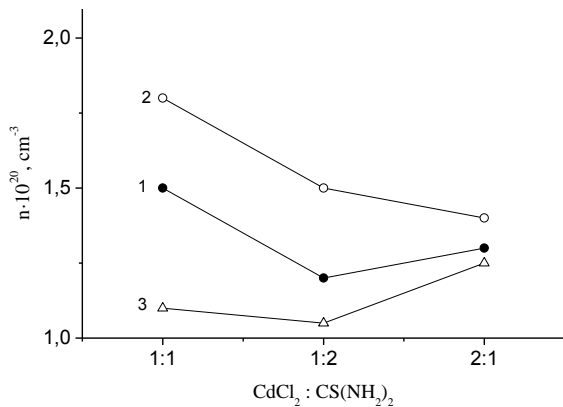


Fig. 5. Charge carrier concentration dependence on CdCl₂:CS(NH₂)₂ ratio in CdS layers deposited at T_s=450°C and annealed at: 1 – 350°C; 2 – 250°C; 3 – 450°C.

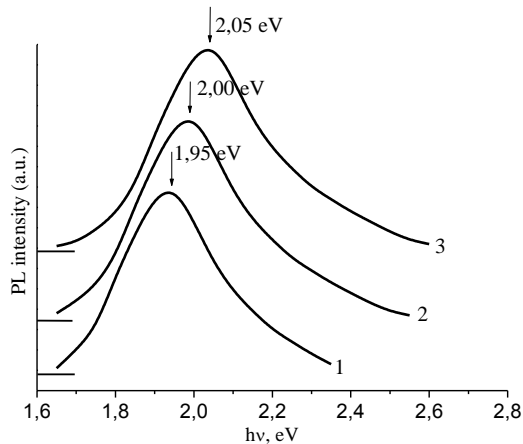


Fig. 6. CdS layers photoluminescence deposited at: 1- T_s=250°C; 2- T_s=350°C; T_s=450°C and annealed at 350°C

The photoluminescence spectra of CdS layers deposited at the temperatures from 250°C to 250°C on the

glass substrates coated with a tampon SnO₂ layer and annealed at 350°C in a hydrogen flow are given in Fig. 6. The photoluminescence spectra represent a large radiation band in the energies range 1,6 – 2,6 eV. As one can see from Fig. 6. the photoluminescence spectrum has a maximum at the energy of 1,95eV for the layer grown at 250°C which is shifting with the growth temperature increase and reaches 2,05eV for the layers grown at 450°C.

The photoluminescence spectra of CdS layers grown at the substrate temperature of 450°C for different CdCl₂: TU ratio and annealed at temperatures of 350°C and 450°C are given in Fig. 7. and Fig. 8. correspondingly. For the layers grown at different CdCl₂: TU ratio the photoluminescence spectra shape is similar with a peak at 2,05eV and have, practically, the same semi-width of the luminescence band.

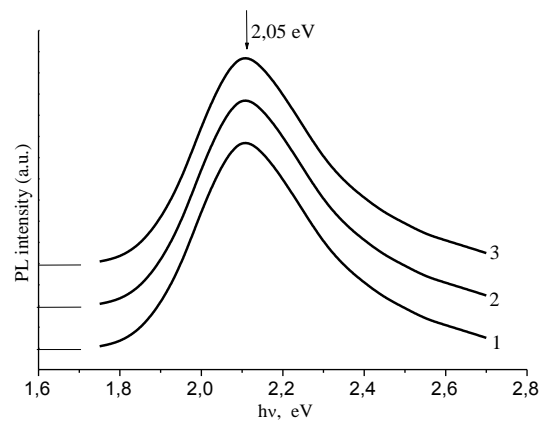


Fig. 7. Photoluminescence spectra of CdS layers grown at different CdCl₂: TU ratio: 1 – 1:2; 2 – 2:1; 3 – 1:1 and annealed at 350°C

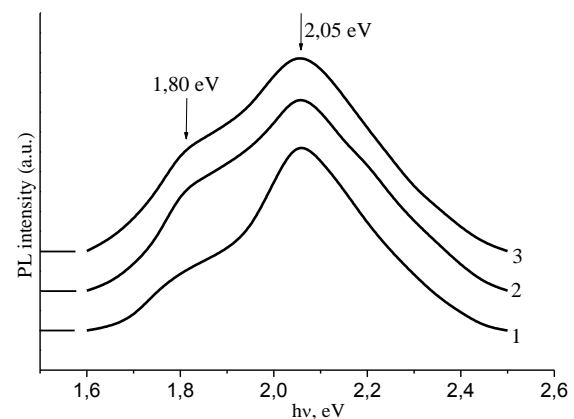


Fig. 8. Photoluminescence spectra of CdS layers grown at different CdCl₂: TU ratio: 1 – 1:2; 2 – 2:1; 3 – 1:1 and annealed at 450°C

As one can see from Fig. 8. in the spectra of CdS layers grown at different CdCl₂: TU ratio and annealed in a hydrogen flow at 450°C, which is characteristic for the layers annealed at 350°C another maximum at 1,80eV is observed.

The maximum at 1,95eV are probable related to the existence of the dislocations in the CdS layers structure.

The growth temperature increase leads to the shift of this maximum to higher energies. The appearance of the radiation band with a maximum at 1,80eV which is characteristic to CdS layers grown and annealed at higher temperatures is, probably, related to the modification of the layer crystallites and enhancement of their crystalline structure.

IV. CONCLUSIONS

The high charge carrier concentration of 10^{20} cm⁻³ in CdS layers grown on glass substrates coated with a SnO₂ layer is related to Sn doping of the layers from the SnO₂ layer.

The analysis of the charge carrier concentration, mobility, and electrical conductivity of CdS layers suggests that crystalline restructuration occurs depending on the growth and annealing temperature. As a result of electro-physical properties investigation in CdS layers it was established that the optimum growth and annealing temperature is around 450°C.

The emission band with the maximum at 1,95 eV in the photoluminescence spectra is probably due to dislocations. The growth temperature increase leads to this maximum shift to higher energies. The observed radiation maximum at the energy of 1,80 eV is characteristic for the layers grown and annealed at higher temperatures. This energy level is due to the crystallites modification and their crystalline structure enhancement.

ACKNOWLEDGMENTS

The work the supported by project of the Republic of Moldova no. 11.817.05.12A

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