

## Zn<sub>1-x</sub>Cd<sub>x</sub>S Nanoparticles, Nanofilms, Nanoscale Junction for Solar Cells

M.A. Jafarov, E.F. Nasirov

*Baku State University, Baku 1045, Z.Khalilov st.23, Azerbaijan*

(Received 26 June 2012; published online 09 August)

In this work the results on the investigation of the peculiarity near the solar spectrum region, of Zn<sub>1-x</sub>Cd<sub>x</sub>S nanoparticles, nanofilms, nanoscale p-n and heterojunction prepared on glass-ceramic and aluminium substrates by precipitation from aqueous solutions are presented. The temperature dependence of dark and light conductivity, spectrum and optical quenching of primary and impurity photoconductivity are investigated. The obtained results show that when controlling ionic composition and heat-treatment (HT) conditions, one can purposely control the properties of Zn<sub>1-x</sub>Cd<sub>x</sub>S (0 ≤ x ≤ 0.6) films, achieve the appropriate degree of compensation of different recombination levels and traps attributed to intrinsic defects or impurities, which result in high level of photoelectrical parameters near the IR region. Just after deposition the photoconductivity spectrum maximum of Cd<sub>1-x</sub>Zn<sub>x</sub>S (0 ≤ x ≤ 0.6) films is observed at λ<sub>1</sub> = 0.445 ± 0.495 μm versus the film composition. Subsequent to HT, the photoconductivity spectrum considerably widens and appears the impurity maximums at λ<sub>2</sub> = 0.58 ± 0.69 μm and λ<sub>3</sub> = 0.95 ± 1.05 μm.

**Keywords:** Chemical bath deposition, Nanoparticle, Nanoscale p-n junction, Micro emulsion system

PACS numbers: 78.67.Bf, 81.16.Be

### 1. INTRODUCTION

Among the many different methods available to deposit films of semiconductors, chemical bath deposition (CBD) must rank as conceptually the simplest. CBD refers to depositions from solution (usually aqueous) where the required deposit is both chemically generated and deposited in the same bath. Thus, deposition from a supersaturated solution or spin coating from a colloidal sol are not included under the aegis of CBD: in both cases, the layer material must be pre-prepared. Neither is sol-gel layer formation, although it could be reasonably argued that the cross-linking which occurs during the process constitutes a chemical reaction. Successive ion layer adsorption and reaction (SILAR) is a related technique, where a substrate is first dipped in an ionic solution of one component, rinsed, then dipped in a solution of the second component and rinsed; this ideally results in a single monolayer of the desired compound. Liquid phase deposition (LPD) is a specific subset of CBD often used for acidic oxides. In spite of it being so simple, it is one of the least known. If scientists or engineers in general would be asked to name some semiconductor film deposition methods, evaporation, chemical vapour deposition, sputtering, may be even electrodeposition, would be the most obvious techniques that would spring to mind: CBD would probably be well down the list (with the obvious exception of those who work with the method). A part of the reason (probably not the main part, which remains non-obvious) is the many different terms used to denote CBD: chemical solution deposition (used to be more popular, but a consensus is beginning to appear favoring CBD), chemical deposition (when it is clear that chemical vapour deposition—a very different technique—is not meant) and liquid phase deposition (used for certain oxide depositions).<sup>1,2</sup>

The last decade sharply increased, the interest to nano-objects with the most distinguishes features. It related with the unique properties of particles with this sizes which differ them from according macro phase. The

investigation of the properties of nanoparticles is one of the main aims of the novel directions of physical chemistry. Developing of this direction is closely connected with the simple and accessible methods of synthesis, which allow preparing of nanoparticles with the simulated size and rather narrow separation on sizes. The reverse micro emulsion systems are thermodynamically sustainable double phase systems, that consist of polar phase micro drops, separated in nonpolar ambient. Surface-active materials (SAM) are used for stabilization of the systems like this. It makes possible caring out chemical reactions among materials in polar phase and forming hard-solved compounds. The advantage of this preparing method of nanoparticles is relatively simplicity and also possibilities of simultaneous synthesis and stabilization of prepared particles.

The obtained results show that when controlling ionic composition and HT conditions, one can control properties of the Zn<sub>1-x</sub>Cd<sub>x</sub>S films. Furthermore, the above films are nearly similar in their main photoelectric properties and parameters to such model crystals as CdS and ZnS, to allow for the effect of sticking centers, conditioned polycrystalline structure. Since the Zn<sub>1-x</sub>Cd<sub>x</sub>S films can be used as photodetectors of the near IR region. To determine the general regularities and characteristic of recombination and electron-molecular processes, determinant high sensitivity in IR region, versus the composition and heat-treatment (HT) conditions, the photoelectrical properties of Zn<sub>1-x</sub>Cd<sub>x</sub>S (0 ≤ x ≤ 0.6) films deposited from the solution is the purpose of present investigations<sup>3-5</sup>.

### 2. EXPERIMENT

In this paper, it was investigated preparing of nanoparticles of ZnCdS in micro emulsion system stabilized with nonionic surface active materials and impact of volume of the drops and supersaturation to size of forming ZnS particles. Hexamethylene was used as a non polar phase. We used water, water solution of Cd(Ac)<sub>2</sub>, ZnCl<sub>2</sub> and precrystallized Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as a polar phase.

All solutions have been prepared in bidistilled water. Reverse micro emulsion systems were prepared by solubilization of water, water solutions according to salts in reverse micelles system, which Tx-100 concentration was 0.3 M and SAM/n-SAM ratio was 4:1. The water or water solutions of corresponding salts were added to the defined volume of this solution with drops in such amount that  $W=[H_2O]/[SAM]$  ratio have been varied in the range of 5-15. Equal volume of micro emulsion with similar content, containing ions of reacting substances in aqueous phase was mixed for preparing cadmium sulfide.

Particle size of cadmium sulfide prepared during reaction process has been defined by spectrophotometrical method. Dependence of optical density on wavelength was measured by spectrophotometer in cuvette in the range of wavelength 320-500 nm.

The  $Zn_{1-x}Cd_xS$  ( $0 \leq x \leq 0.6$ ) films of 0,8-2 $\mu$ m thickness were deposited on glass ceramic substrates from aqueous solution by the method described in<sup>3</sup>. This was prepared by adding into the beaker containing the stirred deionized water at 85 °C,  $Cd(CH_3COO)_2$ ,  $Zn(CH_3COO)_2$ ,  $NH_4OH$ , and  $Na_2S_2O_3$ , from 0.05, 0.05, 12 and 0,2M stock solutions, respectively, in that order. The nanofilms composition ( $0 \leq x \leq 0.6$ ) was changed by partial substitution of the thiourea and was controlled by chemical, spectral and X-ray phase analyses. XRD pattern of  $Zn_{1-x}Cd_xS$  thin films were using in fig.1a,b. The spectral dependence of optical transmittance of  $Zn_{1-x}Cd_xS$  films were using in fig.2. A part of films was subjected to heat-treatment in the air at temperatures of 400-500 °C for 0-30 min.

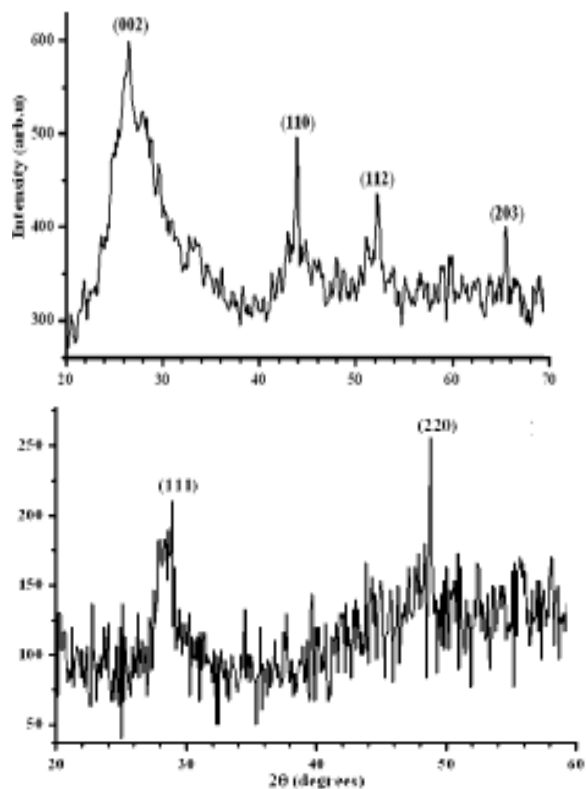


Fig. 1 – XRD pattern of thin films : (a) CdS, (b) ZnS

The temperature dependence of dark ( $\sigma_{dk}$ ) and light

conductivity ( $\sigma_{ph}$ ), the spectrum and optical quenching of photoconductivity ( $\sigma_{oq}$ ), the current-illumination characteristics, thermostimulated conductivity in the range of 80-400 K has investigated. According to thermopower measurements, the films were n-type. The dark conductivity of  $Zn_{1-x}Cd_xS$  films was found to vary with x, from  $10^{-4}$  to  $10^{-5}$  S/cm.

The ratio of photocurrent to the dark current reached  $10^2$  to  $10^3$ . The carrier concentration determined from Hall measurements was  $3-5 \times 10^{14} cm^{-3}$  and  $10^{16} cm^{-3}$  for the films with  $x=0$  and  $x=0.3$ , respectively.

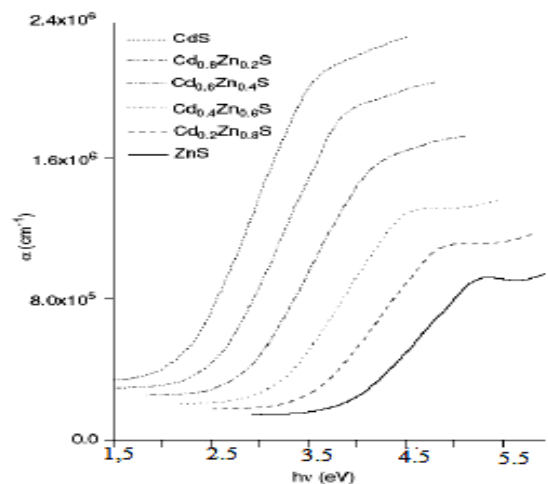
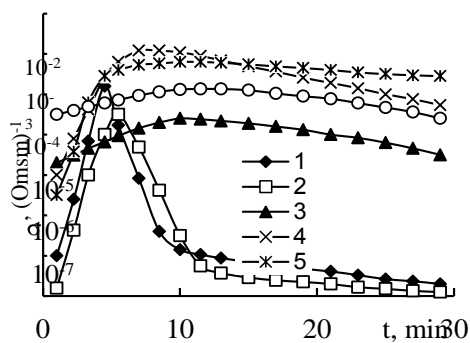


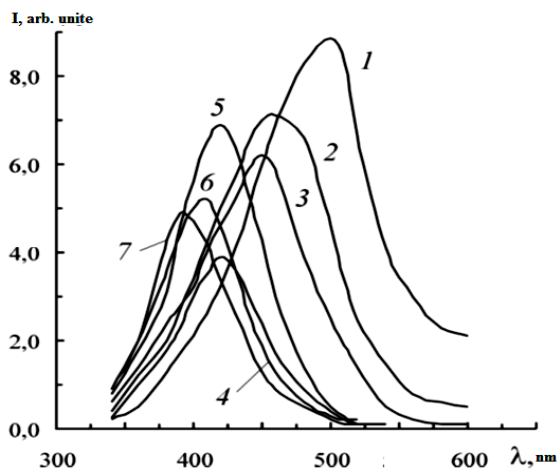
Fig. 2 – The spectral dependence of optical transmittance of  $Zn_{1-x}Cd_xS$  films

Just after deposition the above films are characterized by long-term relaxation photoeffects. Subsequent to heat-treatment, the considerable changes in photoelectric (PE) properties versus the composition, temperature and annealing time ( $\tau_a$ ) are observed (Figure 3). The dependence of conductivity as a function of time ( $\tau_0$ ) has nonmonotonically character, i.e. with low  $\tau_a$ , the conductivity of films increases and achieves a maximum value exceeding the initial one by more than four orders of magnitude. The further increase of annealing time up to 15min leads to a sharp decrease of conductivity. The  $\sigma_c(\tau_a)$  dependence has an extremum character, i.e. primarily it increases at annealing times to 15min, then ( $t \geq 15$  min) a slow decay is observed. With increasing annealing temperature and x, a shift of the above dependence extremums toward the lower times takes place (Figure 3, curves 2,3). Photoconductivity spectrum maximum of  $Cd_{1-x}Zn_xS$  ( $0 \leq x \leq 0.6$ ) films is observed at 0.445-0.495 $\mu$ m versus the composition (Figure 4, curves 1-7). Subsequent to heat treatment, the photoconductivity spectrum considerable widens and the peaks at (0.58-0.70)  $\mu$ m and (0.90-1.13)  $\mu$ m appear. With increasing time, to  $4 \leq \tau_a \leq 15$ min, the intensities of additional maximum increases and intensity of principal maximum decreases. (Figure 5, curves 1-5). The  $Cd_{1-x}Zn_xS$  ( $0 \leq x \leq 0.6$ ) films after the heat treatment at 500 °C for 5-10min exhibit high sensitivity ( $\sigma_{ph}/\sigma_{dk} = 10^7$  to  $10^8$ ) over a wide spectral range (Figure 5, curve 4).

The photosensitivity in near IR region is comparable with proper photoconductivity. But with increasing



**Fig. 3** – Semilog plot of (1,2,3) dark conductivity and (4,5,6) photoconductivity in Cd<sub>1-x</sub>Zn<sub>x</sub>S (0 ≤ x ≤ 0.6) films vs. annealing time; x = (1,4) 0.1, (2,5) 0.2, (3,6) 0.4



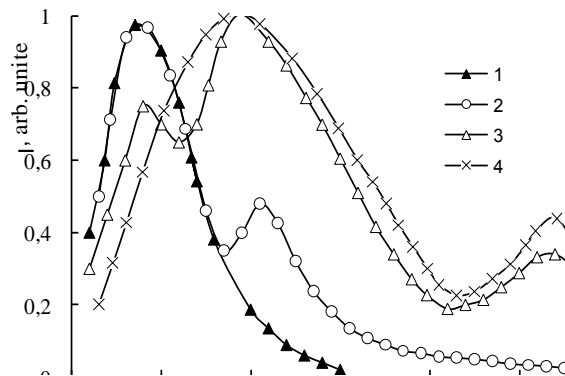
**Fig. 4** – The photoconductivity spectrum of Cd<sub>1-x</sub>Zn<sub>x</sub>S (0 ≤ x ≤ 0.6) films, versus x; 1- (0.1), 2- (0.2), 3- (0.4)

temperature from nitrogen to room, the photosensitivity stays constant. At low temperatures the Cd<sub>1-x</sub>Zn<sub>x</sub>S (x = 0.2) films have a complex spectrum of the impurity photoeffects, i.e. a superposition of several bands with 0.60 μm, 0.64 μm and 0.69 μm maximums attributed to impurity and defect centres.

The energy positions of the photoactive levels (impurity and defects levels) were determined from the impurity photoconductivity spectra when comparing them with the calculated data for deep compensated centres with a spectral dependence of photoionisation section in the c-band S<sub>n</sub>(hν) and the v-band S<sub>p</sub>(hν)<sup>6</sup>.

In the photoluminescence spectra of solid solutions is usually observed several bands correlate with different types of defects in the crystal structure of the films. The spectra of the studied films are similar in appearance and are characterized by the presence of two intense bands with maxima at 840-870 nm in the region and 970 nm.

Depending on the intensity of these bands have a maximum temperature of t = 320 °S and at t = 400 °S band disappears completely. These features show that the luminescence in the red due to the holiday-type defects (V<sub>d</sub> all). Vacancies are formed due to the presence of selenium coordination related halogen atoms.



**Fig. 5** – spectral response of the photocurrent through Cd<sub>1-x</sub>Zn<sub>x</sub>S (0 ≤ x ≤ 0.6) films annealed in air at 500 °C for (1) 0, (2) 3, (3,5) 10, (4) 15 min

With increasing annealing temperature increases to a certain limit of vacancies of selenium, which are then filled with oxygen to form complexes (V<sub>cd</sub>-O<sub>s</sub>), so the maximum emission is shifted slightly to longer wavelengths. Adding cadmium interstitial ions enriches the film, which is manifested in the detection of orange light. The excitation spectrum has a maximum for hν<sub>m</sub> = 2,95 eV. Narrow band in the excitation spectrum corresponds to the zone zonnomu excitation.

The main influence on the spectrum of radiative recombination factor is the presence of potential fluctuations caused by the distribution of intrinsic defects. The increase in content in the solution selenouera similarly annealed in selenium vapor and observed induced disordering of the anion sublattice of sulfide with the formation of defects Se and Vse. When using thiourea precipitate more thermodynamically stable wurtzite modification. Another mechanism for data analysis rentgenofaznogo observed in the case of cadmium sulphoselenides. In this case, the simultaneous use of thio- and determines the allocation selenomocheviny cubic phase

Until now, converters based on CdS produced mainly as a heterostructure. Create a p-n junction is difficult because of the receipt of CdS with hole conductivity. The literature contains only a few data concerning single-crystal film-p-n-junction. In this paper we present the results of studies of nanoscale p-n junction based on CdS, precipitated out of solution. The samples were prepared by precipitation from solution onto an aluminum substrate. Before applying the lower aluminum electrode, the sample was kept in air at 300 °S, for 10 min. Based on measurements of current-voltage (I-V) and capacitance-voltage (C-U) characteristics and thermally stimulated conductivity (TSC) of the samples it was established that the conductivity due to the presence p-n junctions. The research I-U, C-U characteristics and thermally stimulated conductivity in the temperature range 80-400 K. The I-U was removed in a pulsed, static and dynamic mode and the C-U characteristics by the method of RLC bridge, allowing simultaneous measurement of the barrier capacitance and the differential resistance of the barrier, as well as resistance in the neutral part semiconductor. Volt-ampere characteristic (VAC) nanoscale p-n transition p-CdS/n-CdS has rectifying properties by a factor of 10<sup>3</sup>-10<sup>4</sup> with a voltage of U = 1,5 ÷ 2B. It is shown that

the barrier width is 100 nm at zero bias and reaches 150nm at a voltage of 2 V reverse mixing. Hence, the space charge region in the investigated structures is only part of the film thickness and the space charge region in p-CdS is very narrow, due to the sharp asymmetry of the conductivity. In the beginning, the external voltage drops on the space charge region in CdS n-type. The presence of n-CdS with high resistivity excludes the presence of a strong field at the edge of the metal contact and forms p-n transition, parallel to the barrier Al/p-CdS. The conductivity of the tunnel transparent dielectric Al<sub>2</sub>O<sub>3</sub> present on the surface of aluminum is much higher than the conductivity is inversely biased p-n junction and most of the applied external voltage drops on the p-n junction. Direct current-voltage characteristic structure of Al/p-CdS/n - CdS is almost identical to the current-voltage characteristics of p-n junctions. In this case, the current through the structure increases exponentially with increasing applied voltage. In the course of temperature dependence of the slopes of the lines  $\ln I \sim U$  can be divided into two temperature range. Below is 250K slope remains almost constant, which corresponds to the dominant role of tunneling processes, and above 250K with increasing temperature the slope increases, indicating the increasing role of thermal processes. Direct parts of the VAC (in logarithmic scale) consist of two parts, corresponding to different mechanisms of current flow. With an increase in forward voltage observed at the beginning section of the VAC with a large slope, which corresponds to when a current flow mechanism is replaced by another. Reverse saturation current of two orders of magnitude smaller than the current through the tunnel-transparent oxide layer of Al<sub>2</sub>O<sub>3</sub> and 10<sup>-10</sup> cm<sup>2</sup> for high temperature region (T>250K). The activation energy of the saturation current in this case is 0.9 eV, which is less than the barrier and the current is not purely thermal emission, and the corresponding emission-recombination mechanism. In the film sandwich structures of CdS-Al in the presence of an intermediate layer Al<sub>2</sub>O<sub>3</sub> show the effect of switching to a steady state conduction, which in some approximation can be regarded as the prebreakdown and breakdown after state. After the breakdown condition, studies show that at T = 80K, can be of two types - low and high conductivity. These states are also reproduced. The physical nature of the state can only be understood by studying the mechanisms of conduction film systems at different stages of change. On basis of measurement data volt-ampere characteristics of samples established the presence of conduction due to the presence of reverse bias p-n junctions. Was found to be high hole concentration (10<sup>21</sup> cm<sup>-3</sup>), characteristic of the conducting state.

In the solar cell of CdTe, the lattice mismatch between n-CdS and p-CdTe and the low bandgap of CdS window layer are known to have some drawback on cell performance. Using higher bandgap materials like ZnS or Zn<sub>1-x</sub>Cd<sub>x</sub>S as a heterojunction partner to CdTe can improve the window bandgap, but the lattice mismatch of these materials is worse than that of CdS. Trading off the latter mismatch for the higher bandgap may not be the solution, for the loss in cell performance due to lattice mismatch outweighs the gain due to the increase in window bandgap. Therefore, to retain the

compatibility of CdS and CdTe and still improve the short wavelength spectral response of CdTe solar cell, its traditional CdS/CdTe structure should be changed to Zn<sub>1-x</sub>Cd<sub>x</sub>S /CdTe. In other words, a Zn<sub>1-x</sub>Cd<sub>x</sub>S /CdS layer should replace the CdS-only window layer. Since the CBD-grown CdS layer has produced some of the best performing cells, the growth of the new Zn<sub>1-x</sub>Cd<sub>x</sub>S /CdS window layer by CBD should therefore be explored. Each experimental solution contained 300 ml of deionized water.

We have demonstrated using chemical and thermal activated diffusion that Zn<sub>1-x</sub>Cd<sub>x</sub>S thin films can be synthesized from electrochemical deposited ZnS/CdS multilayers. A more homogeneous Zn<sub>1-x</sub>Cd<sub>x</sub>S film is obtained at low processing temperature if the stacked layers are thin. Of great importance is that the grown structure is almost homogenized in the chemical bath at the temperature below 90°C. The homogenization of our structure is achieved by annealing at 400°C, the temperature generally used for processing solar cells. The low processing temperature developed here in the fabrication of Zn<sub>1-x</sub>Cd<sub>x</sub>S means that the proposed Zn<sub>1-x</sub>Cd<sub>x</sub>S/CdS solar cell window could be grown at temperatures that will not damage the glass or the underlying transparent conducting oxide generally used as substrate in solar cells. To achieve the new Zn<sub>1-x</sub>Cd<sub>x</sub>S /CdS structure proposed for the CdTe window layer, what is required is simply an additional growth of CdS on top of the Cd<sub>1-x</sub>Zn<sub>x</sub>S layer obtained from a chemical deposition ZnS/CdS multilayer. The structures are Al/p-CdTe/Zn<sub>1-x</sub>Cd<sub>x</sub>S /contact, type 1 Al/CdTe/CdS /Cd<sub>1-x</sub>Zn<sub>x</sub>S and type 2 Al/p-CdS/CdTe/Zn<sub>1-x</sub>Cd<sub>x</sub>S. In type 1 Cd<sub>1-x</sub>Zn<sub>x</sub>S /CdS window, a 0.15µm-thick ZnCdS film was first deposited on Al substrate. This was then dipped in CdCl<sub>2</sub> methanol solution for about 30 s to improve the conductivity, then dried with an infrared lamp, and then rinsed in the deionized water. This was followed by an additional deposition of 0.05µm CdS thin film to complete the window fabrication. In type 2 CdS/Zn<sub>1-x</sub>Cd<sub>x</sub>S window, a 0.15µm thick CdS film, sandwiched between two 0.04 µm-thick ZnS films, was first deposited by CBD on Al substrate. The sample was then annealed in CdCl<sub>2</sub>/Ar ambient at 400 °C for 15 min. The window fabrication was completed by the deposition of an additional 0.035µm-thick CdS film. In the following order, CdTe /CdS/ Zn<sub>1-x</sub>Cd<sub>x</sub>S structure have 75% or slightly higher quantum efficiency in the 400–850 nm wavelength region. We note that the structure with the Zn<sub>1-x</sub>Cd<sub>x</sub>S layer generally has better short wavelength response, as expected.

### 3. DISCUSSION OF RESULTS

The interpretation of experimental results becomes complicated due to a simultaneous occurrence of several processes (evaporation, generation and transformation of intrinsic defects) in films at the heat treatment. The kinetics of every process has a complicated character<sup>5</sup>. The dependence observed in photoelectric properties of films point out the changes of concentration of defects of donor and (or) acceptor character due to film annealing. The decreases of film photosensitivity at low annealing times (τ<sub>a</sub>) indicate the increase in concentration of fast-recombination centres (s-centres),

i.e. the increase of the recombination flux ( $g_s$ ), and hence the decrease in the life of electrons takes place. The measurements of the current-illumination characteristics of samples show that at low annealing times the decrease in hole concentration on the slow recombination centres (r - centres) is observed. This fact can be attributed either to increase of compensating shallow donor concentration or decrease of the r-centre concentration. A simultaneous increase in concentration of shallow donor centres responsibly for increase of dark conductivity and the fact recombination centres causing the decrease of photosensitivity allows to assume that the s-centres are the complexes consisting of shallow donors<sup>7</sup>.

The change observed at  $\tau_a \geq 5$ min can be explained when the anion and the cation vacancies diffusing into the volume are formed on their surfaces. Due to heavy evaporation of metal at initial stages of annealing, the near-surface region is mainly enriched by cadmium and sulfur vacancies playing the role of slow recombination centres. Their diffusion to the volume leads to increase of photosensitivity and to decrease of dark conductivity. In this case, the complexes of cadmium, sulfur and selenium vacancies, i.e. the recombination r-centres, are formed.

The decrease of photoconductivity of annealing times  $\tau_a > 15$ -20min is attributed to a single electron-molecular mechanism considering the initial state of film surface as were as local and collective phenomena at chemisorption. At initial state of annealing the increase of surface potential barrier due to chemisorption leads to increase of film sensitivity due to slow recombination. When the recombination controlled by the r-centres, the increase in their occupancy by holes due to chemisorption results in decrease of the lifetime of photoholes, i.e. the photoconductivity decreases. In this case, with increasing sulfur concentration in films the effect of oxygen becomes lower.

The main peculiarities of the POQ process are determined by the energy structure of r-centres with the excited state of holes: the hole transfer from the ground state to the excited one followed by thermal preexcita-

tion of holes to the v-band at phonon absorption leads to the occurrence of the long-wavelength POQ maximum. The short-wavelength POQ maximum is attributed to optical transition of the hole directly to the v-band.

The experiments carried out shown that there are no difference in kinetics of photocurrent reduction under illumination with the wavelengths corresponding to the both quenching maximum and this testifying their relations to one type of recombination centres.

The curve of photocurrent reduction is characterized only by the time of that recombination centre where the electrons from v-band are transferred by impurity light.

The obtained results show that when controlling ionic composition and heat treatment conditions, one can control the properties of Zn<sub>1-x</sub>Cd<sub>x</sub>S ( $0 \leq x \leq 0.6$ ) films, achieve the appropriate degree of compensation of recombination levels and traps attributed to intrinsic defects or impurities. In this way model crystals, as CdS and ZnS, can explain the main photoelectrical properties and parameters of Zn<sub>1-x</sub>Cd<sub>x</sub>S ( $0 \leq x \leq 0.6$ ) films.

#### 4. CONCLUSION

The Zn<sub>1-x</sub>Cd<sub>x</sub>S ( $0 \leq x \leq 1$ ) films deposited from solution the sensitivity condition of these films have been determined. The obtained results show that when controlling ionic composition and HT conditions, one can control the properties of Zn<sub>1-x</sub>Cd<sub>x</sub>S ( $0 \leq x \leq 1$ ) films.

Furthermore, the above films are nearly electron similar on their main photoelectric properties and parameters to such model crystals as CdS and ZnS. The recombination schemes and electron transitions in Zn<sub>1-x</sub>Cd<sub>x</sub>S ( $0 \leq x \leq 1$ ) films and A<sup>2</sup>B<sup>6</sup> crystals are identical. Not only a chemical composition but also a degree of crystallization are not determining, and the difference in photoelectric properties is attributed to the nature and the concentration distribution of recombination centres and trapping levels.

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