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Photodetectors Based on CdTe:Li

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The optimal modes for doping CdTe with Li impurity have been established. Photodetectors based on Au-CdTe:Li surface barrier diodes have been manufactured. The optical parameters and photoelectric characteristics of heterostructures have been studied, the region of their photosensitivity of 1.4÷5.0 eV and the mechanisms of its formation during interband transitions and through local Li_{Cd} centers have been determined. Au-CdTe:Li structures with high photosensitivity were obtained due to the high potential barrier φ_0 formed on the modified CdTe surface. The high quantum efficiency η = 12% of CdTe:Li determines the production of photodetectors with typical values of open circuit voltage V_{oc} and short circuit current I_{sc}, which are 0.7 V and 10 mA/cm² under AM2 solar illumination. Their efficiency can be 10%. Temperature coefficient of change in efficiency CdTe-based solar cells are almost four times smaller than silicon ones. A high quantum efficiency of η = 12% radiation in the edge region was obtained. The proposed approach to modifying the CdTe surface and doping with Li allows for a significant increase in the photosensitivity of structures and opens up new possibilities for developing highly sensitive photodetectors for different spectral ranges.

Keywords: Cadmium telluride, Li impurity, Photosensitive heterostructures, High quantum intensity, Li_{Cd} centers, Interband transitions.

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1. INTRODUCTION

Photodetectors play an important role in modern electronics. In systems with radiation sources (including LEDs), they solve several important problems in diagnostics and conversion of optical radiation energy [1, 2]. At the same time, solar energy is of particular importance. It solves important problems of supplying electrical energy to various devices. They use different types of photodetectors. Their capabilities depend significantly on the design of the device and the material used. In the case of solar energy, cadmium telluride is of particular importance, since the direct gap nature of its energy structure and its parameters (E_g = 1.5 eV at 300 K) are consistent with most parameters of solar radiation. This is an important condition for converting solar energy into electrical energy with high efficiency [3, 4]. At the same time, the photostructures used on its basis, when obtained, require further improvement of the technological processes of manufacturing and design of energy structures. Note that the density and atomic number of CdTe, combined with high radiation resistance, contribute to the efficient and stable operation of CdTe-based devices in a wide range of ionizing radiation energies [5, 6]. Therefore, the selection of doping impurities and processes to increase the photosensitivity of CdTe-based structures requires further development. Accordingly, it is relevant to obtain highly efficient structures and study processes in them for the formation of photosensitivity.

2. EXPERIMENT

2.1 Tested Samples

Basic CdTe crystals were obtained using the well-known Bridgman method [7]. Based on the monitoring of their electrical properties, *n*-type conductivity and a resistivity of $\rho\sim$100 Ohm cm were established. Substrates with a standard size of 4 × 4 × 1 mm³ were made from them and chemical-mechanical processing was carried out. Chemical treatment of the surface of the substrates was carried out for 10-20 s in a solution of the composition $K_2Cr_2O_7$:H_2O:HNO_3 = 4:20:10 at 300 K, which made it possible to obtain a mirror surface. Its high level is confirmed by the formation of intense photoluminescence, which is not observed on samples without the specified treatment. The absence of a surface of the resulting CdTe layers of a different chemical nature is confirmed by optical reflection studies. Doping with Li impurity was carried out by diffusion from the vapor phase in a sealed quartz ampoule at T = 980 °C and a diffusion time of at least 1.5 hours. This process was carried out with the CdTe substrate and Li_2CO_3 diffuser located at opposite edges of the ampoule.

Surface barriers on Au-CdTe:Li photostructures were created by deposition of an Au film. For this purpose, the technique of applying them in a vacuum using a VUP-2K installation was used. The degree of vacuum was no less than 10^{-4} Torr. Immediately before deposition, short-term temperature treatment of CdTe substrates was carried out

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in vacuum. Au films were deposited at appropriate substrate temperatures, which ensured high adhesion of the films to the base material.

2.2 Research Methods

The photoelectric and electrophysical properties of Au-CdTe structures were studied. Measurements were made to determine both the electrical conductivity of the resulting material and the parameters of the resulting rectifying structures.

Measurements of current-voltage characteristics (CVC) were carried out according to the generally accepted method at direct current in a standard installation. The power was supplied by a stabilized voltage source TES 7, and the voltage at 10^{-2}-$5\cdot10^{2}$ V and the current 10^{-11}-10^{-1} A were measured with a digital device V7-21A and a microvoltammeter F 116/2 with an accuracy of 0.5 %. Based on such studies, both the electrical conductivity value and the parameters of the resulting structures were also determined. For this purpose, the equivalent circuit structures were considered. Graphs of the voltage U and current I was plotted in the coordinates $lnI - eU/kT \sim f(I)$, from which R was determined from the slope of the straight line.

Spectral studies of photosensitivity were carried out on a universal spectral installation using standard methods [8]. The radiation source was an ELS/L halogen lamp with a monotonic spectral distribution over a wide range of wavelengths. The spectral device was an MDR-23 monochromator, the diffraction grating of which provided irradiation of photostructures in the wavelength range 380-1270 nm when it was focused by a system of quartz lenses to sizes with a diameter of 2÷3 mm (according to sample dimensions). The photocurrent was recorded by a system with an F116/2 microvolt-microammeter. To do this, the samples were placed in a standard cell with two electrodes, which made it possible to connect the structures through ohmic contacts.

The above installation made it possible to carry out spectral studies to diagnose the properties of the base material, the effect on them of physicochemical surface treatment and doping with Li impurities. Optical reflection, absorption and photoluminescence were studied. The signal was recorded by a FEP-112 photomultiplier. Measurements were also made using modulation spectroscopy, namely, the λ-modulation method [9]. The latter significantly increased the resolution and made it possible to reveal the fine structure of generation-recombination processes. The signals were recorded by a standard synchronous detection system. Optical processes were studied with an ELC/C halogen lamp (1), and luminescence was excited by an LGN-21 laser with λ = 337 nm, which corresponds to an excitation energy of 3.68 eV.

3. RESULTS AND DISCUSSION

Photodetectors are based on surface barrier diodes (SBDs) Au-CdTe: Li. Comprehensive studies of their photoelectric and electrophysical properties, as well as the optical and luminescent properties of the original CdTe and doped Li impurity, have been carried out. Additionally, the effect of temperature on the properties of the material under Li alloying conditions was determined.

Photodetectors made based on Au-CdTe:Li are characterized by a high potential barrier φ_0. It is one of the more fundamental characteristics of the diode structure. It has been established that the value φ_0 determines the open-circuit voltage V_{oc} (all other things being equal, $V_{oc} \sim \varphi_0$). An increase in φ_0 causes a decrease in the dark current and an increase in the signal-to-noise ratio [10]. In addition, significant φ_0 allow the operation of devices with a rectifying barrier at higher temperatures [11]. Accordingly, to increase the barrier height, a search was carried out for the corresponding processes of modifying the surface of cadmium telluride. It has been established that the production of a modified surface significantly increases the height of the potential barrier during the formation of SBDs based on Au-CdTe:Li [12].

Surface modification was carried out by additional treatment of samples with ohmic contacts in an aqueous suspension of $LiCO_3$ salt in air for t = 10-20 minutes. The correctness of the modes is confirmed by the results obtained when comparing them with unmodified SBDs, which is displayed in the graphs in Fig. 1.

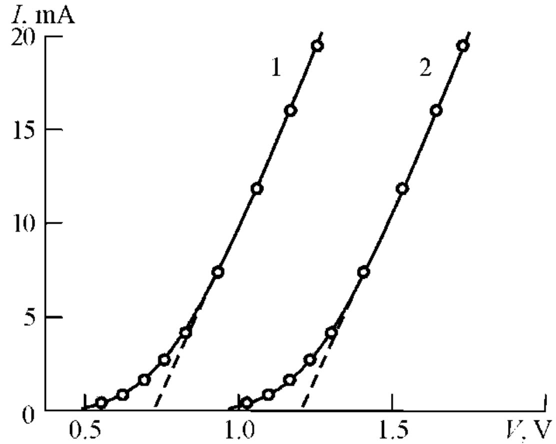

Fig. 1 – Straight branches of the current-voltage characteristics of diodes with conventional (1) and modified (2) surfaces

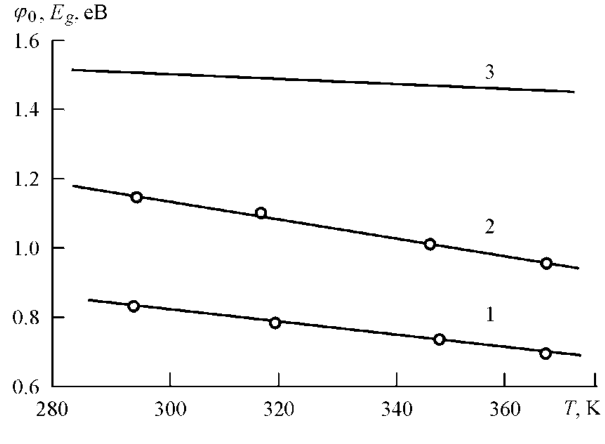

Fig. 2 – Temperature dependences of E_g (3) and φ_0 (1, 2) for diodes with conventional (1) and modified (2) surfaces. Points – experiment, curve 3 calculated using the formula $E_g(T) = 1.6 - 4.1\cdot10^{-4}\,T$

The fundamental thing for these samples is the invariance of the slope of the straight section of the CVC, which indicates the identity of the resistance sequence R_0. As is known, it is the sum of the resistances of the ohmic contacts and the diode base. In addition, the contribution of the resistance of the modified layer to R_0 is negligibly small.

It is also important that the temperature coefficient of change in the height of the potential barrier increases by almost an order of magnitude compared to the temperature coefficient of change in the band gap width, Fig. 2.

The established properties indicate a significant contribution of surface levels in the formation of the Au-CdTe:Li potential barrier. Therefore, when forming photosensitive surface-barrier structures, the structural perfection of the CdTe substrate, the state of its surface, and the absence of foreign impurities were controlled. Optical reflection R'_ω studies using λ modulation allowed us to determine a band gap of E_g = 1.5 eV, a cubic energy structure, and a spin-orbit coupling value of Δ_{SO}= 0.9 V, which is consistent with the literature data for *CdTe* [13]. A feature was established at $\hbar\omega$ = 1.442 eV, determined by optical transitions involving centers formed by lithium, Fig. 3, curve 3. Their depth is $E_g - \hbar\omega_m$ = 0.058 eV, which is in good agreement with the *Li* centers formed during doping with an impurity [3]. Their nature is due to vacancies in the metal sublattice V_{Cd} [14]. Therefore, it is logical to assume that they are replaced by lithium atoms, which form substitution centers Li_{Cd}. This conclusion is also confirmed by studies on the change in the type of electrical conductivity of the surface layer from *n*-type to *p*-type due to the formation of acceptor centers, namely Li_{Cd} [12, 15].

Optical absorption studies confirmed the perfection of the crystal structure, as well as the absence of uncontrolled impurities. A typical differential curve T'_ω from λ-modulated absorption studies is characterized by a maximum at E_g=1.5 eV, Fig. 3, curve 2, insert in Fig. 5.

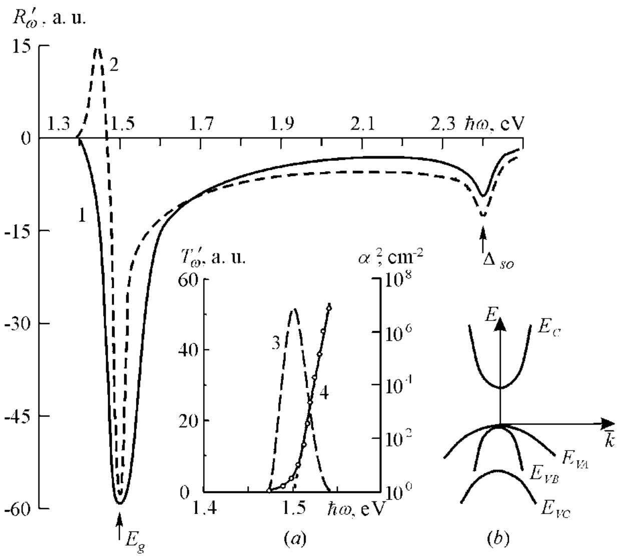

Fig. 3 – Spectra of λ-modulated optical reflection of CdTe (1) and Li-doped diffusion layers (2). In inset (a) the transmission spectrum was measured using the λ-modulation method (3), as well as the absorption spectrum (4) of diffusion layers of cadmium telluride doped with a Li impurity; (b) – energy structure of the Brillouin zone centers. T = 300 K

No other features in the area $\hbar\omega < E_g$ were found in the studies conducted. This is also confirmed by studies of optical transmission on CdTe plates ~ 45 μm thick, Fig. 3, curve 3. A rapid decrease in transmission intensity is observed at $\hbar\omega \geq$1.5 eV. The nature of its change is well approximated by the well-known expression for the optical absorption coefficient α in the case of allowed direct transitions $\alpha = A^*(\hbar\omega - E_g)^{\frac{1}{2}}$, where A^* is the known value, which is determined by the effective masses of charge carriers m_n^* and m_p^* [3,16]. The spectral dependence α in coordinates $\alpha^2 \sim \hbar\omega$ is characterized by linearity. It is from this that the band gap of E_g = 1.5 eV was determined when it is approximated to the intersection with the photon energy axis.

A fundamental and important characteristic of the obtained Au-CdTe:Li photostructures is the spectral region of photosensitivity S_ω. At 300 K it covers the photon energy range 1.4÷5.0 eV, Fig. 4.

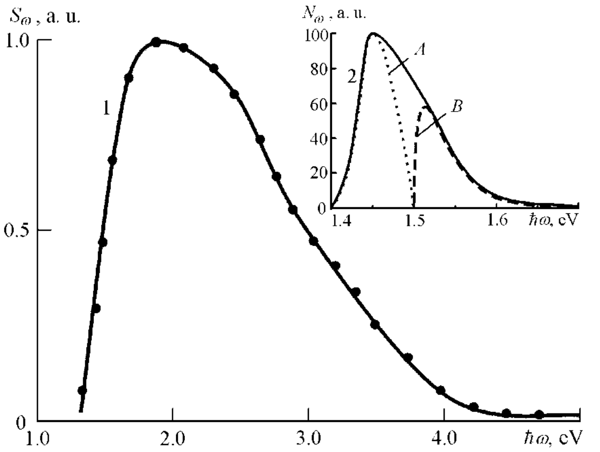

Fig. 4 – Photosensitivity spectrum (1) of surface-barrier structures obtained based on CdTe:Li. The inset shows the photoluminescence spectrum (2) of Li-doped cadmium telluride and the component PL bands (bands *A* and *B*). T = 300 K

Note that the established region of photocurrent generation consists of two ranges corresponding to $\hbar\omega > E_g$ and the region $\hbar\omega < E_g$. Note that the base *CdTe:Li* is characterized by intense photoluminescence (PL) because of the indicated processing processes. Its quantum efficiency is η = 12 %. The maximum of the spectrum is at $\hbar\omega$ = 1.442 eV and covers the region of interband emitting transitions, inset in Fig. 4.

The composite nature of the radiation in the edge region ($\hbar\omega < E_g$ and $\hbar\omega > E_g$) correlates with photosensitivity. High quantum efficiency confirms the structural perfection of the surface, which is fundamental in the formation of SBDs with a high potential barrier φ_0. The maximum of the PL spectrum occurs at a photon energy of $\hbar\omega$ = 1.442 eV and is characterized by properties typical for recombination through local levels – the independence of the position of $\hbar\omega_m$ from the excitation level L and the linearity of the dependence of its intensity I on L [15]. The energy position $E_g - \hbar\omega_m$ is 0.058 eV, which is consistent with the burial depth Li_{Cd}. Thus, in the formation of generation-recombination processes, Li_{Cd} centers play an important role. They also determine the formation of photosensitivity of Au-CdTe:Li structures at $\hbar\omega < E_g$.

In the photon energy $\hbar\omega \geq E_g$ region, intense radiation is formed, the spectrum of which is consistent with the analytical curve calculated from the well-known expression for interband transitions of free charge carriers [1, 15]

$$N_\omega \sim (\hbar\omega)^2 \sqrt{\hbar\omega - E_g}\, exp\left(-\frac{\hbar\omega - E_g}{kT}\right) \qquad (1)$$

where k is the Boltzmann constant, T is the temperature, N is the number of photons in a unit energy interval. Note that the maximum occurs at $\hbar\omega_m$= 1.51 eV, and its position does not depend on L and the intensity depends on the excitation level according to the quadratic law [17]. The properties of highly efficient radiation indicate the interband nature of recombination in CdTe:Li. Note that similar bands are observed in the above results of optical reflection studies.

Suitable interband generation processes in region $E_g - \hbar\omega_m$ determine the photosensitivity of the *Au*-CdTe:Li SBDs. Note that the spectral distribution of photosensitivity and radiation are characterized by similar curves, Fig. 4. The mechanisms during interband transitions of carriers are confirmed by studies carried out under the conditions of the CVC of an illuminated diode. This CVC of a bleached diode can be described by the following expression [10, 13]

$$I = I_0[\exp(eV/nkT) - 1] - I_p, \qquad (2)$$

where I_p is the photocurrent, I_0 is the cut-off dark current at voltage $V = 0$, n is the ideality coefficient determined by the current flow mechanism.

Analysis of the obtained integral light characteristics confirmed the indicated mechanism. Following this, the transition to the open-circuit voltage V_{oc} (at $I = 0$) and the short-circuit current I_{sc} (putting $V = 0$) allows us to obtain the following dependence for $eV \geq 3nkT$

$$I_{sc} \approx I_{sc}^0 exp(eV_{oc} / nkT) \qquad (3)$$

Here, I_{sc}^0 must be understood as the cutoff luminous flux at $V_{oc} = 0$, which can coincide with I_0 only in the case of identical mechanisms for the formation of light and dark currents. Accordingly, it becomes possible to establish not only the mechanisms of their formation, but also to determine the common and distinctive features between the electrical and energy properties of [19].

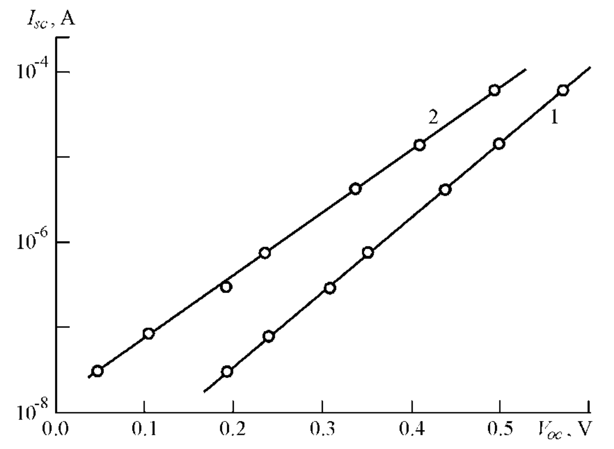

Fig. 5 – Dependences of I_{sc} (V_{oc}) at different temperatures: 1 – 300 K, 2 – 400 K

Therefore, the obtained light CVC of Au-CdTe:Li photostructures are plotted in ln I_{sc} – V_{oc} coordinates; they represent straight lines, the slope of which changes with temperature, Fig. 5.

The ideality coefficient determined by the characteristics is $n = 2$ and it does not depend on T in the range under study. Note that the obtained dependences are characteristic of the recombination of carriers in the space charge region (SCR) through single local centers [20]. According to this model, the parameter $I_{sc}^0 \sim \exp(-E_g / 2kT)$, which allows one to determine the band gap of the material in which recombination occurs. The experimental dependence $I_{sc}^0(T)$ is approximated by a straight line in coordinates ln I_{sc}^0 – $10^3/T$. The energy slope of the straight lines is ~ 1.6 eV and is consistent with E_g for cadmium telluride at 0 K.

The results obtained indicate that, along with generation-recombination processes involving local Li_{Cd} centers, interband generation of photocarriers in the Au-CdTe:Li photostructures under study is important. This also indicates the spectral range of photosensitivity, Fig. 4. The dominant processes in the formation of light CVC of Au-CdTe:Li are transitions through local centers. This is confirmed by the following circumstances. Under stationary conditions, the generation rate of G should be equal to the recombination rate, although they may be due to different mechanisms. Therefore, they are described by different analytical expressions. At the same time, measurements of the $I_{sc}(V_{oc})$ dependences were carried out in the mode of photocurrent compensation by dark current at forward bias. Accordingly, the recombination of photocarriers, which can be described by an expression like dark current, was monitored. The conducted studies of dark current indicate that in the objects of study at small forward biases, the current is controlled by recombination processes in the space charge region through single centers. Since in SBDs the generation of photocarriers occurs in the SCR with fundamental absorption (interband transitions), their recombination will also occur in the same region, but with the participation of local centers. As shown above, the latter is also possible, as are the established interband transitions of nonequilibrium charge carriers.

Thus, it is possible to create Au-CdTe:Li SBDs based on crystalline cadmium telluride. Their photosensitivity is formed by generation-recombination processes involving local LiCd centers and interband transitions of photocarriers. Surface modification during additional processing of CdTe:Li with ohmic contacts in an aqueous suspension of $LiCO_3$ salt determines high photosensitivity due to a significant increase in the height of potential barrier 0 during the formation of SBDs. The perfection of CdTe:Li is confirmed by high quantum efficiency η = 12 % photoluminescence of CdTe:Li and localization of radiation in the edge region. It is advisable to monitor the influence of technological processes on the selection of optimal modes for the manufacture of photodetectors, the influence of doping processes and surface modification when studying the processes of optical reflection, absorption and photoluminescence using λ-modulation. The processes of interband generation of photocarriers and with the participation of local Li_{Cd} centers determine the photosensitivity S_ω at 300 K of Au-CdTe:Li photostructures in the photon energy range 1.4÷5.0 eV. The high quantum efficiency of η = 12 % when localizing radiation in the edge region makes it possible to obtain typical values of the V_{oc} and I_{sc} parameters of 0.7 V and 10 mA/cm^2 at 300 K on Au-CdTe:Li structures under AM2 solar illumination. Under such conditions, the efficiency coefficient (efficiency factor) reaches 10 %, and the temperature coefficient of change of efficiency factor photocells are almost four times smaller than silicon ones.

REFERENCES

1. M. Fox, *Optical Properties of Solids* (Oxford: New York: 2010)
2. V.P. Makhniy, M.M. Berezovskiy, O.V. Kinzerska, M.P. Mazur, T.M. Mazur, V.V. Prokopiv, *Sensor Electronics and Microsystem Technologies* **16**, 2, 42 (2019).
3. D.V. Korbutiak, S.V. Melnychuk, Ye.V. Korbut, M.M. Borysiuk, *Teluryd kadmiiu: domishkovo-defektni stany ta detektorni vlastyvosti* (Kyiv: Ivan Fedorov: 2000).
4. Tetiana Mazur, Myroslav Mazur, Marian Halushchak, *J. Nano- Electron. Phys.* **15** No 2, 02006 (2023).
5. Ji-Hui Yang, Shiyou Chen, Wan-Jian Yin, X.G. Gong, *Phys. Rev. B*, **79**, 245202 (2009).
6. T.M. Mazur, M.M. Slyotov, O.M. Slyotov, M.P. Mazur, *Phys. Chem. Solid State*, **23** No 2, 317 (2022).
7. T.K. Al-Hamdi et al., *J. Cryst. Growth* **534**,125466 (2020).
8. Yu.V. Vorobev, V.Y. Dobrovolskyi, V.Y. Strykha, *Metody yssledovanyia poluprovodnykov* (K.: Vyshcha shkola: 1988).
9. V.P. Makhniy, M.M. Slyotov, E.V. Stets, I.V. Tkachenko, V.V. Gorley, *Thin Solid Films,* **450**, 222 (2004).
10. M.V. Demych, *Elektrychni ta fotoelektrychni vlastyvosti diodnykh struktur na bazi monokrystalichnoho telurydu kadmiiu,* (Dys. kand. fiz.-mat. nauk: Chernivtsi: 2000).
11. 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).
12. M.V. Demych, O.S. Lytvyn, V.P. Makhnii, M.M. Slotov, O.V. Stets, *Fizyka i khimiia tverdoho tila*, **3**, 3 (2002).
13. P.Y. Yu, M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer-Verlag: Berlin: 2010).
14. V.P. Makhnii, M.M. Berezovskyi, *Tochkovi defekty v binarnykh napivprovidnykakh: Navchalno-metod. Posibnyk* (Chernivtsi: Chernivetskyi un-t.: 1995).
15. J.I. Pankove, *Optical Processes in Semiconductors* (Prentice-Hall Inc. Englewood Cliffs: New Jersey: 1971).
16. Sadao Adachi, *Properties of Semiconductor Alloys: Group-IV, III-V and II-VI Semiconductors* (New Jersey: Wiley: 2009).
17. M.M. Slotov, O.M. Slotov, *Liuminestsentsiia u pryladakh i systemakh optoelektroniky* (Chernivtsi: Chernivets. nats. un-t im. Yu. Fedkovycha: 2019).
18. V.P. Makhniy, T.M. Mazur, M.M. Berezovsky, O.V. Kinzerska, V.V. Prokopiv, *Phys. Chem. Solid State* **19** No 4, 313 (2018).
19. O. Oda, *Compound Semiconductor Bulk Materialsand Characterization* (London: World Scientific Publishing Co. Pte. Ltd.: 2007).
20. A.V. Savytskyi, V.R. Burachek, *Fotoprovidnist napivprovidnykiv: Navchalnyi posibnyk* (Chernivtsi: Ruta: 2002).

Фотодетектори на основі *CdTe:Li*

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Встановлено оптимальні режими легування CdTe домішкою Li. Виготовлено фотодетектори на основі поверхнево-бар'єрних діодів Au-CdTe:Li. Досліджено оптичні параметри і фотоелектричні характеристики гетероструктур, визначено область їх фоточутливості 1,4÷5,0 еВ і механізми її формування при міжзонних переходах та через локальні центри Li_{Cd}. Отримано структури Au-CdTe:Li з великою фоточутливістю внаслідок високого потенціального бар'єру φ_0, що формується на модифікованій поверхні CdTe. Висока квантова ефективність η = 12 % CdTe:Li обумовлює отримання фотодетекторів з типовими значеннями напруги холостого ходу V_{oc} і струму короткого замикання I_{sc}, які складають 0,7 В і 10 мА/см^2 за умов сонячного освітлення AM2. Їх коефіцієнт корисної дії може бути 10 %. Температурний коефіцієнт зміни к.к.д. фотоелементів на основі CdTe практично в чотири рази менший за кремнієві. Отримано високу квантову ефективність η = 12 % випромінювання у крайовій області. Запропонований підхід до модифікації поверхні CdTe та легування Li дозволяє суттєво підвищити фоточутливість структур і відкриває нові можливості для розробки високочутливих фотодетекторів для різних діапазонів спектра.

Ключові слова: Телурид кадмію, Домішка Li, Фоточутливі гетероструктури, Висока квантова інтенсивність, Центри Li_{Cd}, Міжзонні переходи.