Journal of Nano- and Electronic Physics
Vol. **14** No 6, 06001(5pp) (2022)

Журнал нано- та електронної фізики
Том **14** № 6, 06001(5cc) (2022)

Mechanisms of Current Generation in Graphene/*p*-CdTe Schottky Diodes

I.P. Koziarskyi[1,*], M.I. Ilashchuk[1], I.G. Orletskyi[1], L.A. Myroniuk[1,2], D.V. Myroniuk[1,2], E.V. Maistruk[1],
D.P. Koziarskyi[1], V.V. Strelchuk[3]

[1] *Yuriy Fedkovych Chernivtsi National University, 2, Kotsyubynskyi St., 58002 Chernivtsi, Ukraine*
[2] *I.M. Frantsevich Institute for Problems of Materials Science, NASU, 3, Krhyzhanovsky St., 03142 Kyiv, Ukraine*
[3] *V. Lashkaryov Institute of Semiconductor Physics, NASU, 45, Nauky Ave, 03028 Kyiv, Ukraine*

(Received 03 October 2022; revised manuscript received 20 December 2022; published online 27 December 2022)

Graphene/*p*-CdTe Schottky diodes are obtained on *p*-CdTe substrates by spaying aqueous solutions of polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$), which contain particles of multilayer graphene mechanically exfoliated from graphite. The diode properties of the obtained graphene/*p*-CdTe surface barrier structures are determined by the energy barrier $q\varphi_k = 0.8$ eV, which is formed in the near-contact region of *p*-CdTe. The temperature dependence of the *I-V*-characteristics is analyzed and the dynamics of change in the barrier height with temperature and the main mechanisms of current generation in the studied diodes under forward and reverse voltages are established. In the region of forward biases at $V < 0.2$ V and reverse biases at $-0.5\text{ V} < V$, recombination-generation currents flow through the diode. The reverse current is due to the generation processes, and the forward current is due to recombination in *p*-CdTe charge carrier depleted region. At higher, both forward and reverse voltages, current formation is dominated by the tunneling of charge carriers through the potential barrier of the electrical junction.

Keywords: Graphene, Schottky Diode, CdTe, Mechanisms of current generation.

DOI: 10.21272/jnep.14(6).06001 PACS numbers: 73.61.Le, 81.15.Lm

1. INTRODUCTION

Graphene is a two-dimensional material that has unique electrical and optical properties. The quality of graphene for the phenomenon of charge transfer is determined by such a parameter as the mobility of charge carriers. Since electron-phonon scattering in graphene is much weaker, the value of mobility can reach $2\cdot10^5\ \text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ at room temperature [1]. The light transmission coefficient for graphene in the visible region of the optical range does not depend on the wavelength and is equal to $T \approx 0.977$ [2]. At the same time, the transparency of graphene remains quite high when the number of layers increases: graphene layers corresponding to a thickness of 1 µm have a transparency of approximately 70 % [3]. In addition, the reflectivity of graphene R is very low: $R = 1.3\cdot10^{-4}$, although this value slightly increases to 2 % for 10 layers [3]. The specified parameters make it possible to obtain graphene films on silicon substrates with high transmittance values and fairly low values of surface resistance, which for films obtained under different technological conditions varied within $T = 90\text{-}97.4$ % and $R_S \sim 30\text{-}120\ \Omega\cdot\text{sq}^{-1}$ [4]. The given electrical and optical parameters of graphene films are one of the reasons for their use as transparent frontal contacts in organic [5], hybrid organic-inorganic perovskite [6, 7] and silicon [8] solar cells.

The paper investigates the electrical properties of graphene/*p*-CdTe surface barrier structures obtained by applying multilayer graphene by the method of mechanical exfoliation of graphite in an aqueous solution of polyvinylpyrrolidone (PVP) on freshly cleavage crystalline cadmium telluride plates.

2. METHODOLOGY OF THE EXPERIMENT

Cadmium telluride substrates grown by the vertical Bridgman method were used for the manufacture of graphene/*p*-CdTe Schottky diodes. Their specific electrical conductivity was $\sigma = 3\cdot10^{-3}\ \Omega^{-1}\cdot\text{cm}^{-1}$, the concentration and mobility of holes were $p = 3.5\cdot10^{14}\ \text{cm}^{-3}$ and $\mu_H = 56.0\ \text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ (at $T = 301$ K), respectively. To obtain graphene layers on the surface of the substrate, the method of mechanical exfoliation of graphite in organic solvents using a kitchen blender was used. Powdered casting graphite (GL-1) and an aqueous solution of PVP $(C_6H_9NO)_n$ were used to form a dispersed mixture. The exfoliation process of graphite to graphene occurred as a result of the dynamics of the dispersed graphite mixture under the influence of a mechanical blender. Further separation of the liquid and solid fractions of the mixture was carried out using a centrifuge. The resulting precipitate was diluted with ethyl alcohol and applied to the cleaned substrates using a pneumatic atomizer. The complete removal of volatile components of the solution from the deposited films occurred at a substrate temperature not higher than $T_S = 523$ K. This ensured the stability of the electrical parameters of the base material in the process of manufacturing structures. The formation of graphene layers by the indicated method was confirmed by the results of Raman scattering spectra studies using a Jobin Yvon t64000 Raman spectrometer under excitation by unpolarized light with a wavelength of 514.5 nm.

The problem of obtaining ohmic contacts to *p*-CdTe substrates [9] was solved by creating a p^+-region in the near-surface layer. For this, their surface was pretreated with a ruby laser (wavelength $\lambda = 0.694$ µm, photon energy $h\nu = 1.79$ eV). High-power laser radiation with

---

[*] i.koziarskyi@chnu.edu.ua

photon energy greater than the band gap of CdTe ($h\nu > E_g = 1.5$ eV) leads to melting, recrystallization, and evaporation of surface components. At the same time, it is enriched with its own point defects of the acceptor type, cadmium vacancies (V_{Cd}), which causes the formation of the p^+-region. Further formation of the ohmic contact occurred by deposition of gold and copper from aqueous solutions of their salts. The contact to the graphene layers was formed using a silver-based conductive paste.

The *I-V*-characteristics of the investigated graphene/*p*-CdTe Schottky diodes were measured using a hardware-software complex implemented on the basis of the Arduino platform, an Agilent 34410A digital multimeter and a Siglent SPD3303X programmable power source, which were controlled by a personal computer using software created by the authors in the LabView environment.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Graphene is characterized by one sharp and symmetrical peak of the 2D band in the Raman scattering spectra. Since graphite consists of several graphene monolayers, the 2D band observed in its spectrum is wider and more asymmetric compared to the 2D band in the graphene spectrum [10]. This indicates the presence of several components from several phonon modes, as can be seen from the comparison of the spectra shown in Fig. 1. Some observed asymmetry of the 2D band in the graphene spectrum indicates its multilayered nature. Raman scattering spectra of the casting graphite GL-1 and obtained few-layer graphene (FLG) are presented in Fig. 1.

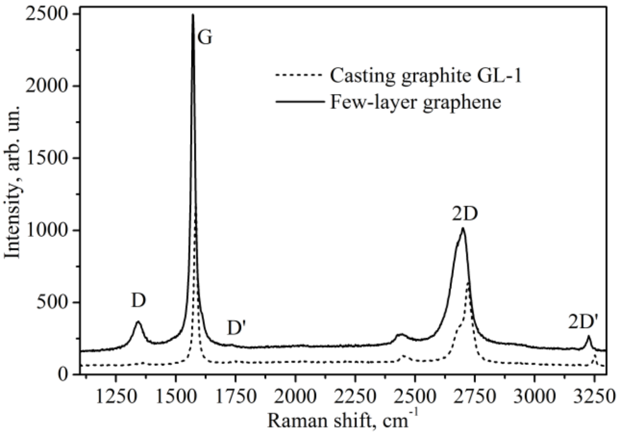

Fig. 1 – Raman spectra of casting graphite and FLG

The *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes measured in the temperature range $T = 301$-340 K are shown in Fig. 2. Current rectification ratio in the manufactured structures at $T = 301$ K and voltages $|V| = 1$ V was $\sim 10^2$. The value of the voltage φ_k, at which a significant increase in the forward current occurs and which, in the first approximation, can be interpreted as the value of the built-in potential, was estimated by extrapolation of the linear sections of the *I-V*-characteristics at a forward bias to the voltage axis (at $T = 301$ K, the value of $\varphi_k = 0.75$ V).

Determined from the temperature dependence of the potential barrier height $q\varphi_k$, the temperature coefficient of its change was $d(q\varphi_k)/dT = -2.6 \cdot 10^{-3}$ eV/K (Fig. 2, inset *a*), which correlates well with the results obtained for barrier structures based on CdTe and solid solutions based on it $Cd_{1-x}Zn_xTe$ [11, 12].

The value of the series resistance of the structure ($R_S \approx 1.4 \cdot 10^2$ Ω) correlates well with the resistance of the CdTe base material, taking into account the geometric dimensions of the substrates. The almost absent temperature dependence of R_S is explained by the presence in the temperature range of measurements of the depletion region of the shallow acceptor level E_V of $+ 0.05$ eV. It determines the equilibrium conductivity of low-impedance undoped *p*-CdTe obtained under the specified technological conditions [13]. It is known that this energy level corresponds to a singly charged vacancy of cadmium V_{Cd}^{-1} or a complex with its participation [13].

The mechanisms of the carrying of charge carriers through the potential barrier in the region of forward biases were determined based on the analysis of the forward branches of the *I-V*-characteristics plotted on a semi-logarithmic scale (Fig. 3).

In the area of small currents at $3kT < V < 0.2$ V, the diode coefficient A is 2.6. Therefore, in the first approximation, at the indicated voltages, the forward branches of the *I-V*-characteristics of graphene/*p*-CdTe diodes are described by the expression for the recombination current [14]:

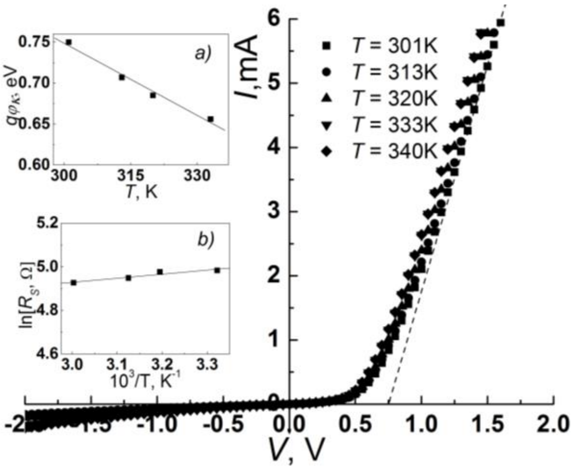

Fig. 2 – *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes in the temperature range $T = 301$-340 K. The inset shows temperature dependences of the potential barrier height $q\varphi_k$ (*a*) and series resistance of the structure R_S (*b*)

$$j = \frac{qn_i d}{\tau}\left(e^{\frac{qV}{2kT}} - 1\right) = \frac{n_i}{\tau}\sqrt{\frac{2q}{N_A}(\phi_k - V)}\left(e^{\frac{qV}{2kT}} - 1\right), \qquad (1)$$

where n_i is the value of the intrinsic concentration of charge carriers in *p*-CdTe, d is the depleted region thickness in *p*-CdTe, τ is the lifetime of charge carriers in this region, N_A is the concentration of acceptors. At the same time, recombination of charge carriers occurs in the *p*-CdTe depleted region through deep levels that are incompletely filled with electrons, since the Fermi level in this region at low forward voltages is located near the middle of the band gap of the semiconductor.

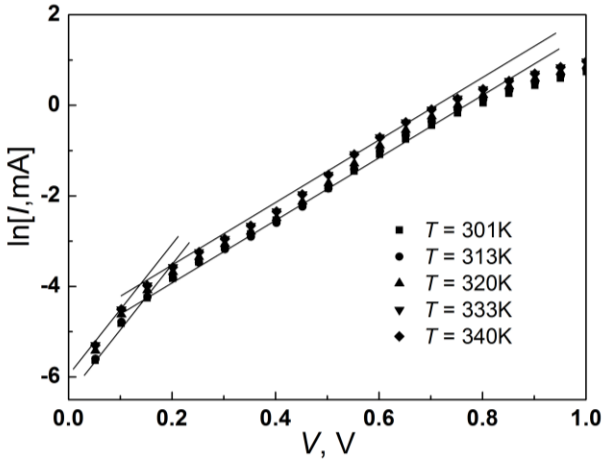

Fig. 3 – Forward branches of the *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes in a semi-logarithmic scale (T = 301-340 K)

At forward voltages of $0.2\text{ V} < V < 0.8\text{ V}$, the diode coefficient $A \approx 5.6$. Its value, as well as the observed absence of the temperature dependence of the tangent of the angle of inclination $\ln I = f(V)$ indicates the tunneling mechanism of the forward current, which for sharp surface-barrier structures is determined by the expression [15]:

$$I(V) = BN_t\exp[-\alpha(\varphi_k - V)], \tag{2}$$

where B is a constant, N_t is the concentration of traps in the band gap, a is a value that depends on the effective mass of electrons in the band gap, the dielectric constant, the equilibrium concentration of carriers, and the shape of the barrier. The linearity of the forward branches of the *I-V*-characteristics in the coordinates $\ln I = f(\varphi_k - V)$ (Fig. 4) confirms the tunneling mechanism of the forward current.

The most probable, in this case, is tunneling of electrons from graphene to unfilled states of the valence band of CdTe with a decrease in the height and size of the potential barrier at forward bias. This is confirmed by the independence of the probability of filling the energy levels, from which tunneling occurs, on temperature, since the value $\ln[BN_t] = \ln I$ at $(\varphi_k - V) = 0$ is unchanged in the temperature range of the study (Fig. 4).

At reverse biases in the range $-0.7\text{ V} < V < -3kT/q$, the dependence of the reverse current on the voltage for graphene/*p*-CdTe Schottky diodes indicates the generation mechanism of current formation (Fig. 5) [14, 16]:

$$I = \frac{qn_i d}{\tau} = \frac{n_i}{\tau}\sqrt{\frac{2q}{N_A}\left(\phi_k - V\right)}, \tag{3}$$

where n_i is the value of the intrinsic concentration of charge carriers in *p*-CdTe, d is the thickness of the depleted region in *p*-CdTe, τ is the lifetime of charge carriers in this region, N_A is the concentration of acceptors.

I-V-characteristics in $I = f((\varphi_k - V)^{1/2})$ coordinates (Fig. 5) at reverse biases $-0.5\text{ V} < V < -3kT/q$, according to expression (3), are linear. Determined from the temperature dependence of the generation current, the ionization energy of the energy level from which charge carriers are generated is $\Delta E = 0.05$ eV (Fig. 5, inset). As already noted, this level is near the edge of the *p*-CdTe valence band. Therefore, the reverse current is formed by the transfer of the positive charge of holes generated in the *p*-CdTe depleted region into its bulk and the movement of the negative charge of electrons from the conduction zone of cadmium telluride to the conduction zone of graphene.

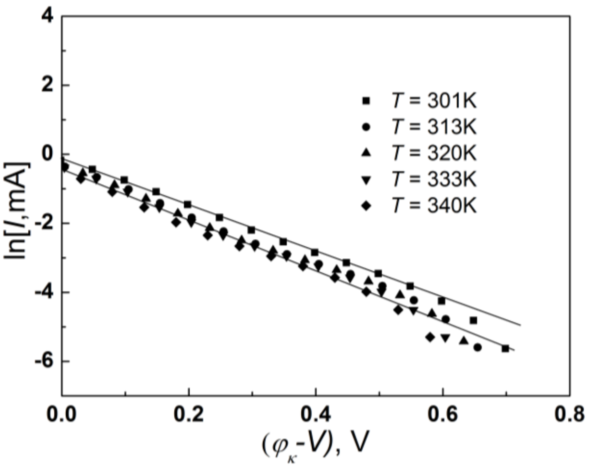

Fig. 4 – Forward branches of the *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes in $\ln I = f(\varphi_k - V)$ coordinates in the temperature range T = 301-340 K

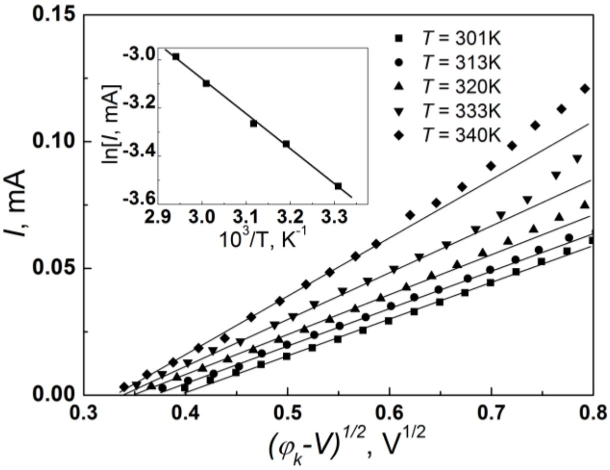

Fig. 5 – Linear dependence of the reverse *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes for generation current at voltages $-0.5\text{ V} < V < -3kT/q$. The inset shows the temperature dependence of the generation current at a constant value of the reverse voltage

At reverse voltages $V_r > 0.5$ V, the *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes are described by the expression for the tunneling current [15]:

$$I^t_{rev} = a_0\exp\left(-b_0\left(\phi_k - V\right)^{-1/2}\right), \tag{4}$$

where a_0 is a parameter that depends on the probability of filling the energy levels from which electrons are tunneled, b_0 is determined by the dynamics of current change on voltage. According to (4), the *I-V*-characteristics of graphene/*p*-CdTe Schottky diodes in coordinates $\ln I^t_{rev} = f((\varphi_k - V)^{-1/2})$ are linear (Fig. 6).

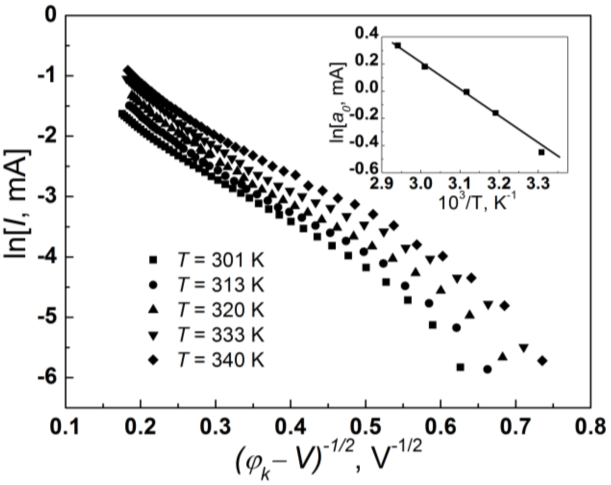

Fig. 6 – Linear dependence of the reverse *I*-*V*-characteristics of graphene/*p*-CdTe Schottky diodes for the tunneling current at voltages $V_r > 0.5$ V. The inset shows the temperature dependence of parameter a_0

The value of the parameter a_0 is determined by extrapolation of the linear sections of the dependence $\ln I = f(\varphi_k - V)^{-1/2}$ constructed at different temperatures to the ordinate axis. The value of the ΔE determined from the temperature dependence $\lg a_0 = f(10^3/T)$, which is approximated in the specified coordinates by a straight line (Fig. 6, inset), was $\Delta E = 0.17$ eV. Taking into account the shift of the Fermi levels at reverse biases both in *p*-CdTe and in graphene, it can be assumed that electron tunneling occurs from the acceptor level E_V of + 0.17 eV, which is located in the band gap of *p*-CdTe, into the conduction band of graphene. It should be noted that the found level is manifested in cadmium telluride crystals with hole conductivity and corresponds to a complex defect – $(V_{Cd}{}^{-2}D^{+})^{-1}$ [13].

4. CONCLUSIONS

Graphene/*p*-CdTe surface-barrier structures with a current rectification ratio of ~ 10^2 were fabricated by mechanical exfoliation of graphite with the formation of FLG in a PVP aqueous solution. The height of the potential barrier, which determines the rectifying properties of the studied diodes, was 0.8 eV. The formation of graphene layers on the surface of *p*-CdTe substrates by this method is confirmed by the presence of an intense asymmetric 2D band in the Raman scattering spectra of graphene.

In the regions of forward (up to 0.2 V) and reverse (up to 0.5 V) biases, the current transfer mechanism is determined by recombination-generation processes in the region of *p*-CdTe depleted of majority charge carriers. With an increase in voltage in the formation of both forward and reverse currents, the tunneling of charge carriers through the potential barrier prevails.

REFERENCES

1. S.V. Morozov, K.S. Novoselov, M.I. Katsnelson, F. Schedin, D.C. Elias, J.A. Jaszczak, A.K. Geim, *Phys. Rev. Lett.* **100**, 016602 (2008).
2. M.I. Katsnelson, *Mater. Today* **10**, 20 (2007).
3. A.D. Bartolomeo, *Phys. Rep.* **606**, 1 (2016).
4. S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H.R. Kim, Y. Song, Y.-J. Kim, K.S. Kim, B. Ozyilmaz, J.H. Ahn, B.H. Hong, S. Iijima, *Nat. Nanotechnol.* **5**, 574 (2010).
5. Y. Wang, X. Chen, Y. Zhong, F. Zhu, K.P. Loh, *Appl. Phys. Lett.* **95**, 063302 (2009).
6. L. Fagiolari, F. Bella, *Energ. Environ. Sci.* **12**, 3437 (2019).
7. L. Zhang, T. Liu, L. Liu, M. Hu, Y. Yang, A. Mei, H. Han, *J. Mater. Chem. A* 3, 9165 (2015).
8. S. Tongay, T. Schumann, X. Miao, B.R. Appleton, A.F. Hebard, *Carbon* **49**, 2033 (2011).
9. A. Niemegeers, M. Burgelman, *J. Appl. Phys.* **81**, 2881 (1997).
10. E.Y. Polyakova (Stolyarova), K.T. Rim, D. Eom, K. Douglass, R.L. Opila, T.F. Heinz, A.V. Teplyakov, G.W. Flynn, *ACS Nano* **5**, 6102 (2011).
11. E.V. Maistruk, I.G. Orletsky, M.I. Ilashchuk, I.P. Koziarskyi, D.P. Koziarskyi, P.D. Marianchuk, O.A. Parfenyuk, *Semicond. Sci. Tech.* **34**, 045016 (2019).
12. I.P. Koziarskyi, E.V. Maistruk, I.G. Orletskyi, M.I. Ilashchuk, D.P. Koziarskyi, P.D. Maryanchuk, M.M. Solovan, K.S. Ulyanytskiy, *Semicond. Sci. Tech.* **35**, 025018 (2020).
13. K.R. Zanio, *Semiconductors and Semimetals. Volume 13: Cadmium Telluride* (NY: San Francisko, Acad. Press.: 1978).
14. S.M. Sze, K.N. Kwok, *Physics of Semiconductor Devices* (NY: Core Publ., John Wiley & Sons, Inc.: 2006).
15. B.L. Sharma, R.K. Purohit, *Semiconductor Heterojunctions* (Pergamon Press: 1974).
16. I.G. Orletskyi, M.I. Ilashchuk, M.M. Solovan, P.D. Maryanchuk, E.V. Maistruk, G.O. Andrushchak, *Mater. Res. Express* **6**, 086219 (2019).

Механізми генерації струму в діодах Шотткі графен/*p*-CdTe

І.П. Козярський[1], М.І. Ілащук[1], І.Г. Орлецький[1], Л.А. Миронюк[1,2], Д.В. Миронюк[1,2], Е.В. Майструк[1], Д.П. Козярський[1], В.В. Стрельчук[3]

[1] *Чернівецький національний університет імені Юрія Федьковича, вул. Коцюбинського, 2, 58002 Чернівці, Україна*
[2] *Інститут проблем матеріалознавства імені І.М. Францевича НАН України, вул. Кржижановського, 3, 03142 Київ, Україна*
[3] *Інститут фізики напівпровідників імені В.Є. Лашкарьова НАН України, пр. Науки, 45, 03028 Київ, Україна*

Діоди Шотткі графен/*p*-CdTe були отримані на підкладках *p*-CdTe розпиленням водних розчинів полівінілпіролідону (PVP, $(C_6H_9NO)_n$), які містять частинки багатошарового графену, механічно відлущені з графіту. Діодні властивості отриманих поверхневих бар'єрних структур графен/*p*-CdTe визначалися енергетичним бар'єром $q\varphi_k = 0,8$ еВ, який формується в приконтактній області *p*-CdTe. Проаналізовано температурну залежність ВАХ та встановлено динаміку зміни висоти бар'єру з температурою та основні механізми генерації струму в досліджуваних діодах під дією прямої та зворотної напруг. В області прямого зміщення при $V < 0,2$ В і зворотного зміщення при $-0,5$ В $< V$ через діод протікають рекомбінаційно-генераційні струми. Зворотний струм зумовлений процесами генерації, а прямий – рекомбінації в збідненій на основні носії заряду області *p*-CdTe. При вищих, як прямих, так і зворотних напругах, формування струму відбувається за рахунок тунелювання носіїв заряду через потенціальний бар'єр електричного переходу.

Ключові слова: Графен, Діод Шотткі, CdTe, Механізми генерації струму.