ОПТИЧНІ, ОПТОЕЛЕКТРОННІ І РАДІАЦІЙНІ СЕНСОРИ

OPTICAL AND OPTOELECTRONIC AND RADIATION SENSORS

UDC 621.315.592
DOI http://dx.doi.org/10.18524/1815-7459.2019.2.171227

PROSPECTS OF USING SURFACE AND BARRIER CdTe-DIODES IN SOLAR ENERGY

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Abstract. The paper discusses the advantages and disadvantages of the most used today semiconductor materials of different structural perfection (single crystals, polycrystalline and amorphous) to create solar cells. The main attention is paid to the study of the possibilities of using surface-barrier diodes (SBD) as photoconverters based on single-crystal cadmium telluride. A number of technological methods for modifying n-CdTe substrates are analyzed, which lead to a significant improvement in the electrical and photoelectric parameters and characteristics of SBD. It is shown that the photoconversion efficiency of SBD based on substrates with surface nanostructure ($CdTe:O_2$) reaches 13% at 300 K in AM2 lighting conditions. The use of technologies used in the creation of surface-barrier solar cells based on cadmium film telluride is discussed.

Keywords: cadmium telluride, surface barrier diode, solar cell, photoconversion efficiency

ПЕРСПЕКТИВИ ВИКОРИСТАННЯ ПОВЕРХНЕВО-БАР'ЄРНИХ CdTe-ДІОДІВ В СОНЯЧНІЙ ЕНЕРГЕТИЦІ

В. П. Махній, М. М. Березовський, О. В. Кінзерська, М. П. Мазур, Т. М. Мазур, В. В. Прокопів

Анотація. В роботі обговорюються переваги і недоліки найбільш використовуваних на сьогоднішній день напівпровідникових матеріалів різної структурної досконалості (монокристали, полікристалічні і аморфні) для створення сонячних елементів. Особлива увага приділяється вивченню можливостей використання в якості фотоперетворювачів поверхнево-бар'єрних діодів (ПБД) на базі монокристалічного телуриду кадмію. Аналізується ряд технологічних способів модифікації підкладинок n-CdTe, які призводять до суттєвого покращення електричних та фотоелектричних параметрів і характеристик ПБД. Показано, що ефективність фотоперетворення ПБД на базі підкладинок з поверхневою наноструктурою ($CdTe:O_2$) досягає 13% при 300 K при умовах освітлення АМ2. Обговорюються варіанти застосування використаних в роботі технологій для створення поверхнево-бар'єрних сонячних елементів на основі плівкового телуриду кадмію.

Ключові слова: телурид кадмію, поверхнево-бар'єрний діод, сонячний елемент, ефективність фотоперетворення

ПЕРСПЕКТИВЫ ИСПОЛЬЗОВАНИЯ ПОВЕРХНОСТНО-БАРЬЕРНЫХ CdTe-ДИОДОВ В СОЛНЕЧНОЙ ЭНЕРГЕТИКЕ

В. П. Махний, М. М. Березовский, О. В. Кинзерская, М. П. Мазур, Т. М. Мазур, В. В. Прокопив

Аннотация. В работе обсуждаются преимущества и недостатки наиболее используемых на сегодняшний день полупроводниковых материалов разного структурного совершенства (монокристаллы, поликристаллические и аморфные) для создания солнечных элементов. Основное внимание уделено изучению возможностей применения в качестве фотопреобразователей поверхностно-барьерных диодов (ПБД) на базе монокристаллического теллурида кадмия. Анализируется ряд технологических способов модификации подложек n-CdTe, которые приводят к существенному улучшению электрических и фотоэлектрических параметров и характеристик ПБД. Показано, что эффективность фотопреобразования ПБД на базе подложек с поверхностной наноструктурой ($CdTe:O_2$) достигает 13% при 300 K в условиях освещения АМ2. Обсуждаются варианты применения используемых в работе технологий для создания поверхностно-барьерных солнечных элементов на основе пленочного теллурида кадмия.

Ключевые слова: теллурид кадмия, поверхностно-барьерный диод, солнечный элемент, эффективность фотопреобразования

INTRODUCTION

The urgency of the energy problem necessitates the development and production of renewable sources, among which a special place is occupied by semiconductor solar cells (SC), which provide direct conversion of solar energy into electrical energy. Despite the many semiconductors that are suitable for creating an SC [1], their real number is limited to several materials that have received the most attention in recent years [2]. Among them, Si_{cr} monocrystalline silicon should be distinguished, which so far continues to occupy a leading position, although the production of the substrates themselves and the structures based on it is a complex and expensive process. On the other hand, the production technology of solar cells on Si_{cr} is in almost perfect condition, and therefore it is quite difficult to find new ways to improve existing technologies that have been worked out for many years as part of the mass production of microelectronic devices. In addition, a theory of photoelectric processes in structures based on single-crystal semiconductors has been developed quite well, and on its basis, appropriate computer programs have been created for optimizing the parameters of silicon SC.

Therefore, in recent times, more and more attention has been paid to other materials, which, in particular, include amorphous silicon (α-Si:H), copper-indium diselenides (CIS) and copper-indium-gallium (CIGS), as well as cadmium telluride (CdTe). Another advantage of these semiconductors compared with Si_{cr} is their more efficient absorption of optical radiation, which allows the manufacture of cheaper thin-film SC. We also pay attention to the sharp increase in thin-film technologies after 2005, the share of which, according to the Institute of Solar Systems. Fraunhofer increased to 8%, of which 5% is accounted for by CdTe films [3]. Meanwhile, the average efficiency achieved by that time η of the heterostructures (HS) of n-CdS/p-CdTe at 300 K in AM1.5 lighting conditions is ~ 16%, which is almost two times less than the theoretical value [2].

It is believed that one of the reasons for this is the short lifetime τ_s of minority carriers causing a high recombination υ_s rate at the interfaces between the HS components and the grains of the polycrystalline CdTe film. In this regard, the decrease υ_s (increase τ_s) should lead to an improvement in the main parameters of the SC – short circuit current $J_{s\,c}$ and open circuit voltage $V_{o\,c}$. Experimentally this is confirmed by the authors [4], who observed an increase $V_{o\,c}$ from 0.84 to 0.93 V when replacing a polycrystalline CdTe film with a single-crystal substrate in a heterostructural n-CdS/p-CdTe SC. Low values $J_{s\,c}$, and ultimately efficiency these samples are due to the high resistance of sufficiently thick basic p-CdTe substrates, the concentration of free holes in which at 300 K does not exceed $7\cdot10^{15}$ cm^{-3}. The improvement in the structural perfection of the photoactive p-CdTe layer in the thin-film n-CdS/p-CdTe EE allowed us to increase η to ~21%, although $V_{o\,c}$ it grew by only 0.03 V [5]. The increase in efficiency in this case is associated with an increase $J_{s\,c}$ due to a sharp decrease in the series resistance of the HS, determined by a thin layer of p-CdTe. A small increase $V_{o\,c}$, taking into account the above, allows us to conclude that the lifetime of minority carriers is determined mainly by recombination processes at the interface of the HS components. Meanwhile, using various methods for passivation the surfaces of single crystals and coarse-grained semi-crystalline films, one can reduce the value υ_s by 1-2 orders of magnitude [6].

This paper discusses a number of technological methods for changing (modifying) the physicochemical properties of the surface of single-crystal n-CdTe substrates, leading to an improvement in the basic electrical and photoelectric parameters of metal-semiconductor contacts, hereinafter referred to as surface barrier diodes (SBD).

TECHNOLOGY OF MANUFACTURING AND BASIC PARAMETERS SBD

The initial substrates were plates of the size $5\times5\times1$ mm^3, which were cut from a bulk crystal of cadmium telluride with a specific resistance of ~20 Ohm·cm at 300 K. The crystals were grown by the Bridgman method from a melt, did not contain any doping impurities, and had properdefect electronic conductivity. The plates were staged mechanically and chemically polished in a solution of $K_2Cr_2O_7$:H_2O:HNO_3=4:20:10, thoroughly washed in distilled water and dried. The substrates prepared in this way had mirror surfaces, and when excited by a He-Ne laser, they had a weak edge luminescence.

An indium ohmic contact was deposited on one of the large sides of the plate, after which part of the substrates were subjected to a series of additional treatments. The first group includes samples that underwent the operation of thermal annealing in air and are further designated by the symbol CdTe:O_2 [7]. Another group consists of samples that were processed in an aqueous suspension of alkali metals [8], in particular, Li-CdTe:Li. And finally, the third group includes chemically etched substrates that have not undergone any additional treatments and are conditionally labeled CdTe. The SBD created on them served as reference, with which the parameters and characteristics of other types of diode structures are compared. The rectifying contact to all groups of samples was vacuum-deposited translucent layers of gold or nickel, and a schematic representation of the structure of the SBD and its lighting conditions are shown in Fig. 1.

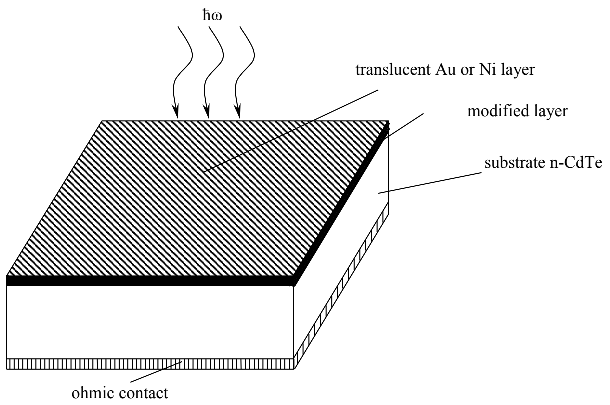

Fig. 1. Schematic representation of the SC structure.

Studies have shown that SBD based on CdTe:Li and CdTe:O_2 substrates have a much higher potential barrier φ_0 height than reference ones. This is illustrated by the data in Fig. 2, which depicts the straight branches of the current-voltage characteristics (CVC) of the objects of research in the field of their linearity. We draw attention to the insignificant difference in the slopes of the rectilinear sections of the current – voltage characteristics of all the diode groups under study. On the one hand, this indicates the proximity of the values of the series resistance R_0 of the diodes, and on the other hand, the negligible contribution of the resistance of the modified layers to the magnitude R_0.

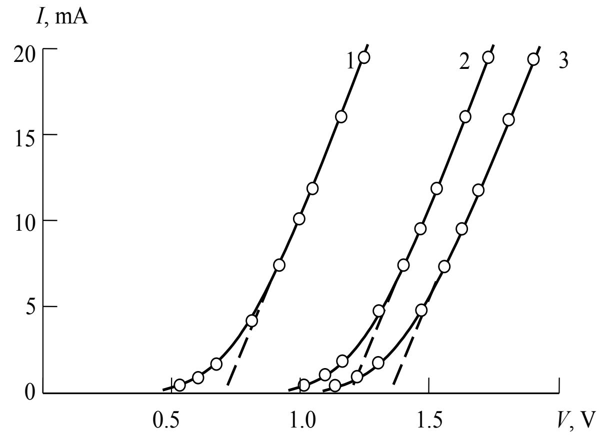

Fig. 2. Straight branches of the current – voltage characteristics of SBD based on CdTe (1), CdTe:Li (2) and CdTe:O_2 (3) substrates at 300 K.

Further analysis of the properties of the objects of research showed that surface modification affects not only the magnitude φ_0, but also significantly changes the nature of the flow of electronic processes, including photoelectric ones. Separate interest in this aspect is caused by CdTe:O_2 substrates, in which surface nanostructure is formed under certain conditions of annealing [7]. This is illustrated by topograms (Fig. 3), obtained using a Nanoscope-III atomic force microscope in the periodic contact mode. It is seen that the surface of CdTe:O_2 samples is characterized by a granular structure with lateral grain sizes of 10–50 nm, which can unite in more (100–500 nm) subgrain, fig. 3a. Note that each of these groups of grains plays its role in the formation of the physical properties of the surface of CdTe:O_2 substrates and SBD based on them, which is discussed in a number of papers [7,9,10]. We also note that the surface morphology of CdTe:Li substrates remains similar to unmodified (Fig. 3a), although the φ_0 SBD are much higher on their basis, Fig. 2. A number of photovoltaic parameters and characteristics of the studied SBD groups are also significantly different, which requires separate consideration.

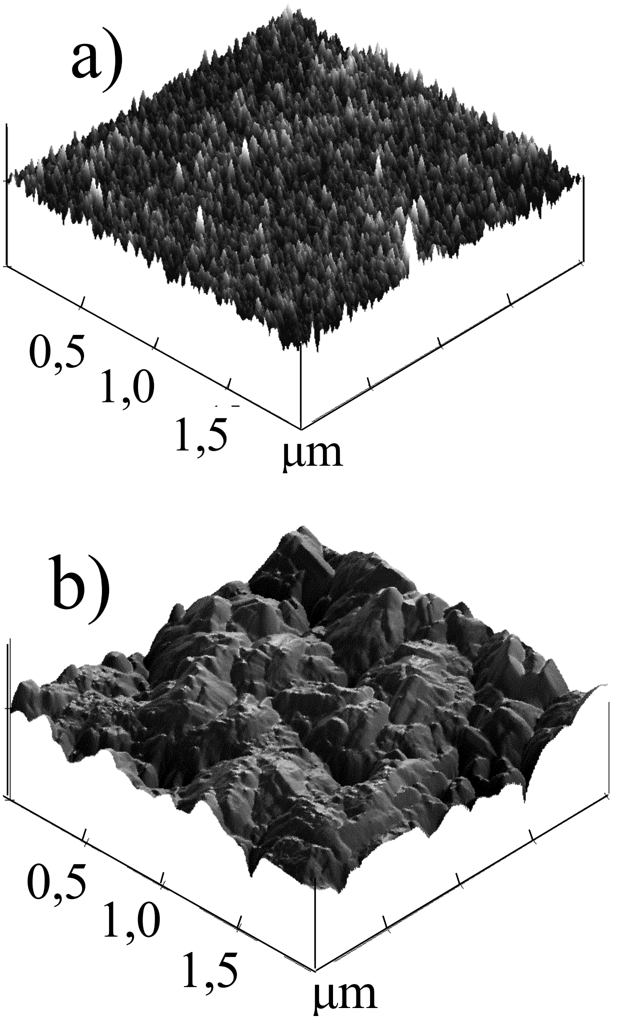

Fig. 3. Fragments of ASM topograms of surfaces of CdTe and CdTe:Li - a, $CdTe:O_2$ - b substrates.

PHOTOELECTRIC PROPERTIES OF SBD

The study of integrated light characteristics showed that qualitatively similar dependences are observed for all diodes. They were measured using a xenon lamp-based solar simulator and a calibrated set of neutral light filters. In this case, the short circuit current I_{sc} is a linear function of the level of illumination L when it changes within more than four orders of magnitude. Open circuit voltage V_{oc} is proportional $\lg L$ at low and tends to saturate at high levels of illumination, fig. 4. Absolute values I_{sc} are V_{oc} determined by the type of SBD and magnitude L, and their averaged values, measured for five samples of each group, at 300 K under solar lighting conditions AM2 are given in Table. 1. The short-circuit current density was $J_{sc} = I_{sc} / S$ calculated taking into account the effective photosensitive area, which for the studied samples was ~$2 \cdot 10^{-1}$ cm^{-2}.

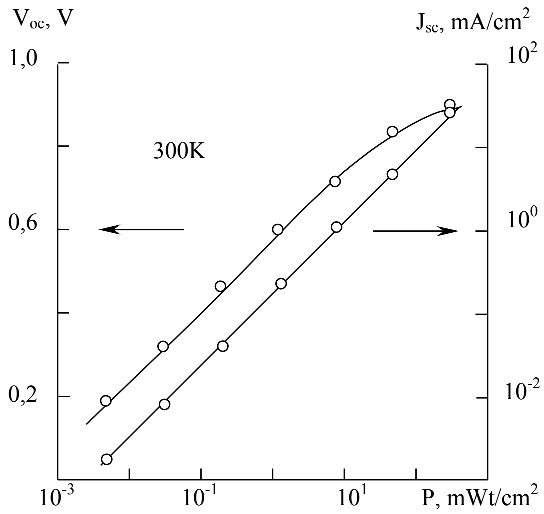

Fig. 4. Dependencies J_{sc} and V_{oc} for SBD based on the $CdTe:O_2$ substrate on the flux density of solar radiation.

Data analysis table. 1 shows that the modification of the substrates leads to an increase in the efficiency of the SC, and the greatest η is observed for SBD with a quantum-size surface. Note that the change in the efficiency of photoconversion is due to the change in other parameters of the SC associated with it by the well-known expression [1]

$$\eta = \frac{J_{sc} \cdot V_{oc}}{P} \cdot FF . \quad (1)$$

Here FF is the filling factor of the load characteristics of the SC, and P is the power of solar radiation, which with AM2 is 69 mW/ cm^2. Obviously, to maximize the efficiency of photoconversion, one should maximize all three factors in the numerator of the right-hand side of expression (1). Solving this problem requires experimental studies to establish the effect on the above-mentioned parameters not only of the manufacturing techniques of SBD, but also of their operating conditions – temperature, light level, etc.

Table. 1.

The main parameters of the solar cell at 300 K.

Substrate / Parameter	CdTe	CdTe:Li	$CdTe:O_2$
φ_0, eV	0,7	1,25	1,35
R_0, Ohm	30	30	32
V_{oc}, V	0,4	0,75	0,9
I_{sc}, mA/cm^2	10	15	25
FF	0,76	0,78	0,51
η, %	5	9	13

The temperature dependences I_{sc} and V_{oc} of two types of SBD with modified surfaces in AM2 lighting conditions are presented in Fig. 5. It is seen that the increase T leads to an increase in short circuit current, which is caused by a decrease in the diode series resistance, as well as an increase in the number of absorbed low-energy photons, due to a decrease in the width of the band gap. The decrease in the open circuit voltage with an increase in temperature is mainly due to the stronger temperature dependence of the dark current compared to the photocurrent [1]. An additional factor is also a drop in the height of the potential barrier with increase T, characteristic of SBD.

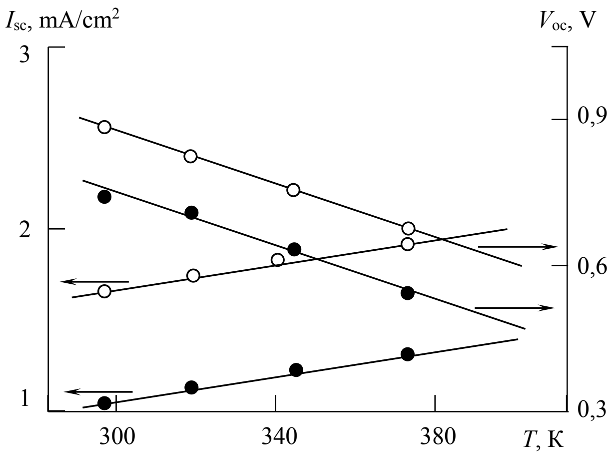

Fig. 5. Temperature dependences for SBD based on CdTe: Li (●) and $CdTe:O_2$ (○) substrates.

In contrast to the integral, the spectral characteristics are more diverse, since for the studied SBD they significantly depend on the parameters of the interface (i.e., the actual state of the substrate surface), which in turn are determined by the type of structure, Fig. 6.

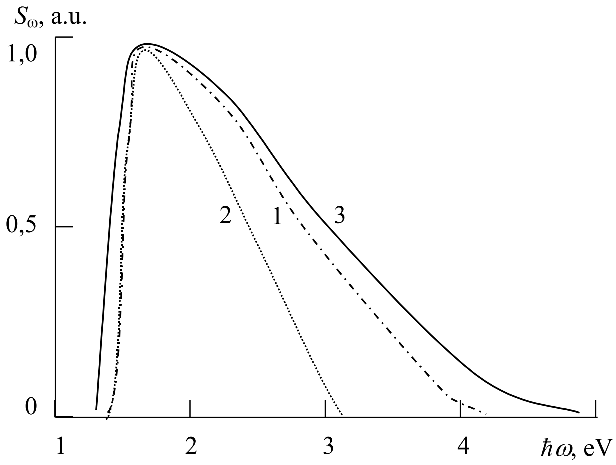

Fig. 6. Photosensitivity spectra of SBD based on CdTe (1), CdTe:Li (2) and $CdTe:O_2$ (3) substrates at 300 K.

Let us discuss the reasons for these differences using the example of metal $CdTe:O_2$ PBBs, which possess the widest range of photosensitivity S_ω, curve 3 in Fig. 6. First of all, we note that the low-energy edge S_ω of these samples is significantly shifted towards lower energies compared to the reference one. In this case, the cutoff on the abscissa axis is also significantly less than the band gap of cadmium telluride ($E_g \approx 1.5$ eV [1]) and is ~1.3 eV. The observed effect in photosensitivity spectra completely correlates with the features of the optical transmission T_ω spectra of CdTe:O_2 substrates [10] .They are explained by the presence on the modified surface of subgrains with sizes of 100–500 nm (Fig. 3a), which can cause processes of multiple reflection and scattering of light, leading to an increase in the absorption length. This leads to a significant decrease in the absolute value of the transmittance and an adequate increase in the absorption coefficient α_ω, since in the first approximation we can assume that $\alpha_\omega \approx 1 - T_\omega$. We draw attention to the fact that the most efficient scattering will occur on subgrains with a size of $d \le 0{,}1\text{-}0{,}2\lambda$, the intensity of the scattered light I_d in the first approximation obeys the Rayleigh law $I_d \sim \lambda^{-4}$. The wavelength λ_0 corresponding to the edge of fundamental absorption is easily determined by the well-known formula $\lambda_0 = 1{,}24 / E_g \approx 1{,}24/1{,}5 \approx 0{,}825$ μm. The sizes of inhomogeneities for this λ_0 lie in the range of 80–160 nm and fall into the range of lateral sizes of subgrains on the modified surface of CdTe:O2 substrates, Fig. 3a. A decrease λ (increase ω) leads to a decrease T_ω, an adequate growth α_ω and a corresponding shift of the absorption edge to a region of lower energies as compared to E_g CdTe. Since the photocurrent is proportional α_ω, an increase in the latter causes the appearance of photosensitivity in the region $\hbar\omega < E_g$, Fig. 6. Note that a similar behavior of the transmission spectra of samples with SNS is also observed on other semiconductor substrates [16–18] and is most likely a law than an exception to the rule.

We also pay attention that this effect is due precisely to the surface morphology, and not to the appearance of another chemical compound as a result of annealing. This is confirmed by several experimental facts. The first of these is that the differential reflection spectra of CdTe and CdTe:O_2 substrates are the same and contain a peak corresponding to the band gap of CdTe. Secondly, the temperature dependence of the low-energy edge of the curve S_ω (cut-off $\hbar\omega_0$ in Fig. 7) practically tracks the course $E_g(T)$, since the coefficient $\gamma_{\hbar\omega_0} = d(\hbar\omega_0)/dT \approx 4.3\cdot10^{-3}$ eV/K within the accuracy of the experiment is consistent with $\gamma_{E_g} = dE_g/dT \approx 4.1\cdot10^{-4}$ eV/K cadmium telluride.

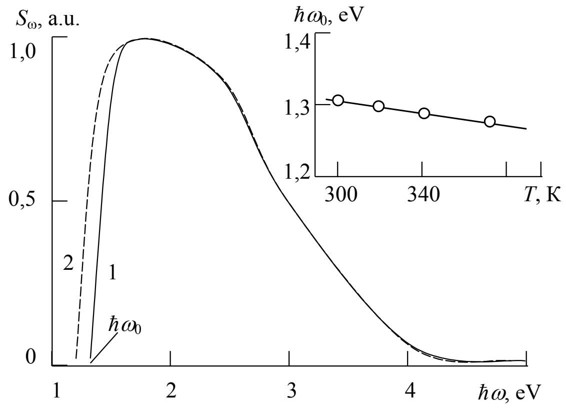

Fig. 7. Photosensitivity spectra of SBD based on CdTe:O_2 substrates at different temperatures: 1 – 300, 2 – 370 K. The inset shows the temperature dependence $\hbar\omega_0$ of the cutoff at $S_\omega = 0$.

In the photon energy $\hbar\omega > E_g$ region, the photosensitivity spectrum of an ideal photodiode can be represented by the expression [11]

$$S_\omega \approx \eta / \hbar\omega, \text{ A/W} \quad (2)$$

which does not describe any of the curves in fig. 6, which also have different high-energy boundaries (here η quantum efficiency). Let us pay attention to the fact that these differences are not related to the different thickness of the semitransparent rectifying contact, since for all presented in fig. 6 diodes it was deposited simultaneously in one technological cycle. Meanwhile, the above-noted discrepancies between the expected and experimental spectra are due to the different contributions of surface effects. Indeed, in the region of direct transitions $\hbar\omega > E_g$, taking into account the CdTe direct gap, the absorption coefficient quickly increases to 10^5 cm^{-1}. This causes a sharp increase in the effective penetration depth of radiation to $\alpha_\omega^{-1} \le 0.1$ μm, and therefore most of it is absorbed in the near-surface layer, where surface recombination processes dominate. The velocity of the latter can be estimated by comparing the experimental photosensitivity spectra with the theoretical expression for S_ω, obtained from the continuity equation with allowance υ_s, as well as for the drift and diffusion components of the photocurrent [12]. Studies have shown that the surface recombination rate in diodes made on $CdTe:O_2$ substrates is one and two orders of magnitude lower than in structures based on CdTe:Li and CdTe, respectively [12].

This pattern of behavior υ_s is also confirmed by a number of experimental facts. First of all, we turn our attention to higher values S_ω in the high-energy region of the spectrum of Au-$CdTe:O_2$ diodes in comparison with samples of other types, Fig. 6. Secondly, given that the photoluminescence I_{ph} intensity in the first approximation is inversely proportional to the surface recombination rate, one should also expect differences in the values I_{ph} for substrates of different types. Studies do show that the intensity of photoluminescence in a series of $CdTe:O_2$, CdTe: Li, CdTe substrates decreases by almost three orders of magnitude. At the same time, the efficiency of the edge emission band of $CdTe:O_2$ substrates at 300 K reaches several tenths of a percent [10].

Note that SBD made on substrates with a maximum edge luminescence intensity have the highest photoconversion efficiency. In this regard, luminescence can be used as a non-destructive method to optimize the size η of SBD made on n-CdTe substrates with other parameters. In conclusion, we note that rather high values of $\eta \approx 13\%$ were obtained in the absence of antireflection coated, as well as optimization of the basic electrophysical parameters of the base substrates and the design of the SC. This indicates additional potentialities for increasing the efficiency of photoconversion of SBD based on cadmium telluride.

CONCLUSION

Thus, the above results indicate that it is possible in principle to use cadmium telluride-based SBD as an SC. Note that although they were obtained for single-crystal substrates, the proposed technological methods can be successfully transferred to thin films. The basis for this, in particular, is the work [14], which reports on the creation of a quantum-size surface in thin CdTe films synthesized by the hot wall method. A relatively simple technology for producing thin layers of cadmium telluride with high hole conductivity may also be very promising [15]. Films created with its help can be the basis for fairly simple and cheap n-ITO/p-CdTe heterostructures with potentially high photoconversion efficiency.

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Стаття надійшла до редакції 18.04.2019 р.

UDC 621.315.592
DOI http://dx.doi.org/10.18524/1815-7459.2019.2.171227

PROSPECTS OF USING SURFACE AND BARRIER CdTe-DIODES IN SOLAR ENERGY

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Summary

The paper discusses the advantages and disadvantages of the most used today semiconductor materials of different structural perfection (single crystals, polycrystalline and amorphous) to create solar cells. The main attention is paid to the study of the possibilities of using surface-barrier diodes (SBD) as photoconverters based on single-crystal cadmium telluride. A number of technological methods for modifying n-CdTe substrates are analyzed, which lead to a significant improvement in the electrical and photoelectric parameters and characteristics of SBD. It has been established that the treatment of substrates in an aqueous suspension of alkali metal salts causes the potential barrier φ_0 height and the open circuit voltage of diodes V_{oc} based on them to increase by about 1.8 times compared with similar parameters of SBD on the base substrates. Annealing of the latter under certain conditions in air leads to the formation of a surface nanostructure, as a result of which not only almost a twofold increase is observed φ_0 and $V_{o\,c}$, but also a significant expansion of the photosensitivity S_ω spectrum of diodes based on unmodified substrates. It was established that the surface recombination rate of SBD on the basis of substrates with surface nanostructures is two and one orders of magnitude lower than in structures based on basic substrates and treated in suspension of alkali metal salts, respectively.

It is shown that the photoconversion efficiency of SBD based on substrates with surface nanostructure ($CdTe:O_2$) reaches 13% at 300 K in AM2 lighting conditions. The use of technologies used in the creation of surface-barrier solar cells based on cadmium film telluride is discussed.

Keywords: cadmium telluride, surface barrier diode, solar cell, photoconversion efficiency

УДК 621.315.592
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ПЕРСПЕКТИВИ ВИКОРИСТАННЯ ПОВЕРХНЕВО-БАР'ЄРНИХ CdTe-ДІОДІВ В СОНЯЧНІЙ ЕНЕРГЕТИЦІ

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Реферат

В роботі обговорюються переваги і недоліки найбільш використовуваних на сьогоднішній день напівпровідникових матеріалів різної структурної досконалості (монокристали, полікристалічні і аморфні) для створення сонячних елементів. Особлива увага приділяється вивченню можливостей використання в якості фотоперетворювачів поверхнево-бар'єрних діодів (ПБД) на базі монокристалічного телуриду кадмію. Аналізується ряд технологічних способів модифікації підкладинок n-CdTe, які призводять до суттєвого покращення електричних та фотоелектричних параметрів і характеристик ПБД.

Встановлено, що обробка підкладинок в водній суспензії солей лужних металів викликає зростання висоти потенціального бар'єру φ_0 і напруги холостого ходу $V_{o\,c}$ діодів на їх основі приблизно в 1,8 разів в порівнянні з аналогічними параметрами ПБД на базових підкладинках. Відпал останніх при певних умовах на повітрі призводить до утворення поверхневої наноструктури, в результаті чого спостерігається не тільки збільшення майже в два рази φ_0 і $V_{o\,c}$, але й суттєве розширення спектру фоточутливості S_ω діодів на базі не модифікованих підкладинок. 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.

Показано, що ефективність фотоперетворення ПБД на базі підкладинок з поверхневою наноструктурою ($CdTe:O_2$) досягає 13% при 300 К при умовах освітлення АМ2. Обговорюються варіанти застосування використаних в роботі технологій для створення поверхнево-бар'єрних сонячних елементів на основі плівкового телуриду кадмію.

Ключові слова: телурид кадмію, поверхнево-бар'єрний діод, сонячний елемент, ефективність фотоперетворення