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Radiation resistance of $Hg_3In_2Te_6$ near-infrared photodiodes

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ABSTRACT

The design and technology for manufacturing of photodiodes with a potential barrier created by a Schottky contact on a substrate of radiation-resistant *n*-$Hg_3In_2Te_6$ single crystal are presented. The photosensitivity of the photodetector covers the wavelength range λ≈0.6-1.6 μm at the maximum current monochromatic sensitivity S_λ≈1.15 A/wt for λ_{max}≈1.55 μm. To study the effect of the contact material on the effect of the absorbed dose of ionizing radiation, two types of photodetectors Ni/n-$Hg_3In_2Te_6$/In and Cr/n-Hg3In2Te6/Cr were fabricated. A study of the effect of absorbed doses of ionizing radiation $D_{\gamma1}\approx10^5$, $D_{\gamma2}\approx10^6$ i $D_{\gamma3}\approx10^7$ Gray on the main parameters of photodetectors (i.e., S_λ, λ_{max}, dark currents at forward and reverse bias, open circuit voltage, and short circuit current). Photodiodes, based on mercury-indium telluride (HgInTe), showed a high resistance to ionizing radiation. The best resistance to ionizing radiation was shown by Cr/HgInTe/Cr photodiodes, which slightly changed their basic parameters at the absorbed dose of $D_{\gamma3}\approx10^7$ Gray. The Ni/HgInTe/In photodetectors lost their function after exposure to an absorbed dose of $D_{\gamma3}\approx10^7$ Gray. In Ni/HgInTe/In photodetectors the absorbed dose of $D_{\gamma3}\approx10^7$ Gray practically destroyed the indium contact. 30-50 % of the nickel front contact was also destroyed. For comparison, similar studies were performed with photodetectors based on cadmium telluride Cr/CdTe/In prepared by the authors as well as silicon. The silicon-based photodetectors used in this study were provided by industrial sources.

Key words: photodetector with potential Schottky barrier, radiation resistance, $Hg_3In_2Te_6$, Cr.

1. INTRODUCTION

An important disadvantage of classical Ge, Si, InGaAs, GaInAsP photodiodes with a potential barrier (based on p-n junctions, Schottky-type barriers or heterostructures) is the low level of radiation resistance [1]. The problem of radiation resistance is quite acute for solar cells used on board spacecraft. Under the influence of high-energy particle irradiation, the power of solar cells decreases due to the formation of defects in the semiconductors. When the semiconductor photodiodes are exposed to ionizing X-ray/γ-neutron radiation with energies of 0.01-10 MeV, a large number of radiation defects are formed, which are effective recombination centers. Under the influence of neutrons, whole clusters of radiation defects with a characteristic size of 30-100 nm are formed. Due to the presence of such large traps, the recombination rate increases significantly.

At exposure levels when other semiconductor devices (diodes and transistors) can still function, many types of photodiodes are already destroyed, which complicates the design of radiation-resistant fiber-optic systems for signal transmission and conversion. It is important to note that the process of increasing the recombination rate of charge carriers and reducing the photosensitivity of photodiodes does not depend on the doping profiles, the area of the p-n junctions used in photodiodes, or many other design features of standard photodiodes. Due to the high penetration of neutron radiation (up to 10 cm and more), photodetectors cannot be protected by simple housings and/or screens with acceptable characteristics - mass and dimensions. Typical levels of dose for stable operation of commercial silicon photodiodes are in the range of $5\times(10^1\text{-}10^3)$ Gray, depending on the application of the silicon devices. In this regard, the development of radiation-hardened designs for photodiodes has become relevant, in which the use of special semiconductor materials and the use of radiation-resistant materials can be used as barrier frontal and ohmic contacts to significantly increase their radiation resistance. It should be noted that the lethal dose for humans is about 6 Gray (≈600 Rad). In the case of optical systems operating under conditions of high radiation, it is optimal to use photodetectors based on $Hg_3In_2Te_6$ crystals [2]. On the one hand, this is due to the fact that this semiconductor is characterized by photosensitivity in the spectral range of 0.5-1.6 μm [3, 4], on the other - its increased radiation resistance to ionizing radiation [5, 6] is due to the presence of its crystal structure and concentration of electrically neutral cationic vacancies [7].

In addition, the spectral operating range of photodetectors, based on $Hg_3In_2Te_6$ crystals, is in the region of transparency of quartz fiberglass, with a maximum in the region of the best transparency of quartz λ≈1.5-1.55 μm [8]. As shown in [9, 10], in terms of optical, electrical, chemical and adhesive properties, and most importantly radiation resistance, the optimal metal for rectifier and ohmic contacts is a layer of chromium. The aim of this work is to develop and study photodetectors, based on $Hg_3In_2Te_6$, characterized by high radiation resistance, in which the barrier and ohmic contacts are Cr layers. We compare their radiation resistance with photodetectors, in which a layer of nickel was used as a barrier contact, and an ohmic layer was prepared using indium.

2. EXPERIMENTAL

We studied the effects of the absorbed dose of ionizing radiation on two types of photodetectors based on single crystals of *n*-$Hg_3In_2Te_6$ with a resistivity $\rho \approx 5\times10^3$-10^4 Ω·cm: Ni/n-InHgTe/In and Cr/n-HgInTe/Cr: Ni/n-HgInTe/In and Cr/n-HgInTe/Cr. All crystals were grown at Chernivtsi National University by a modified method of zone recrystallization [11, 12]. Radiation-resistant single crystals, obtained by this method, are characterized by improved homogeneity of electro-physical parameters over the whole volume of the single crystal. Plates with a size of 4×4×0.5 mm^3 were cut with a saw. After high-quality mechanical grinding and polishing, the samples were etched in a solution of bromine in methanol (1 %) for 60 seconds and then washed in methanol. After such treatment, the size of the plates of single crystals were equal to 4×4×0.4 mm^3. The prepared single crystals were annealed for 12 hours in mercury vapor at a temperature t ≈240-250 °C.

Next, the frontal contact surface was protected by a chemically stable substance and etched in a 5 % solution of bromine in methanol for 60 seconds and washed in methanol. After removing the protective coating, the single crystals were etched in a 1 % solution of bromine in methanol for 10-15 seconds and then washed in methanol. Ohmic contact was applied to the entire surface of the crystal by thermal spraying of indium or chromium in a vacuum (10^{-5} Torr) at a temperature of t≈120-130 °C. The thickness of the metal film was d≈0.1-0.12 μm. Similarly, the front translucent contact was applied by spraying nickel and chromium through a molybdenum mask 3×3 mm^2 at 100-120 °C; the metal film thickness was d≈0.012-0.015 μm. The thickness of the Cr or Ni layer was determined not only by the maximum optical transmission, but also for good conductivity [13]. Before applying the metals for both ohmic and rectifying contacts, the surface of the single crystal was treated in an argon plasma. For ohmic contacts the treatment continued 10-15 minutes (200-250 V, 40-50 mA) and for rectifier ones - 5-10 minutes (350-400 V, 10-15 mA).

Such technological techniques, as shown by the AFM, led to the formation on the semiconductor surface, where the rectifying contact was created on a porous near-surface layer [4]. Cr/n-CdTe/In photodetectors were created similarly, only there was no annealing in mercury vapor. Thus, our technology allowed the use of the same metal (chromium) to create both ohmic and rectifying contact to n-HgInTe. That is, for one type of photodiode the rectifying contact was nickel and the ohmic contact was indium, and for the second type of photodiode both the ohmic and rectifying contacts were made using the same metal - chromium. This was done in order to improve the desired resistance of the obtained structure to the absorbed dose of ionizing radiation, because chromium is a more resistant metal to the action of ionizing radiation than indium and nickel [9, 10]. In addition, for comparison, we used an industrial silicon photodiode without a housing.

A typical spectrum of current monochromatic photosensitivity vs. the wavelength for photodetectors is shown in Fig. 1. Fig. 1 also shows the theoretical dependence $S_\lambda=0,806\cdot\eta\cdot\lambda$, where η is the efficiency of photoconversion equal to one.

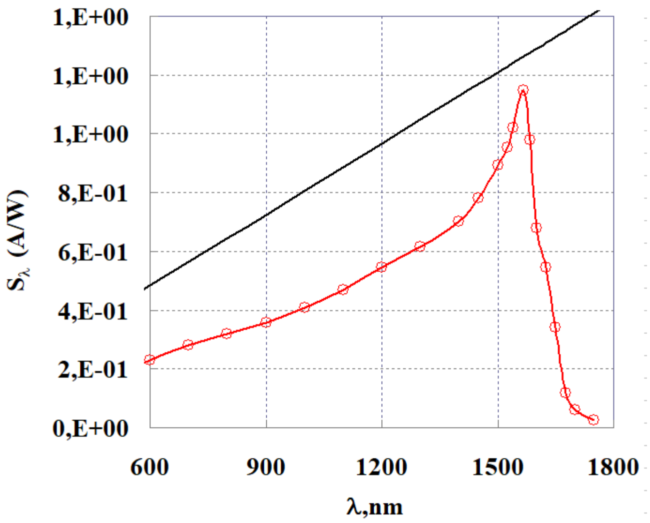

Fig. 1. Typical current spectrum of monochromatic photosensitivity vs. wavelength for photodetectors Ni/n-HgInTe/In and Cr/n-HgInTe/Cr. The solid line is the theoretical dependence of S_λ (293 K).

3. CONTROL OF THE PHOTODETECTOR PARAMETERS AND CHARACTERISTICS BEFORE AND AFTER IRRADIATION

The effect of ionizing radiation on semiconductor crystals and devices, such as semiconductor photodiodes, leads to a change (deterioration) of their important parameters and characteristics. The band gap of the semiconductor changes, which leads to a change in the current monochromatic sensitivity of the photodiode S_λ and the maximum. The resistivity also changes and the voltage drop increases when the photodiode is switched on directly. New energy levels are formed in the band gap of the semiconductor, and the dark current rises at a fixed reverse voltage. All these factors change the I-V curves. Therefore, for control measurements to study the effect of ionizing radiation, the following important parameters of photodiodes were selected: short-circuit current, open-circuit voltage, current monochromatic sensitivity at maximum - S_λ, and dark voltage at a fixed direct current.

Prior to the tests, the main parameters and characteristics of the photodetector were measured by the action of a relatively low level of ionizing radiation: open circuit voltage, short-circuit current, and current monochromatic sensitivity - S_λ at the maximum photosensitivity (λ = 1.55 μm). A certified germanium photodiode was used to measure S_λ. I–V curves were also measured both in forward and inverse bias directions. The photoelectromotive force was measured by the compensation method. The control of photodiode parameters during the action of ionizing radiation was not performed.

4. THE INFLUENCE OF IONIZING RADIATION ON THE BASIC PARAMETERS OF HgInTe PHOTODIODES

The irradiation of photodiodes was carried out using a gamma installation MPX-25M under atmospheric conditions in air at 300 K. The energy of the gamma rays was $E_\gamma \approx$ 1.2 MeV (^{60}Co). The irradiation dose rate of photodiodes was $N_\gamma \approx$ 0.06 Gy×s^{-1}. Irradiation was performed in three stages, which differed in the absorbed doses of ionizing radiation. At the first stage the absorbed dose of ionizing radiation was $D_{\gamma 1} \approx 10^5$, at the second stage - $D_{\gamma 2} \approx 10^6$ and at the third stage - $D_{\gamma 3} \approx 10^7$ Gray. It should be noted that at each stage, we used fresh, non-irradiated samples. Since after the first stage of studies ($D_{\gamma 1} \approx 10^5$ Gray) silicon photodiodes lost their efficiency, their I–V characteristics and other parameters are not given here.

Fig. 2 shows the I–V curves of the Cr/n-CdTe/In photodetector before and after the absorbed dose of ionizing radiation $D_{\gamma 1} \approx 10^5$ Gray.

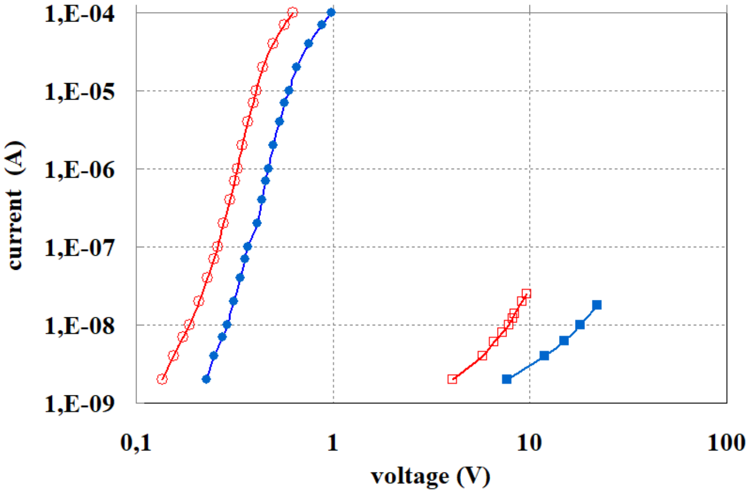

Fig. 2. I-V curves of the Cr/n-CdTe/In photodiode before the action of ionizing radiation - unfilled circles (direct forward bias) and squares (reverse bias), and after the action of ionizing radiation - filled circles (direct bias) and filled squares (inverse bias), respectively. Absorbed dose is $D_{\gamma 1} \approx 10^5$ Gray.

Visually, on the surface of silicon photodiodes, damage of both rectifying and ohmic contacts was observed, as well as changes in the state of the surface, where one can observe a noticeable matte sheen. No changes in the parameters of the Ni/n-HgInTe/In and Cr/n-HgInTe/Cr structures within the measurement error were observed. For Cr/n-CdTe/In, the change in the main parameters predictably affected the change in the magnitude of the direct voltage drop at a fixed current (e.g., at a direct current of 100 μA, the voltage drop increased from 0.7 to 1.0 V). On the other hand, at a fixed direct voltage of 0.7 V the direct dark current decreased ~10 times. This is obviously due to the fact that not only the electro-physical properties of the crystal volume have changed significantly, but also the properties of the barrier region (i.e., the space charge region).

The open circuit voltage decreased by approximately 25-30 % from 0.5 to 0.37 V, indicating a decrease in the height of the potential barrier. On the other hand, the dark current decreased significantly under reverse bias, approximately 10 times at 10 V. The decrease in dark current cannot be considered an improvement of the parameter, because the short-circuit current significantly decreased (approximately twice). The current monochromatic sensitivity S_λ for λ = 1.06 μm decreased from $S_\lambda \approx 0.95$ to $S_\lambda \approx 0.45$ A/wt, which may indicate a change in the band gap of the crystal. After the action of the absorbed dose of $D_{\gamma 2} \approx 10^6$ Gray, Cr/n-CdTe/In photodetectors completely lost their efficiency. Instead, the photodetectors Ni/n-HgInTe/In and Cr/n-HgInTe/Cr did not change their basic parameters. For the absorbed dose $D_{\gamma 2} \approx 10^6$ Gray, as can be seen from Fig. 2, the changes in the I–V curves are not significant and are almost within the measurement error. Other important parameters did not change within the error (i.e., open circuit voltage, short-circuit current and current monochromatic sensitivity at maximum). This also applies to the photodetector Cr/n-HgInTe/Cr, therefore we do not show the I – V curves for this structure.

In Fig. 3 we present the I–V curves after exposure to the absorbed dose $D_{\gamma 2} \approx 10^6$ Gray for only Ni/n-HgInTe/In.

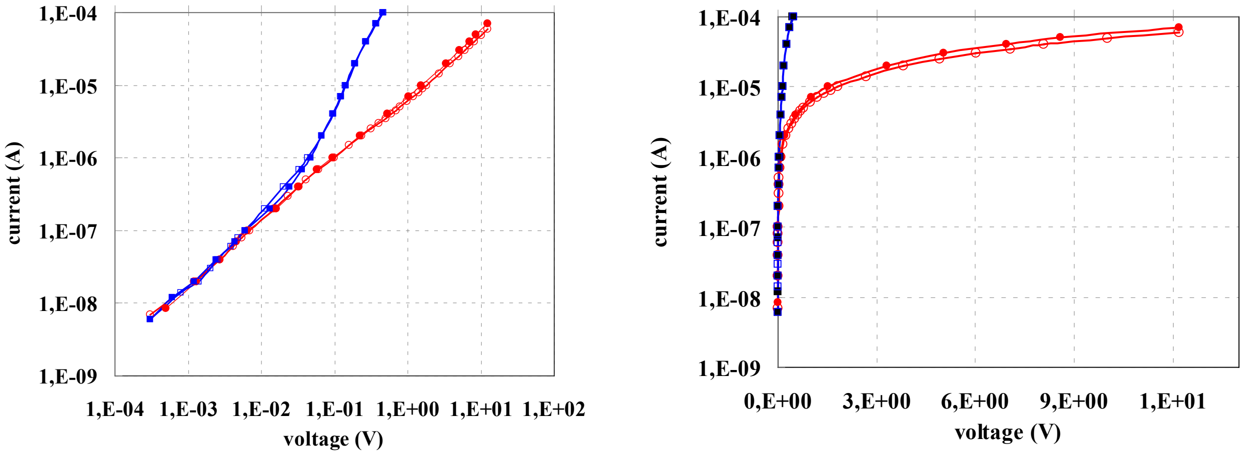

Fig. 3. I-V curves of the Ni/n-HgInTe/In photodiode before irradiation (unfilled circles, direct bias) and squares (reverse bias) and after irradiation (filled circles, direct bias) and squares (reverse bias), respectively. On the left - double logarithmic scale, on the right - semi-logarithmic. Absorbed dose was $D_{\gamma 2} \approx 10^6$ Gray.

For greater clarity Fig. 4 shows the initial part of the Ni/n-HgInTe/In I-V curves before and after the action of the absorbed dose $D_{\gamma 2} \approx 10^6$ Gray.

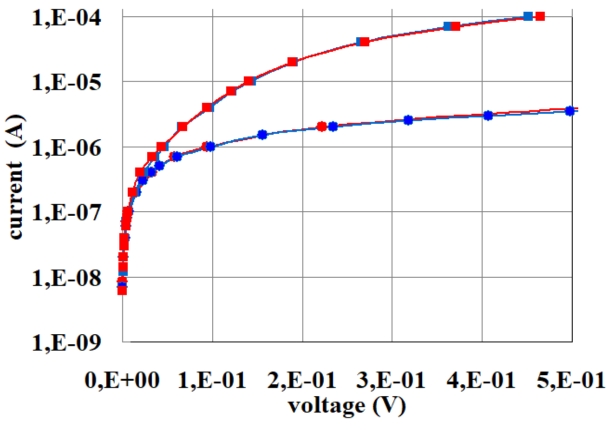

Fig. 4. Initial section of the I–V curves of the Ni/n-HgInTe/In photodetector before and after the action of the absorbed dose of ionizing radiation $D_{\gamma 2} \approx 10^6$ Gray.

I–V curves for the Ni/n-HgInTe/In structure at the absorbed dose $D_{\gamma 3} \approx 10^7$ Gray are not shown, because after the irradiation destruction of metal contacts was observed, especially for the indium contact. The indium contact lost strength, became loose, powdery and somewhat "crumbled" with little mechanical action. A reduction of integrity for the nickel contact was also observed, which manifested itself in spontaneous detachment of approximately 30-50 % of the contact area. It is clear that the measurements of the I–V curves for this case were impossible. After the action of the absorbed dose of ionizing radiation $D_{\gamma 3} \approx 10^7$ Gray, the photodetector Ni/n-HgInTe/In practically lost its functionality. Visual inspection showed the catastrophic change in the parameters of the photodetector after irradiation was associated primarily with the amorphization of the lower ohmic indium contact and its complete destruction [19]. The nickel contact was partially destroyed (by 30-50)%). Amorphization of the metal due to the action of irradiation leads to a deterioration of adhesion, and, as a consequence, to the destruction of electrical contacts between the single-crystal substrate $Hg_3In_2Te_6$ and these layers of metal. The photodetector Cr/n-HgInTe/Cr after the action of the absorbed dose $D_{\gamma 3} \approx 10^7$ Gray did not lose efficiency. More importantly, the basic parameters and characteristics were not changed. Fig. 4 shows the I–V curves of the photodetector Cr/n-HgInTe/Cr after the action of the absorbed dose $D_{\gamma 3} \approx 10^7$ Gray. For clarity, the I–V curves are shown in double logarithmic and semi-logarithmic coordinates.

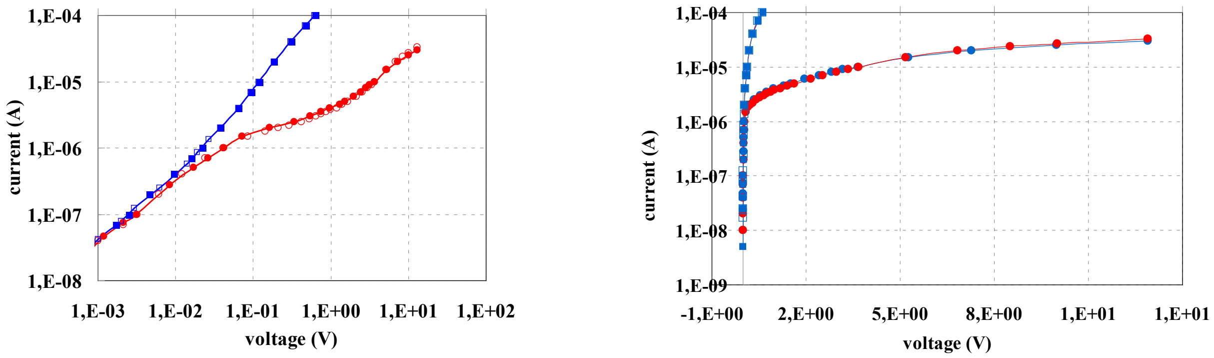

Fig. 5. I–V curves of the Cr/n-HgInTe/Cr photodiode before the action of ionizing radiation - unfilled circles (direct bias) and squares (reverse bias) and after the irradiation - unfilled circles, direct bias, and squares - inverse bias, respectively. On the left - double logarithmic coordinates, on the right - in semi-logarithmic. Absorbed dose was $D_{\gamma 3} \approx 10^7$ Gray.

For clarity Fig. 6 it shows the initial section of the I–V curves before and after the action of the absorbed dose $D_{\gamma 3} \approx 10^7$ Gray.

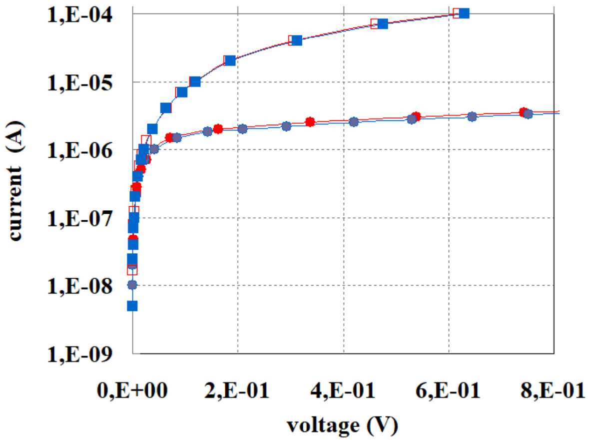

Fig. 6. The initial section of the I–V curves of the Cr/n-HgInTe/Cr photodetector, blank circles (forward offset) and squares (reverse offset); after the action of ionizing radiation - unfilled circles (direct bias) and squares (reverse bias), respectively.

As we see from Figs. 5-6, after the action of the ionizing radiation for the absorbed dose of $D_{\gamma 3} \approx 10^7$ Gray, the changes in the I–V curves of the Cr/n-HgInTe/Cr photodetector are insignificant. The I–V curves under direct bias practically did not change within the measurement error. Under reverse bias there is a slight, within ≈5 %, increase in the dark current. With regard to the photoelectric parameters, we recorded a decrease of approximately 7 % percent for the short-circuit current and current monochromatic sensitivity - S_λ. The open circuit voltage decreased by approximately 10 %. Upon visual inspection of the contacts, we noticed a slight darkening of the chrome contacts, but no loss of mechanical integrity was observed.

The results of the studies confirmed the high radiation resistance of *n*-$Hg_3In_2Te_6$ crystals. According to the results of the tests, it is clear what changes need to be made in the design of photodetectors based on *n*-$Hg_3In_2Te_6$, in particular, what material should be used for rectifying and ohmic contacts to create structures with greater radiation resistance. It should be noted that an important factor is the developed technology for creating photodiodes with a porous near-surface layer, which makes it possible to use a wide range of materials to make an electrical contact. Thus, using this approach, one can design a device with the desired parameters. For example, instead of indium, which is traditionally used as an ohmic contact, one can use chromium for greater radiation resistance. Since $Hg_3In_2Te_6$ is a n-type semiconductor, for an ohmic contact it is necessary to use indium or aluminum (i.e., metals with low output work, and for a rectifying contact one can use gold, platinum, nickel as metals with high output work). Given that chromium has better radiation resistance, it is better to use chromium. But the disadvantage of chromium is that its yield is less than that of gold, platinum, nickel and more than that of indium. Therefore, in general, although it is a radiation-resistant metal, it is not ideal as a contact for n-$Hg_3In_2Te_6$ Schottky diode. However, the technology for the manufacture of photodiodes with a porous near-surface layer, developed by us, makes it possible to use almost any material to make contact without compromising the quality of the Schottky contact.

5. CONCLUSIONS

Photodiodes based on n-HgInTe showed high resistance to ionizing radiation. Moreover, among the two types of photodiodes, Ni/n-HgInTe/In and Cr/n-HgInTe/Cr, the best resistance to ionizing radiation were Cr/n-HgInTe/Cr photodiodes, which slightly changed their parameters at the absorbed dose $D_{\gamma 3} \approx 10^7$ Gray. Photodetectors based on Ni/n-HgInTe/In completely lost their ability to work after an absorbed dose of $D_{\gamma 3} \approx 10^7$ Gray due to the complete destruction of the indium contact and partial (30-50)% destruction of the nickel contact. The better stability of the Cr/n-HgInTe/Cr photodiodes is obtained due to the fact that instead of nickel and indium as rectifying and ohmic contacts, a chromium contact was used, which has greater radiation resistance. Cadmium telluride and cadmium telluride-based photodiodes showed better stability than silicon photodiodes. Although photodiodes based on CdTe significantly changed their parameters after the absorbed dose of $D_{\gamma 1} \approx 10^5$ Gray, they did not lose their efficiency, while at the same dose, silicon photodiodes are predicted to completely lose their efficiency.

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