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PHOTOELECTRIC PROPERTIES OF THIN FILM $Si/Cd_{1-x}Zn_xS$ HETEROJUNCTIONS

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Abstract. Photoelectric properties of thin film $Si/Cd_{1-x}Zn_xS$ heterojunctions have been studied in rather wide range of light wavelength (0.3÷1,4 μm), temperature (100÷500^{0}C) as well as duration (0÷20 min) of thermal processing (TP). In the course of carrying out the experiments it was found that the $Si/Cd_{1-x}Zn_xS$ heterojunctions that were undergo to thermal processing possess higher photosensitivity in the wavelength range of (0,4÷1,25 μm). When these structures are illuminated from the side of semiconductor with wide band gap ($Si/Cd_{1-x}Zn_xS$) is developed the photo electromotive force whose sign does not change in all range of photosensitivity. Chief parameters of the investigated structures were estimated for their illumination by W = 100÷500 mW/sm^2 intensity. It has been found that values of these parameters in addition to other factors depend also on the composition of films.

Keywords: Photoelectric properties, thin film, heterojunctions

1. INTRODUCTION

Wide progress and entrance of semiconductor devices to all spheres of science and engineering often causes their use in conditions of both external and internal ionizing radiation. First of all it belongs to semiconductor emitters [1,2], solar cells [3] and radiation detectors [4]. Radioactive action as a rule causes fast degradation of basic modern semiconductor materials - silicon, germanium [5] and A^2B^6 compounds [6-8] that is revealed in variation (usually to become worst) of characteristics of devices on their basis. The fundamental problem in this sphere becomes finding the regularities of interaction between light and nanoparticles [9]. Interaction of impurities, point and structural defects plays key role in semiconductor materials in both stages; obtaining of single crystals and films with necessary set of properties and management with these properties upon device fabrication [10-12]. Compounds of A^2B^6 group find widespread application in modern optoelectronic facilities due to their unique emitting characteristics and high photosensitivity [13-15]. In reality potential of unique properties of these materials was not perfectly realized in result of weak study and complexity of management the processes of impurity-defect interaction in them. In this connection the question of development of radioactive reliable semiconductor materials keeping functionality of traditional ones becomes actual. An interest to semiconductor materials is not limited with bulk materials and epitaxial films. For series of practice applications (solar cells, matrix electroluminescent screens etc.) are required the small dispersed semicrystalline films of A^2B^6 group compounds. In these materials significance of processes of impurity-defect interactions is multiply increasing. On the other hand complex processes of structural reconstruction occur in semicrystalline films during their TP and device fabrication. Methods of obtaining of thin film semiconductors significantly determine their properties. Therefore the actual becomes not only development of representations on chemistry of solid body but also the techniques allowing to act on synthesized material in the process of its obtaining. In recent years in the obtaining technology of the thin films of metal sulfides dominate the methods based on chemical processes.

2. EXPERIMENT.

Photoelectric properties of thin film $Si/Cd_{1-x}Zn_xS$ heterojunctions have been studied in rather wide range of light wavelength (0,3÷1,4 μm), temperature (100÷500 C) as well as duration time (0÷20 min) of thermal processing (TP).

The studied heterojunctions possessed "sandwich" structure. Upon their creating the Si single crystalline plates of 0.4÷0.5 mm thickness and oriented along the axis (100) were used as the substrate (cathode). Resistivity of p-Si were 8÷20 Ohm sm respectively. As a anode material the molybdenium plate of coal rods have been used. With the aim of dismearing of different mechanical defects, oxide films and other pollutions the silicon substrates were undergo to etching first in HCI and further in KOH+KNO (1:3) mixture at 250-500°C according to preliminary found regime before dipping into operating solution.

The process of electrochemical deposition has been carried out by us on the silicon plates in a special quartz vessel at room temperature. Composition of obtained films was varying in the $0 \leq x \leq 0.5$ range and was controlled by chemical, thermal and X-ray analyses. For different samples their thicknesses were 2 μm. The films possessed n-type conductance which was determined due to sing of thermal e.m.f. Concentration of free charge carriers defined by the value of conductivity and Current-voltage characteristic possessed $(0.2 \div 8)x10^{16}$ sm^{-3} depending on composition percentage of films. Operating areas of obtained heterojunctions were in the $0.04 \div 2$ cm^2 range. Depending on requirements of measurements metallic indium or silver paste were used as materials of ohmic contacts to ohm city of contacts were examined by us according to voltage-current characteristics (VCC) recorded in character graph. Measurement of electro physical characteristics of $Si/Cd_{1-x}Zn_xS$ nanofilms on a glass and estimation the VCC of p-$Si/Cd_{1-x}Zn_xS$ structure alb owed to reveal the optimum composition of chemical width: 1:12:500 ($1,5 \div 2,2x10^{-3}$M Zn $(CH_3OOO)_2$, $1,5 \div 2x10^{-3}$M $Cd(CH_3OOO)_2$, $0,01 \div 0,02$ M $Na_2S_2O_3$, 1,05 M NH_4OH).

The structural characterization of the films has been performed by using X-ray diffractometer in the range of scanning angle 20–70 using Rigaku D/Max-IIIC diffractometer. The surface morphology has been inspected by using ZEISS SUPRA 50VP scanning electron microscope with an attached energy dispersive X-ray analysis (EDAX) analyser to qualitatively measure the sample stoichiometry. The X-ray diffraction patterns (XRD) are analysed to obtain the structural information of thin film. The structural analysis of $Cd_{1-x}Zn_xS$ thin film was carried out by using X-ray diffractometer in the range of scanning angle 20–70. The $Cd_{1-x}Zn_xS$ films were found to have polycrystalline nature and grown in the hexagonal crystal structure with strongly preferred orientation along the (002) plane parallel to the as-revealed from the XRD studies. Fig.1 shows SEM images of as-grown $Si/Cd_{1-x}Zn_xS$ thin films. It is seen that well-crystallized grains in the first image belong to these films. As can be seen in fig.1. the $Cd_{1-x}Zn_xS$ films were dense, uniform and homogeneous without visible pores and covered well with substrate. From the image of $Si/Cd_{1-x}Zn_xS$ thin films, it is clearly seen that the particles forming the films are in nano scale. One of the important applications of the SEM is to obtain the knowledge of the material composition. This microanalysis mode of SEM replied upon the monitoring X-rays emitted by surface of the sample under electron irradiation. These X-rays may be collected and analyzed to give information on the elemental compounds present in the sample. The quantitative analysis of the films was carried out by using the EDAX technique to study stoichiometry of films.

In the course of fulfilled measurements it was known that the $Si/Cd_{1-x}Zn_xS$ heterojunctions that have not been undergo to TP had high photosensitivity in the $0,4 \div 1,25$ μm range of wavelength. When these structures are illuminated from the side of broad band semiconductor $Si/Cd_{1-x}Zn_xS$ is arised the photo electromotive force (e.m.f) whose sign does not change along the range of photosensitivity. Basic parameters (open-circuit voltage (V_{OC}) and $I_{S.C.C.}$ – short circuit current) of these structures were estimated due to their illumation with $W = 100 \frac{mW}{cm^2}$ intensities.

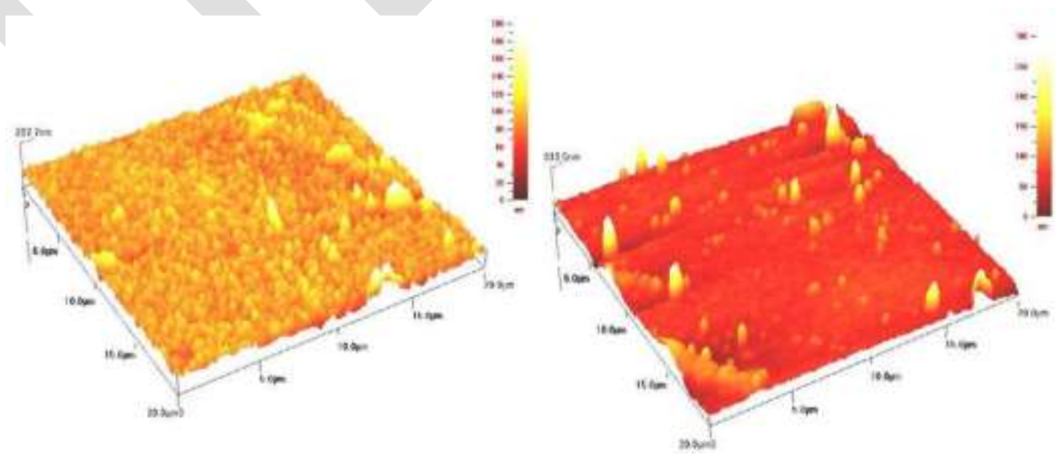

Fig.1. SEM images of as-grown $Si/Cd_{1-x}Zn_xS$ thin films, deposited and annelained at various temperaturs. a- just deposited films, b-after heat-treatment HT in air at 400^0C, for 15 min.

Is found that values of these parameters in addition to other factors are also the function of film composition (value of x) (Fig.1).

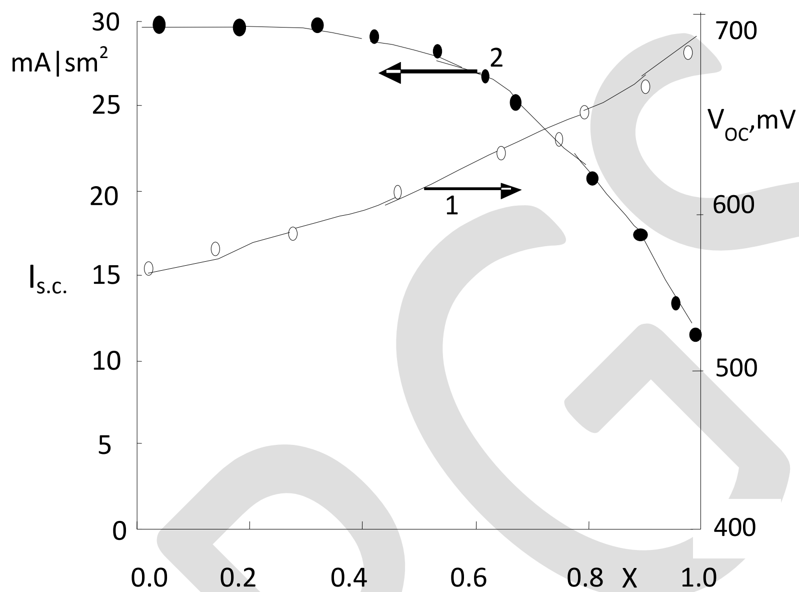

Fig.1. Dependence of open-circuit voltage (1) and short circuit current (2) in p-Si/ $Cd_{1-x}Zn_xS$ versus composition of $Cd_{1-x}Zn_xS$ films: W=100 mW/cm^2

Investigations carried out by us allow to point that the $Cd_{1-x}Zn_xS$ based thin film structures reveal remarkable results under other identic conditions. With the aim of obtaining the photosensitive samples the influence of TP on the photoelectric properties of heterostructures have been studied. The thermal processing has been carried out in the open air at $t=100\div500^0$C with duration time range $\tau=0\div20$ min. It should be noted that under considered conditions the current of short circuit for studied structures was found to be no monotonic not only with temperature but also versus duration period of TP process (Fig.2). For the heterojunctions that passed TP in air at 400^0C τ=12 min values of open-circuit voltage and short circuit current reach V_{oc}=0,6 V and $J_{s.c}$=23 mA/sm^2 respectively. With increasing of the percentage of selenium in obtained films with thickness from 0 to 0,2 photoelectrical efficiency for thin film structures considerably increases and it shows enough binding of constants of Si and $Cd_{1-x}Zn_xS$ crystalline lattices. Light current – voltage diagrams of thermally processed heterojunctions are presented in Fig.3.

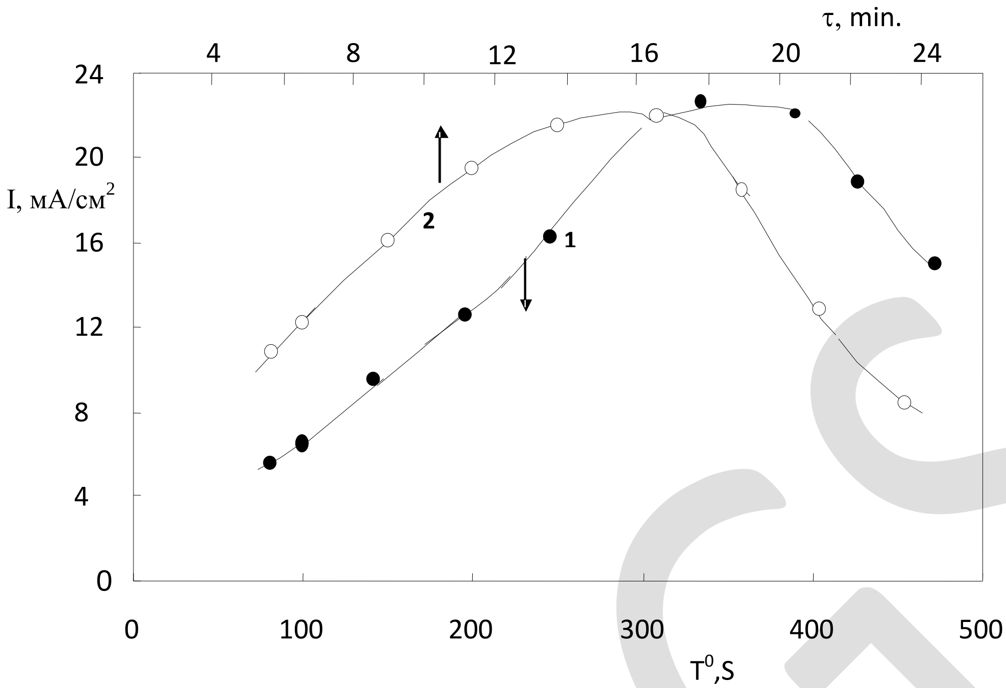

Fig.2. Dependence of short circuit current in p-Si/ $Cd_{1-x}Zn_xS$ heterojunctions versus temperature (1) and duration time(2) of TP; x= 0,5;

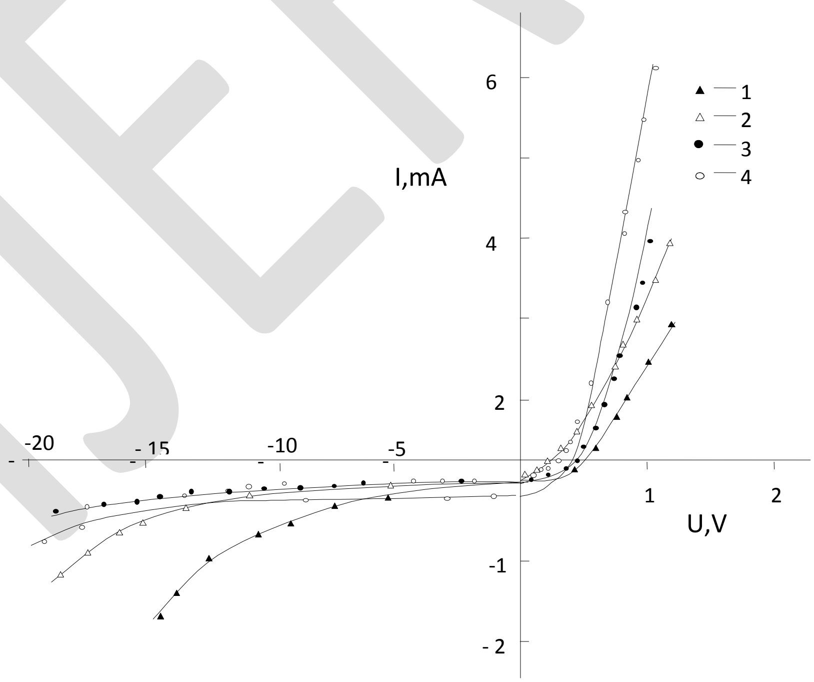

Fig.3. Light CVC of thermally processed p-Si/ $Cd_{1-x}Zn_xS$ heterojunctions;

x: 1-0,2; 2-0,3; 3-0,4; 4-0,5; $t=400^0C$, $\tau=10$ min

The photocurrent of p-Si/ $Cd_{1-x}Zn_xS$ heterojunctions (short circuit regime) as a function of power of incident light flux before and after TP is illustrated. For the structures which were not undergo to TP this dependence in the beginning is linear, further has sub linear portions, that tells about presence of recombination centers at intersections. After TP at 400^0S $\tau=10$ min, this dependence becomes linear in absorbed excitation interval.

Fig.4 demonstrates characteristics curves of spectral dependence of short circuit current for the p-Si/$Cd_{1-x}Zn_xS$ heterojunctions obtained by TP under 300^0C temperature. As can be seen from this Figure long wave edge of photosensitivity is defined by their interband transition when heterojunctions are illuminated from the side of substrate (silicon films). In the case of illumination of the studied heterojunctions from the side of Si the spectral dependence of photocurrent process the most intense long wave peak only. For the heterojunctions with x=0 more pronounced short wave peak is observed at 0,450 μm and 1,125 μm related to direct band-to-band transitions in a p, n-Si monocrystal. Illumination the heterojunctions from the side of wideband gap semiconductor ($Cd_{1-x}Zn_xS$ films) leads to change of pattern. With increase in x the displacement of this peak toward more shortwave part of the spectrum is observed. In our option it is related to the change of width of band gap of $Cd_{1-x}Zn_xS$ films. It is assumed, that variation of photosensitivity of heterojunctions dependently on illumination geometry observed by us first of all is related to the features of optical absorption of materials Si and $Cd_{1-x}Zn_xS$ being in contact. Illumination of investigated heterojunctions from the side of $Cd_{1-x}Zn_xS$ films leads to the rise in total width of spectral distribution of short circuit current (Fig.4, curve 2). Most large-strip photosensitivity is reached in heterojunctions obtained by contact with $Cd_{1-x}Zn_xS$ films whose thickness were d=0,5÷1 μm. after TP the spectral distribution of short circuit current in studied heterojunctions considerably varies – the spectrum becomes larger and an increase about 5÷6 times in photocurrent is observed. Increase in annealing temperature up to 350÷380^0C leads to sharply rise of photosensitivity of heterojunctions in a wide spectral range of 0,8÷1,34 μm (Fig.4, curve 4). At the same time long period annealing ($\tau \geq 15$ min) of heterojunctions at temperatures above 450^0C leads to degradation of parameters and finally to destroy of studied structures.

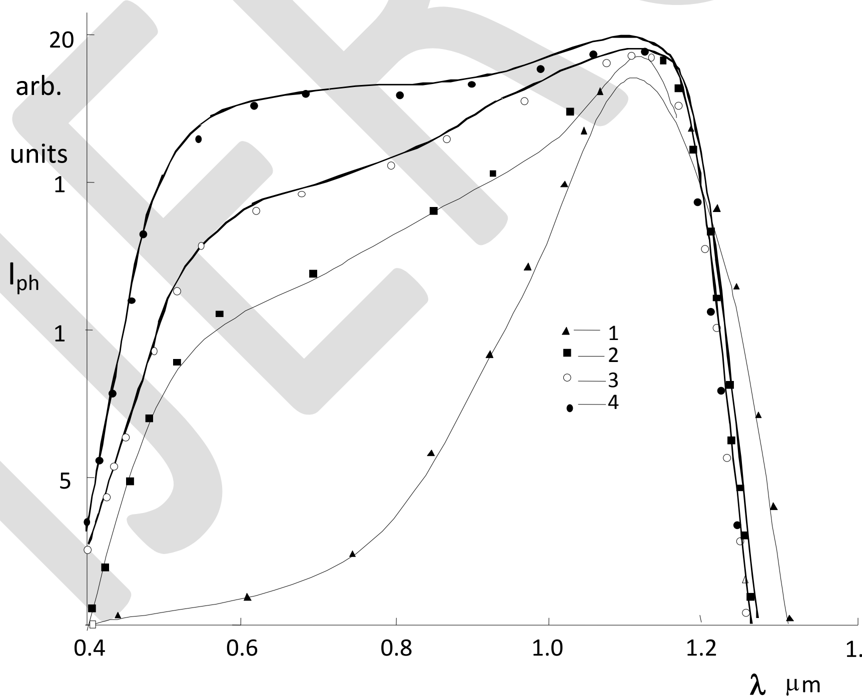

Fig.4. Spectral distribution of photosensitivity of p-Si/$Cd_{1-x}Zn_xS$ heterojunctions after TP, when is illuminated from the side of: 1-Si, 2,3,4- $Cd_{1-x}Zn_xS$, x=0.5; t^0C: 1,2-0, 3-300; 4-420; $\tau=10$ min,

Curves of voltage-capacitance characteristics (VCC) for the structures which were not undergo to TP have been studied. For the isotype structures with x=0,6 the straight line extrapolated up to $C^{-2}=0$ cuts from axis of "voltage" a portion equal 0,59 V, but for unisotype structures with the same composition it becomes 0,65 V. The observed increase in the value of U_d with decrease x in our measurements can be explained with increase of band gap width in films depending on their percentage composition. Character of VCC in investigated p-Si/$Cd_{1-x}Zn_xS$ structures strongly depends on the percentage composition of films (Fig.5).

When a percentage of selenium in $Cd_{1-x}Zn_xS$ solid solutions increases the sharply decrease of divergence between constants of crystals lattices of absorbing and substrate layers causes increase of degree of linearity of curves in $C^{-2}=f(U)$ coordinates. Then a weak dependence of capacitance versus frequency is observed. Note, that capacitance, consequently concentration of surface states are regulated also by regime of TP.

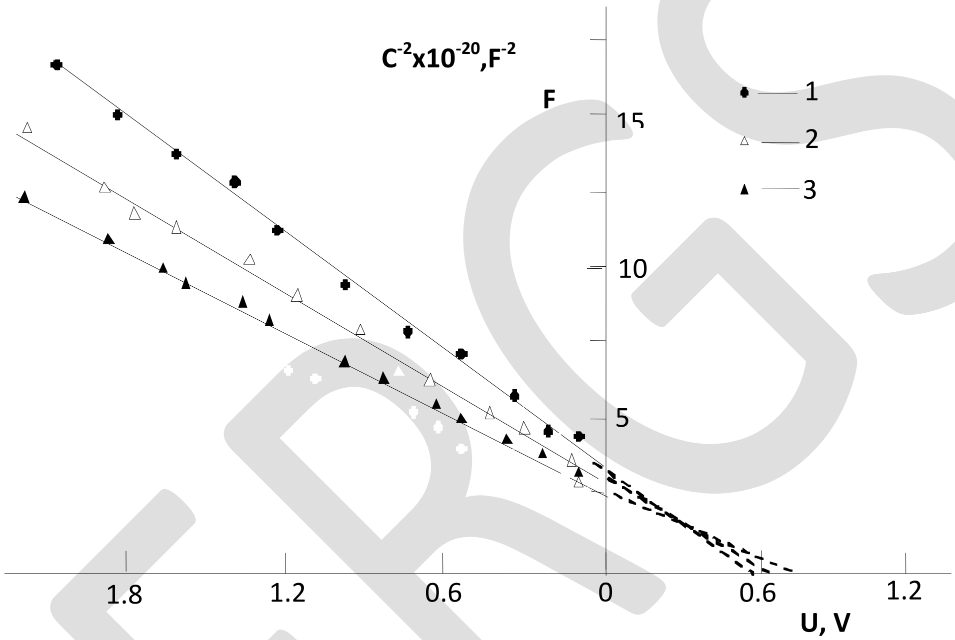

Fig.5. VCC of investigated p-Si/$Cd_{1-x}Zn_xS$ structures:

1-x=0,6; 2-x=0,5; 3-x=0,4

After TP at 380^0C for τ=10 min degree of sharpness for $C^{-2}=f(U)$ dependence strongly increases and then capacitance of structures almost does not depend on the frequency of reference signal. It shows that in the given case concentration of surface states on hetero-boundary, being responsible for frequency dependent contribution to capacitance decreases.

3. DISCUSSION OF RESULTS.

The changes observed in parameters of Si/$Cd_{1-x}Zn_xS$ heterojunctions after TP is explained by us a result of possibility of electronic-molecular interaction between film surfaces and oxygen in considered conditions. In particular, it is assumed, that surface adsorption of oxygen in $Cd_{1-x}Zn_xS$ films just after taking out these films from water solution into opened atmosphere leads to formation of deep acceptor states in boundary layer. Further, through electron capture from the volume these oxygenic centers create interface potential barrier and it in its turn causes low shortwave photosensitivity of created heterojunctions in origin state. Heights of intercrystallite barriers, which mainly are characteristic for semicrystalline films are less in comparison with barriers created by oxygen. Therefore basic properties of p-Si/$Cd_{1-x}Zn_xS$ heterojunctions in a short wave region of spectrum are determined by concentration of oxygen centers only. Values of U_d determined from VAC and CVC do not coincide. In our opinion it can be explained by no optimum fabrication regime as well as zero correspondence of constants of crystalline lattices of materials in contact. Fabrication of heterojunctions by electrochemical method leads to formation of large mumber surface states in interface which are related with inhomogeneouties of semicrystalline films, but this divergence decreases with increase in values of x. It is assumed that increase in percentage of zinc in composition of films leads, first, to enhancement of potential barrier, and, second, to decrease in discorrespondence between constants of lattices of materials in contact. This in its turn can lead to decrease in concentration of surface states taking part in condition of heterojunction's interface.

4. CONCLUSION.

Photoelectric properties of thin film Si/$Cd_{1-x}Zn_xS$ heterojunctions have been studied in enough wide range of light wavelength, temperature and duration of thermal processing (TP). In measurements was observed that p-Si/$Cd_{1-x}Zn_xS$ that were undergo to TP process high photosensitivity in the wavelength range of 0,4÷1,28 μm. When these structures are illuminated from the side of semiconductor with large band gap ($Cd_{1-x}Zn_xS$) is developed photo e.m.f., whose sign does not change in all range of photosensitivity. Chief parameters of investigated structures were estimated. It is found that, values of these parameters depend on film composition in addition to other factors.

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