Chalcogenide Letters Vol. 18, No. 1, January 2021, p. 31 - 38

PHOTOELECTRICAL PROPERTIES OF p-Si/$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ HETEROJUNCTIONS

H. M. MAMMADOV, M. A. JAFAROV[*], E. F.NASIROV, D. PIRIYEVA
Baku State University, Baku, Azerbaijan

In this paper the photoelectrical properties of p-Si/$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ type thin film heterojunctions in a wide range of wavelengths (300 - 1400 nm) were characterized depending on the quantitative composition ($0 \le x \le 1$ and $0 \le y \le 1$) of $Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ type films, electrochemical deposition potential, mode and medium of heat treatment (HT). In order to clarify the effect of these factors on the photoelectric properties and basic parameters of heterojunctions with different composition, the spectral distribution of photoconductivity, volt-ampere characteristics (I-U characteristics), amper-light characteristics were studied.

(Received October 13, 2020; Accepted January 15, 2020)

Keywords: Electrochemical deposition, Thin film, H eterojunction, Heat treatment, Solar cell, Rectifier diodes

1. Introduction

The photovoltaic heterojunction based on $A^{II}B^{VI}$ type compounds has been found to be candidate for inexpensive and high performance alternative to the homojunction photovoltaic device [1-8]. Many methods were used to prepare films of $A^{II}B^{VI}$ type compounds e.g. vacuum evaporation, sputtering, spray pyrolysis, chemical bath deposition etc. [9-15]. It shown, that properties of $A^{II}B^{VI}$ type films such as electrical, optical, and structural are depends strongly on the preparation method. One of the promising method for producing of large areas of inexpensive $A^{II}B^{VI}$ type films for photovoltaic applications is electrochemical deposition and here we are followed this method to prepare $Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ films. Electrochemical deposition has advantages over other methods such as: simple, inexpensive, possibility of large area deposition does not need high vacuum apparatus, and stoichiometry preservation. Furthermore, the properties of grown film can be varied and controlled by proper optimization of deposition conditions.

In the present work, the effect of electrochemical deposition potential, chemical and composition of the films and heat treatment regimens on the photoelectrical properties of p-Si/$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ heterojunction deposited by electrochemical deposition from aqueous solution was investigated.

2. Materials and methods

The thickness and resistivity of the monocrystalline p-Si substrates were 0.4 mm and 0.2 Ω·cm, respectively. Films of Cd1-xZnxS(Se)1-ySe(Te)y and heterojunctions on their basis with different composition were manufactured and characterized via the same methods as reported in our previous work [4,13,16,17].

---

[*] Corresponding author: maarif.jafarov@mail.ru

https://doi.org/10.15251/CL.2021.181.31

3. Result and discussion

The photovoltaic effect is observed in all types of heterojunctions just after the deposition. Thus, the photosensitivity is strongly dependent on the electrochemical deposition potential (cathode potential). Fig. 1 shows the graphs of the relative photosensitivity (values of wavelength corresponding to the maximum photo-sensitivity for each sample in 1 sm^2 area and 100 mVt/sm^2 illuminations) for heterojunctions of different compositions. As can be seen from the figures, the maximum photosensitivity is observed at a specific value of the cathode potential and takes different values for different components.

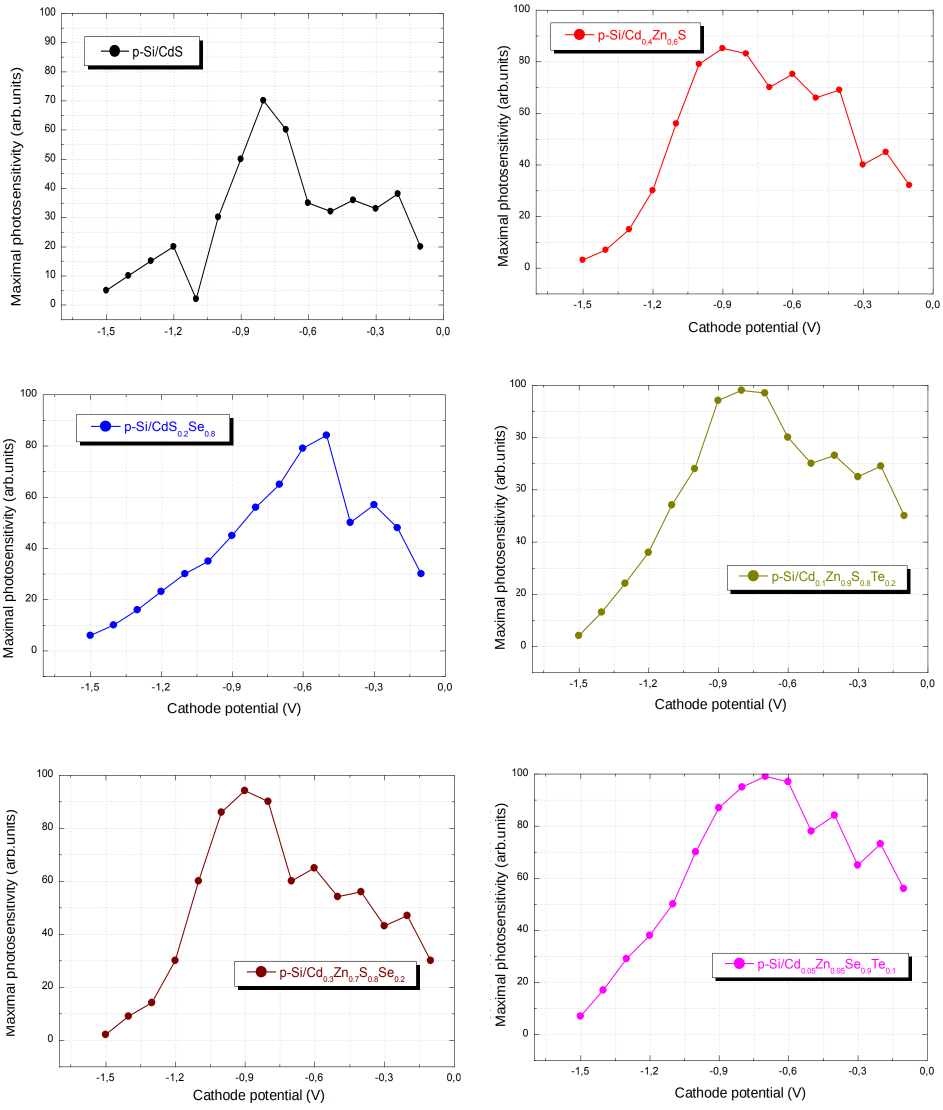


Fig. 1. Dependence of the relative photosensitivity (values of wavelength corresponding to the maximum photosensitivity for each sample in 1 cm^2 area and 100 mW / cm^2 illumination) for p-Si/ $Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ heterojunctions of different composition just after deposition.

Photosensitivity is oscillating at cathode potentials where relative photoresistivity is weak. We think that this is due to the fact that the thin layers deposited at these values of the cathode potential are not yet fully formed. The oscillation of the photocurrent can be explained by the presence of a small CdS-ZnS-ZnSe(Te)-CdSe(Te) mixed system or a metal/chalcogenide excess in the thin layer matrix. However, at optimal values of the deposition potential for films of a given composition, the photosensitivity in the short-wavelength range of the spectrum increases sharply, and the oscillations of the photocurrent disappear and heterojunctions exhibit maximum photosensitivity. With a further increase in the cathode potential (U≥ – 1.0 V) the photosensitivity of the heterojunctions in the short-wavelength region of the spectrum become worse again. Such non-monotonous variation of photosensitivity depending on the deposition potential proves once again that the stoichiometric composition of films $Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ type solid solutions can be obtained only at an optimal value of the potential. Thus, at high and little values of cathode potential, the violation of thermodynamic equilibrium on the cathode surface and the sharp difference in the electrochemical activity of ions (Cd^+, Zn^+, S^+, Se^+, Te^+) lead to excess metal or chalcogenide that causes the formation of a system consisting of mixtures.

The photosensitivity of heterojunctions is determined not only by the cathode potential but also by the thickness of the layer. It is well known that one of the ways to further reduce the cost of electricity generated by solar photovoltaic cells is to minimize the thickness of the semiconductor layer from which the working element is made. This, on the other hand, reduces material consumption and, most importantly, reduces the series resistance of the solar cell. However, reducing the thickness of the layer also creates certain problems – reducing the thickness will lead to an increase in the internal electric field in the junction region, and this additional field will contribute to the separation of light-generated carriers, i.e, at the end, efficiency will increase. According to investigations, by depositing nano-dimensional metal electrodes on the surface of nanometer-thick layers, it is possible to achieve the absorption of the entire spectrum of solar radiation due to surface polarization. In other words, maximum efficiency can be achieved by depositing an extra thin films. According to theoretical data, if the electron-hole pair is generated in the order of diffusion lengths Lp and Ln calculated from the junction boundary under the influence of light, they can be successfully separated. That is, in principle, the active thickness can be defined as the d = Lp + Ln + width of the bulk region (WBR). If we assume that the sum Lp + Ln is close to zero, the active thickness is determined only by the width of the bulk region. Since there is a relationship $d \sim 1/\alpha$ between the absorption coefficient (α) and the thickness of the thin layer, it can be concluded that for a material with a very high absorption coefficient, d~(WBR) and for them the photocurrent is too large. In general, the absorption coefficient of Cd1-xZnxS(Se)1-ySe(Te)y type thin films is not too large.

Therefore, for maximum efficiency, an optimal thickness must be selected for the specific material.

Figure 2 shows the graphs of the relative photosensitivity dependence on the thickness of films just after deposition for heterojunctions deposited at the optimal value of cathode potential (cathode deposition potential corresponding to the maximum photosensitivity of heterojunctions according to Figure 1). As can be seen from the graphs, the dependence of photosensitivity on the thickness of the layer is extreme. At small thicknesses, the photosensitivity decreases sharply and is oscillating. The oscillation nature of the photosensitivity can be explained as follows: since films under study are polycrystalline, the total photosensitivity of the layer is determined by the photosensitivity of the individual islets. Because the resistance of each part is different, the absorption of light and generation of electron-hole pairs also take place in different ways. Since the difference between the islets at small thicknesses is significant, the photosensitivity of the heterojunction also depends non-monotonously on the change in thickness. As the thickness increases, the boundaries of the islets overlap and these oscillations decrease. As can be seen from the figure, the oscillations are weak in the thin films based on the four-component compounds containing S-Te and Se-Te. This once again proves that tellurium compounds are more durable, and on their basis it is possible to make flexible, durable solar elements. At greater thicknesses, photosensitivity is decreases because most of the radiation is absorbed in thin layers. Based on the graphs, the optimal thickness was selected to determine the maximum photosensitivity for each composition of heterojunction, and the spectral distribution of the photocurrent, ampere-light characteristics, light I-U characteristics just after deposition and depending on the environment and mode of HT were studied.

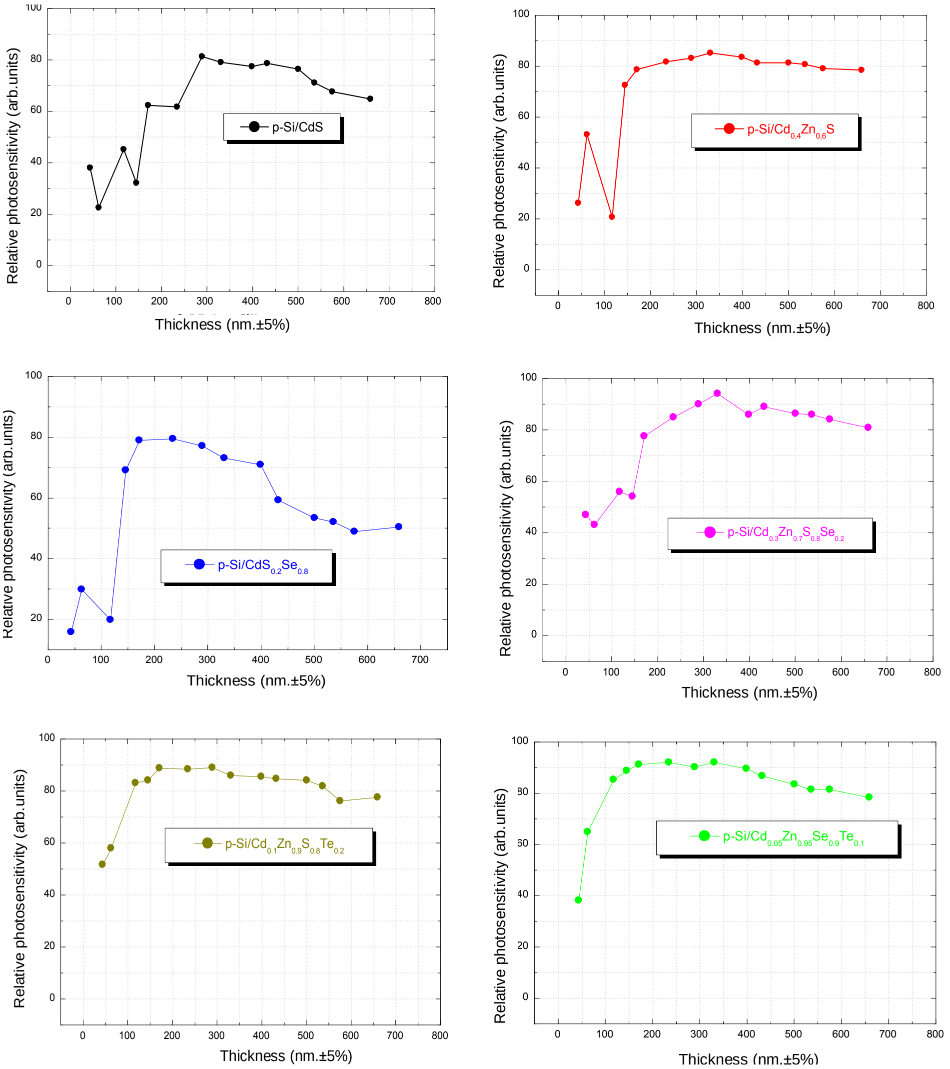


Fig. 2. Dependence of the relative photosensitivity (values of wavelength corresponding to the maximum photosensitivity for each sample in 1 cm2 area and 100 mW/cm2 illumination) for p-Si/ $Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ heterojunctions of different composition after deposition.

Fig. 3 shows the spectral distribution curves of short-circuit current density at 100 mW/cm^2 illumination after direct deposition in thin-layer heterojunctions deposited at the optimal value of the cathode potential and optimal thickness. As can be seen from the figure, the short-wavelength range of the spectrum for all composite heterojunctions is determined by the width of the band gaps of thin films Cd1-xZnxS(Se)1-ySe(Te)y, and the long-wavelenght range boundary is determined by the band gap of Si (Eg = 1.12 eV) wafers.

Despite the choice of the optimal thickness of the thin films and the optimal value of the cathode deposition potential, the low sensitivity in the short-wavelength region of the spectrum and the oscillation of the photocurrent in all composite heterojunctions indicate that the thin films deposited by electrochemical deposition at low temperature are not fully formed. Thus, the absorption of oxygen molecules to the surface during direct exposure to the open air, the presence of various complexes on the surface during the reaction, as well as the unreacted *metal/semiconductor* excess can cause poor photosensitivity and oscillations.

As can be seen from the figure, as the composition of the thin films changes, the maximum in the region of the short-wavelength shifts to the longer wavelengths with the increasing of the amount of Se and Te and the shifts in the direction of the shorter waves as the amount of Zn increases. This once again proves that thin films of double, three-component and four-component compounds with stoichiometric composition are deposited from an aqueous solution by electrochemical deposition. Our experimental studies have shown that, regardless of the environment in which it is carried out, HT changes the photosensitivity of all composite heterojunctions quantitatively and qualitatively.

Figure 4 illustrates the spectral distribution and ampere-light curves of the short-circuit current before HT of heterojunctions and in optimal HT modes in different environments. As can be seen from the figure, after the HT not only increase the photosensitivity in the short-wavelength region, but also expand their spectrum towards the shorter wavelength range.

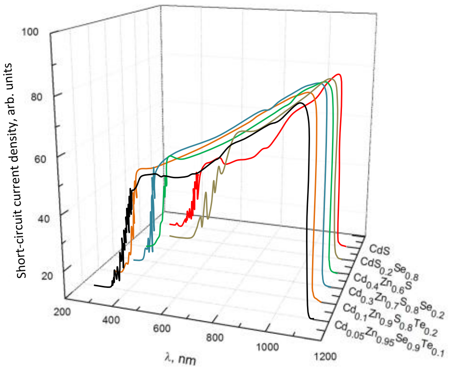
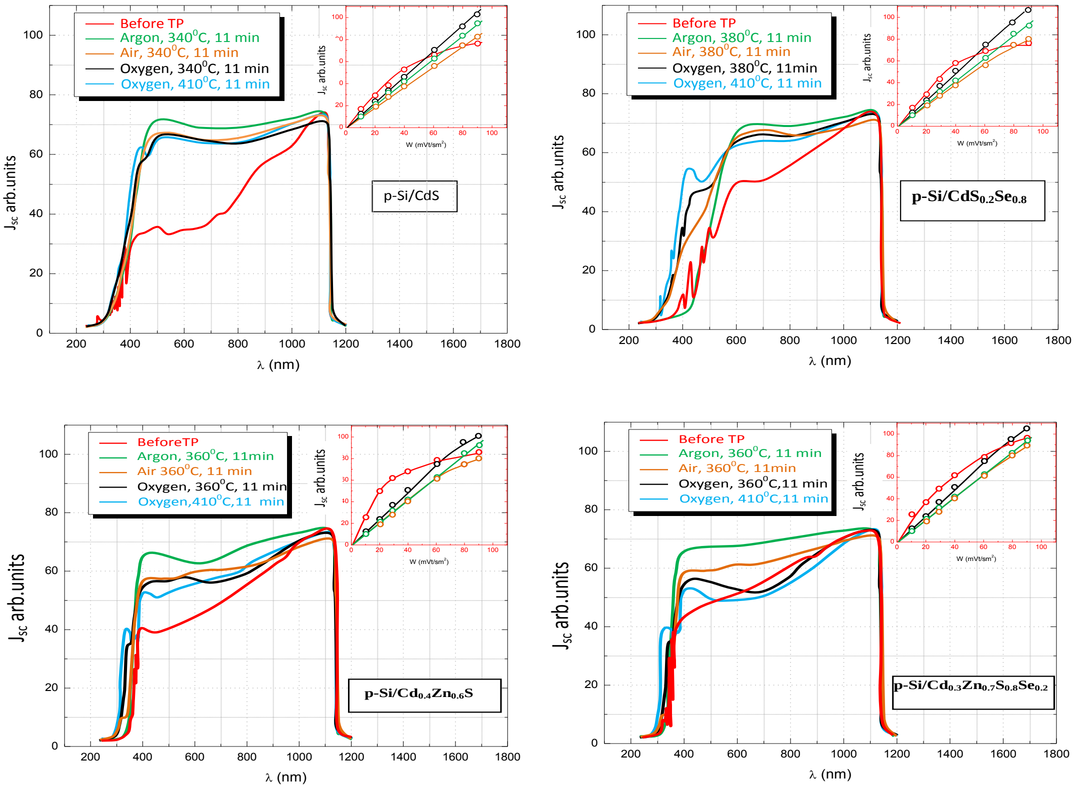


Fig. 3. Spectral distribution of short-circuit current density at 100mW/cm2 illumination just after deposition for heterojunctions p-Si/$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ deposited at the optimal value of the cathode potential and the optimal thickness.



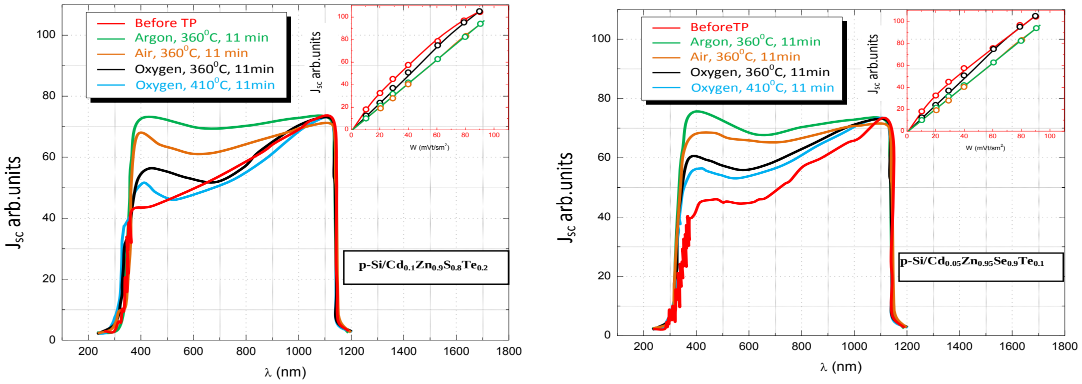


Fig. 4. Spectral distribution curves of short-circuit current and ampere-light characteristics before and after the HT for heterojunctions ***p-Si****/$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ with different compositions.*

During HT in the open air and oxygen environment, another maximum is formed in the short-wavelength region of the spectrum, which once again proves the formation of $Cd_{1-x}Zn_xO$ thin films on the surface of heterojunctions. It should be noted that this effect is less observed in heterojunctions based on four-component compounds. This proves once again that they are environmentally strong. As can be seen from the figure, the photosensitivity of heterojunctions after the HT in the argon environment increases sharply in the entire region of the spectrum. Although the sensitivity of the whole spectrum in the oxygen environment is lower than in the argon, the increase in sensitivity in the short-wavelength region allows them to be used as both high-efficiency and sensitive solar cells and light detectors in the ultraviolet region of the spectrum. After the HT in such an environment and regime, the sensitivity of the heterojunctions, as well as in the visible region of the spectrum increases and stabilizes. After the optimal HT, these heterojunctions exhibit high stable photosensitivity over a wide range of spectra (385–1100 nm). As can be seen from Figure 4, a little increasing in the HT temperature or duration from the optimal value, sharply reduces the photosensitivity of these heterojunctions in the short-wavelength region and increases the oscillation of the photosensitivity. The short-circuit current is nonlinearly dependent on the intensity of the incident light (Figure 4, appendices). This non-linear dependence is due to the presence of easily and difficult-to-manage donor or acceptor centers in thin layers. As can be seen from the figures, in four-component compounds, ampere-light characteristics exhibits a close dependence to linearity even just after deposition. This shows that in four-component compounds, all reaction products are fully reacted along the entire surface and volume of the layer, without violating the thermodynamic equilibrium during the reaction, which prevents *metal/semiconductor* excess and vacancies and, consequently, oxygen absorption to the surface. High temperature and longer-duration HT leads to intensive evaporation of film components from the surface, which results in the non-linear dependence.

As the series resistance of the heterojunctions changes after the HT, the value of the short-circuit current (J_{sc}) and the open circuit voltage (U_{oc}) change significantly. Table 1 shows the photoelectrical parameters of the studied heterojunctions. As can be seen from the table, heterojunctions based on thin films of four-component compounds exhibit the best photoelectrical parameters. During 5 years, heterojunctions show a maximum of 0.2% degradation, while Te-based compounds show almost no degradation.

Table 1. Photoelectrical parameters of **p-Si/**$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ *heterojunctions before and after the HT in argon for* 360^0C *and 11 min.*

Sample		Active area	J_{sc}, mA/cm^2	U_{ad}, V	FF	η, %
p-Si/$Cd_{0.4}Zn_{0.6}S$	before the HT	1 cm^2	10,8	0,56	0,58	3,5
	after the HT	1 cm^2	23,4	0,58	0,7	9,5
p-Si/$CdS_{0.2}Se_{0.8}$	before the HT	1 cm^2	11	0,5	0,56	3,1
	after the HT	1 cm^2	25	0,53	0,66	8,7
p-Si/$Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$	before the HT	1 cm^2	16	0,54	0,63	5,4
	after the HT	1 cm^2	22,8	0,6	0,65	8,9
p-Si/$Cd_{0.1}Zn_{0.9}S_{0.8}Te_{0.2}$	before the HT	1 cm^2	24	0,63	0,53	8,6
	after the HT	1 cm^2	34	0,64	0,55	11,9
p-Si/$Cd_{0.05}Zn_{0.95}Se_{0.9}Te_{0.1}$	before the HT	1 cm^2	32	0,6	0,56	10,7
	after the HT	1 cm^2	42	0,61	0,57	14,6

4. Conclusions

The results indicate that, the maximum values of the maximum photoelectric parameters for heterojunctions **p-Si/**$Cd_{1-x}Zn_xS(Se)_{1-y}Se(Te)_y$ can be provided only at a certain optimal value of the cathode deposition potential and the thickness of the thin layers. The weak dependence of photoelectric parameters on the HT mode in four-component compounds (mainly in Te compounds), as well as the weak oscillations at the values indicate that they are more stable than two- and three-component compounds.

References

[1] A. Hermann, Solar Materials and Solar Cells **55**, 85 (1998).
[2] C. Feredikes, J. Britt, Y. Ma, L. Killian, IEEE PVSC **23**, 83 (1993).
[3] N. Sans, D. Mao Y. Zhu, J. Tang, J. Trefny, IEEE PVSC 25 (1996).
[4] A. Sh. Abdinov, H. M. Mamedov, S. I. Amirova, Thin Solid Films **511-512**, 140 (2006).
[5] H. M. Mamedov, M. B. Muradov, Z. Konya, A. Kukovecz, K. Kordas, S. I. Shah, V. C. Mamedova, K. M. Ahmedova, E. B. Tagiyev, V. U. Mamedov, Photonics Letters of Poland **10**, 73 (2018).
[6] H. M. Mamedov, A. Kukevecz, Z. Konya, K. Kordas, S. I. Shah. V. U. Mamedov, K. M. Ahmedova, V. J. Mamedova, R. M. Rzaev, Sh. A. Shamilova, E. A. Khanmamedova, L. E. Agazade, Russian Journal of Applied Physics **61**, 96 (2018).
[7] H. M. Mamedov, V. U. Mamedov, V. J. Mamedova, K. M. Ahmedova, E. B. Tagiyev, L. E. Agazade, J. Optoelectron. Adv. M. **20**, 468 (2018).
[8] H. M. Mamedov, S. I. Shah, A. Chirakadze, V. U. Mamedov, V. J. Mamedova, K. M. Ahmedova, Photonics Letters of Poland **10**, 26 (2018).
[9] K. Senthil, D. Mangalaraj, K. Narayandass, S. Adachi, Mat. Sci. Eng. **53**, B78 (2000).
[10] A. Oliva, O. Solis, R. Castro , P. Quintana, Thin Solid Film **28**, 391 (2001).
[11] P. Hoffman, K. Hom, A. Bradshaw, R. Johson, D. Fuchs, M. Cardona, Phys. Rev. B **47**, 1693 (1993).
[12] D. Mazón, M. Lerma, M. Quevedo, M. El-Bouanani, H. Alshareef, F. J. Espinoza-Beltrán, R. Ramírez, Applied Surface Science **254**, 499 (2007).
[13] H. M. Mamedov, H. A. Hasanov, S. I. Amirova. Thin Solid Films **480-481**, 388 (2005).
[14] A. A. Albassan, Solar Energy Mater. Sol. Cells **57**, 323 (1999).
[15] M. C. Baykul, Orhan, Thin Solid Films **518**, 1925 (2010).
[16] H. Mamedov, H. Hasanov, Proc. SPIE **5834**, 264 (2005).
[17] H. Mamedov, S. Amirova, Proc. SPIE **6636**, 121 (2007).

[18] V. E. Primachenko, J. F. Kononets, B. M. Bulakh, E. F. Venger, E. B. Kaganovich, I. M. Kizyak, S. I. Kirillova, E. G. Manoilov, Y. A. Tsyrkunov, Semiconductors **39**, 565 (2005).

[19] O. Yu. Shevchenko, D. N. Goryachev, L. V. Belyakov. O. M. Sresli, Semiconductors **44**, 642 (2010).

[20] Y. K. Xu, S . Adachi, Journal of Applied Physics **101**(10), 2007.

[21] G. Laukaitis, S. Lindroos, S. Tamulevičius, M. Leskelä, M. Račkaitis, Appl. Surf. Sci. **161**, 396 (2000).

[22] T. Yamaguchi, Y. Yamamoto, T. Tanaka, Y. Demizu, A. Yoshida, Thin Solid Films **281-282**, 375 (1996).

[23] T. L. Chu, S. S. Chu, J. Britt, C. Ferekids, C. Q. Wu, J. Appl. Phys. **70**, 2688 (1991).

[24] S. Chandra, R. K. Pandy, R. C. Agrawal, J. Phys. D. Appl. Phys. **13**, 1757 (1980).

[25] K. L. Chopra, S. R. Das, Thin Film Solar Cells, Plenum Press, New York, 1983.

[26] F. I. Ezema, S. C. Ezugwu, R. U. Osuji, P. U. Asogwa, B. A. Ezekoye, A. B. C. Ekwealor, M. P. Ogbu, Non-Oxide Glasses **1**, 45 (2010).

[27] C. I. Yah, Z. Zulkarnain, K. Anuar, M. Wan, Int. J. Electrochem. Sci. **6**, 2898 (2011).