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# Perspective of surface modification of CdTe single crystal substrate for creation of photosensitive barrier structures

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**Abstract.** Analyzed in this paper is the influence of various modifications of substrate surface in n-CdTe single crystals (laser, thermal and photothermal) on electric and photoelectric properties of diode structures based on them.

**Keywords:** surface-barrier diode, modificated surface, current-voltage characteristic.

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## 1. Introduction

Cadmium telluride continues to remain one of the most perspective materials for creation of various devices in semiconductor electronics, which is caused by the number of their physical-and-technical parameters. The relatively wide bandgap provides work of devices at high temperatures and is optimum for converting sun energy into the electric one [1]. The high density and atomic number in combination with high radiation hardness promote effective and stable work of various types of CdTe-detectors in a wide range of ionizing radiation energies.

It is noteworthy that the basis for most of above devices is rectifying structures, the separate class of which is represented by surface-barrier diodes (SBDs). It is caused by a number of their advantages in comparison with other types of diode structures. The first advantage consists in relatively simple technology providing creation of single- and multi-element active structures with arbitrary topology on mono- or polycrystalline substrates in a unique cycle. Second, anomalous low temperatures for deposition of barrier contacts do not change the parameters of base substrates. Third, presence of strong electric surface field causes more effective separation of photocarriers born by high energy photons. And finally, SBDs can possess lower values of the serial resistance as compared with that of homo- and heterojunctions, since one of semiconductor ranges is eliminated in the first case.

Despite the above advantages of SBDs, the main problems in their production are to obtain a maximal height of the potential barrier and provide minimal speed of surface recombination. Application of the known technological methods does not result in successful solution of these tasks, which requires new approaches and principles.

One of possible ways to solve the above problems lies in additional special treatment (modification) of semiconductor substrate surface before creation of the rectifying contact. In this work, influence of various types of annealing (thermal, photothermal and laser) on electric and photoelectric properties of SBDs based on n-CdTe is analyzed.

## 2. Technology and methodology

As initial substrates, we used the plates with typical dimensions 4×4×1 mm, which were cut out from the bulk single-crystals of CdTe with the specific resistance 10 to 20 Ohm·cm at 300 K. Crystals were obtained using the Bridgmen method growing from melt, non-doped additionally with any impurities and had electronic conductivity. Plates passed stage-by-stage mechanical and chemical polishing in solution of composition $K_2Cr_2O_7$:$H_2O$:$HNO_3$ = 4:20:10, and also careful cleaning in deionized water and final drying. The prepared substrates had mirror surfaces, in one of which the conductive indium contacts were infused. Before creation of the rectifying contact made of semi-transparant gold layer deposited in vacuum, some substrates were treated in specific ways described below.

First group of substrates was processed in the water suspensions of salts of alkaline metals and, in what follows, marked as CdTe:AS [8]. Substrates from second and third groups were treated by laser annealing (CdTe:L) and thermal annealing in air, i.e., in molecular oxygen (CdTe:$O_2$) [9]. It is necessary to note that photothermal oxidation of plates (annealing in atomic oxygen) results in formation of new compound CdO [9], and, consequently, in creation of the heterojunction CdO-CdTe. As the latter cannot be related to the class of SBDs, they will not be considered in this work. Note also that annealing of CdTe substrates in the same conditions but in molecular oxygen results in formation of quantum size surface [10]. The fourth group of samples consists of chemically etched substrates that were not treated in addition and marked as CdTe. SBDs based on them served as the standard ones when comparing their characteristics with those of diode structures in other groups.

## 3. Results and discussion

Researches showed that SBDs based on CdTe:AS and CdTe:$O_2$ substrates have a considerably higher height of the potential barrier than that in standard ones. Unlike the above mentioned treatments, the laser annealing causes some decrease in the value $\varphi_0$. It is illustrated in Fig. 1, where the direct branches of *I-V* characteristic for objects under study are shown in the range of their linearity. Let us pay attention to the insignificant difference of slopes in linear parts of *I-V* characteristic for diode structures in all the groups. It testifies to the close values of the serial resistance $R_0$ that is the sum of resistances of contacts and the base of diode. On the other hand, it is also indicative of negligibly low contribution to the value $R_0$ from surface layers modified by different methods. Further analysis of investigated electric properties showed that the change of surface modification method considerably influences not only on the value $\varphi_0$ but also on the character of flowing physical processes. First of all, it can be seen from the dependences of forward and backward currents, which are considered in detail below. As obvious from Fig. 2, the initial parts of *I-V* characteristics of SBDs based on CdTe, CdTe:AS and CdTe:$O_2$ substrates at $eV > 3kT$ are described by the known expression [1, 5-7, 11]

$$I = I_0 \exp(eV/nkT), \quad (1)$$

where $I_0$ is the cut-off current for $V = 0$, $n$ – coefficient of ideality. The latter can be easily determined from the linear part of *I-V* characteristics, built in semi-logarithmic coordinates. For the diodes Au-CdTe $n = 1$, which indicates the over-barrier character of the forward current origin and is characteristic for SBDs created on reasonably doped substrates. Beside, it means that an intermediate layer between metal and semiconductor is tunnel transparent, and the height of barrier does not exceed the half of the bandgap for the substrate base. Unlike the contacts of Au-CdTe, the latter condition is not valid for SBDs based on CdTe:AS and CdTe:O, as the value $\varphi_0$ for them is noticeably higher than $E_g/2 \approx 0.75$ eV (Fig. 1). For these structures at low voltages in accord with [5, 11], the recombination current becomes dominating in the space charge region (SCR) which is described by the formula (1) at $n = 2$. As it is evident from Fig. 1, the initial parts of direct branches in *I-V* characteristics of SBDs with $\varphi_0 > E_g/2$ well follow the expression (1), and the energy dependence slope is 1.6 eV and agrees with $E_g$ of cadmium telluride at 0 K [2].

Note that deviation of experimental points from the expected dependences in Fig. 1 is caused by a voltage drop on the serial resistance $R_0$ in this diode structure. Calculating the resistance results in straightening the $I_f(V)$ dependences in semi-logarithmic coordinates. In this case, the slope of straight lines for all SBDs in Fig. 1 is the same and equals $e/\kappa T$. It is indicative of the over-barrier character of the forward current at a large bias and does not contradict to the known mechanisms of current transfer in SBDs [1, 4-6, 11].

The considered above over-barrier current and generation-recombination cut-off one $I_0$ at 300 K do not exceed $10^{-10}$ A (Fig. 1), and, moreover, in obedience to the theory depend on reverse bias not stronger than $\sqrt{V}$ [1, 5, 11]. On the other hand, there observed in experiment are more sharp dependences $I_r(V)$, which indicates other current transfer mechanisms. It is

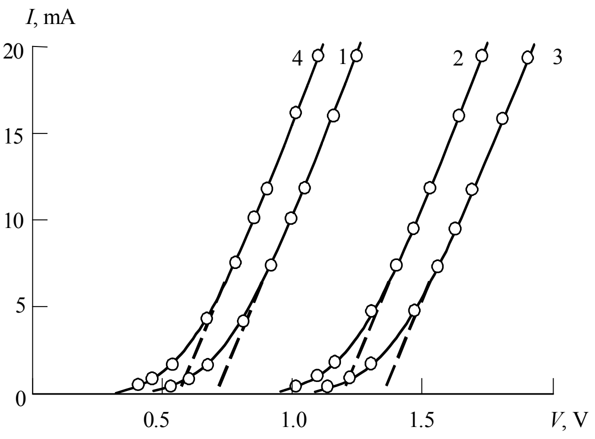


**Fig. 1.** Forward branches of *I-V* characteristics of surface-barrier diodes based on CdTe (*1*), CdTe:AS (*2*), CdTe:$O_2$ (*3*) and CdTe:L (*4*) substrates at 300 K.

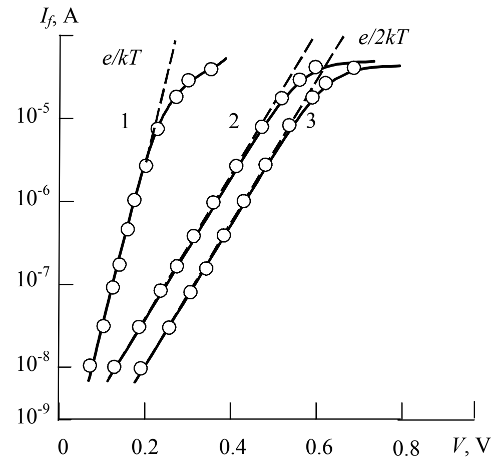


**Fig. 2.** Initial parts of forward branches of *I-V* characteristics for the diodes based on CdTe (*1*), CdTe:AS (*2*) and CdTe:$O_2$ (*3*) substrates at 300 K.

reasonable to assume that for diodes based on wide-bandgap semiconductors (including the surface-barrier ones), tunnelling of charge carriers can be both interband and with participation of local levels [11]. This assumption is confirmed by Fig. 3, from which it is evident that the reverse *I-V* characteristics are described by the known expression for a tunnel current through a sharp barrier [5, 11].

$$I = a \cdot \exp\left(-\frac{b}{\sqrt{\varphi_0 - eV}}\right). \quad (2)$$

Here, $a$ and $b$ are the coefficients defined by the parameters of a substrate and diode structure. The sign "–" under the root indicates the reverse bias, and the voltage should be put with the negative sign. Different slopes of initial parts in reverse *I-V* characteristics for the objects under study testifies to the difference just of the diode parameters, and not of the substrate ones, since the latter are identical for all of them. Note that the coefficient $b$ depends on the height and width of barrier, energy depth of local centres in SCR, their distribution and other reasons [11], and in this relation needs separate more detailed consideration. Also, the same concerns explanation of various dependences in Fig. 3 at large biases, in the range of which, except for the factors marked above, avalanch processes can take part yet [6, 11].

Unlike to the considered above SBD current-voltage characteristics, the ones based on laser annealled substrates have quite another character. As seen from Fig. 4, they follow the law

$$I \sim V^m, \quad (3)$$

where the exponent takes values from the interval 1 to 6 in dependence on the sign and magnitude of the applied bias voltage. The analysis shows that dependence of the type (3) is characteristic for currents limited by the space charge. In accord with the theory of mono-polar injection, the initial part of *I-V* characteristics should be described by the Ohm law ($m = 1$), and at higher $V$ should be changed with the quadratic one named as trapless. Instead, in our case the exponent in this part is larger and equals to 3, which does not coincide with the expected one $m = 2$.

Similar dependences were observed, in particular, in thin CdS crystals, which was explained by the authors [12] accounting for the presence of a large number of traps with the shallow energy depths. Note that in our case it is fully probable, as after the laser annealing in this modified layer there can be a large number of defects, authentication of which needs additional researches. Further growth of the forward current in the part with $m = 6$ corresponds to the complete filling of traps, which is again changed with a slower growth region, namely, by the expected trapless quadratic law. The reverse branch of *I-V* characteristic (curve 2 in Fig. 4) in a wide range of changing voltages follows the Ohm law, and at high $V$ values is changed with the sharper one. It can be caused by many mechanisms, the most probable of which are tunneling with participation of local levels and impact ionization.

Researches of light characteristics showed that dependences for all the diodes are qualitatively similar. So, in particular, the current of short circuit $I_{sc}$ is the linear function of the illumination level $L$ when the latter changes within the limits of more than four orders. The open circuit voltage $V_{oc} \sim \lg L$ at low illumination levels and follows to the saturation at the larger ones. The absolute values $V_{oc}$ depends on the type of diode and $L$, and their maximal values are summarized in Table.

It is noteworthy that the effective photosensitive area of the samples was $\sim 2 \cdot 10^{-2}$ cm$^2$, and photoelectric parameters were measured at the maximal illumination level provided with a 100-W tungsten filament lamp. Note also the substantial improvement of basic electric and photoelectric parameters ($\varphi_0$, $V_{oc}$ and $I_{sc}$) of SBDs with the modified surface as compared with the standard barrier structure.

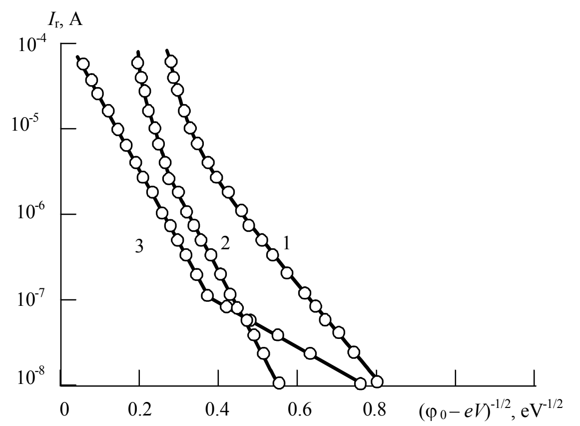


**Fig. 3.** Comparison to (*2*) experimental reverse branches of *I-V* characteristics for the diodes based on CdTe (*1*), CdTe:AS (*2*) and CdTe:$O_2$ (*3*) substrates at 300 K.

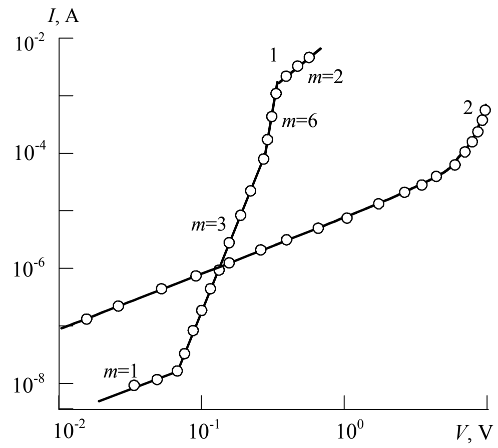


**Fig. 4.** Forward (*1*) and reverse (*2*) *I-V* characteristics of diodes Au-CdTe:L at 300 K.

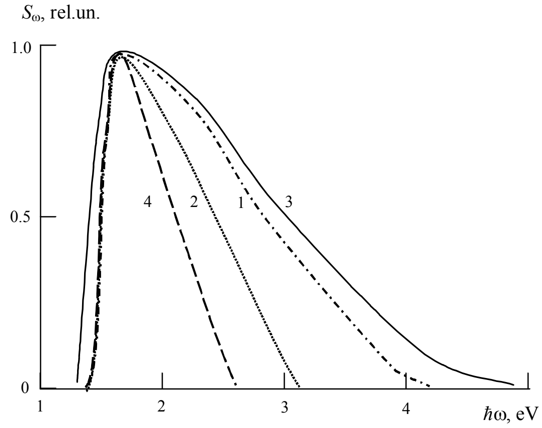


**Fig. 5.** Photosensitivity spectra of surface-barrier base substrates CdTe (*1*), CdTe:AS (*2*), CdTe:$O_2$ (*3*) and CdTe:L (*4*) at 300 K.

**Table. Parameters and types of the diode structures.**

| Diode type | | Au–CdTe | Au–CdTe:AS | Au–CdTe:$O_2$ | Au–CdTe:L |
|---|---|---|---|---|---|
| Parameter | $\varphi_0$, eV | 0.7±0.1 | 1.2±0.1 | 1.35±0.1 | 0.55±0.05 |
| | $R_0$,Ohm | 30±2 | 30±2 | 35±2 | 30±2 |
| | $V_{oc}$, V | 0.4±0.05 | 0.75±0.05 | 0.9±0.05 | 0.45±0.05 |
| | $I_{sc}$, mA | 0.1±0.02 | 0.2±0.02 | 0.3±0.02 | 0.4±0.02 |

At the end, let us analyze the influence of modification on the concentration of surface defects $N_s$ that usually form the undesirable channels of recombination in the impurity range. As the effective length of absorption for radiation with the quantum energy $\hbar\omega > E_g$ in cadmium telluride $l_e \leq 10^{-5}$ cm, non-equilibrium electron-hole pairs are practically generated in a subsurface layer. In this relation, in the first approximation it is possible to conceive that the efficiency of edge luminescence and photosensitivity in the area of fundamental absorption are inversely proportional to the concentration $N_s$. As it is seen from Fig. 5, the highest photosensitivity in the high-energy spectral range inherent to SBDs based on CdTe:$O_2$ substrates, the surface of which has a quantum-size structure [10]. These substrates provide also the highest efficiency of edge luminescence that can reach 10 % at 300 K. The least short-wave photosensitivity is observed for the contacts of Au-CdTe:L, which is well explained by a considerable number of surface defects appearing after the laser annealing. It is confirmed by the results of measuring *I-V* characteristics in these diodes, and also complete absence of mentioned above edge luminescence at 300 K.

## 4. Conclusions

Thus, the obtained results testify to perspectives of modification of n-CdTe substrate surface to control electric and photoelectric properties of surface-barrier structures based on them. In this case, every method has its advantages and deficiencies as compared to each other both in technological aspect and in achieving the maximal values of physical-and-technical parameters of photodiodes. In this relation, the following investigations should be aimed at not only development of new technologies for surface modification but also at searching the optimum combinations of treatments considered in this work in application to cadmium telluride substrates.

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