**Preparation of Nanosized A²B⁶ Compound Multilayer 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/p-CdTe/ZnTe/Zn₁₋ₓCdₓS heterojunctions, were prepared by the method of electrochemical deposition from solution in a uniform work cycle. The open-circuit photovoltage (Uoc), short circuit-current density (I_sc) and efficiency of the Al/p-CdS/p-CdTe/ZnTe/Zn₁₋ₓCdₓS heterojunctions were 600-650 mV; 22-25 mA/cm² and 9-12 %, accordingly. The value of Uoc increases and I_sc decreases by increasing of Zn in Zn₁₋ₓCdₓS material.

**Keywords**

Thin Film, Solar Cell, Heterojunctions, Compounds, Potential Barrier

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1. **Introduction**

II-VI group compound semiconductors such as CdS, ZnTe 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, sol gel synthesis. In recent years, there has been considerable interest in use of 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 nonideal heterojunctions. The big set of various effects and phenomena in nonideal heterojunctions connected to various properties of semiconductors on both junction regions of heterocontacts have been observed. Perspectivity of practical application of the nonideal heterojunctions is connected first of all to more economic technology of creation polycrystalline heterostructure in comparison with the monocrystal. One of directions in studying of the nonideal heterojunctions is the opportunity of solar cells application on the basis of A²B⁶ compound multilayer structures. The p-CdS/p-CdTe/ZnTe/ZnCdS system represents a nonideal unizotype heterojunction at which difference of Zn₁₋ₓCdₓS and CdTe 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.

2. **Experimental**

Heterojunctions were prepared by a method of electrochemical deposition from a solution in a uniform work cycle (Fig.1.). The solution was stirred and thus local heating was avoided. The deposition solution for A²B⁶ compounds contained 0.5 mM CdCl₂, 50 mM ZnSO₄, TeO₂ and 250 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 electrodeposition condition. Cyclic voltammeter was used to study the electrochemical reactions in 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.

![Figure 1. Schematic diagram of the thin films electrodeposition apparatus.](image-url)
Reductive electrodeposition of alloys with large difference in the standard redox potentials of their constituents becomes thermodynamically possible at potentials positive of the standard redox potential of the less noble constituent due to the energy gain by compound formation. 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 CdTe deposited on aluminum substrate by a method of deposition from a solution, contained Cd and Te concentration ratio 1:2.5.

In the typical synthesis, CdCl₂ (0.5 mmol), ZnSO₄ (0.35 mmol) and Na₂S₂O₃ (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 thickness of the layers p-CdTe, n-ZnTe, n-ZnCdS films determined ellipsometric method. All layers were deposited on Al substrate serially - first of all p-CdS with thickness of about 150 nm, p-CdS with thickness of about 200-500 nm and ZnCdS with thickness of about 200-800 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 diffractometer in the range of scanning angle 20–70 using Rigaku D/Max-IIIC diffractometer. The films have been investigated by scanning electron microscopy (Fig. 2) and X-ray diffraction (Fig. 3, 4) for the structure analysis and morphology study, respectively.

Figure 2. The scanning electron microscopy (SEM) micrographs of the p-CdTe (A), n-ZnTe (B) and ZnCdS (C) thin films.

Figure 3. X-ray diffraction (XRD) patterns of the p-CdS films electrodeposited at different bath temperatures ranging from 20 °C to 90 °C.

Indium tin oxide (ITO) glass slides were 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 3 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 p-CdTe, n-ZnTe and n-ZnCdS thin films (Fig.4)

![X-ray diffraction patterns](image)

Figure 4. X-ray diffraction (XRD) patterns of the p-CdTe (a), n-ZnTe (b) and Zn_{1-x}Cd_xS (x=0.4) (c) thin films

However, there seems a slight decrease in the number of grains for the films deposited at 40 and 60°C. The surface of the substrate is not covered completely at these bath temperatures. The grain formation is observed as irregular agglomeration with the grain sizes completely different from each other (2-5 μm). These observations suggest an incomplete nucleation step with irregular growth rate of the grains.

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/p-CdTe/ZnTe/Zn_{1-x}Cd_xS heterojunctions increases by increasing of illumination intensity [4]. Have been observed the peaks on the photosensitivity spectrum of the p-CdS/p-CdTe/ZnTe/Zn_{1-x}Cd_xS heterojunctions at 0.48-0.49 μm and 0.72-0.75μm. The photo answer in long-wave area of a spectrum explains by presence of a high-resistance layer at the edge of near-surface areas of the CdTe films (Figure 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/p-CdTe/ZnTe/Zn_{1-x}Cd_xS heterojunctions and features of spectral distribution of a current in them depending on a thickness of the Zn_{1-x}Cd_xS films. Photocurrent in long-wave area of spectral sensitivity increases by increasing of the Zn_{1-x}Cd_xS film thickness (Figure 5, curves 2 and 3).
Preparation of Nanosized A₂B₆ Compound Multilayer Structures for Solar Cells

Figure 5. The photo answer spectrum of the p-CdS/p-CdTe/ZnTe/Zn₁₋ₓCₓS heterojunctions. Thickness of the Zn₁₋ₓCₓS films, nm: 1-200, 2-500, 3-800.

Under AM1.5 illumination the open-circuit photovoltage (U_{oc}), short circuit-current density (I_{sc}) and efficiency of the Al/p-CdS/p-CdTe/ZnTe/Zn₁₋ₓCₓS heterojunctions were 600-650 mV, 22-25 mA/cm² and 9-12 %, accordingly (Fig.6). The value of U_{oc} increases and I_{sc} decreases by increasing of Zn in Zn₁₋ₓCₓS material.

Figure 6. VAX heterojunctions p-CdS/p-CdTe/ZnTe/Zn₁₋ₓCₓS, (x: 1,3-0.2, 2,4 - 0.4) before (1, 2) and after (3, 4) heat treatment at temperatures 300°C, t = 20 min.

3. Results and Discussions

Researches show that essential changes occur in p-CdS/p-CdTe/ZnTe/ZnCdS heterojunctions during heat treatment. The nature of a change of electric and photo-electric properties of heterojunctions depending on the heat treatment shows, that due to presence acceptor levels in near-surface of the Zn₁₋ₓCₓS layer there is an expansion of a layer of a volumetric charge (Figure 5). Therefore, the capacity of p-n heterojunctions decreases. Increase of the photoanswer 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.

Tunnel currents prevail in the p-CdS/p-CdTe/ZnTe/Zn₁₋ₓCₓS heterojunctions prepared by chemical way even at temperatures of 270 K. Improving the technology it is possible to reduce a tunnel current considerably, first, due to increases potential barrier, through which tunnel electrons and second, due to reduction of centers’ concentration at interface. Electrons tunnel from the conductivity zone of wide-band material on narrow-band by the tunnel mechanism. Appear nonequilibrium electrons and holes during photoexcitation by quantum from area of own absorption of Zn₁₋ₓCₓS 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 Zn₁₋ₓCₓS 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/p-CdTe/ZnTe/Zn₁₋ₓCₓS heterojunction 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 - nonequilibrium - is high 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 Zn₁₋ₓCₓS 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 450-520 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 recombinated 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/p-CdTe/ZnTe/ZnCdS 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 CdTe layer.

4. Conclusion
Thus, the device prepared on the base of p-CdS/p-CdTe/ZnTe/ZnCdS 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. Spectral distribution of a short circuit current allows characterizing the shape of image signals as green sensitive on a basis of the p-CdS/p-CdTe/ZnTe/Zn_{1-x}Cd_xS heterojunction, on the standard classification for photographic layers. Hence, record of the optical information is most effective at wavelengths of about 520 nanometers.

REFERENCES