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Heat treatment effects in $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}/CdTe$ hetero-junction solar cells

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The electric and photoelectric properties of $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}/CdTe$ hetero-junctions have been investigated as a function of heat treatment. Solar cells were prepared by the method of electrochemical deposition. The performance of the cells after heat treatment in air at 300 °C for 10 min was improved. Under AM1.5 conditions the open-circuit voltage, short-circuit current, fill factor and efficiency of our best cell, were V_{oc} = 784 mV, J_{sc} = 16 mA/cm^2, FF = 0.6 and η = 7.4 %, respectively.

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1. Introduction

Despite their polycrystalline nature, thin-film solar cells based on the CdTe thin films achieve surprisingly high conversion efficiencies approaching 16-16.5 % [1-3]. As far as we know the band gap of buffer material needs to be sufficiently wide that as few photons as possible are absorbed in the buffer [4]. In spite of the 9% lattice mismatch between polycrystalline CdS and CdTe, good match of their electron affinity makes cadmium sulfide as perspective buffer material for CdTe -based solar cells. Nevertheless, weak sensitivity of CdTe/CdS solar cells in shorter wavelength region of spectrum demands replacement of buffers with alternative higher band-gap materials. The mixed films of $Cd_{1-x}Zn_xS$ at x = 0.6 was originally chosen for its lattice match to CdTe substrates and it is shown, that the discontinuities in conduction-band, ΔE_c, drop to zero for heterojunctions $Cd_{0.4}Zn_{0.6}S/CdTe$ and these structures are suitable for producing effective solar cells [5].

The quaternary compounds of $Cd_{1-x}Zn_xS_{1-y}Se_y$ have been attracting much attention for the buffer materials of the solar cells, since their band-gaps are ranging from 1.8 eV to 3.8 eV, which correspond to red to ultra-violet spectral region [6]. It is shown in our paper that the efficiency of $In_2O_3/Cd_{0.4}Zn_{0.6}S/CdTe$ solar cells can be improved by addition of selenium to $Cd_{0.4}Zn_{0.6}S$ films.

On the other hand, it is well known that, the stoichiometry of electrodeposited thin films can be controlled by the deposition potential but the photosensitivity of as-deposited films are poor. Heat treatment (HT) allows a remarkable improvement of these properties along with a complete recrystallization [6-8].

In this paper, we report the preparation of In2O3/$Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe solar cells by the method of electrochemical deposition, which is currently attracting considerable attention, as it is relatively inexpensive, simple and convenient for large area deposition [9-11]. The basic goal of paper is to explore the benefits of the utilization of the wide-gap $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ buffers in place of traditional CdS, to begin a more in-depth analysis of the current transport and to study the effect of HT on the electric and photoelectric properties of $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}/CdTe$ cells.

2. Experimental

Firstly, we deposit layers of $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ (with E_g = 2.94 eV) from $CdCl_2$ + $ZnCl_2$ + $Na_2S_2O_3$ + SeO_2 aqueous solution onto the layers In_2O_3 prepared by magnetron sputtering from pure indium targets onto the cleaned surface of quartz substrates. Deposition was carried out for 48 hour at potentials of – 0.7 V and current density of 15 mA/cm^2. The final thickness of the $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ films was 0.4 – 1 μm and their resistivity essentially depends on the solution pH (HCl and NaOH). With increasing pH, resistivity of films decreases (from 3000 up to 150 Ohm·cm).

Polycrystalline films of p-CdTe were prepared by the method of electrochemical deposition on the $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ substrates by using a three-electrode system with the saturated calomel electrode from aqueous solution containing $CdSO_4$ (1.0 M) and TeO_2 (0.1 mM), 25 mM citric acid, and 10% ethanol by volume. Electro deposition was carried out at room temperature (25 – 35 °C). The films were deposited using a deposition potential of –0.6 V and current density of 11 mA/cm^2. In order to deposit a 3 μm thick film, a deposition time of 20 – 22 min was used.

For ohm contacts for p-CdTe we used Cu/graphite [12]. The active area of the cells was 0.5 ÷ 4 cm^2.

Heat treatment of cells was carried out in N_2 atmosphere at temperature T_a = 100 – 300 °C for τ_a = 1 - 14 min.

3. Results and discussion

The forward *I-V* characteristics of the $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}/CdTe$ cells in the temperature range of T = 100 – 350 K consist of two plots (Fig. 1). For the first plot the forward currents exponentially depends on the applied voltage:

$$I \sim I_0 \, exp(eV / W) \qquad (1)$$

Where e is the electron charge, W is the characteristic energy, I_0 is the preexponential factor. The second plot is due to influence of residual resistance of the structure base. Characteristic energy of exponential region of the forward *I-V* characteristics practically does not depend on the temperature. The pre-exponential factor, in particular, exponentially depends on the temperature. The experimental results suggest a determining role of the forward tunnel currents in investigated cells. The analysis of the forward *I-V* characteristics with different models of current transport shows that the transport of current through the $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells is due to multiple step tunneling model by Riben and Feucht [4]. According to this model, the following relation can describe the forward currents:

$$I \sim N_0 \exp(V_d) \exp(eV / W) \qquad (2)$$

where N_0 is the state density through which there is a tunneling charge carriers, V_d – is the cut-off voltage. The forward *I-V* characteristics of cells are qualitatively well described within the framework of this model, and temperature dependence of the current is determined by the temperature factor of V_d.

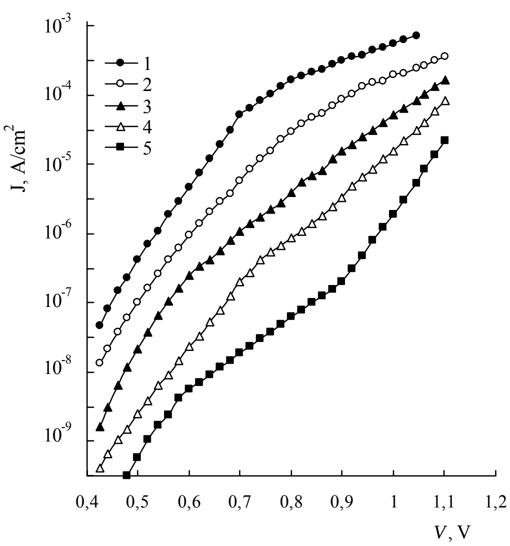


Fig. 1. Temperature dependence of forward I-V characteristics of the $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells. T, K: 1 – 100, 2 – 200, 3 – 250, 4 – 300, 5 – 350.

The reverse current obeys a power law at relatively low ($V < 2$ V), i.e. reverse currents on this region is determined by the generation process of carriers in the space charge layer (Fig. 2). At relatively high voltages ($V > 2$ V) the reverse currents practically do not depend on the temperature and is well described within the framework of multiple step tunnel model [4].

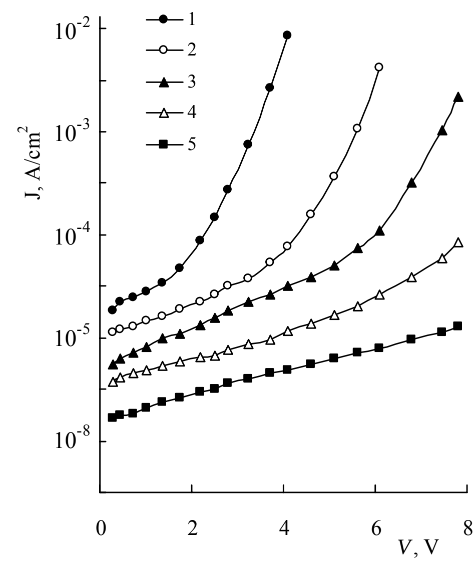


Fig. 2. Temperature dependence of reverse I-V characteristics of the $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells. T, K: 1 – 100, 2 – 200, 3 – 250, 4 – 300, 5 – 350.

The voltage dependence of capacitance in all annealed in air at 200 °C for 3 min cells showed linear variation of C^{-2} against V. From the plot in the figure we find V_d =1.02 V (Fig. 3).

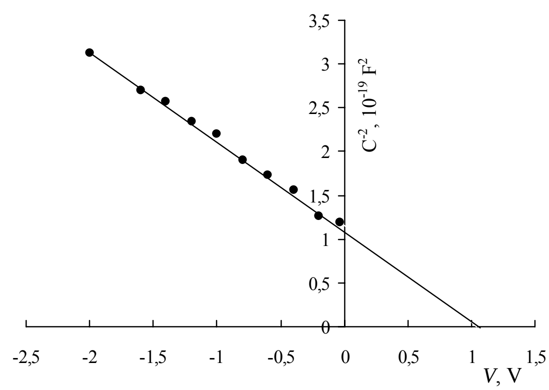


Fig. 3. C-V characteristics of the annealed $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells at 300 K.

Quantum efficiency and light *I-V* characteristics of as-deposited and annealed $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells were measured by the standard technique (Fig. 4 and 5). The values of all photoelectrical parameters of the cells strongly depend on the annealing regime. At illumination, as-deposited cells have the following photoelectrical parameters: $I_{sc} \approx 1.23$ mA/cm², $U_{oc} \approx 120 - 130$ mV (Table 1). After the HT the photosensitivity spectrum considerably changes - the spectral contour extends and strongly pronounced maxima are observed (Fig. 4). The long wavelength fall off for all cells indicated CdTe absorber band gap. After the HT at temperature T_a = 300 °C for τ_a = 10 min, the photosensitivity of cells reaches a maximum value. Thus under AM1.5 conditions the cells possess the following photoelectrical parameters: V_{oc} = 784 mV, J_{sc} = 16 mA/cm^2, FF = 0.6 and η = 7.4 %, respectively (Fig. 5, curve 3 and Table 1). The further increase of annealing temperature and duration ($T_a \geq$ 450 °C and $\tau_a \geq$ 12 min) results in sharp decrease of photosensitivity in all spectral range.

Table 1. The characteristics of glass/In_2O_3/$Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells depending on the HT temperature and time.

Heat treatment (temperature and time)	Thickness of films $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ (μm)	Band gap energy of films $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ (eV)	Under light Characteristics			
			J_{sc} (mA/cm^2)	V_{oc} (volt)	*FF*	η (%)
1. before annealing	0.52	2.940	1.23	0.130	0.42	0.07
2. 100°C; 3 min	0.50	2.940	3.46	0.48	0.46	0.8
3. 100°C; 5 min	0.51	2.940	9.65	0.534	0.58	3.0
4. 200°C; 5 min	0.53	2.940	13.6	0.731	0.58	5.7
5. 300°C; 10 min	0.53	2.941	16	0.784	0.6	7.4
6. 350°C; 10 min	0.52	2.941	11.2	0.357	0.53	2.0
7. 450°C; 13 min	0.52	2.942	1.2	0.120	0.4	0.06

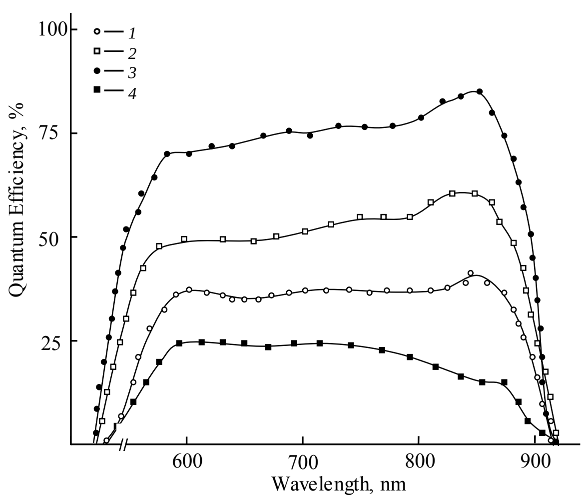


Fig. 4. Quantum efficiency curves of In_2O_3/$Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe cells as a function of annealing conditions: T_a, °C: 1 – 0; 2 – 200; 3 – 300; 4- 450, τ_a, min: 1 – 0; 2 – 5; 3 – 10; 4 – 13.

The observed effect of HT on the photoelectric properties of the cells demonstrates that the donor and acceptor concentrations in the junction region of structures depend on HT conditions. In particular, it seems likely that, HT promotes grain growth within both CdTe and $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ layers, diffusion of Cu from back contact into the cell junction and inter-diffusion between CdTe and $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ resulting in the formation of $CdTe_{1-x}(SSe)_x$ alloys at the interface.

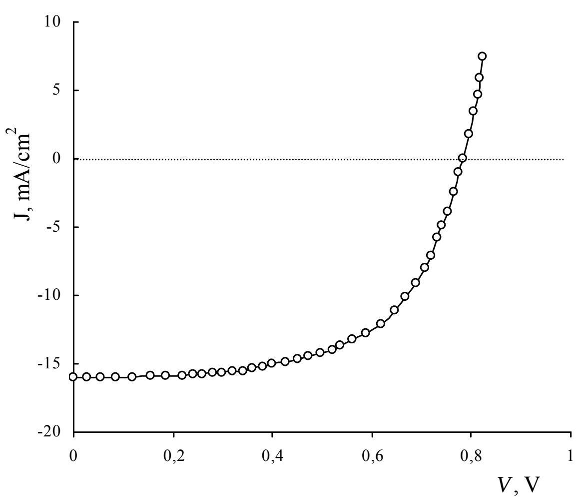
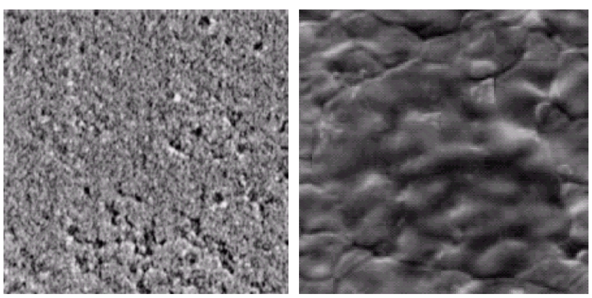


Fig. 5. Light I-V characteristics of In_2O_3/$Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe after HT at 300 °C for 10 min.

It is supposed that oxygen adsorption after the removal of $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ films from the solution leads to the formation of deep acceptor states in the surface layer of the films [6-8]. The oxygen- related acceptors capture electrons from the film bulk, creating a near-surface potential barrier, which is responsible for the low short-wavelength photosensitivity of the as-deposited cells (Fig. 4, curve 1). Because of the small height of the inter-granular barriers in polycrystalline films as compared to the oxygen-related barriers, these states govern the short-wavelength photosensitivity of the cells. In the initial stages of HT, oxygen desorbs firstly. At the same time, as show scanning electron microscope (SEM) images, the CdTe films grain size increases (Fig. 6). The crystallites of as-deposited films CdTe grown on $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ substrates are very small (Fig. 6 a). The films annealed at 300°C for 10 min already exhibits planar surface morphology and grain size up to 7 µm, which enhances the long-wavelength photosensitivity of cells (Fig. 6 b). Thus, inter-diffusion between $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$ and CdTe occurs, and at the interface forms a $CdTe_{1-x}(SSe)_x$ layer. It has been suggested that formation of the interlayer reduces the structural defects, which also leads to improvement in cell performance.



a) b)

Fig. 6. SEM photograph of CdTe surface: a) before HT; b) after HT at 300 °C for 10 min.

The sharp decrease in photosensitivity upon heat treatment at 400 °C or higher temperatures indicates that some of the oxygen does not desorbs and Cu starts to diffuse from the back contact into the junction region. At the cell junction, Cu was proposed to form recombination centers and shunt pathways [12,13]. As a result, the concentration of holes captured by these centers increases sharply, reducing the photosensitivity of the devices.

4. Conclusion

Rather high values of FF, V_{oc} *and* J_{sc} allow to conclude that there is an effective division of the generated by light electron-hole pairs in the contact region of cells. The films of CdTe and $Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$, because of HT, forms a continuous number of solid solutions on the contact region (thin layer), which reduces the amount of defects adversely influencing on the electric and photoelectric parameters of the hetero-junction $In_2O_3/Cd_{0.4}Zn_{0.6}S_{0.9}Se_{0.1}$/CdTe solar cells.

References

[1] T. Aramoto, S. Kumazawa, H. Higuchi, T. Arita, S. Shibutani, T. Nishio, J. Nakajima, M. Tsuji, A. Hanafusa, T. Hibino, K. Omura, H. Ohyama, M. Muronzo. Jpn. J. Appl. Phys. **36**, 6304-6305 (1997).
[2] K. Durose, P. R. Edwards, D. P. Halliday. J. Cryst. Growth **197**, 733-736 (1999).
[3] A. Morales-Acevedo. Solar Energy Materials and Solar Cells **90**, 2213-2220 (2006).
[4] A. G. Milnes, D. L. Feucht, “Heterojunctions and metal-semiconductor junctions,” Academic Press, New York/London, 1972.
[5] T. M. Razykov, B. Kh.Kadyrov, M. A. Khodyaeva. Phys. Stat. Sol. (a) **91**, 87-91 (1985).
[6] A. Sh. Abdinov, H. M. Mamedov, S. I. Amirova. Thin Solid Films **511-512**, 140-142 (2006).
[7] H. M. Mamedov, G. A. Gasanov, S. I. Amirova. Inorganic Materials **41**, 276-280 (2005).
[8] A. Sh. Abdinov, H. M. Mamedov, H. A. Hasanov, S. I. Amirova. Thin Solid Films **480-481**, 388-391 (2005).
[9] A. E. Rakhshani. J. Appl. Phys. **90**, 4265-4271 (2001).
[10] R. K. Sharma, K. Jain, A. C. Rastogi. Current Appl. Phys. **3**, 199-204 (2001).
[11] N. B. Chaure, Sh. Chaure, R. K. Pandey. Solar Energy Materials and Solar Cells **81**, 39-60 (2004).
[12] K. D. Dobson, I. Visoly-Fisher, G. Hodes, D. Cahen. Solar Energy Materials and Solar Cells **62**, 295-325 (2000).
[13] D. Grecu, A. D. Compaan, Appl. Phys. Lett. **75**, 361-365 (1999).

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