

## PHOTOELECTRIC PROPERTIES OF THIN FILM p-CdS/n-CdS/n-CdZnSSe HETERO JUNCTIONS

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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/n-CdZnSSe hetero junctions. These hetero junctions were prepared by the method of chemical deposition from solution in a uniform work cycle. The open circuit photo voltage ( $U_{oc}$ ), short circuit current density ( $I_{sc}$ ) and efficiency of the Al/p-CdS/n-CdS/n-CdZnSSe hetero junctions were 650 mV, 29-32 mA.cm<sup>-2</sup> and 12%, accordingly. The  $I-U$  fill factor was 0.69. Hence, record of the optical information is most effective at wavelengths of about 510-550 nanometers.

**Keywords:** Thin Film, Solar Cell, Hetero Junctions, Compounds, Potential Barrier.

### I. INTRODUCTION

II-VI group compound semiconductors such as CdS, ZnSe and CdZnSSe are important because of their photovoltaic, photo electrochemical, and electroluminescent applications and, thus, they have got much attention. Recently, there have been many efforts to produce nano sized 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 hetero junctions have found practical application in phototransistors and in solar cells. However, the physics and technology of hetero junctions have also other prominent aspect - creation, research and practical application of non-ideal hetero junctions. The big set of various effects and phenomena in non-ideal hetero junctions related to various properties of semiconductors on both junction regions of hetero contacts have been observed.

Perspectivity of practical application of the non-ideal hetero junctions is related first of all to more economic technology of creation of polycrystalline hetero structure in comparison with the mono crystalline [4-6]. One of directions in studying of the non-ideal hetero junctions is the opportunity of solar cells application on the basis of A<sup>2</sup>B<sup>6</sup> compound multilayer structures.

The p-CdS/n-CdTe/n-CdZnSSe system represents a non-ideal unizotype hetero junction at which difference of CdZnSSe and CdTe lattice constants make 4%. Such significant difference of the lattice constants at hetero junction 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 their 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 [7-9].

The semiconductor compound CdZnSSe (CZSSe) is considered as one of the ideal photovoltaic absorber layer materials for low-cost thin film solar cells, since CZSSe has a large absorption coefficient and all the constituent elements are naturally abundant. The CZSSe absorber layer can be prepared by various vacuum approaches, such as co-evaporation and sputtering, or non-vacuum approaches, such as sol-gel sulfurization and ink-based method [10-12]. Compared with the vacuum approaches, the no vacuum approaches are recognized as the more desired techniques to achieve low production costs, because of their advantages such as simplicity, easy to scale up, and high material utilization.

In this study, we applied a low-temperature colloid technique to synthesize CZSSe nanoparticles for application in low-cost solar cells. This technique provides a relatively safe process for the fabrication of nanoparticles. To the best of our knowledge, this is the first reported synthesis of CZSSe nanoparticles by this technique [13, 14].

### 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 A<sup>2</sup>B<sup>6</sup> compounds contained 0.5 mM CdCl<sub>2</sub>, 50 mM ZnSO<sub>4</sub>, SeO<sub>2</sub> and 250 mM Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. 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  $\text{CdCl}_2$  + 0.2 mM  $\text{H}_2\text{SO}_3$  + 0.25 M  $\text{Na}_2\text{S}_2\text{O}_3$ . 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 p-type ZnSe deposited on aluminum substrate by a method of deposition from a solution, contained Zn and Se concentration ratio 1/2.5.

In the typical synthesis,  $\text{CdCl}_2$  (0.5 mmol),  $\text{ZnSO}_4$  (0.35 mmol),  $\text{Na}_2\text{S}_2\text{O}_3$  (0.3 mmol) and  $\text{SeO}_2$  (0.3 mmol) were added into pyridine as a metal source and the Cd/Zn molar ratio was determined to be 2/1.5.

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 thickness of the layers p-CdS, n-CdS, n-CdZnSSe films determined ellipse metric method. 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 200-500nm and CdZnSSe with thickness of about 800 nm.

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 structural characterization of the films has been performed by using X-ray diffract meter in the range of scanning angle 20-70 using Rigaku D/Max-IIIC diffract meter. The films have been investigated by scanning electron microscopy (Figure 1) and X-ray diffraction for the structure analysis and morphology study, respectively.

Surface photo voltage spectroscopy (SPV), which is a sensitive probe of surface states, was used to show that adsorbed water passivated surface states. Figure 2 shows the X-ray diffraction (XRD) patterns of the films electrodeposited at different bath temperatures ranging from 20°C to 90°C. There is only single peak corresponding to (111) plane is obtained for the films prepared at lower bath temperature of about 60°C. The results obtained from X-ray diffraction analysis reveal some interesting nature of the CdS materials. The surface of the substrate is not covered completely at these bath temperatures.

The grain formation is observed as irregular accumulation with the grain sizes completely different from each other. These observations suggest an incomplete formation step with irregular growth rate of the grains. No nanoparticles were observed when  $\text{Na}_2\text{S}_2\text{O}_3$  was used as the chalcogenide source. In contrast, the nanoparticles were detected when  $\text{SeO}_2$  was used as the chalcogenide source. However, it was found that the particle size distribution was wide. When  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{SeO}_2$  were used as the chalcogenide sources, the synthesized nanoparticles showed a narrow diameter distribution, suggesting that they are the optimum chalcogenide sources for the

fabrication of nanoparticles in our case. It is obvious that the chalcogenide source affects results of synthesis reaction.

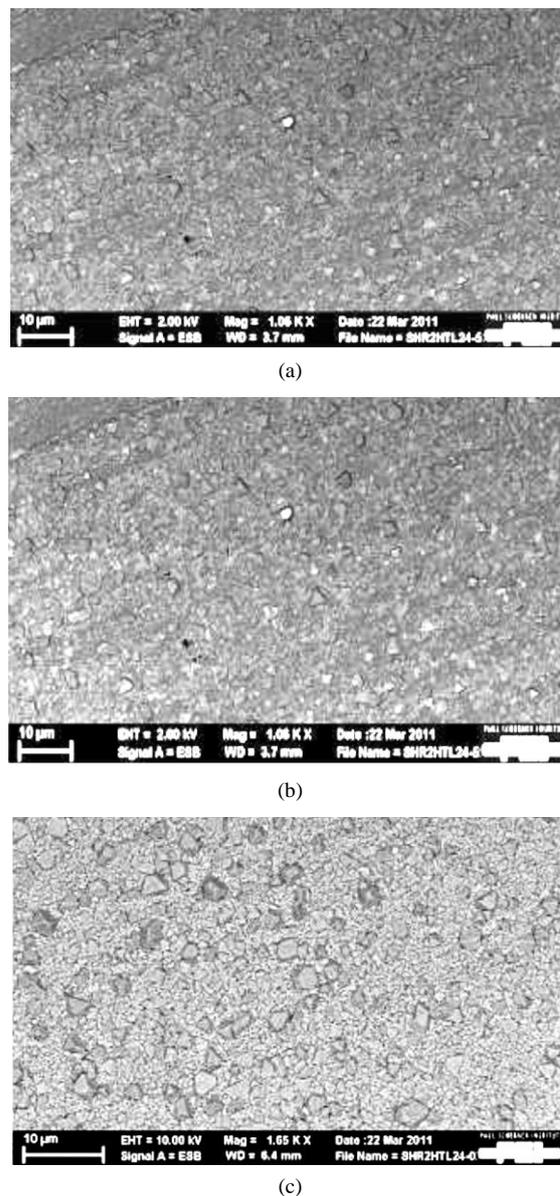


Figure 1. The scanning electron microscopy (SEM) micrographs of the (a) p-CdS, (b) n-CdS and (c) CdZnSSe thin films

The possible reason for this is the different nucleation and growth speeds caused by the different chalcogenide sources. The nucleation speed was fast and it resulted in the formation of numerous small nuclei when  $\text{Na}_2\text{S}_2\text{O}_3$  was used. The small nuclei quickly agglomerated together by van der Waals attractive forces detected. The slow nucleation speed caused growth of nuclei, which occurred with nucleation at the same time, resulting in the wide range of nucleus size when  $\text{SeO}_2$  was used as the chalcogenide source. Therefore, the size of CZSe nanoparticles, which grew from the nuclei, shows a wide distribution range. The appropriate nucleation and growth speeds with  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{SeO}_2$  were applied at the same time, resulting in a narrow distribution of diameter, and the average size of the nanoparticles was about 80 nm.

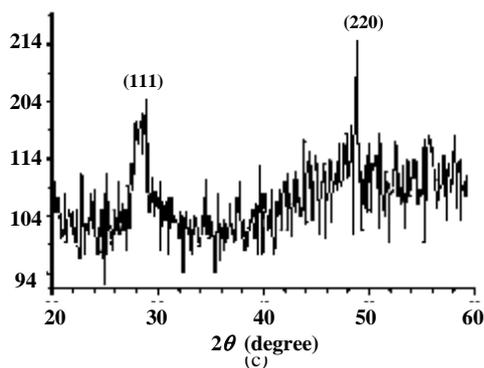
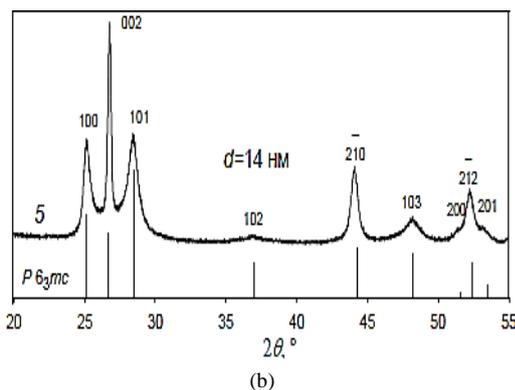
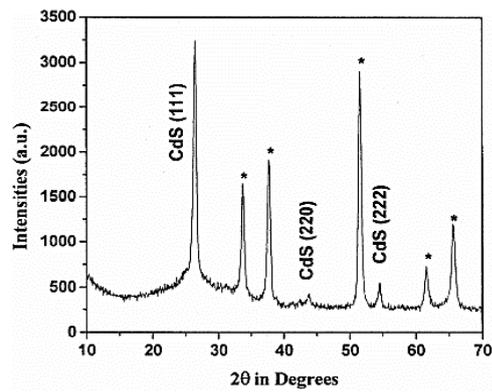


Figure 2. X-ray diffraction (XRD) patterns of the (a) p-CdS, (b) n-CdS and (c) CdZnSSe films

Under AM1.5 illumination (100Lux) the Al/p-CdS/n-CdS/CdZnSSe photo cells generated open circuit voltages of about 580–650 mV and short circuit current density of about 29–32 mA.cm<sup>-2</sup> also had efficiency up to 12% (Figure 3). On the other hand, discrepancy of constant lattices of contacting materials results in reduction of concentration of states in junction region of the hetero junctions, and also speeds up the degradation process. The dependence of an open-circuit voltage on illumination intensity differs from logarithmic. Therefore, the efficiency of Al/p-CdS/n-CdS/CdZnSSe hetero junctions increases by increasing of illumination intensity [4].

The peaks on the photosensitivity spectrum of the Al/p-CdS/n-CdS/CdZnSSe hetero junctions have been observed at 0.40–0.65μm (Figure 4). 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 CdZnSSe films. Peaks correspond to edge of own absorption.

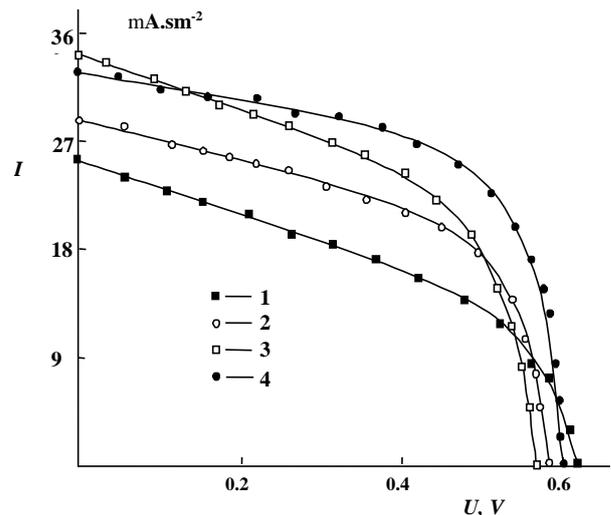


Figure 3. Volt-Ampere characteristics of the Al/p-CdS/n-CdS/CdZnSSe hetero junctions before (1) and after (2) heat treatment at temperatures 425°C, *t* in min: 1-10, 2-20, 3-30, 4-40

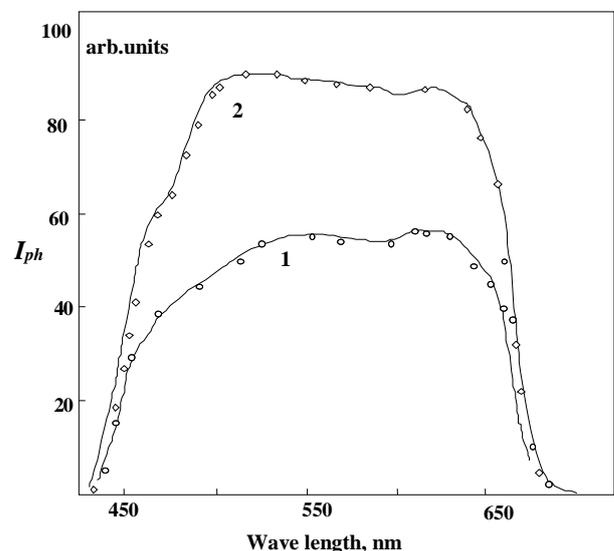


Figure 4. The photo answer spectrum of the Al/p-CdS/n-CdS/CdZnSSe hetero junctions before (1) and after (2) heat treatment at temperatures 425°C for *t* = 20 min

It has been investigated that the dependence of the spectral distribution nature of a photocurrent on a mode of deposition of the Al/p-CdS/n-CdS/CdZnSSe hetero junctions and features of spectral distribution of a current in them depending on a thickness of the CdS films.

Curves of voltage-capacitance characteristics (VCC) for the structures which were not undergo to TP have been studied. Character of VCC in investigated structures strongly depends on the percentage composition of films (Figure 5). When a percentage of selenium in CdZnSSe 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. (Figure 5, curve 1) Note, that capacitance, consequently concentration of surface states are regulated also by regime of TP.

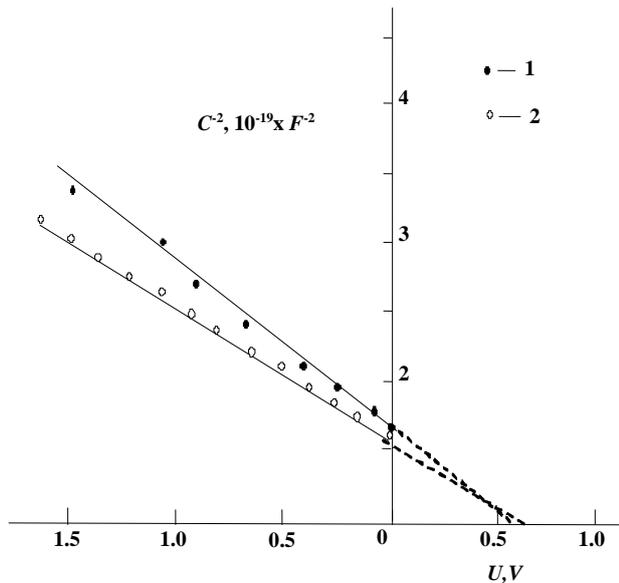


Figure 5. Volt-capacitance characteristics of the Al/p-CdS/n-CdS/CdZnSSe hetero junctions, before (1) and after (2) heat treatment at temperatures 425°C for  $t = 20$  min

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 (Figure 5, curve 2). It shows that in given case concentration of surface states on hetero boundary, being responsible for frequency dependent contribution to capacitance decreases.

### III. DISCUSSIONS AND RESULTS

Researches show that essential changes occur in Al/p-CdS/n-CdS/n-CdS/n-CdZnSSe hetero junctions during heat treatment. The nature of a change of electric and photoelectric properties of hetero junctions depending on the heat treatment shows, that due to presence acceptor levels in near surface of the CdZnSSe layer there is an expansion of a layer of a volumetric charge (Figure 5).

Therefore the capacity of p-n hetero junctions 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 hetero junctions raises [15].

Rise in temperature of storage results in faster thermal hole liberation to a valence band. The composition of the CZSSe nanoparticles as-synthesized for 2 min was confirmed by Energy-dispersive X-ray spectroscopy (EDS). The yields of the CZSSe nanoparticles exceeded 90%, which was determined after the evaporation treatment of the solvent. Annealing treatment has been performed to improve the crystallinity of the films in a quartz box with a volume of 16 cm<sup>3</sup> at various temperatures for 60 min. The intensity of the peaks increased when the annealing temperature up from 380 to 450°C, indicating the improvement of film crystalline.

The increase of the CZSe peak intensity confirmed the improvement of crystallinity, which is similar to the XRD results. The low-energy shift in the CZSe peak and the decrease of the CZS peak intensity were observed with increasing annealing temperature from 400 to 450°C, indicating the substitution of the annealing process. The Al/p-CdS/n-CdS/n-CdZnSSe hetero junction can be in two various states. One of them - equilibrium - possesses low sensitivity to the infra-red light and allows to receive low value of short-circuit current. Other state - non equilibrium - is high sensitive to infrared light and gives considerably high short-circuit current value.

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 photo excitation 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 510 nanometers.

Short wave lights are strongly absorbed in a base layer. Therefore the thickness of CdZnSSe layer and the diffusion length of charge carriers in this material determine the photo excited hole concentration in vicinities of the spatial charge area. The spatial charge area is not reached by all photo generated 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 CdZnSSe layer, not being in time to reach to the spatial charge area, i.e. there is absorption of light in a superficial layer of CdZnSSe.

The wane of sensitivity in long-wave area speaks about reduction of gathering factor of Al/p-CdS/n-CdS/n-CdZnSSe and about presence of the impurity centers in CdZnSSe, 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 hetero junctions by electrochemical method leads to formations of large member surface states in interface which are related with in homogeneities 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 disco response 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 hetero junction's interface.

### IV. CONCLUSIONS

Thus, the device prepared on the base of Al/p-CdS/n-CdS/n-CdZnSSe hetero junction can operate in all area of the visible spectrum with different sensitivity. Spectral distribution of a short circuit current allows characterizing

the shape of image signals as green sensitive on a basis of the Al/p-CdS/n-CdS/n-CdZnSSe hetero junction, on the standard classification for photographic layers. Hence, record of the optical information is most effective at wavelengths of about 510 nanometers.

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#### BIOGRAPHIES



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