

Al-P-Cds/N-Cds/Zn_{1-x}Cd_xS Structures for Solar Cells

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Abstract

In this paper we report some properties of thin film photocells prepared on the basis of Al/p-CdS/n-CdS/Zn_{1-x}Cd_xS heterojunctions. These heterojunctions were prepared by the method of chemical and electrochemical deposition from solution in a uniform work cycle. The open-circuit photovoltage (U_{oc}), short circuit-current density (I_{sc}) and efficiency of the Al/p-CdS/n-CdS/Zn_{0.6}Cd_{0.4}S heterojunctions were 650 mV; 35 mA/cm² and 11%, accordingly. The I-U fill factor was 0.68. The value of U_{oc} increases and I_{sc} decreases by increasing of Zn in Zn_{1-x}Cd_xS material.

Keywords: thin film, solar cell, heterojunctions, compounds, potential barrier.

I. INTRODUCTION

II-VI group compound semiconductors such as CdS, ZnSe and CdTe are important because of their photovoltaic, photoelectrochemical, and electroluminescent applications and, thus, they have got much attention. Recently, there have been many efforts to produce nanosized materials, because electrical and optical properties can be varied via chemical control over the size, stoichiometry, and interparticle separation. These materials have been synthesized by various techniques including pyrolysis of organometallic compounds and sol gel synthesis. In recent years, there has been considerable interest of using thin films in solar cells [1-3]. Photoelectrical properties of these heterojunctions have found practical application in phototransistors and in solar cells. However, the physics and technology of heterojunctions have also other prominent aspect - creation, research and practical application of non-ideal heterojunctions. The big set of various effects and phenomena in non-ideal heterojunctions related to various properties of semiconductors on both junction regions of heterocontacts have been observed [4-6]. Perspectivity of practical application of the non-ideal heterojunctions is related first of all to more economic technology of creation of polycrystalline heterostructure in comparison with the monocrystalline. One of directions in studying of the non-ideal heterojunctions is the opportunity of solar cells application on the basis of A²B⁶ compound multilayer structures. The Al/p-CdS/n-CdS/Zn_{1-x}Cd_xS system represents a non-ideal unizotype heterojunction at which difference of Zn_{0.6}Cd_{0.4}S and CdS lattice constants make 4%. Such significant difference of the lattice constants at heterojunction formation creates the high density of discrepancy dislocations on an interface. Torn off connections in dislocations result in occurrence of power levels in the band gap, responsible for capture of the carriers or for them recombination and render essential influence on charge carrying through the impoverished area. 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 p-n junction film based on p-CdS, precipitated out of solution.

II. EXPERIMENTAL

Heterojunctions were prepared by a method of deposition from a solution in a uniform work cycle. The solution was stirred and thus local heating was avoided. The deposition solution for A²B⁶ compounds contained 30 mM CdCl₂, 50 mM ZnSO₄, 125 mM SeO and 125 mM Na₂S₂O₃. It should be noted that the solution for CdS was Cd-rich has a large Cd or S concentration ratio, as in the usual electro-deposition condition. Cyclic voltammetry is used to study the electrochemical properties of solution containing 0.2 M CdCl₂ + 0.2 mM H₂SO₃ + 0.25 M Na₂S₂O₃. All voltammetry curves were scanned first in the cathode direction, and the negative current density

indicates a cathode current. The p-type CdS deposited on aluminum substrate by a method of deposition from a solution, contained Cd and S concentration ratio 1/3.

The films have been investigated by X-ray diffraction and scanning electron microscopy for the structure analysis and morphology study, respectively. Aluminum plate was used as the substrate during the deposition process. Surface photovoltage spectroscopy (SPV), which is a sensitive probe of surface states, was used to show that adsorbed water passivated surface states. Figure 1 shows the X-ray diffraction (XRD) patterns of the p-CdS (a), n-CdS (b), Zn_{1-x}Cd_xS (c) thin films.

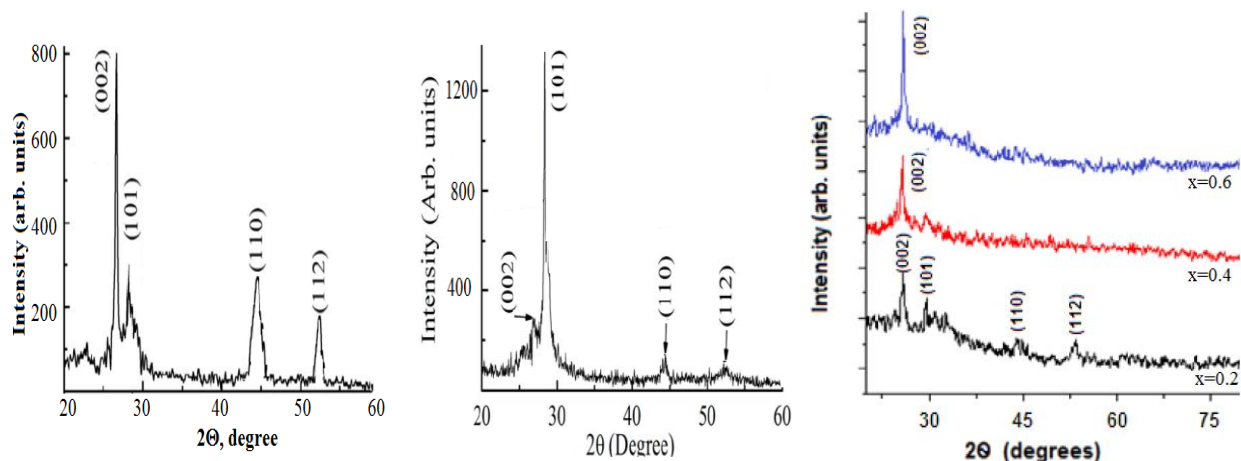


Fig.1. X-ray diffraction (XRD) patterns of the p-CdS (a), n-CdS (b) and Zn_{1-x}Cd_xS (c) films.

The grain formation is observed as irregular accumulation with the grain sizes completely different from each other (2-5 μm). These observations suggest an incomplete formation step with irregular growth rate of the grains. The scanning electron microscopy (SEM) micrographs of the p-CdS (a), n-CdS (b), Zn_{1-x}Cd_xS (c) thin films show in Fig.2.

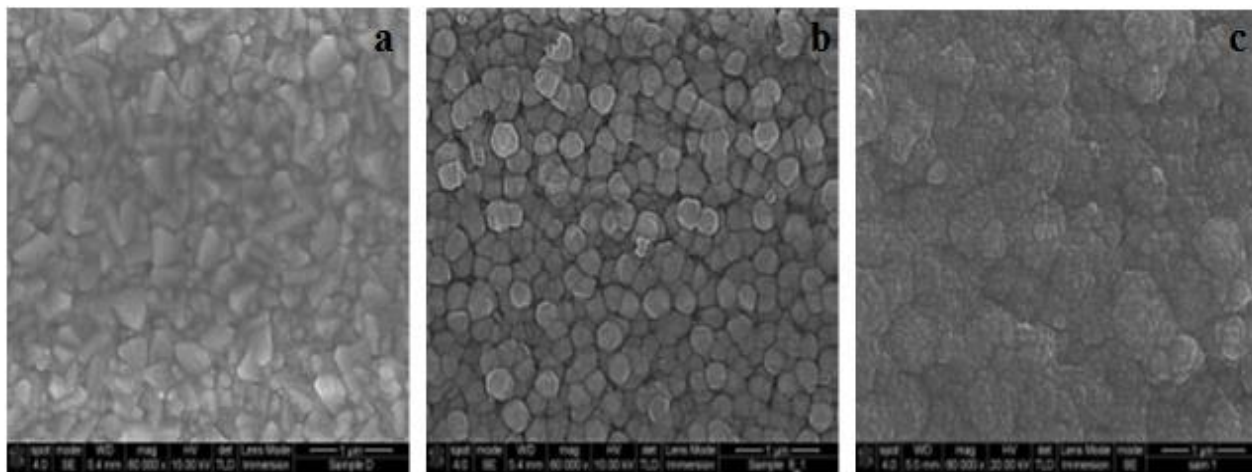


Fig.2. The scanning electron microscopy (SEM) micrographs of the p-CdS (a), n-CdS (b), Zn_{1-x}Cd_xS (X=0,4) (c) thin films

Fig. 2a shows p-CdS with uniform coverage of the Al substrate without any visible pinholes at the magnification of 60,000 \times used. This is a good sign as mentioned earlier for the growth of CdS. The estimated sizes of the grains are in the range 208–417 nm. In Fig. 2b, the nature of n-CdS growth is revealed. The crystallites and therefore the grains tend to grow in an upward direction perpendicular to the substrate, leaving some gaps

between them. This can pose serious problems in solar cell fabrication when CdS is deposited directly on the Al. The estimated grain sizes are in the 167–375 nm range. These observed CdS grains actually consist of groups of crystallites that agglomerated together. Zn_{1-x}Cd_xS crystallites can go through these gaps between the grains and tend to deposit on the uncovered (exposed) portions of Al when there is no buffer layer, since this is the path of least resistance. A possible way of preventing this is using a buffer layer (such as p-CdS in this case) or by making the CdS crystallites and grains grow laterally and fatter instead of growing as vertically oriented rods, so that they can close up the gaps when they touch each other. Growing thick CdS layers helps to achieve this but at the same time this increases the light absorption near the surface of CdS and drastically reduces the amount of photons that reach the depletion region for creation of electron-hole pairs due to the position of the depletion region. Zn_{1-x}Cd_xS tends to grow also in upward direction as columns. However, due to the large thickness grown compared to CdS, the grains touch each other towards the surface of the layer and tend to close up the gaps between them so that the micrograph shows no visible pinholes or gaps between the grains as shown in Fig.2c. What is seen therefore are clusters of tightly-packed grains with these clusters of grains touching each other. The grains are also made up of tightly-packed smaller crystallites. The estimated grain sizes (or clusters) in Figure 6c are in the 217–870 nm range.

The thickness of the layers p-CdS, n-CdS and Zn_{1-x}Cd_xS films was monitored by ellipsometric measurements. All layers were deposited on Al substrate serially- first of all p-CdS with thickness of about 150nm, second n-CdS with thickness of about 200nm and Zn_{1-x}Cd_xS with thickness of about 800 nm. Finally ZnO layer was deposited by vacuum evaporation, which is a highly conducting window used as transparent electrode. The films were characterized by spectral, X-ray diffraction and chemical analyses. X-ray diffraction showed that the p-type CdS films were single-phase and had a hexagonal structure.

The experimental measurement of $\alpha(T)$, $\sigma(T)$ and $R(T)$ correspond hole conductivity in the temperature range 250–400K. The mobility of holes was $\mu_p = 6-7 \text{ cm}^2/\text{V}\cdot\text{sec}$. and the concentration was $6 \times 10^{19} \text{ cm}^{-3}$. The p-n junction was formed between p-CdS and n-CdS layers.

Figure 3a,b shows the LogI vs. V graphs under dark conditions for the Al/p-CdS/n-CdS/Zn_{1-x}Cd_xS.

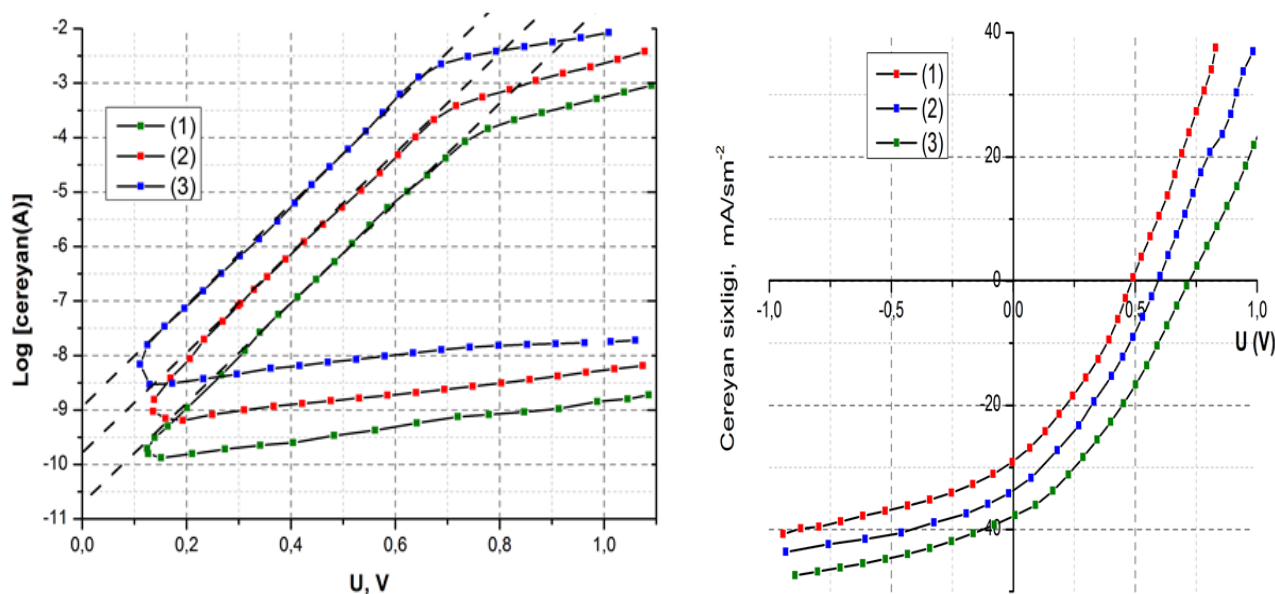


Fig.3. the LogI vs. V graphs under dark and light conditions for the Al/p-CdS/n-CdS/Zn_{1-x}Cd_xS solar cell, x:-1-0,2, 2-0,4, 3-0,6

Each of the figures is a combination of LogI-V for both forward and reverse bias conditions. The diode parameters under dark condition (such as barrier height, ϕ_B , ideality factor, n , rectification factor, $R.F.$, and reverse saturation current density, J_0) are obtained from these graphs. The Schottky barrier heights estimated for the two device structures were >1.13 eV for Al/p-CdS/n-CdS/Zn_{1-x}Cd_xS devices. These values most likely represent the average values of all the barrier junctions present in the devices. The diode ideality factors obtained were respectively 2.3 and 2.45. The large ideality factor values in excess of 2.00 indicate the possible presence of high series resistance, a contribution from tunnelling and the presence of high concentration of recombination and generation centres in the device structures and these underestimate the potential barrier heights of the devices. The diode rectification factor [$R.F. = (I_F/I_R)V=1$] of each solar cell was obtained as the ratio of the forward current, I_F , to the reverse current, I_R , at the maximum bias voltage of 1.0 V. The intercept of the straightline portion of the forward current on the LogI axis is used to calculate the reverse saturation current density of the solar cells using the cell active area of ~ 0.03 cm². The large Schottky barrier heights $\phi_B > 1.10$ eV and the high rectification factors, $R.F. > 10^4$ obtained for both solar cell structures indicate how strong the electric field in the depletion region is for effective separation of photo-generated charge carriers. This high field actually imposes high drift velocity on the photo-generated charge carriers, and due to the high quality of the electrodeposited materials, this leads to high short-circuit current densities observed for the devices. Low efficiencies could arise due to existence of shunting paths through pinholes and detrimental defects via recombination.

Curves of voltage-capacitance characteristics (VCC) for the structures which were not undergo to TP have been studied. For the unisotype structures with $x=0,6$ the straight line extrapolated up to $C^{-2}=0$ cuts from axis of "voltage" a portion equal 0,65 V, but for structures with the same composition it becomes 0,58V. 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 structures strongly depends on the percentage composition of films (Fig.4).

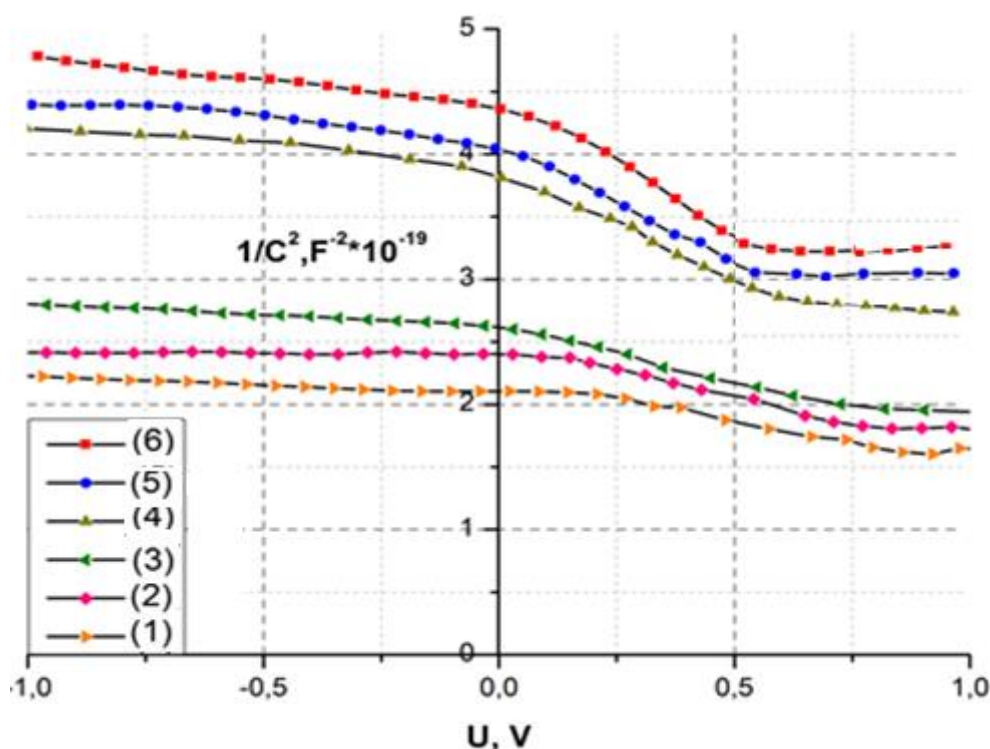


Fig.4. Volt-capacitance characteristics (VCC) of the p-CdS/n-CdS/Zn_{1-x}Cd_xS heterojunctions,

X:1,4- 0,2 2,5- 0,4, 3,6- 0,6 before and after heat-treatment HT at 380°C for $\tau=10$ min

When a percentage of selenium in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 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. After TP at 380°C for $\tau=10$ 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.

Under AM1.5 illumination (100 Lux), the p-CdS/n-CdS/ $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ photocells generated open circuit voltages of about 550÷650 mV and short circuit current density of about 25÷29 mA/cm² also had efficiency up to 11 %. On the other hand, discrepancy of constant lattices of contacting materials results in reduction of concentration of states in junction region of the heterojunctions, and also speeds up the degradation process. Consecutive resistance limits the short circuit current, and its dependence on illumination intensity is superlinear. The dependence of an open-circuit voltage on illumination intensity differs from logarithmic. Therefore, the efficiency of the p-CdS/n-CdS/ $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ heterojunctions increases by increasing of illumination intensity [4]. The peaks on the photosensitivity spectrum of the p-CdS/n-CdS/ $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ heterojunctions have been observed at 0.45-0.49 μm and 0.62-0.65 μm . The photo response in long-wave area of a spectrum explains by presence of a high-resistance layer at the edge of near-surface areas of the CdS films (Fig. 5). Peaks correspond to edge of own absorption. Have been investigated the dependence of the spectral distribution nature of a photocurrent on a mode of deposition of the Al-p-CdS/n-CdS/ $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ heterojunctions and features of spectral distribution of a current in them depending on a thickness of the CdS films.

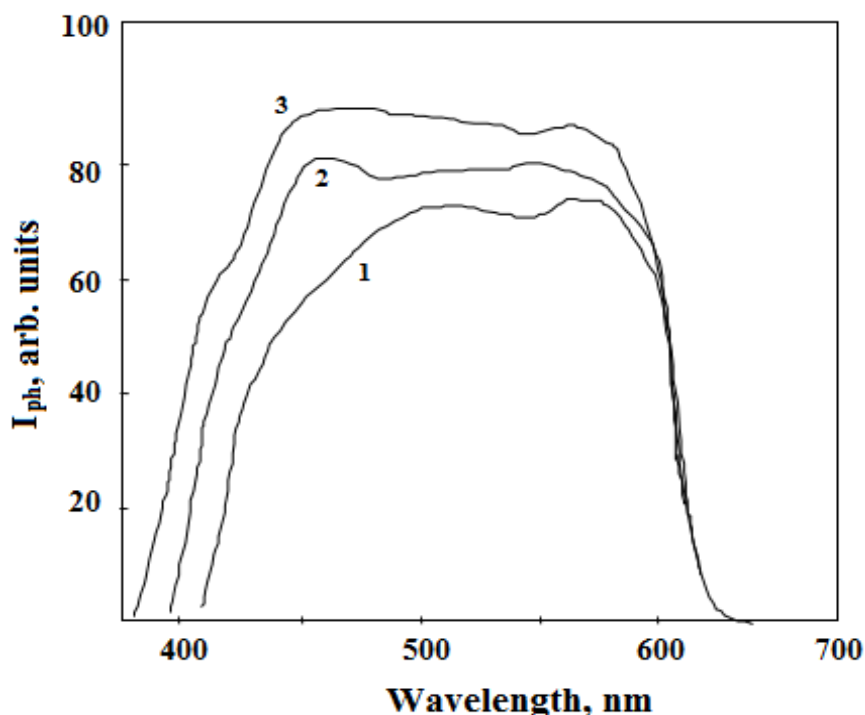


Fig.5. The photo answer spectrum of the p-CdS/n-CdS/ $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ heterojunctions,

X: 1- 0,2, 2- 0,4, 3- 0,6

III. RESULTS AND DISCUSSIONS

Researches show that essential changes occur in p-CdS/n-CdS/ZnCdS heterojunctions during heat treatment. The nature of a change of electric and photoelectric properties of heterojunctions depending on the heat treatment shows, that due to presence acceptor levels in near-surface of the $Zn_{1-x}Cd_xS$ layer there is an expansion of a layer of a volumetric charge. Therefore the capacity of p-n heterojunctions decreases. Increase of the photo response on all spectrums specifies that fact, that due to compensation of donor type natural defects by acceptor levels formed a high resistance layer in a near-surface layer and increases the rectification factor. Absorption of light becomes more effective due to a high-resistance layer, i.e. the usefulness of an absorbed beam and accumulating of carriers by the p-n heterojunctions raises.

Appear nonequilibrium electrons and holes during photoexcitation by quanta from area of own absorption of $Zn_{1-x}Cd_xS$ film. A barrier field in the base area removes electrons and holes are captured near interface on traps and the recombination centers. Presence of such compensating centers with the big concentration actually is one of the basic properties of the considered heterojunction. The barrier field promotes electron accumulation in the spatial charge area; therefore, distribution of a positive charge in $Zn_{1-x}Cd_xS$ considerably changes even at an insignificant level of photoexcitation, which results in growth of the transition capacity. Herewith sharply increases the intensity of the electric field at interface of the heterojunction. The short circuit current is in direct dependence on spatial distribution of electric potential, and this distribution is directly related to electron's concentration located on traps. At displaying on a sample of any image, its points are illuminated differently that results in various electron concentration, captured on traps and accordingly to a various bend of power zones in the spatial charge area. If displaying to stop, distinction in the electron concentration is kept enough long time that allows using this heterojunction as the device recording the optical information. Reading of this information is possible by scanning a sample with infrared light. Using infrared illuminations also makes it possible to delete the image; herewith a sample must be illuminated with pulses of the long duration with high frequency of following. Then the sample is suitable for repeated storing other image. Processes of record and reading can be considerably carried in time, however long storage is accompanied by a thermal devastation of traps that results in gradual loss of the optical information. Reading the information is possible during several days at storage of a sample at the temperature about 80K. Rise in temperature of storage results in faster thermal hole liberation to a valence band.

The p-CdS/n-CdS/ $Zn_{1-x}Cd_xS$ heterojunction can be in two various states. One of them - equilibrium – possesses low sensitivity to the infrared light and allows to receive low value of short-circuit current. Other state - nonequilibrium - is highly sensitive to infrared light and gives considerably high short-circuit current value. Transition from an equilibrium state to nonequilibrium is carried out under illumination of shortwave light due to the effect of capture and the accumulation of nonequilibrium holes on traps in the spatial charge area of $Zn_{1-x}Cd_xS$ film. Time of preservation of the nonequilibrium state in structure is determined by the recombination barrier size and the process of hole emission from the traps, going alongside with accumulation. The emission starts to play a main role in current passage after cancellation of short-wave illumination so releasing of the captured charge causes inverse changes of parameters of a barrier and transition of structure from a nonequilibrium state to equilibrium. Intensity of emission determines rate and speed of this change of barrier parameters, so and short circuit current. Therefore it is obviously important to know, how emission influences on barrier parameters after the termination of photoexcitation by short-wave light. Let's consider possibility using such system for registrations of the optical image of the different spectral composition. The maximal effect is achieved at 520 nanometers. Short-wave lights are strongly absorbed in a base layer. Therefore the thickness of $Zn_{1-x}Cd_xS$ layer and the diffusion length of charge carriers in this material determine the photoexcited hole concentration in vicinities of the spatial charge area. The spatial charge area is not reached by all photogenerated electrons, which result in reduction of the short-wave stimulation rate. Sharp recession of sensitivity of a sample in the shortwave area of a spectrum is caused by that the generated charge carriers are recombined in volume of $Zn_{1-x}Cd_xS$ layer, not being in time to reach to the spatial charge area, i.e. there is absorption of light in a superficial layer of $Zn_{1-x}Cd_xS$. The wane of sensitivity in long-wave area speaks about reduction of gathering factor of p-CdS/n-CdS/ $Zn_{1-x}Cd_xS$ and about presence of the impurity centers in $Zn_{1-x}Cd_xS$, participating in

generations of current carriers. In order to increase of sensitivity it is necessary or to reduce thickness of a base layer, or to create the optical image on the part of thin CdS layer. Values of U_d determined from VAC and VCC 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 number surface states in interface which are related with inhomogeneities of semi crystalline 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 discordance 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.

CONCLUSION

Thus, the device prepared on the base of p-CdS/n-CdS/Zn_{1-x}Cd_xS heterojunction can operate in all area of the visible spectrum with different sensitivity. As in the given device reading of the image is made by infrared light but not by an electronic beam, and it does not need the vacuum and the high voltage, used for formation of an electronic beam. These heterojunctions were prepared by the method of electrochemical deposition from solution in a uniform work cycle. The open-circuit photovoltage (U_{oc}), short circuit-current density (I_{sc}) and efficiency of the Al/p-CdS/n-CdS/Zn_{0.6}Cd_{0.4}S heterojunctions were 650 mV; 35mA/cm² and 11%, accordingly.

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