Chemical Surface Deposition of CdS Ultra Thin Films from Aqueous Solutions

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1. Introduction

Solar cells (SC) are the most effective devices that allow direct one-stage conversion solar energy into electricity from the view of energy. The last yers tendency in traditional energetic forced to direct a significant part of research on the establishment of modern technology for production available and effective thin film SC that would not require the use of high temperature and pressure, a large number of rare and expensive materials. At the same time, to find ways for increase the conversion efficiency of solar energy it is necessary to understand the processes that occur in the elements. Therefore it is necessary to establish a correspondence between characteristics of elements and main structural, electronic and optical properties of initial semiconductor films. Therefore, the investigation of CdS thin films deposition process with desire photoelectric properties and fabrication on their base thin-film SC have great significance.

CdS is the main material for buffer layer in thin-film CdTe and Cu(In, Ga)Se$_2$ solar cells. It has a high photosensitivity and absorption, favorable energy band gap (Eg) 2,4 eV and photoconductivity (σ) 10^2 Om^{-1}cm^{-1} and does not change the properties with SC surface temperature increase during the work. One more peculiarity of this material is absence of the hole conduction due the acceptor additives and point defects recombination. Effective lifetime of the main carriers is very large (10...100 ms), that causes a initial photocurrent increase up to 10^5 times (Hamakawa, 2002). An important advantage of CdS thin films use in SC is possibility of their synthesis by different methods, including chemical deposition from solution which has significant preference over others: 1) grown nanocrystalites with a form close to spherical, while the electrochemical deposition - non-spherical (Jager-Waldau, 2004); 2) CdS thin films deposited from solution have structural, optical and electrical parameters thet do not inferior parameters of films received by other methods, but used equipment is available, simple, does not require use of the high temperatures and pressures compared, for example, with the vacuum evaporation or ion (sputtering or pulverization, spraying) methods; 3) the method is not explosive and low-toxic, compared with the vapor deposition methods; 4) enable control of the film growth and dynamically change the fabrication conditions for polycrystalline or smooth solid films.

2. Deposition of CdS thin films and structures based on

2.1 Fabrication methods

The thin film semiconductor properties largely depend on fabrication technology. Therefore development of actual methods, which would allow an influence on material parameters in the synthesis process and to obtain coating with the set properties, is an important scientific and technological problem. Recently the methods based on chemical processes dominate in the technology of metal sulfides thin films semiconductor. The semiconductor films with a thickness from several tenth of nanometers to hundreds of microns can be fabricated by a large number of so-called thin-film and thick-film methods. For large area in ground conditions aplication of thin-film solar cells crucial are not only their energy characteristics, but also their economic indicators. This causes use of bough thin film and thick-film technology methods for satisfying of such requirements as: fabrication simplicity, low cost, ability to create homogeneous films with a large area, controlling the deposition process, and ability to obtain the films with preferred structural, physical, chemical and electrooptical properties.

The deposition methods for wide range of semiconductors in detail are considered in literature (Aven & Prener, 1967, Chopra & Das, 1983, Green, 1998, Möller, 1993, Sze, 1981, Vossen & Kern, 1978,). We will consider only those methods that are used for cadmium sulfide films fabrication and are the best for solar cells producing. Thin film deposition process consists of three stages: 1) obtaining of substance in the form of atoms, molecules or ions; 2) transfer of these particles through an intermediate medium; 3) condensation of the particles on substrate. The methods of thin films fabrication are classified in several ways. Depending on the film grown phase are four methods of films deposition: 1) from the vapor phase; 2) from the liquid phase; 3) from the hydrothermal solutions; 4) from the solid phase. Depending on which way the vapour particle were obtained: using physical (thermal or ion sputtering), chemical or electrochemical processes, it is possible to classify deposition methods: physical vapor deposition; chemical vapor deposition; chemical deposition from the solution; electrochemical deposition. On the basis of physical and chemical vapor deposition were developed combined methods, such as: reactive evaporation, reactive ion sputtering and plasma deposition. Among the nonvacuum deposition methods of cadmium sulfide thin films for inexpensive solar cells with a large area perspective are: chemical deposition from baths (CBD), electrochemical deposition, mesh-screen printing, pyrolysis and pulverization followed by pyrolysis. Selection of the films deposition method first of all are specified by structural, mechanical and physical parameters, which should have thin-film sample.

Although, cadmium sulfide is the most widely studied thin film semiconductor material, interest of researchers to it is stable, and the number of scientific publications increasing all the time. Changing the deposition conditions drasticly alter electrical properties of CdS thin films. CdS films, obtained by vacuum evaporation have specific resistance $1 \bullet 10^3$ Om$\bullet$cm and carrier concentration of 10^{16}-10^{18} cm^{-3}. Films always have n-type conductivity, that explains their structure deviation from stoichiometry, by sulfur vacancies and cadmium excess. Electrical properties of the films are largely depended from the concentration ratio of Cd and S atoms in the evaporation process and the presence of doping impurities. Electrical properties of CdS films, fabricated by pulverization followed by pyrolysis, are determined mainly by the peculiarities the chemisorption process of oxygen on grain boundaries, which accompanied by concentration decreaseing and charge carriers mobility. Due to presence of

the sulfur vacancies such films always have n-type conductivity, and their resistance can vary widely, differing by the amount of eighth order. Epitaxial CdS films are characteristic due to carrier high mobility. With the increase of substrate temperature concentration of carriers grows by an exponential law. This increase the electron mobility. Optical properties of CdS films are strongly dependent on their microstructure and thus on the method and conditions of deposition. For example, evaporation of CdS results in smooth mirror reflective films, but increasing their thickness leads to a predominance of diffuse reflection. The CdS films, obtained by ion sputtering have the area with rapid change of transmission at 520 nm, corresponding CdS band gap. In the same time in the long-wave spectral range films have high transparency.

2.2 Use of the CdS films in photovoltaic cells

Edmund Becquerel, a French experimental physicist, discovered the photo-voltaic efect in 1839 while experimenting with an electrolytic cell, made up of two metal electrodes placed in an electricity-conducting solution. He observed that current increased when the electrolytic cell was exposed to light (Becquerel, 1839). Then in 1873 Willoughby Smith discovered the photoconductivity of selenium. The first selenium cell was made in 1877 (Adams, 1877), and five years later Fritts (Fahrenbruch & Bube, 1983) described the first solar cell made from selenium wafers. By 1914 solar conversion eficiencies of about 1 % were achieved with the selenium cell after it was finally realized that an energy barrier was involved both in this cell and in the copper/copper oxide cell.

The modern era of photovoltaics started in 1954. In that year was reported a solar conversion efficiency of 6 % (Chapin at al., 1954) for a silicon single-crystal cell. In 1955 Western Electric began to sell commercial licenses for silicon PV technologies. Already in 1958 silicon cell efficiency under terrestrial sunlight had reached 14 %. At present, available in the market SC are mainly represented of monocrystalline silicon SC. Through high-temperature process of their formation, crystal (from ingots grown from melt by Czochralski method) and polycrystalline silicon solar cells have too high price, to be seen as a significant competitor to the formation of energy from solid fuels. Polycrystalline silicon provides lower expenses and increase production, rather than crystalline silicon. In 1998, approximately 30 % photovoltaic world production was based on the polycrystalline silicon wafers. Nowadays solar cells conversion efficiency based on monocrystalline silicon is 25 %, polycrystalline – 20 % (Green at al., 2011).

In 1954 reported 6 % solar conversion efficiency (Reynolds at al., 1954) in what later came to be understood as the cuprous sulfide/cadmium sulfide heterojunction (HJ). This was the first all-thin-film photovoltaic system to receive significant attention. In following years the efficiency of Cu_xS/CdS increased up to 10 % and a number of pilot production plants were installed, but after several years of research it was realized that these solar cells have unsolvable problems of stability owing to the diffusion of copper from Cu_xS to CdS layers. By taking advantage of new technology, work out on Cu_xS/CdS, researchers have rapidly raised the effciency of the gallium arsenide based cell with 4 % efficiency (Jenny at al., 1956) to present eficiencies exceeding 27 % (Green at al., 2011).

However in the last 20 years other thin films solar cells have taken the place of the cuprous sulfide/cadmium sulfide, and their eficiency have raised up to almost 20 %. The most predominant are two: copper indium gallium diselenide/cadmium sulfide $(Cu(In,Ga)Se_2$/CdS) and cadmium telluride/cadmium sulfide (CdTe/CdS). The first CdTe heterojunctions were constructed from a thin film of n-type CdTe material and a layer of p-

type copper telluride ($Cu_{2-x}Te$), producing ~7 % eficient CdTe-based thin-film solar cell (Basol, 1990). However, these devices showed stability problems similar to those encountered with the analogous $Cu_{2-x}S/CdS$ solar cell, as a result of the difuusion of copper from the p layer. The lack of suitable materials with which to form heterojunctions on n-type CdTe, and the stability problems of the $Cu_{2-x}S/CdS$ device, stimulated investigations into p-CdTe/n-CdS junctions since the early 1970s. Adirovich (Adirovich at al., 1969) first deposited these films on TCO-coated glass; this is now used almost universally for CdTe/CdS cells, and is referred to as the superstrate configuration. In 1972 5-6 % eficiencies were reported (Bonnet & Rabenhorst, 1972) for a graded band gap CdS_xTe_{1-x} solar cell.

The research for $CuInSe_2/CdS$ started in the seventies, a 12 % efficiency single-crystal heterojunction p-$CuInSe_2$/n-CdS cells were made by in 1974 (Wagner, 1975) and in 1976 was presented the first thin film solar cells with 4-5 % eficiency (Kazmerski at al., 1976). In the last 30 years a big development of these cells was given by the National Renewable Energy Laboratories (NREL) in U.S.A. and by the EuroCIS consortium in Europe.

Nowadays CdS among Si, Ge, CdTe, Cu(In, Ga)Se$_2$, ZnO belongs to the widespread group of semiconductors. Beyond the attention of researchers are still many issues associated with cadmium sulfide as componenet of thin-film semiconductor devices, although the CdS is one of the most studied semiconductor materials.

2.3 Peculiarities of chemical bath deposition (CBD)

CBD technology consist of the deposition of semiconductor films on a substrate immersed in solution containing metal ions and hydroxide, sulfide or selenide ions source. The first work on CBD is dated 1910 and concerns to the PbS thin films deposition (Houser & Beisalski, 1910). Basic principles underlying the CBD of semiconductor films and earlier studies in this field were presented in the review article (Hass at al., 1982), which encouraged many researchers to begin work in this direction. Further progress in this area is presented in review article (Lokhande, 1991), where references are given for 35 compounds produced by the mentioned method, and other related links. Chemical reactions and CBD details for many compounds were listed in the next paper (Grozdanov, 1994). The number of materials which can be produce by CBD, greatly increased, partly due to the possibility of producing multilayer film structures by this method with subsequent annealing, which stimulates crosboundary diffusion of metal ions and thereby motivates fabrication of new materials with high thermal stability. For example, crossboundary diffusion of CBD coatings PbS/CuS and ZnS/CuS leads to materials such as $Pb_xCu_yS_z$ and $Zn_xCu_yS_z$ with p-type conductivity and thermal stability up to 573 K (Huang at al., 1994). Annealing of Bi_2S_3/CuS coatings at temperatures 523-573 K leads to formation of new Cu_3BiS_3 compounds with p-type conductivity (Nair at al., 1997). In recent years we counted approximately 120 CBD semiconductor compouns.

Among the first applications of CBD semiconductor films were photodetectors based on PbS and PbSe (Bode at al., 1996). Although the chemically precipitated CdS films were made back in the 60's of last century, for photodetectors were used CdS layers, obtained by screen printing and sintering (Wolf, 1975). Chemically deposited CdSe films are fully suitable for use in photodetectors (Svechnikov & Kaganovich, 1980). At late 70's and early 80-ies the main direction in chemical bath deposition technology was deposition of thin films for use in solar energy conversion. One of the first developments in this area was the coating producing that absorbs sunlight (Reddy at al., 1987), and its use in glass vacuum tube collectors (Estrada-Gasca at al., 1992). Application of the chemically deposited films in

coatings for controlling the flow of sunlight was first proposed in 1989 (Nair at al., 1989). The efficiency improving of such coatings in glass vacuum tube collectors were presented in (Estrada-Gasca at al., 1993). One of the main applications of chemically deposited semiconductor films has been their use in photoelectrochemical SC, mostly CdS and CdSe films (Hass at al., 1982, Boudreau & Rauh, 1983, Rincon at al., 1998). The use of chemically deposited semiconductor films in thin SC has a short history. In the structure Mo/CuInSe$_2$/CdS/ZnO, which showed 11% efficiency (Basol & Kapur, 1990), was by the first time used chemically deposited CdS thin film. Further structure improvement allowed to reach 17% efficiency (Tuttle at al., 1995). Chemically deposited CdS film with thickness of 50 nm has been an essential element of this structure. The biggest, confirmed today for SC based on CdS/CdTe, is 16,5% efficiency in which CdS film was chemically deposited in bath (Green at al., 2011). Entering highly resistive CdS film in p-CuInSe$_2$/CdS/n-CdS solar cell structure deemed necessary step towards improving of the solar cells stability (Mickelsen & Chen, 1980). Performed theoretical calculations (Rothwarf, 1982) showed that the thickness of CBD CdS films should be as small as possible to increase efficiency of solar cells with its use. Therefore, chemical deposition technology, which allows to fully cover the substrate at small film thickness was selected for the fabrication of thin films and showed significantly better results (Basol at al., 1991). Efficiency of n-CdSe or n-Sb$_2$S$_3$ chemically deposited films with WO$_3$ inclusions as absorber material in solar cells based on the Schottky barrier has been proved in practice. For example, elements on the Schottky barrier ITO/n-CdSe(5 μm)/Pt/Ni/Au (13 nm) shows U_{xx}=0,72 V, $I_{к3}$=14,1 mA·cm^{-2}, fill factor 0,7, and 5,5% efficiency (Savadogo & Mandal, 1993 & 1994). Abovementioned possible applications of chemical bath deposition, particularly in solar energy conversion, provided the growing interest to chemical deposition of semiconductor thin films. Chemical deposition is perfect for producing thin films on large areas and at low temperatures, which is one of the main requirements for the mass use of solar energy.

2.4 The advantages of chemical surface deposition (CSD) over CBD

In the CBD process, the heat necessary to activate chemical reaction is transferred from the bath to the sample surface, inducing a heterogeneous growth of CdS on the surface and homogeneous CdS formation in the bath volume. The reaction is better in the hottest region of the bath. Therefore, for baths heated with thermal cover deposition also occurs on the walls, and bath, which heat up immersed heater, significant deposition occurs on heating element. Additionally, the solution in the bath should be actively mixed to ensure uniform thermal and chemical homogeneity and to minimize adhesion of homogeneously produced particles to the surface of CdS film. The disproportion of bath volume and that which is necessary for the formation of CdS film, leads to significant proportion of wastes with high cadmium content. Different groups of researchers put efforts for decreasing the ratio of volumes bath/surface through use of overlays. However the clear way for unification of large areas deposition with high cadmium utilization and high speed of growth, to achieve high efficiency of transformation is not represented.

The chemical surface deposition (CSD) technology demonstrated in this paper overcomes these limitations through use of the sample surface as a heat source and use of solution surface tension to minimize the liquid volume. The combination of heat delivery method to surface and small volume of solution leads to high utilization of cadmium and its compounds.

This paper describes CSD technology of CdS thin films from aqueous solutions of cadmium salts CdSO$_4$, CdCl$_2$, CdI$_2$. The properties of CdS films deposited on glass and ITO/glass from the nature of the initial salt and solar cells based on CdTe/CdS with CSD CdS films as windows was investigated.

3. Chemical surface deposition of CdS thin films from CdSO$_4$, CdCl$_2$, CdI$_2$ aqueus solutions

3.1 Introduction

One of the methods to increase SC efficiency based on CdS/CdTe, CdS/CuIn$_{1-x}$Ga$_x$Se$_2$, with the CdS film as the window is increasing the current density value (Stevenson, 2008). This can be achieved by reducing losses in the photons optical absorption from $\lambda > 500$ nm by reducing CdS film thickness. To provide a spatially homogeneous work of the device the CdS films should not only be thin, but solid, durable and resistant to further technology of SC production. To produce ultra-thin (from 30 to 100 nm) and homogeneous CdS films the technology of bath chemical deposition is widely used (Estela Calixto at al., 2008, Mugdur at al., 2007).

Chemical deposition technology is quite simple, inexpensive and suitable for the deposition of polycrystalline CdS films on large areas. Deposition of thin CdS films from aqueous solutions is a reaction between cadmium salt and thiocarbamid (thiourea) in alkaline medium. Mostly are used simple cadmium salts: CdSO$_4$ (Chaisitsak at al., 2002, Contreras at al., 2002, Tiwari & Tiwari, 2006, Chen at al., 2008), CdI$_2$ (Nakada & Kunioka, 1999, Hashimoto at al., 1998), Cd(CH3COO)$_2$ (Granath at al., 2000, Rau & Scmidt, 2001) and CdCl$_2$ (Qiu at al., 1997, Aguilar-Hernández at al., 2006). Thiourea (TM) is used as sulfide agent in the reactions of sulfide deposition, as has a high affinity to metal cations and decomposes at low temperatures. Deposition process can be described by two mechanisms (Oladeji, 1997, Soubane, 2007). Homogeneous mechanism involves formation of layer with the CdS colloidal particles, which are formed in solution and consists of several stages.
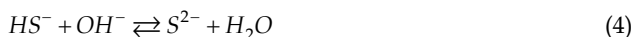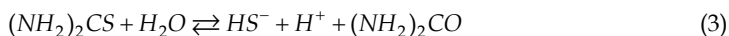
1. Ammonium dissociation:

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O \tag{1}$$

In alkaline medium due to interaction Cd^{2+} ions with the OH$^-$ environment ions is possible formation of undesirable product - Cd(OH)$_2$:

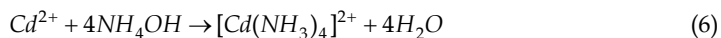$$Cd^{2+} + OH^- \rightarrow Cd(OH)_2 \downarrow \tag{2}$$

2. Thiourea hydrolysis (NH$_2$)$_2$CS with the the formation of sulfide ions

$$(NH_2)_2CS + H_2O \rightleftarrows HS^- + H^+ + (NH_2)_2CO \tag{3}$$

$$HS^- + OH^- \rightleftarrows S^{2-} + H_2O \tag{4}$$

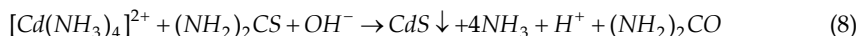3. Final product formation

$$Cd^{2+} + S^{2-} \rightleftarrows CdS \downarrow \tag{5}$$

Deposition of thin CdS films from the aqueous solutions through the stage of cadmium tetramin $[Cd(NH_3)_4]$ $^{2+}$ complex ion formation, which reduces the overall speed of reaction and prevents Cd(OH)$_2$ formation by the heterogeneous mechanism.

$$Cd^{2+} + 4NH_4OH \rightarrow [Cd(NH_3)_4]^{2+} + 4H_2O \tag{6}$$

$$[Cd(NH_3)_4]^{2+} + S^{2-} \rightarrow CdS \downarrow + 4NH_3 \tag{7}$$

In general form:

$$[Cd(NH_3)_4]^{2+} + (NH_2)_2CS + OH^- \rightarrow CdS \downarrow + 4NH_3 + H^+ + (NH_2)_2CO \tag{8}$$

The sulphides films deposition from thiocarbamid coordination compounds has some chemical peculiarities. Depending on the nature and the salt solution composition may be dominated different coordination forms, and with thiourea molecules in complex inner sphere may contain anions Cl-, Br-, J-, and SO$_4$$^{2-}$ under certain conditions. Thus, the cadmium atoms close environment are atoms of sulfur, halogens and oxygen, and at the thermal decomposition part of the Cd-Hal or Cd-O bonds are stored and in the sulfide lattice are formed Hal$_S$• and O$_S$•defects. In conjunction with the substrate the thiocarbamid complexes orientation on active centers of its surface is observed. The complex particles that can interact with active centers on the substrate are the link that provides sulfide link with the substrate. The nature of this interaction determines the nature of film adhesion. In the case of cadmium sulfide deposition on quartz or glass substrates the active centers are sylanolane groups (≡Si–OH) which interact with halide or mixed hydroxide complexes. In result of such interaction the Cd–O–Si oxygen bridges are created. This explains the good adhesion of the cadmium sulfide films deposited from thiocarbamid coordination compounds to glass substrates (Palatnik & Sorokin, 1978).

3.2 Chemical surface deposition of CdS thin films
In CSD, a solution at ambient temperature containing the desired reactants is applied to a pretreated surface. Glass or ITO/glass (16×20 mm) substrates, CdTe (10×10 mm) and Si (30×20 mm) wafers were used in the entire work. After that sample with working solution is heated and endured for a given temperature (Fig. 1). To ensure uniformity of heating plate

$$[Cd(NH_3)_4]^{2+} + CS(NH_2)_2 + OH^- \leftrightarrow CdS\downarrow + 4N_3 + H^+ + (NH_2)CO$$
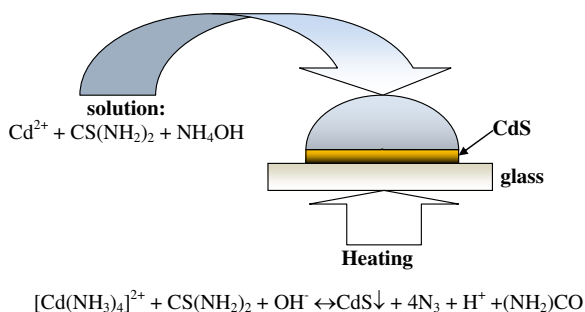
Fig. 1. Scheme of CdS films thin chemical surface deposition

with working solution is previously placed on thermostated (343 K) surface. Surface tension of the solution provides a minimum volume of reaction mixture and its maintenance on the substrate. Film deposition occurs through the heterogeneous growth of compounds on the substrate surface by transfer of heat to the work solution. Heterogeneous growth is preferred over homogeneous loss due to thermal stimulation of chemical activity on warmer surface. At a result we receive a high proportion of cadmium from a solution in film and depending on the substrate, the heteroepitaxial film growth. The outflow of heat from the solution to environment helps to keep the favorable conditions for the film heterogeneous growth in time required for film deposition. After heating the plate was removed, the surface was rinsed with distilled water and dried in the air.

The combination of factors of the heat delivery to phase division surface (substrate-solution) and small volume of working solution in the CSD allows to receive coverage with satisfactory performance, increase the efficiency of the reagents, and therefore simplify their utilization. For deposition of CdS films were used freshlyprepared aqueous solutions of one of three cadmium salts: $CdSO_4$, $CdCl_2$, CdI_2. Solution ingredients and the corresponding concentrations are presented in Table. 1.

salt	C(cadmium salt), mol/l	C(CS(NH$_2$)$_2$), mol/l	C(NH$_4$OH), mol/l
$CdSO_4$			
$CdCl_2$	0,001; 0,0001	0,1; 0,01	1,8; 1,2
CdI_2			

Table 1. Ingredients and concentrations of solutions for CSD of CdS films, T=343 K, pH=12

Several modifications of films CSD were used. First modification (A) includes single applying of working solution and it different time exposure (5 to 12 min.) on the substrate. The second modification (B) provided repeated addition (3 min intervals.) of fresh working solution on the substrate surface. The difference of the third modification (C) consistent in applying (with 3 min. time exposure) and subsequent flushing of working solution on the substrate surface, ie in layer deposition. In such way we achieved increase and regulation of CdS film thickness.

	modifications		
	A	B	C
maximum thickness, nm	62	65	105
deposition rate, nm/min.	≤6	4–6	≥8

Table 2. The CdS films maximum thickness and deposition rate depending on the CSD modification

Aplying of A modification results in the smallest CdS film thickness, as seen from Table. 2. This is because the main part of the film (80-90 % thickness) is deposited in 2-3 min. Further time exposure of the working solution-substrate system is not accompanied by visible changes in the appearance of the formed film, apparently due to exhaustion of working solution. Therefore, during the multistage (CSD modifications B and C) CdS films deposition the duration of elementary expositions deposition was 3 min. Based on the structural studies results for further work modification B was selected.

3.3 Properties of CSD CdS thin films

The film thickness was determined by ellipsometric measurement of light polarization change after light reflection from an air-film interface on the LEF-3M instrument, allowing precision from 5 to 10 nm, for film thickness less then 100 nm. Morphology of the film surface and the elemental composition were investigated using the scanning electron microscopes REMMA-102-02 with EDS and WEDS and JSM-6490LV. Crystallinity of the CdS film structure was investigated using the automated X-ray diffractometer HZG-4A (with CuK$_\alpha$ radiation, λ=0,15406 nm). The optical transmission measurements have been done at room temperature with unpolarized light at normal incidence in the wavelength range from 300 to 1000 nm using Shimadzu UV-3600 double beam UV/VIS spectrophotometer. The optical absorption coefficient α was calculated for each film using the equation

$$I_t = I_0 \exp(-\alpha t) \tag{9}$$

where t is the film thickness, I_t and I_o are the intensity of transmitted light and initial light, respectively. The absorption coefficient α is related to the incident photon energy $h\nu$ as:

$$\alpha \cdot h\nu = A\left(h\nu - E_g\right)^{n/2} \tag{10}$$

where A is a constant dependent on electron and hole effective mass and interband transition, E_g is the optical band gap, and n is equal to 1 for direct band gap material such as CdS. The band gap E_g was determined for each film by plotting $(\alpha h\nu)^2$ vs $h\nu$ and then extrapolating the straight line to the energy axis.

3.3.1 Thickness and deposition rate

The peculiarity of the CSD method is that after the first deposition the function of the substrate is performed not by glass, but by formed CdS film. All subsequent depositions are conducted on the same substrate. Through this growth rate of successive layers is approximately the same, and the total film thickness increases in equal size. The data of film thickness measurements and calculated average growth rate is shown on Fig. 2. The accuracy of ellipsometric measurements of thickness increased as the total thickness of the film growth, so that the absolute error varied from ± 10 nm to ± 5 nm. The highest thickness obtained was in the case of CdSO$_4$, and the least thickness in the CdI$_2$ case.

Apparently, among all other Cd salts, CdI$_2$ always results in a much thinner film. This observation was in agreement with what was reported earlier (Kitaev at al., 1965, Ortega-Borges & Lincot, 1993). This can be explained by different values of stability constant of Cd complexes complementary (Khallaf at al., 2008).While using for CSD the CdCl$_2$ (Fig. 2, a) were obtain almost linear dependence increase of film thickness on the deposition time. For films deposited with CdSO$_4$ and CdJ$_2$ (Fig. 2, b and c, respectively), the dependence of film thickness on deposition time was more complicated, but also had a character close to linear. This fact can be used for CdS films thickness control with high precision in the CdS/SdTe HJ fabrication. The differences in the nature of layer growth of thin CdS films can be explained by the process stages. When solution is applied to the substrate and heated, thiocarbamid complexes start to orient on active centers of the substrate surface and form CdS growth centers. The maximum possible number of growth centers is determined by the number of active centers on the substrate surface, which is considerably less than reactive particles in solution. Under the influence of continuous solution flow the grow centers increases and turn into islands. After a surface filling the islands are merging and form netted
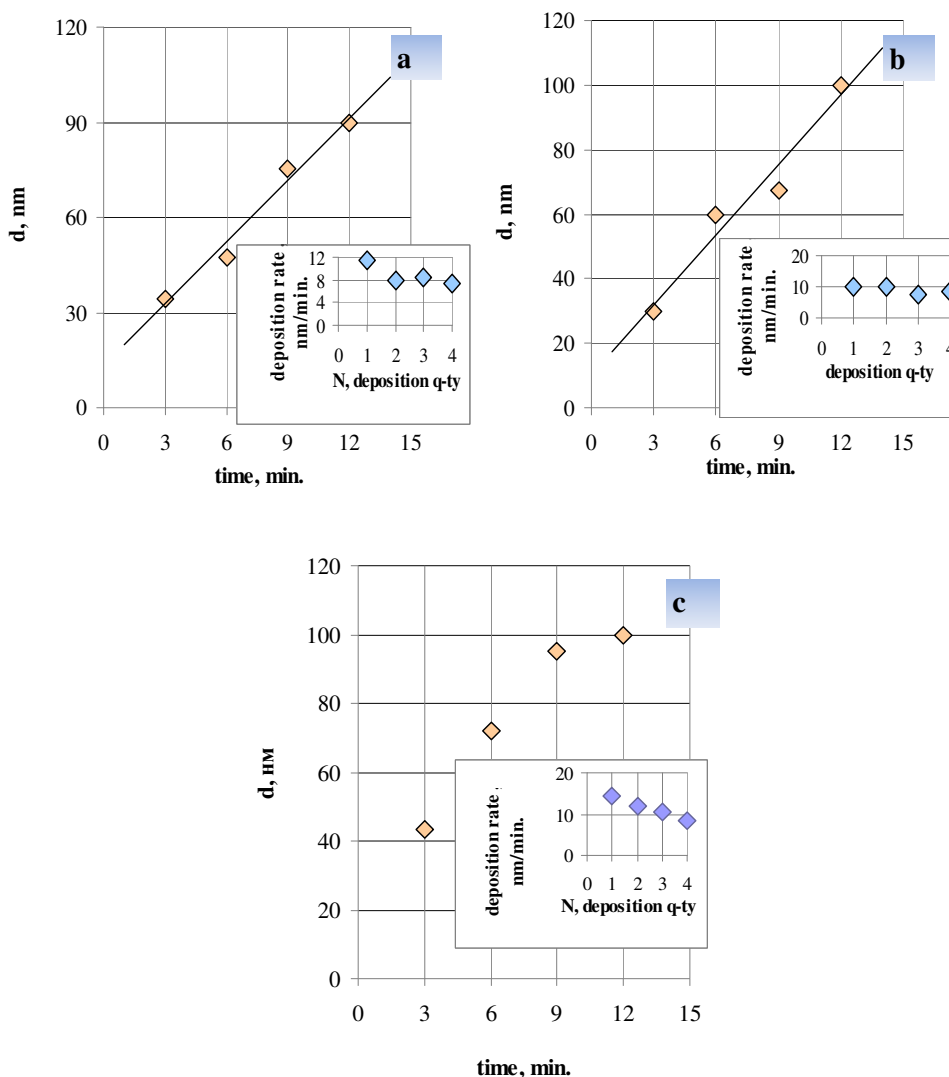
Fig. 2. The CdS thin film thickness dependence on time and quantity of deposition from aqueus solution: $CdCl_2$ (a); $CdSO_4$ (b); CdJ_2 (c). The mean deposition rate of CdS thin films on figure inset.

structures that consist of pores and channels. Further film growth is, in fact, filling the pores and channels. It slows the increase of film thickness, but does not alter the film weight gain. At later stages of the growth occurs reflection of the particles stream from the surface that leads to film growth rate decrease, and in the future - to its almost complete stop. Maximum growth rate of CSD at 343 K had films deposited from CdI_2 solution. Big deposition rates cause to the significant film defections, which confirm the results of their structural studies.

3.3.2 Surface morphology

The results of the CdS films investigation by scanning electron microscopy, deposited from diferent aqueous salt solutions are shown in Fig. 3-7, in the reflected and secondary electrons mode.
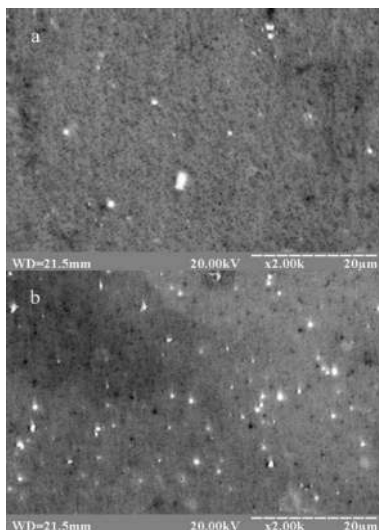
Fig. 3. Surface morphology of CdS film deposited from $CdSO_4$ aqueus solution, A modification (a) and C modification (b). REMMA-102-02, accelerating voltage 20 kV, scale 1:2000
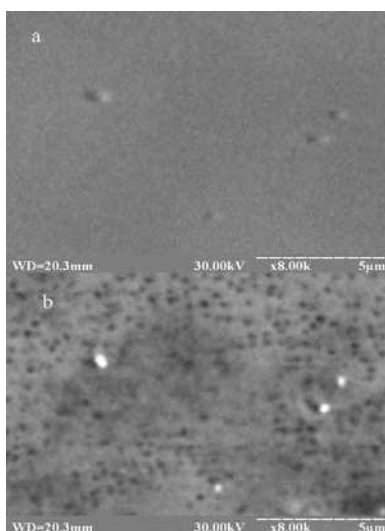
Fig. 4. Surface morphology of CdS film deposited from $CdSO_4$ aqueus solution on ITO coated glass in the secondary-electron mode (a) and reflected-electron mode (b). REMMA-102-02, accelerating voltage 30 kV, scale 1:8000
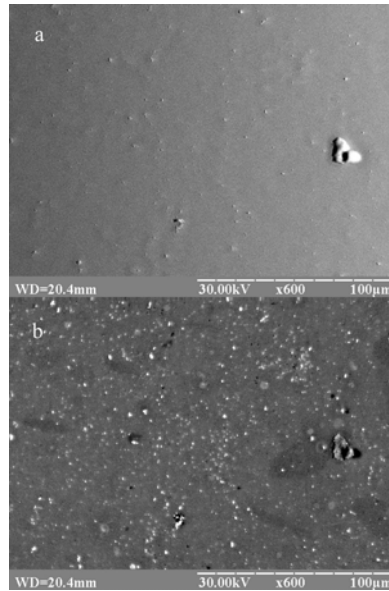
Fig. 5. Surface morphology of CdS film deposited from CdCl$_2$ aqueus solution in the secondary-electron mode (a) and reflected-electron mode (b). REMMA-102-02, accelerating voltage 30 kV, scale 1:600
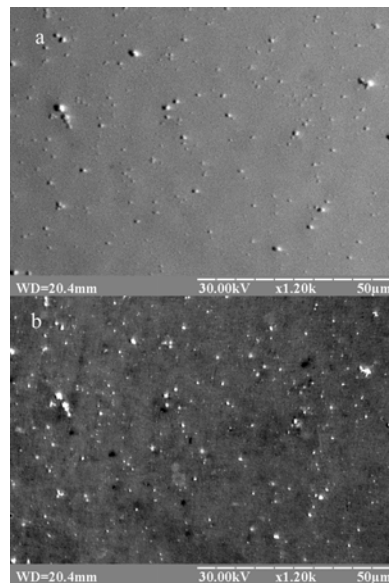
Fig. 6. Surface morphology of CdS film deposited from CdI$_2$ aqueus solution in the secondary-electron mode (a) and reflected-electron mode (b). REMMA-102-02, accelerating voltage 30 kV, scale 1:1200

In reflected electron mode the photo qualitatively displays the surface composition (the lighter point, the heavier elements), and in secondary electron mode - the surface morfology. As seen all CdS film fabricated by C modification completely covers the substrate across the sample area, are homogeneous and solid. In reflected electrons mode are observed white dots indicating the localization heavier compared to the film phase. Comparison of CdS film images, obtained in both reflected and secondary electrons (Fig. 4-6), indicates that the heavier phase inclusions are on the film surface.

So, these heavier phase inclusions are particles on the surface (surface macrodefects) and most likely were formed in the final phase of deposition. The concentration of macrodefects on the surface in the investigated CdS films deposited from varus cadmium salts are presented in table 3. Regardles of applied salt surface macrodefects concentration is almost the same and is 100 times smaler than for CBD films (Romeo at al., 2003). Using EDS and WDS measurements, the stoichiometry of all films were studied. The generalized results of the surface morphology and X-ray microanalysis investigation of thin CdS films, deposited from various cadmium salts are given in Table 3. We determined that the particles on the CdS films surface (macrodefects) are CdS particles with a different stoichiometry than the film. The stoichiometry deviation towards sulfur is quite unexpected because in most nonvacuum deposition methods the lack of sulfur is observed.
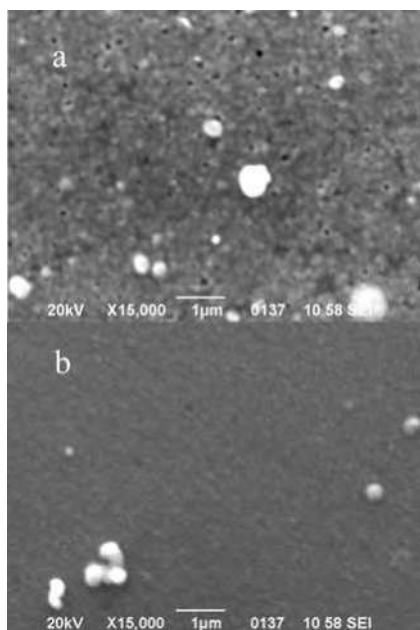

Fig. 7. Surface morphology of CdS film deposited from CdI_2 aqueus solution before (a) and after annealing (b). JSM-6490LV, accelerating voltage 20 kV, scale 1:15000

The CdI_2-based films had composition close to stoichiometric while the $CdSO_4$-based films showed the biggest deviation from stoichiometric composition that agre with results of CBD (Ortega-Borges & Lincot, 1993) (Table 3). Sulfur excess in CSD CdS films gives us the opportunity to perform annealing in the normal (air), not sulfur medium because they do

not need to enter in film extra amount of sulfur to ensure stoichiometry. Analysis of CdS films surface morphology, obtained by AFM (Fig. 8) shows that the method of deposition and the nature of the initial cadmium-containing salt have significant affect on the CdS film surface structures. Using the deposition B modification ensure much more evenly cover over the sample area than A modification. The best results were obtained by C modification. The CdS films deposited from $CdSO_4$ aqueous solution by B and C (Fig. 8, a and b, respectively) have different surface morphology. The surface of all films obtained in the C modifications, is completely packed with crystalline grains. The exception is the film obtained from cadmium iodide aqueous solution. Along with the films surface morphology the results of surface roughness analysis are presented.

salt	surface macrodefects concentration, cm^{-2}	Cd/S rate on film surface	Cd/S rate of surface macrodefects
$CdSO_4$	10^6–10^7	0,880	0,800
$CdCl_2$	10^7	0,898	0,908
CdI_2	10^6–10^7, the pineholes are observed, for films deposited from two other salts the pinholes are almost absent	0,911	1,061

Table 3. Summarized results of surface morphology and X-ray microanalysis investigation of CdS thin films, deposited from various cadmium salts

3.3.3 Crystal structure

Experimental diffraction intensities of CdS films, obtained by B and C modification of (curves 2 and 3), respectively, are shown in Fig. 9. In all tested samples polycrystallinity of CdS films is expressed with the noticeable presence of cubic phase. The curves 2 and 4 on fig. 9. indicates that the samples are almost completely polycrystalline.

The first $26,45^0$ peak of cubic phase (curves 2 and 4) is slightly expressed and shifted compered to the corresponding XRD peak from single CdS crystal (curve 1), which can be explained by the small size of grains as the probability of mechanical stress in films is very small because of low speed growth (Table 2).

In addition to the $26,45^0$ peak on curve 3 (Fig. 9) are present two more – $43,90^0$ and $52,00^0$, corresponding to the cubic phase. Implemented sample heat treatment does not result in a significant increase in the intensity of any of the three peaks, and even the intensity of first one decreases (curve 4). The shift of the first $(26,45^0)$ peak (curves 3 and 4) related with a decrease after annealing of mechanical tensions in the film, and intensity decrease of this peak indicates a simultaneous transition in polycrystalline cubic phase. Size grains expected increase by recrystallization has not occurred. Thus, annealing conditions to improve crystallinity of films need correction. Based on the data diffraction pattern most of the cubic phase is contained in the films deposited by C modification $C(CdSO_4)$ = 0,001 mol/l. The transition to the hexagonal phase after annealing is not observed, unlike CBD CdS film (Archbold at al., 2005, Romeo at al., 2000).

Fig. 10 shows the experimental diffraction intensities obtained from CdS films, deposited from aqueous solutions of $CdSO_4$, $CdCl_2$, CdI_2 salts on glass substrates before and after annealing. In all tested samples polycrystallinity of CdS films is expressed with the noticeable presence of cubic phase. From the curves 2 (Fig. 10, a, b, c) can be seen that as deposited samples are almost entirely polycrystalline. The first peak of 26,45 ° for the cubic
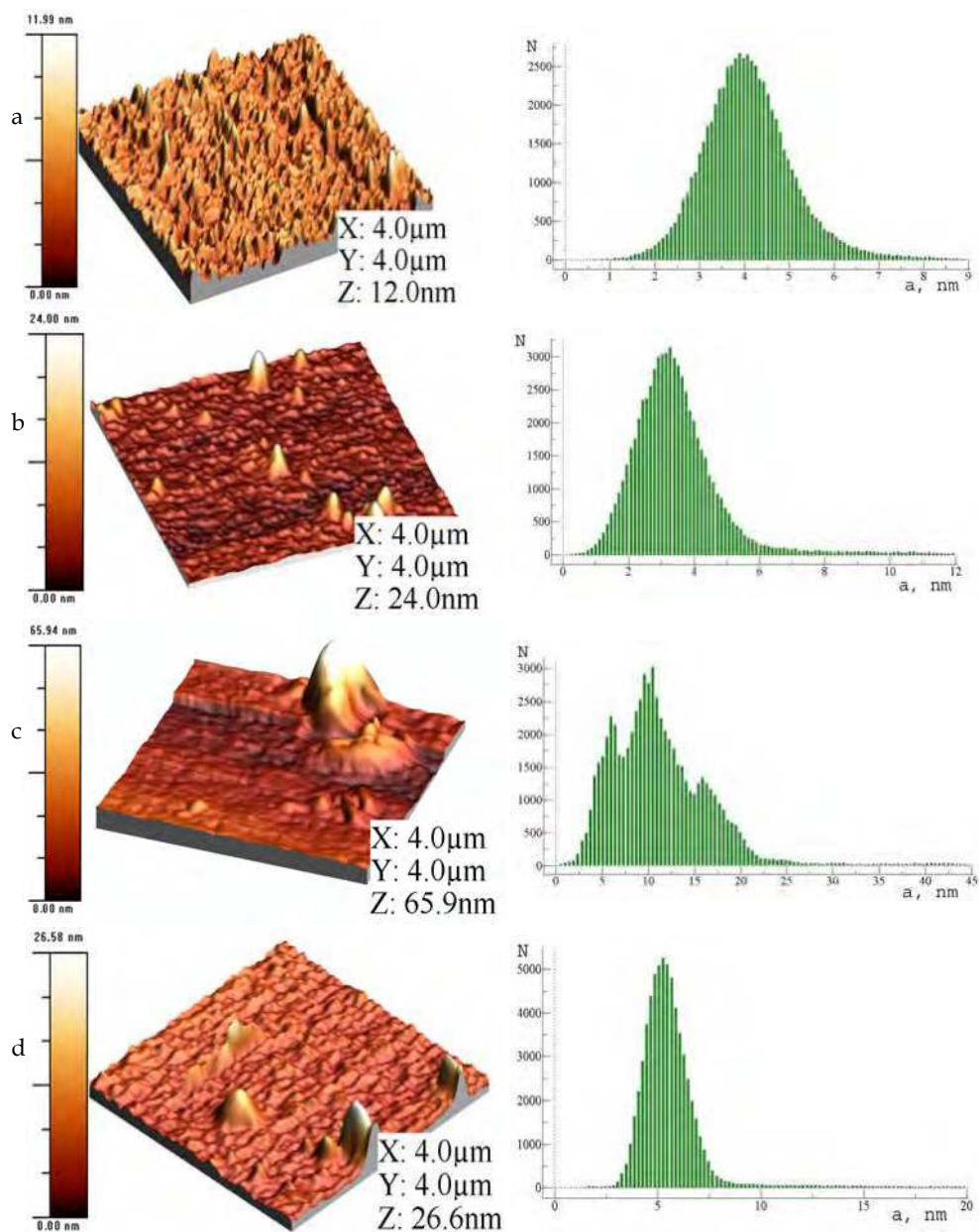
Fig. 8. AFM images and mean roughness distribution of CdS thin films grown from aqueus solution: CdSO$_4$, B modification (a); CdSO$_4$, C modification (b); CdCl$_2$, C modification (c); CdJ$_2$, C modification (d)
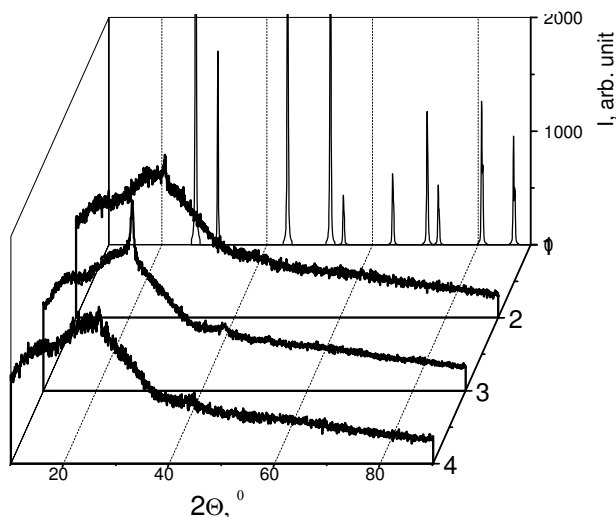
Fig. 9. XRD pattern of CdS film deposited on glass substrate from $CdSO_4$ aqueous solution with $C(CdSO_4)$=0,001 mol/l by B and C modification (curves 2 and 3);
$C(CdSO_4)$=0,001 mol/l by C modification, after annealing (curve 4); with
$C(CdSO_4)$=0,0001 mol/l C modification (curve 5); CdS cubic monocrystal reference pattern (curve 1).

phase have low intensitivity and is slightly shifted against the corresponding peak of CdS single crystal. This can be explained by the small size of grains as the probability of mechanical tensions in films deposited from $CdSO_4$, $CdCl_2$ salts solutions is neglectible due too low growth speed. Besides peak 26,45°, on curve 2 (Fig. 10 b) are present two more - 43,90° and 52,00° corresponding to the cubic phase. The heat treatment of samples leads to a significant increase in the intensity of the first two peaks for films deposited from $CdSO_4$, CdI_2. For films deposited from $CdCl_2$ aqueous solutions, the nature of XRD curve practically unchanges due to annealing. For CdS films, deposited from CdI_2 aqueous solution (fig. 10c curve 1) after annealing were observed intensity increases of 26,45°, 52,00° peaks and the appearance of third peak 43,90°. This indicates a reduction of disordered polycrystalline phase which transforms into crystalline phase and a rather significant restructure of CSD film, that cinsides with the results of the surface morphology investigations (Fig. 7).

Experimental diffraction intensities of CdS films deposited on Si and CdTe substrates are presented in Fig. 11. As seen, the results for various substrates were different, but both express polycrystallinity of CdS films. Besides the peaks of Si (Fig. 11 a, № 3) and CdTe (Fig. 11 b, № 5, 8) substrates are present a significant number of peaks corresponding to different phases of CdS compound. These results indicate the existence of a mixture of two structural phases (cubic and hexagonal) that is often observed for CdS films fabricated by nonvacuum methods (Calixto & Sebastian, 1999). The X-ray diffraction peaks N 1, 2, 7, 4, 9 (Fig. 11a) on silicon corespond to hexagonal structure, cubic may respond only the peak number 1. For films on CdTe substrate peaks intensity of hexagonal and cubic phases is much higher.
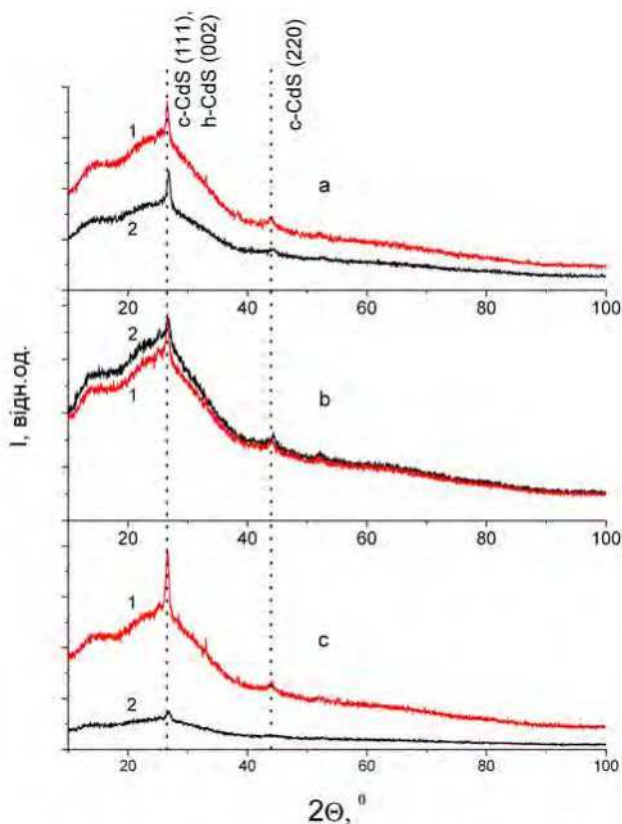
Fig. 10. XRD pattern of CdS film deposited on glass substrate from aqueus solution: CdSO$_4$ (a); CdCl$_2$ (b); CdJ$_2$ (c); as deposited (2); after annealing (1).

3.3.4 Optical properties

Absorption coefficient in the fundamental absorption area for all CdS samples was 10^5 cm^{-1}. The absorption spectra of samples (Fig. 12.) clearly shows the existence of the CdS compounds in all films deposited from aqueous solutions of cadmium-containing salts. Spectral dependence of CdS films absorption in the coordinates $(\alpha^* h\nu)^2$ vs $h\nu$ demonstrate the presence of fundamental absorption edge (Fig. 12), localized in the region 2,5 eV. The calculated band gaps of the films are in good agreement with the reported values (Landolt-Börnstein, 1999, Aven & Prener, 1967) and correspond to the direct allowed band transition. We do not observe a straight-line behaviour on graphs of $(\alpha h\nu)^{2/3}$ vs $h\nu$ (direct forbidden), $(\alpha h\nu)^{1/2}$ vs $h\nu$ (indirect allowed) $(\alpha h\nu)^{1/3}$ vs $h\nu$ (indirect forbidden). These plots (not shown) reveal that the type of transition is neither direct forbidden nor indirect. For films deposited in the same technological modes on glass and ITO coated glass substrates, the location of fundamental absorption edge are olmost the same. A small (0,01 eV) difference between the fundamental absorption edge values for films on glass and ITO/glass are caused by the difference of substrates surface roughness.
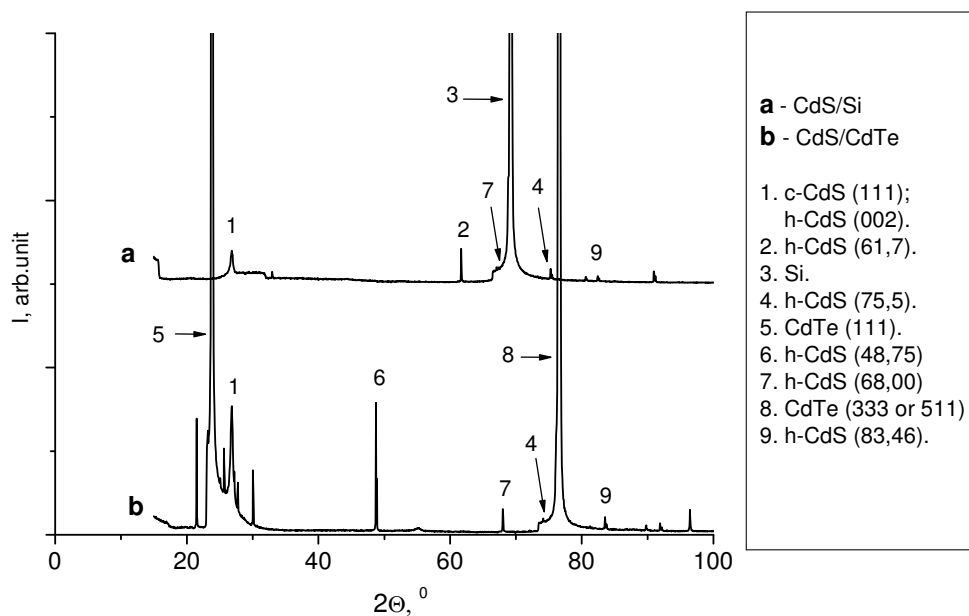
Fig. 11. XRD pattern of CdS films deposited from CdCl₂ aqueus solution on Si (a) and CdTe (b) substrates

The fundamental absorption edge localization feature in CdS films, in comparison with CdS monocrystal, is that in films it is shifted to higher energy region (2,537 eV and 2,547 eV for films on glass and ITO/glass, respectively).
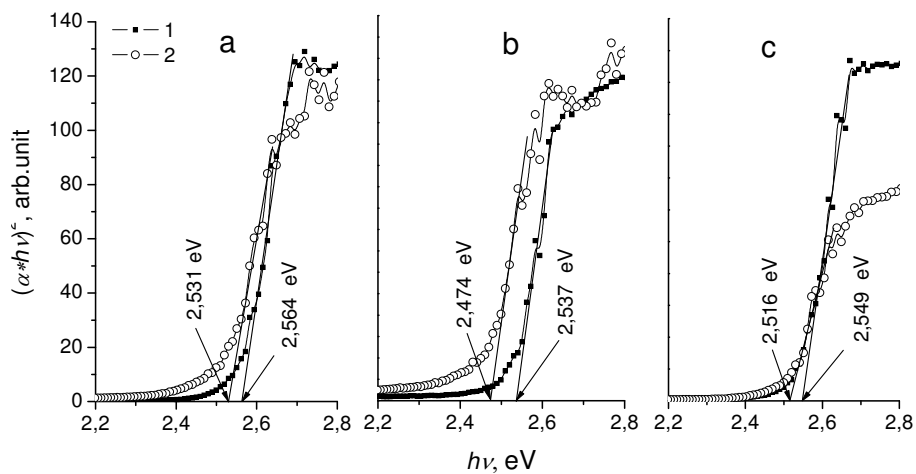

Fig. 12. Optical absorbance spectra of CdS film deposited on glass substrate from aqueus solution: CdSO₄ (a); CdCl₂ (b); CdJ₂ (c); as deposited (1); after annealing (2).

This allows to expand CdS/CdTe solar cells phototransformation area and increase their efficiency. Reducing energy fundamental absorption edge of CdS films after annealing (Fig. 12, curves 2) can be coused by grain growth (Nair at al., 2001). Sharpest edge of fundamental absorption have CdS films, deposited on glass substrate. This indicates a smaller number of macro defects in these films compared with annealed. Energy levels of this defects are lying near the edge zones. The increase long-wave "tail" of the absorption curve for annealed film (Fig. 12, a, b, curve 2) is caused by increase of absorption near the CdS film surface, where in the process of annealing in air CdO can be formed.

All films have high transmission, with the transmission in the CdI_2 case being better than that of the other three films. This was expected, since the SEM micrographs, showed the pinholes on CdI_2-based film. The lowered transmission of our films is caused by their surface roughness, due to coverage by surface macrodefects which are overgrowth crystallite, causes light scattering. Spectral dependence of optical transmission in the visible region of CSD CdS films before and after annealing are shown in Fig. 13. The main feature of the annealed CdS films spectra is small (0.033 eV) shift of fundamental absorption edge in the longwave region and reducing the optical transmission more than 20%. Reducing the transmission is determined not only by absorption and reflection from the film surface, but olso by quite significant changes in the film structure after annealing. From the SEM holes were observed (Fig. 7) after annealing they completely disappeared. X-ray pattern (Fig. 10, c, curve 1) also confirm a significant increase in the film's crystallinity structure as a result of annealing, despite indifferent directing effect of the glass substrate.
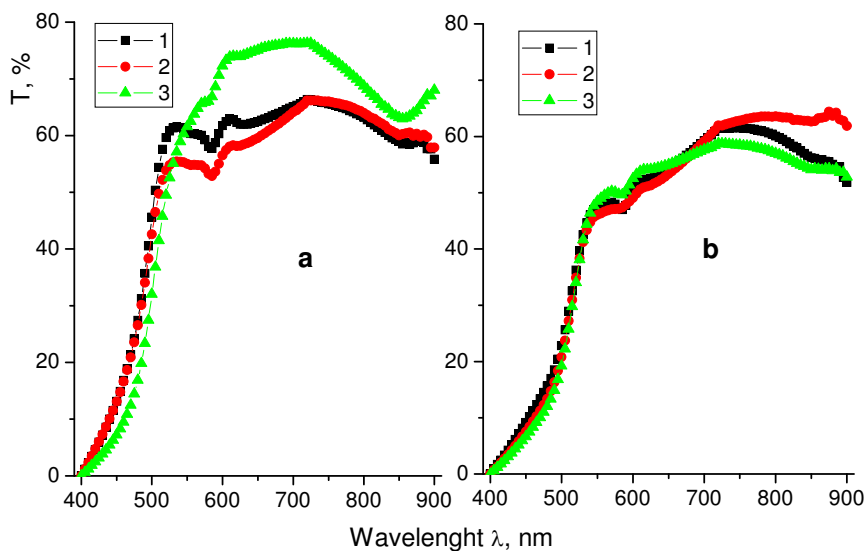

Fig. 13. Optical transmittance spectra of CSD CdS films deposited from aqueus solution: $CdCl_2$ (1); $CdSO_4$ (2), CdJ_2 (3) as deposited (a) and after annealing (b).

4. Solar cell performance

The n-CdS/p-CdTe HJ was fabricated and their electrical and photoelectric properties were investigated. The CdS thin films with 100 nm thickness were deposited by CSD using $CdCl_2$

cadmium chloride solution. Thin polycrystalline CdS films completely covered the substrate across the sample area, hade stoichiometric composition, was solid with a small surface macrodefects concentration ($10^7 sm^{-2}$). Typical spectral dependence of transmission of CSD CdS film is shown on Fig. 13. Resistance of is fabricated n-CdS/p-CdTe SC $R_0 \approx 10^4$-10^5 Ω at T= 300 K and was determined by the electrical properties of the p-CdTe substrates. This is coused by the resistivity of used substrates which is 2-3 orders of magnitude greater than the similar parameter for n-CdS films ($R_{CdS} \approx 10^3$ Ω). Voltage cutoff in n-CdS/p-CdTe structures, as seen in Fig. 14 is $U_0 \approx 1,4$ V and its value is close to CdTe bandgap (Landolt-Börnstein, 1999). Inverse branches of curent-voltage characteristic for anisotropic structures are well described by power dependence $I_R \sim U^m$, where the m ≈ 1 to U> 2, which is typical for charge carriers tunneling or inherent space charge limited currents in velocity saturation mode (Hernandez, 1998, Lamperg & Mark, 1973). Reverse current increase observed in the investigated anisotropic heterojunction with increasing voltage bias can also be caused by imperfections in their periphery.

Fig. 15 shows relative quantum efficiency of photoconversion (ratio of short circuit current to number of incident photons) η(hν) spectra of CdS/CdTe heterojunction fabricated by CSD of CdS film on CdTe wafer. The η(hν) spectra find out to be similar for structures fabricated on different substrates what indicate high local homogeneity of substrates and reproducibility of the CSD films properties. The sharp long wave increase of η(hν) in narrow spectral range 1.4–1.5 eV for CdS/CdTe structure illumination from CdS film side is observed. Its value reach maximum in region $h\nu^m \approx 1.5$ eV what correspond to energy of direct band transitions in CdTe (Landolt-Börnstein, 1999, Aven & Prener, 1967).
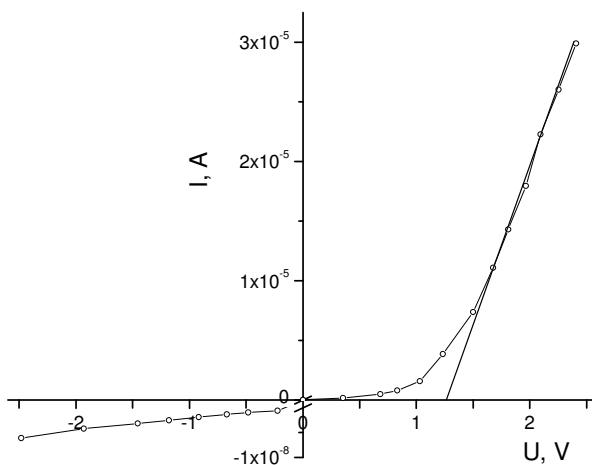

Fig. 14. Curent-voltage characteristic of *n*-CdS/*p*-CdTe HJ at 300 K

It should be notice that photosensitivity of the fabricated CdS/CdTe heterostructures maintain on high level (fig. 15, curve 1, 2) in vide region of incident photons energy. The table like part of η(hν) curve confirm fabrication of the CdS/CdTe high quality heterojunction. The observed η(hν) curve decrease at hν≥2.3 eV is similar to specular transmission spectra of CdS film used for CdS/CdTe heterostructure fabrication. The full wide on half of the maximum (FWHM) of η(hν) spectra δ≈1.1–1.2 eV in our structures is more bigger then FWHM of Ox/CdTe heterostructure (Il'chuk at al., 2000) and indicate higher quality of fabricated structures compared to known.
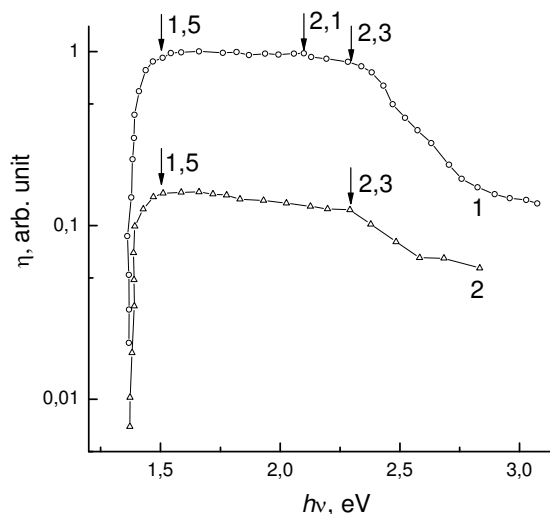
Fig. 15. Spectral distribution of the quantum efficiency of n-CdS/p-CdTe heterojunction at 300 K. Ilumination form CdS film side. The 1 and 2 curves coorespond to samples with diferet thickness of CdS film.

5. Conclusions

The II-VI binary CdS compound semiconductor thin films (30–100 nm) has been successfully deposited from aqueous solutions of $CdCl_2$, $CdSO_4$, CdI_2 salts using Chemical Surface Deposition and employing the direct heating of the substrate.

The linear dependence increase of film thickness on the deposition time was experimentally demonstrated for CSD $CdCl_2$ based films. For the two other salts of the film thickness dependence on deposition time is more complex, but has a character close to linear.

Established that for growth rate <15 nm/min. chemical deposition method allows to growth solid polycrystalline CdS films with 10^6-10^7 cm^{-2} surface macrodefects concentration.

It is proved that CdI_2 based CdS film composition was close to stoichiometric, compared to films deposited from solutions of two ather salts under identical conditions.

The possibility of n-CdS/p-CdTe high quality solar cell fabrication by CSD of CdS thin film is demonstrated. High value of CdS/CdTe heterojunction photoconversion, in region limited by CdS and CdTe band gaps, in our opinion was provided by CdS deposition method.

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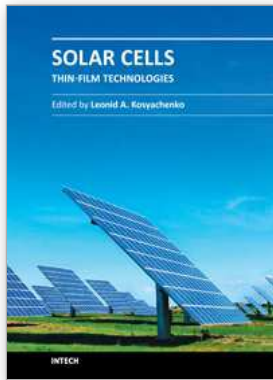
Solar Cells - Thin-Film Technologies

Edited by Prof. Leonid A. Kosyachenko

The first book of this four-volume edition is dedicated to one of the most promising areas of photovoltaics, which has already reached a large-scale production of the second-generation thin-film solar modules and has resulted in building the powerful solar plants in several countries around the world. Thin-film technologies using direct-gap semiconductors such as CIGS and CdTe offer the lowest manufacturing costs and are becoming more prevalent in the industry allowing to improve manufacturability of the production at significantly larger scales than for wafer or ribbon Si modules. It is only a matter of time before thin films like CIGS and CdTe will replace wafer-based silicon solar cells as the dominant photovoltaic technology. Photoelectric efficiency of thin-film solar modules is still far from the theoretical limit. The scientific and technological problems of increasing this key parameter of the solar cell are discussed in several chapters of this volume.

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