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Surface-Barrier CdTe Diodes for Photovoltaics

Tetiana Mazur*, Myroslav Mazur, Marian Halushchak

Ivano-Frankivsk National Technical University of Oil and Gas,
15, Karpatska Str., 76019 Ivano-Frankivsk, Ukraine

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In this paper, a comparative analysis of the use of semiconductor solar cells based on single-crystal, polycrystalline and amorphous silicon (Si), as well as cadmium telluride (CdTe) in the energy sector is carried out. It is shown that the advantages of thin-film technology and CdTe itself as a direct-gap semiconductor open the prospect of large-scale production of competitive CdTe solar modules (batteries). The technology of manufacturing substrates, applying indium ohmic contact to the plates, exposing some of the substrates to a number of additional treatments in an aqueous suspension of alkali metals, in particular Li – CdTe:Li and conducting research on them, as well as on chemically etched substrates that have not undergone any additional processing and conventionally designated CdTe. The possibilities of using devices based on single-crystal CdTe, which are called surface barrier diodes (SBDs), are being studied for converters. Technological advances that lead to changes in the physicochemical properties of single-crystal surfaces of *n*-CdTe substrates (their main optical, electrical, and photoelectric parameters, as well as the characteristics of metal-semiconductor contacts based on single-crystal cadmium telluride) are being discussed. Analyzing the properties of the research objects it should be noted that surface modification not only affects the potential barrier height but also significantly changes the course of electric and photoelectric processes, while the surface morphology of CdTe:Li substrates remains similar to unmodified ones, although the SBDs based on them are noticeably higher. It was also found that the rate of surface recombination of SBDs based on substrates with a surface nanostructure is two and one orders of magnitude lower than in structures based on basic substrates and alkali metal salts treated in suspension, respectively. The modification of substrates leads to an increase in the efficiency of solar cells (SCs), and the highest photoconversion efficiency is observed for SBDs based on substrates with a surface nanostructure and reaches 9 % at 300 K under AM2 illumination. The methods of using the technologies proposed in this work for the creation of surface-barrier photocells based on thin CdTe films are considered.

Keywords: Surface barrier diode, CdTe, Short circuit current, Open-circuit voltage, Quantum efficiency.

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1. INTRODUCTION

One of the urgent problems of our days and the near future is the problem of energy production, including from renewable sources, the development of which modern science pays much attention too. The most attractive, in particular, is the direct generation of electrical energy from the sun in semiconductor devices, the so-called photovoltaics. Photovoltaic energy conversion plays an important role in promoting energy solutions around the world. To date, there are three main generations of photovoltaic cells (PVs): silicon, thin-film and organic SCs [1, 2], among which the most commonly used are PVs based on silicon technologies. For the global solution of energy problems, the development of photovoltaics based on mono- and polycrystalline silicon is predicted to be too protracted due to significant material consumption, low productivity, labor intensity and energy intensity of production, and, as a result, high cost. During the operation of SCs based on amorphous silicon, their efficiency decreases, so only some of the advantages of thin-film technology can be realized in practice. The reasons for the slow growth in the power of traditional silicon solar modules lead to low productivity and high cost of modules with a coefficient of 14-17 % and 12-15 % acceptable in mass production [2]. High-performance SCs based on GaAs and GaInAs, GaInP, AlGaAs, GaAsP solid solutions are also being developed, but not for large-scale implementation in the energy sector, but for special applications, for example, in space, despite their high cost [1, 2].

An alternative to these converters are thin-films SCs designed to reduce the cost of solar modules and increase production using semiconductors deposited on substrates of cheap materials with a large area (glass, metal foil, plastic) [2, 3]. A direct-gap semiconductor is capable of absorbing solar radiation with a layer thickness two orders of magnitude less than the thickness of silicon elements. The use of materials with a higher optical absorption coefficient makes it possible to reduce the PV thickness [4], which reduces production costs. In addition, it is possible to reduce the weight of photovoltaic devices depending on the substrate used. As a result, the use of thin-film semiconductor materials such as copper-indium diselenide (CIS) and copper-indium-gallium diselenide (CIGS), CdTe and CdS and related manufacturing technologies, allows to obtain photovoltaic devices at a relatively low cost, good electrical characteristics, small weight, and high flexibility [3].

A promising direction on the way to solving energy problems is solar energy based on thin-film CdTe [4]. After all, among semiconductor binary compounds II-VI, cadmium telluride is one of the promising materials for the production of inexpensive thin-film photovoltaic

* tetiana.mazur@nung.edu.ua

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devices of the second generation. The material is of great interest among researchers due to its most important properties, such as long-term stability of performance characteristics [2], direct band gap (1.5 eV), close to optimal for converting photovoltaic solar energy [4], high optical absorption coefficient (> 10^5 sm^{-1}) in the visible region of the solar spectrum and high chemical stability [5]. The use of CdTe as a thin-film material for SC has attracted wide attention due to its high availability, low cost, and ease of large-scale production [4]. It is the simple methods of fabricating and forming a barrier structure that do not require complex and expensive equipment that are an important advantage of CdTe-based solar cell technology [3, 4]. In solar energy, the growth rate of CdTe module production over the past decade has been the highest. On the other hand, the quantum efficiency of CdTe-based cells, according to Progress in Photovoltaics, which publishes 6 monthly lists with the highest confirmed efficiency ratings for several photovoltaic cells and module technologies, indicates that the highest efficiency of a large-area CdTe-based module (2.4 m^2, fabricated First Solar) is 19.0 % [6, 7].

The article proposes a technology that modifies the surface properties of the base substrates, while maintaining the parameters of the bulk of the materials without significant changes. An analysis is made of experimental results that improve the basic electrical, optical, and photoelectric properties of n-CdTe substrates with a modified substrate and SBDs based on them. It is shown that annealing of n-CdTe crystals leads to a change in the microstructures of the surface of the samples, without affecting the main band parameters of the material.

2. EXPERIMENT

2.1 Manufacturing Technology of SBDs

Substrates 5×5 mm^2 in size and 1 mm thick served as the basis for the preparation of samples. The starting material was a CdTe crystal with a resistivity of about 20 Ω·cm. The initial crystals were produced by the Bridgman method (growth from a melt) and had electronic conductivity due to intrinsic defects. Doping was not applied. The substrates were subjected to mechanical and chemical treatment in the form of polishing, which was carried out in a solution of $K_2Cr_2O_7:H_2O:HNO_3 = 4:20:10$. After polishing, they washed in deionized water and dried. As a result of treatment, the plates had a reflective surface and, upon irradiation with a He-Ne laser, exhibited moderate edge luminescence.

Next, an ohmic contact was applied. Indium was used as the ohmic contact. The samples were divided into two groups. The first group of samples was processed in a suspension of alkali metals [11] Li-CdTe:Li. The second group of samples was not subjected to treatment and is further designated as CdTe. They were reference samples for comparing parameters. Rectifying contacts for all samples were created by vacuum deposition of semitransparent Au or Ni films. The use of precisely such films is since it creates a rather large barrier from n-CdTe, and its thin layers are characterized by high electrical conductivity and transparency in a wide spectral range (1-6 eV) [5]. An image of the diode structure and its illumination conditions are shown in Fig. 1.

The chemically treated surface of the initial samples is considered to the naked eye as a mirror, while the annealed surface is matte. The surface microstructure was studied using a Nanoscope IIIa atomic force microscope (Digital Instruments) in the periodic contact mode (taping mode) using a silicon probe with a tip radius of 10 nm.

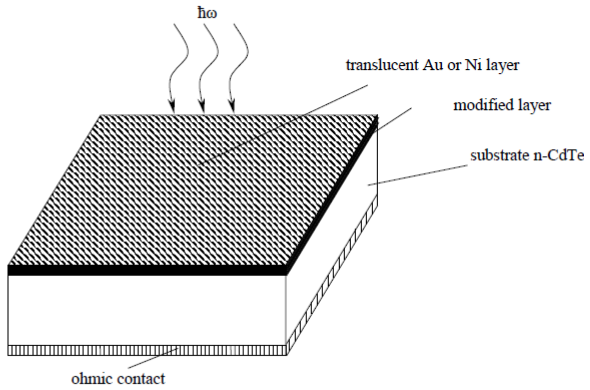

Fig. 1 – Schematic representation of the structure of a solar cell

2.2 Main Parameters of SBDs

According to the research results, surface-barrier diodes based on CdTe:Li substrates have a significantly higher potential barrier φ_0 compared to reference samples. This conclusion is confirmed by the values shown in Fig. 2, which shows the current-voltage characteristics in the areas of their linearity with direct connection of diodes. It follows that the resistance of the modified layers has an insignificant effect on R_0 and, in addition, the values of the series resistances R_0 are close [12].

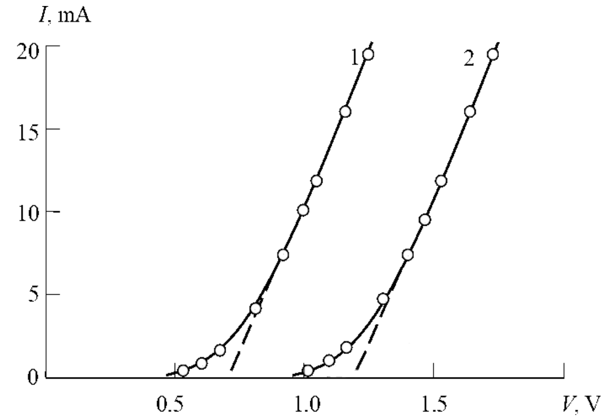

Fig. 2 – Direct branches of current-voltage characteristics of SBDs based on CdTe (1), CdTe: Li (2) substrates at 300 K

It should be noted that the values of φ_0 determined from the direct branches of the current-voltage characteristics are consistent with the results obtained from capacitance measurements. Analyzing the electrical properties, it was investigated that the state of the surface, in addition to the effect of φ_0, leads to a change in the nature of physical processes in SBDs, which is observed in the dependences of the forward current on the voltage. As follows from the further analysis of the samples, the modification of their surface layers affects the value of φ_0, and also significantly changes the value of the occurrence of electronic and photoelectric processes.

During annealing under special conditions, a nanostructure is formed on the surfaces of the samples [13], which can be seen in the topogram obtained using an atomic force microscope Nanoscope – III. As can be seen from the topogram, the surface is characterized by a granular structure with lateral grain sizes of 10-50 nm, which combine into large (100-500 nm) subgrains (Fig. 3). The surface morphology of CdTe:Li substrates is similar to unmodified ones, although the SBD potential barrier is much higher (Fig. 2).

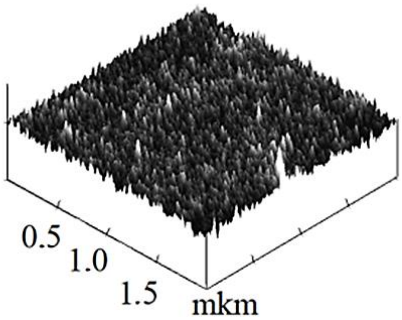

Fig. 3 – Fragments of AFM topograms of substrate surfaces CdTe and CdTe:Li

3. RESULTS AND DISCUSSION

Qualitatively similar dependences of integral light characteristics were observed in all diodes. These characteristics were measured using a xenon lamp and a calibrated ND filter set. The averaged data given in Table 1 (measured for several samples of each group at a temperature of 300 K under AM2 sunlight conditions) show that the dependence of the short-circuit current I_{SC} on illumination L is a linear function when it changes within more than 4 orders of magnitude, and the open-circuit voltage V_{OC} is proportional to lg$L$ at low light levels and saturates at high light levels, Fig. 4. The absolute values of V_{OC} and I_{SC} are determined by the illumination level and the type of diode.

The value of the short-circuit current density was calculated considering the effective photosensitive area according to the formula $J_{SC} = I_{SC}/S$ and for these prototypes had a value of ~$2 \cdot 10^{-1}$ cm ^{2} [14].

According to the data presented in the Table 1 that the modification of substrates leads to an increase in the efficiency of solar cells η, and the maximum efficiency is observed for SBDs with a quantum size surface. It should also be noted that photoconversion is also caused by a change in other parameters of solar cells related to the efficiency by known equations [15]

$$\eta = \frac{J_{SC} \cdot V_{OC}}{P} \cdot ff , \quad (1)$$

where, P is the power of solar radiation, the value of which under the conditions of solar illumination AM2

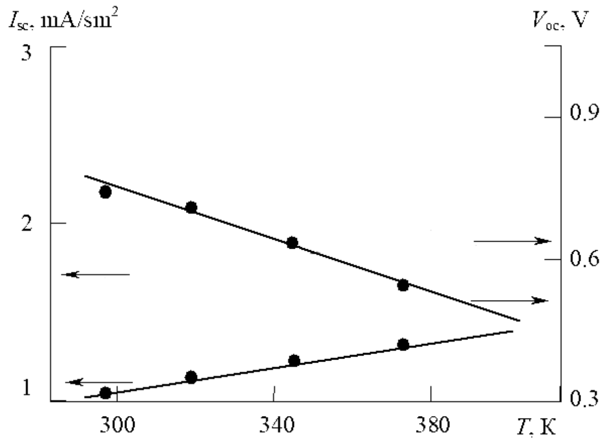

Fig. 4 – Temperature dependences of J_{SC} and V_{OC} for SBDs based on CdTe: Li substrates

at 300 K is 70 mW/cm^2, ff is the duty cycle of the load characteristic of the solar cell. To obtain the maximum photoconversion efficiency, it is necessary to increase all three quantities contained in the numerator of equation (1) [15]. Therefore, there is a need to conduct pilot experiments that will be able to check both the operating conditions of the SBD (illumination level, temperature) and the effect of the diode manufacturing technology on these parameters.

Table 1 – Main characteristics of solar cells at 300 K

Lining / Parameter	CdTe	CdTe:Li
φ_0, eV	0.7	1.25
R_0, Om	30	30
V_{OC}, V	0.4	0.75
I_{SC}, mA/cm^2	10	15
ff	0.76	0.78
η, %	5	9

On Fig. 4 shows the temperature dependences of V_{OC} and I_{SC} for CdTe and CdTe:Li SBBs under AM2 illumination with modified surfaces. As you can see, with an increase in temperature T, an increase in the short-circuit current occurs I_{SC}, which is associated with an increase in the number of absorbed low-energy photons. A consequence of the decrease in the band gap is a decrease in the series resistance of the diode. In addition, with an increase in the temperature T, the value of the open-circuit voltage V_{OC} decreases because of the greater temperature dependence of the dark current compared to the photocurrent [14]. It should also be taken into account that with an increase in temperature T, a drop in the height of the potential barrier is observed, which is inherent in SBBs [14, 16].

The spectral characteristics are more diverse than the integral ones. This is due to the fact that for the studied samples, they significantly depend on the parameters of the separation boundaries, that is, the state of the substrate surface. And the given state of the substrate surface is determined by the type of structure (Fig. 5).

On the modified surface, the absorption of light increases due to the reflection and scattering of light on subgrains, the size of which is from 100 to 500 nm

(Fig. 3). Absorption entails a significant decrease in the absolute value of transmission and, accordingly, an increase in the absorption coefficient α_ω, since we can assume that $\alpha_\omega \approx 1 - T_\omega$. Scattering will be most effective on subgrains with a size of $d \le 0.1$-0.2λ, where the scattered light intensity I_d is subject to the Rayleigh law $I_d \sim \lambda^{-4}$. The wavelength λ_0 corresponding to the extreme limit of fundamental absorption can be calculated from the expression $\lambda_0 = 1.24/E_g \approx 1.24/1.5 \approx 0.825$ μm. The sizes of inhomogeneities obtained for this wavelength λ_0 range from 80 to 160 nm and fall within the range of subgrain sizes on the modified substrate surface, Fig. 3. A decrease λ and, accordingly, an increase in ω leads to an increase in α_ω, a decrease in T_ω, and a shift of the absorption edge to the region of much lower energies compared to the band gap E_g of CdTe [14, 16].

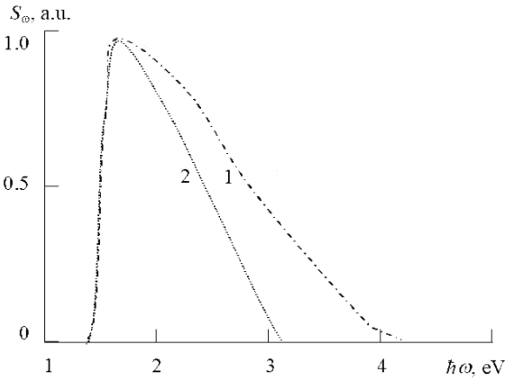

Fig. 5 – Photosensitivity spectra of SBDs based on CdTe (1), CdTe: Li (2) substrates at 300 K

It should be noted that such an effect is caused, in fact, by the surface morphology, and not by the formation of any other chemical compound due to annealing. This is experimentally confirmed by the fact that the differential reflection spectra of the substrates are identical and correspond to the peak value of the CdTe band gap.

Considering the photon energy range $\hbar > E_g$, the photosensitive spectrum of an ideal photodiode can be represented by the equation [15]

$$S_\omega = \eta / \hbar\omega \tag{2}$$

where η is the quantum efficiency.

Expression (2) does not explain the curves shown in Fig. 5. It should be noted that the obtained curves have a different high-energy threshold, which does not depend on the thickness of the rectifying semitransparent contact. Although for all diodes the application of the rectifying contact was carried out under the same technological conditions for the same time. It is the different nature of the surface effects that caused certain disagreements between the obtained spectra. A sharp increase in the value of the absorption coefficient (up to 10^5 cm^{-1}), associated with the direct band gap of CdTe in the region $\hbar\omega > E_g$, leads to a rapid increase in the effective penetration depth of radiation (up to $\alpha_\omega^{-1} \le 0.1$ μm). Surface recombination processes predominate on the diode surface, and a significant absorption of radiation is observed. The rate of surface recombination can be calculated. To do this, the experimental photosensitivity spectra are compared with the expression S_ω obtained theoretically [17]. Based on the continuity equation, taking into account recombination at the separation boundaries and taking into account υ_s, it is possible to analytically describe the spectral distribution of the quantum efficiency of photoelectric conversion.

This behavior υ_s corresponds to some experimental facts, according to which there is a difference in the values of the photoluminescence intensity I_{ph} for different types of substrates, since one should take into account the value I_{ph}, which in the first approximation is inversely proportional to the recombination rate surface. The experiments carried out in this work show that for the studied CdTe, CdTe:Li substrates, the photoluminescence intensity decreases by about three orders of magnitude [14, 18].

Since the CdTe-based SBDs samples under study were produced on substrates with the maximum intensity of edge luminescence, they have a significant photoconversion efficiency. For such structures, J_{SC} depends linearly on the illumination level L, and the open-circuit voltage tends to saturation. Note that the calculated values of J_{SC} and V_{OC} are in good agreement with their experimental values. And the efficiency much less theoretical, which is mainly due to the low fill factor (0.5-0.6) of the loading characteristic. In this regard, further research should be aimed at finding optimal modes of doping and annealing of CdTe crystals. The value of the quantum efficiency of converting solar energy into electrical energy under AM2 illumination conditions for the best samples can reach 9 % at 300 K in the absence of antireflection coatings, generalization of the main parameters of the base substrates and SC design. The short circuit current of such diodes varies from the open circuit voltage according to the law $I_{SC} = I_{OSC} \cdot \exp(eV_{OC}/2kT)$, which indicates the predominant generation of photocarriers in the space charge region. The dependence of Isc on illumination L is linear in a wide range of its configuration. The open-circuit voltage varies according to the $V_{OC} \sim \ln(L)$ law at low illumination values, tending to saturation at large L. The photosensitivity spectrum is limited to the energy range of 1.4-6.0 eV. The wide sensitivity spectrum combined with the high radiation resistance of CdTe make it possible to use such structures in harsh environments, in particular, in outer space. All this points to additional potential opportunities for increasing the efficiency of photoconversion of SBDs based on cadmium telluride.

4. CONCLUSIONS

The paper proposes the use of a special technological method, according to which the surfaces of single-crystal plates of cadmium telluride are subject to special treatment before the deposition of the barrier contact. This significantly improves the electrical and photoelectric properties of SBDs based on them. Annealing of n-CdTe substrates ($\rho \sim 20$ Ω·cm) in an air or aqueous suspension of alkali metals increases the height of the potential barrier. Surface modified SBDs have much better open circuit voltage and short circuit current. The efficiency of solar cells based on diodes studied under AM2 illumination was 9 % at 300 K. The developed technology SBDs is simple, cheap, and environmentally friendly. In this work, the results of single-crystal CdTe substrates are obtained, however, the technology under consideration can be applied to the manufacture of photovoltaic devices based on thin CdTe films. An example is the work [19], which describes the creation of a quantum-well surface in thin CdTe films synthesized by the hot wall method, and work [20], where a relatively simple technology for obtaining thin *p*-CdTe layers with high conductivity and a significant photoconversion efficiency is developed.

REFERENCES

1. Nowshad Amin, et al., *Encyclopedia of Sustainable Technologies* **11**, 26 (2017).
2. L.A. Kosyachenko, E.V. Grushko, *Ukr. Phys. Mag. Rev.* **7** No 1, 3 (2012).
3. R. Yavorskyi, L. Nykyruy, G. Wisz, P. Potera, S. Adamiak, S. Górny, *Appl. Nanosci.* **9** No 5, 715 (2019).
4. T.M. Mazur,V.V. Prokopiv, M.P. Mazur, U.M. Pysklynets, *Phys. Chem. Solid State* **22** No 4, 817 (2021).
5. Rupali Kulkarnia, *Energy Procedia* **110**, 188 (2017).
6. M.A. Green, E.D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, A.W. Ho-Baillie, *Prog. Photovolt.: Res. Appl.* **28** No 1, 3 (2021).
7. M.A. Green, E.D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, H. Xiaojing, *Prog. Photovolt.: Res. Appl.* **30** No 1, 3 (2021).
8. I.N. Duenow, I.M. Burst, D.S. Albin, D. Kuciauscas, S.W. Johuston, R.C. Reedy, W.K. Metzger, *Appl. Phys. Lett.* **105**, 053903 (2014).
9. M.A. Green, K. Emery, Y. Hishikava, W. Warta, E.D. Dunlop, *Prog. Photovolt: Res. Appl.* **24**, 905 (2016).
10. M.O. Reese, C.L. Perkins, I.M. Burst, S. Farrell, T.M. Bames, S.W. Jonston, *J. Appl. Phys.* **118**, 55305 (2015).
11. V.P. Makhniy, M.V. Skrypnyk, Patent of Ukraine for the cinnamon model UA №31891 etc. from 25.04.2008.
12. V.V. Prokopiv, B.S. Dzundza, S.V. Sharyn, T.M. Mazur, L.V. Turovska, O.M. Matkivskyi, *Phys. Chem. Solid State* **21** No 2, 232 (2020).
13. V.P. Makhniy, *Surface X-ray, Synchronous and Neutron Studies* **5**, 93 (2006).
14. V.P. Makhniy, M.M. Berezovskiy, O.V. Kinzerska, M.P. Mazur, T.M. Mazur, V.V. Prokopiv, *Sensor Electron. Microsyst. Technol.* **16** No 2, 32 (2019).
15. S. Zi, *Physics of semiconductor devices* (Mir: M: 1984).
16. B.E. McCandless, J.R. Sites, *Cadmium telluride solar cells* (Handbook of photovoltaic science and engineering, 600-641, 2011).
17. B.E. McCandless, *MRS Online Proceedings Library* **1538** No 1, 249 (2011).
18. V.P. Makhniy, M.M. Slyotov, N.V. Skrypnyk, *Ukr. J. Phys. Opt.* **10** No 1, 54 (2009).
19. T.M. Mazur, V.P. Makhniy, V.V. Prokopiv, M.M. Slyotov, *J. Nano- Electron. Phys.* **9** No 5, 05047 (2017).
20. V.P. Makhniy, T.M. Mazur, M.M. Berezovsky, O.V. Kinzerska, V.V. Prokopiv, *Phys. Chem. Solid State* **19** No 4, 313 (2018).

Поверхнево-бар’єрні CdTe діоди для фотовольтаїки

Тетяна Мазур, Мирослав Мазур, Мар’ян Галущак

Івано-Франківський національний технічний університет нафти і газу, вул. Карпатська, 15, 76019 Івано-Франківськ, Україна

В даній роботі проведено порівняльний аналіз застосування в енергетиці напівпровідникових сонячних елементів на основі монокристалічного, полікристалічного й аморфного кремнію (Si), а також телуриду кадмію (CdTe). Показано, що переваги тонкоплівкові технології й самого CdTe, як прямозонного напівпровідника, відкривають перспективу широкомасштабного виробництва конкурентоспроможних CdTe сонячних модулів (батарей). Описується технологія виготовлення підкладок, нанесення на пластинки індієвого омічного контакту, піддавання частини підкладок ряду додаткових обробок у водяній суспензії лужних металів, зокрема Li – CdTe:Li та проведення досліджень на них, а також на хімічно травлених підкладках, які не пройшли ніяких додаткових обробок і умовно позначені CdTe. Вивчаються можливості застосування для фотоперетворювачів приладів на основі монокристалічного CdTe, які називаються поверхнево-бар’єрними діодами (ПБД). Обговорюються технологічні досягнення, які призводять до змін фізико-хімічних властивостей поверхонь монокристалічних *n*-CdTe підкладок (їх основних оптичних, електричних та фотоелектричних параметрів, а також характеристик контактів метал-напівпровідник на базі монокристалічного телуриду кадмію). Аналізуючи властивості об'єктів досліджень слід відмітити, що модифікація поверхні впливає не тільки на величину висоти потенціального бар'єру, але також істотно змінює характер протікання електричних та фотоелектричних процесів, а морфологія поверхні підкладок CdTe:Li залишається подібною немодифікованим, хоча величина ПБД на їх основі помітно вище. Також встановлено, що швидкість поверхневої рекомбінації ПБД на базі підкладинок з поверхневою наноструктурою на два і один порядок менше, ніж в структурах на основі базових підкладинок і оброблених в суспензії солей лужних металів відповідно. Модифікація підкладок призводить до збільшення ефективності сонячних елементів (СЕ), причому найбільша ефективність фотоперетворення СЕ спостерігається для ПБД на базі підкладок з поверхневою наноструктурою і становить 9 % при температурі 300 К за умови освітлення АМ2. Розглядаються способи використання технологій, запропонованих у роботі, для створення поверхнево-бар’єрних фотоелементів на основі тонких плівок CdTe.

Ключові слова: Поверхнево-бар’єрний діод, CdTe, Струм короткого замикання, Напруга холостого ходу, Квантова ефективність.