High radiation resistant crystals for x-ray and γ-radiation detectors

Sklyarchuk, V., Fochuk, P., Bolotnikov, A., James, R., Zakharuk, Z.

V. Sklyarchuk, P. Fochuk, A. Bolotnikov, R. B. James, Z. Zakharuk, "High radiation resistant crystals for x-ray and γ-radiation detectors," Proc. SPIE 11838, Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XXIII, 1183817 (1 September 2021); doi: 10.1117/12.2594082

Event: SPIE Optical Engineering + Applications, 2021, San Diego, California, United States

High radiation resistant crystals for X-ray and γ-radiation detectors

V. Sklyarchuk[a], P. Fochuk[a], Z. Zakharuk[a], A. E. Bolotnikov[b] and R. B. James[*c]

a – Chernivtsi National University, 2, Kotsiubynskoho Str., Chernivtsi, Ukraine, 58012
b – Brookhaven National Laboratory, Upton, NY, USA, 11973
c – Savannah River Laboratory, Aiken, SC, USA

ABSTRACT

Electrophysical properties of $Hg_2MnInTe_6$ single crystals grown by the modified zone melting method were studied. To expand the band-gap, a multiple part of Hg in 3(HgTe)-In_2Te_3 was replaced by an isovalent metal with a smaller ionic radius - Mn. Single crystals had n-type conductivity and possessed a resistivity of $\rho \approx 5\times10^6$ Ω·cm (293 K), which was determined from the linear region of the current-voltage (*I-V*) characteristics for In/$Hg_2MnInTe_6$/In structure with two ohmic contacts. The product $\mu\tau \approx$ (1.7-3.4)$\times10^{-4}$ $V^{-1}cm^2$ is determined. Compensation degree (≈ 0.99) of the semiconductor material and the energy position of deep level $E_d \approx$ 0.37-0.4 eV responsible for the dark conductivity were determined from measurements of the temperature dependence of the resistivity and space-charge limited currents (SCLC). From the optical measurements, the band-gap of single crystals was determined, which is equal to E_g = 1.15 eV (293 K). Au/$Hg_2MnInTe_6$/In structures with rectifying contacts were fabricated.

Keywords: radiation-resistant single crystals, $Hg_2MnInTe_6$, compensation degree, ohmic contact, Schottky contact, SCLC.

1.INTRODUCTION

Semiconductor crystals of $A_2^3B_3^6$ group and their solid solutions are characterized by the high radiation resistance of electrical and photoelectric parameters [1-3]. The widespread use of such semiconductors as ionizing radiation detectors is hindered by the low mobility of charge carriers, for example, for In_2Te_3 crystals, this value is less than $\mu \sim 10$ $cm^2V^{-1}s^{-1}$. Significantly better values of charge carrier mobility ~ 500 cm^2/(Vs) were achieved for a solid solution of HgTe-In_2Te_3(composition 3:1). But the band-gap of 3(HgTe)-In_2Te_3 is relatively small (E_g = 0.72 eV). To expand the band-gap, a multiple part of Hg in 3(HgTe)-In_2Te_3 was replaced by an isovalent metal with a smaller ionic radius - Mn.

2.EXPERIMENTAL

$Hg_2MnInTe_6$ single crystals grown by the modified zone melting method had n-type conductivity and possessed a resistivity of $\rho \approx 5\times10^6$ Ω*cm (293 K). The resistivity was determined from the linear section of the current-voltage (*I-V*) characteristics for a structure with two ohmic contacts. To create ohmic contacts, the $Hg_2MnInTe_6$ crystals of 4×4 mm^2 size and 0.8 mm thickness after appropriate mechanical grinding and polishing were chemically etched in 1% bromine-methanol solution and then rinsed in methanol. Ohmic contacts were obtained by thermal sputtering of indium after treatment of the crystal surface in an argon plasma. Thereafter, the structure was heated in vacuum at a temperature of T ≈ 445K for several seconds. A Schottky-type rectifying contact to the $Hg_2MnInTe_6$ structure was fabricated by applying a thin semi-transparent (~ 20 nm) layer of Au. The surface was treated in an argon plasma prior to the creation of the rectifying contact. An ohmic contact (In) was sputtered on the opposite side of the semiconductor wafer before the rectifying contact fabrication. The area of the ohmic contact was S ≈ 4 mm^2, and of the rectifying one – S ≈ 3-3.5 mm^2. Thus, Au/$Hg_2MnInTe_6$/In structures were obtained. Au/$Hg_2MnInTe_6$/In structures possessed a pronounced diode-like *I-V* characteristic. The initial section of *I-V* curves at reverse bias was well described in the framework of the Sah-Noyce-Shockley theory. At higher voltages, the *I-V* section, formed by the SCLC, is observed [4].

Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XXIII, edited by Nerine J. Cherepy
Michael Fiederle, Ralph B. James, Proc. of SPIE Vol. 11838, 1183817 · © 2021 SPIE
CCC code: 0277-786X/21/$21 · doi: 10.1117/12.2594082

3.RESULTS AND DISCUSSION

The *I-V* curves measured for Cr/$Hg_2MnInTe_6$/In structure is shown in Fig. 1.

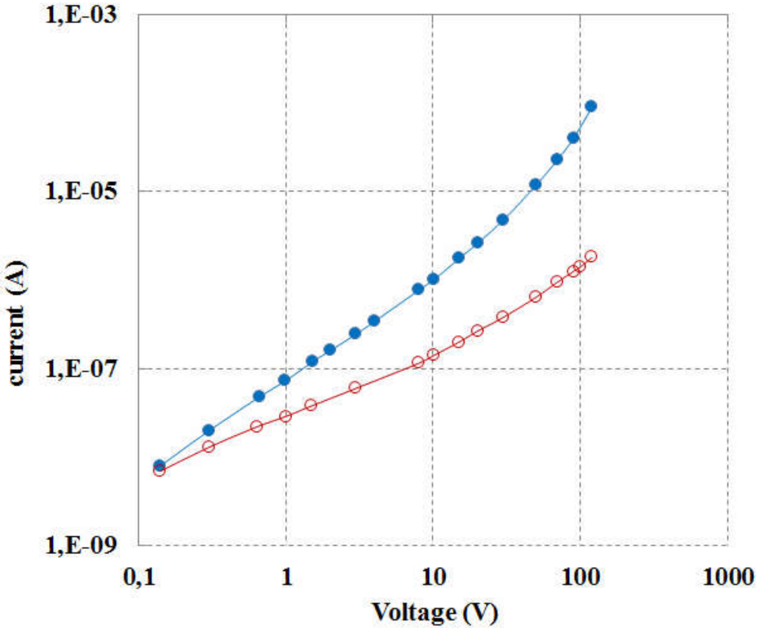

Fig. 1. *I-V* characteristics of Au/n-$Hg_2MnInTe_6$/In structure. Filled circles – direct bias, unfilled circles – reverse one. T = 300 K.

The small rectification coefficient is explained by the relatively large consistent resistance R ≈ (3-4)×10^6 Ohm (293 K) of the crystal's neutral part. When illuminating the structure from the chromium-contact side by an incandescent lamp with a power of 20 W, an open-circuit voltage V ≈ (0.35-0.4) V was observed. The dependence of the differential resistance on the voltage is shown in Fig. 2.

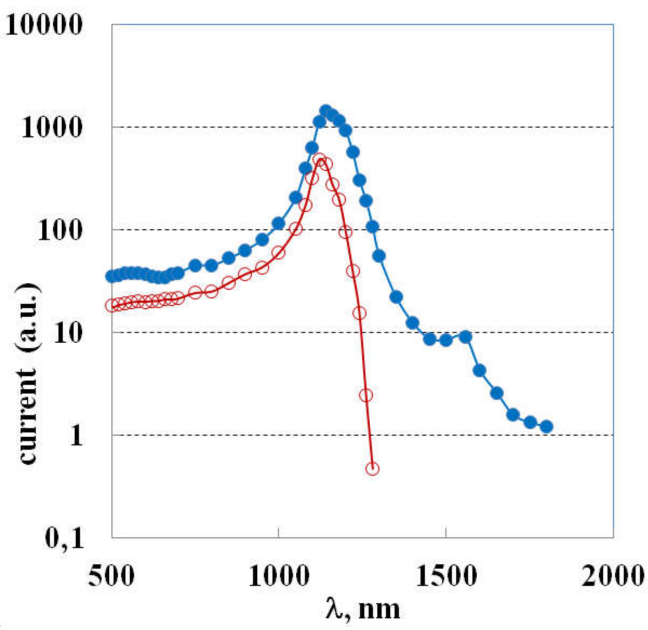

Fig. 2. The photosensitivity spectra of Au/n-$Hg_2MnInTe_6$/In structure vs. the wavelength. Unfilled circles - without offset, filled circles - at reverse voltage V = 5 V.

The photosensitivity spectrum in the photovoltaic mode covers the range of wavelengths from 0.42 to 1.27 μm at λ_{max}≈1.12 μm. At the reverse bias V≈5 V, the photosensitivity spectrum expands to the wavelength range from 0.37 to 1.8 μm at λ_{max}≈1.14 μm. At reverse bias, the voltage is redistributed between the depleted layer of SCLC and the neutral part of the semiconductor, the resistance of which is R≈(3-4)·10^6 Ω at T = 293 K. Therefore, at V = 5 V we observe impurity photosensitivity for λ_d≈1.56 μm due to the resistive photo effect.

Fig. 3 shows the dependence of the differential resistance on the voltage.

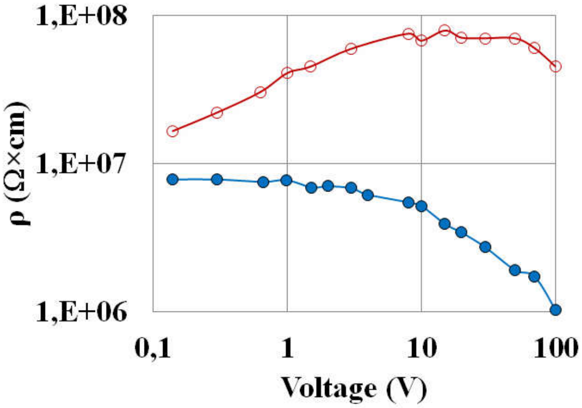

Fig. 3. Dependence of differential resistance on voltage for the structure Au-$Hg_2MnInTe_6$/In. Filled circles - direct, unfilled - inverse offset (T=300 K). Inverse offset - "minus" on the Cr electrode. Crystal thickness was 0.74 mm.

As we see from Fig. 3, the differential resistance at a voltage at ≈100 V is approximately 10 times higher than the resistance of the neutral part of the crystal and is equal to $\rho\approx(7\text{-}8)\times10^7\ \Omega\times$cm. To determine the band-gap, we used the method described in [5,6]. Three plates of $Hg_2MnInTe_6$ single crystal with size 4x4 mm^2 and thickness d_1= 0.5 mm, d_2 = 0.25 mm and d_3 = 0.1 mm were prepared. For each plate from the optical transmission measurements, the width of the band gap $E_g(d)$ of single crystals was determined.

$$\alpha_\omega \sim \left(\hbar\omega - E_g\right)^{1/2} \qquad (1)$$

The value of E_g (d) was determined by extrapolating the rectilinear sections of the dependences α_ω, built in the coordinates $\alpha_\omega^{-1/2}$–$\hbar\omega$, to the intersection with the energy axis $\hbar\omega$. The desired value of the band-gap Eg was determined according to

$$E_g = E_g(d) - \beta \lg d \qquad (2)$$

where $E_g(d)$ is the experimental value of the band-gap for a sample of thickness d, and the coefficient β is found for each semiconductor from the slope of the line depicting the experimental dependence of E_g(d) on lg$d$ at T=const.

Expression (2) in semi-logarithmic coordinates is approximated by a line that cuts off on the abscissa at d=1 μm, the desired value of the band-gap Eg = 1.15 eV (293 K).

As reported in [7], the definition of the product $\mu\cdot\tau$ is based on the use of the Hecht equation. Despite the general recognition of this technique, the assumption of a uniform electric field inside the detector is unjustified. This condition is not fulfilled in practice at relatively low voltages. As a result, it is necessary to measure at relatively high voltages, which leads to significantly lower values of the product μτ. In [7], an original method for determining the product $\mu\cdot\tau$ was proposed. From our point of view, such a method is technically difficult to implement in our case. Therefore, we used the method described in [8] to determine $\mu\cdot\tau$.

To determine the $\mu\cdot\tau$ product, the I–V curves of the In/$Hg_2MnInTe_6$/In structure with two ohmic contacts were used (293K). Voltage V_o is the voltage of the transition of the I–V section, where Ohm's law is fulfilled, to the currents limited by the SCLC. The voltage V_o was found as the point of intersection of the theoretical dependences I~V and I~V^2, respectively (Fig. 3). The product $\mu\cdot\tau$, according to [8], was determined

$$\mu\tau = d^2/V_o \qquad (3)$$

where d is the thickness of the crystal (cm), V_o is the transition voltage of the I–V section, where Ohm's law I~V is valid to the quadratic I~V^2 dependence, which is formed by SCLC, is fulfilled (Fig. 4).

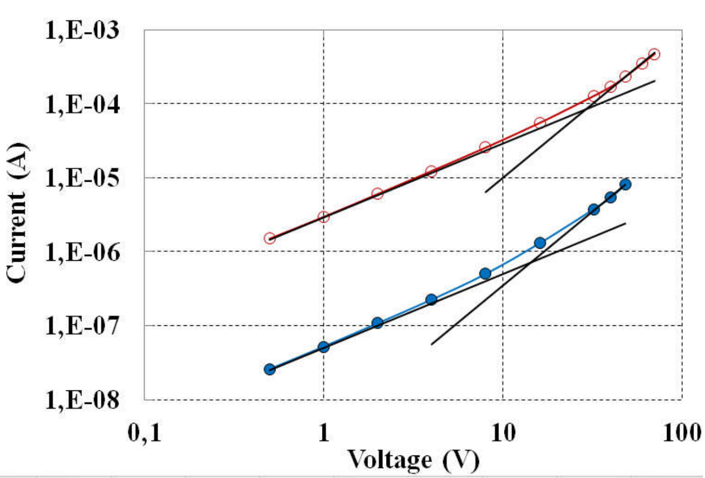

Fig. 4. Direct *I-V* characteristics for In/n-$Hg_2MnInTe_6$/In: filled circles – T = 293 K, unfilled ones – T = 347 K. Crystal thickness was 0.74 mm.

For different single crystals, V_o was equal to ≈ 16-35 V. Thus, from (3), $\mu\tau \approx (1.7–3.4)\times10^{-4}$ $V^{-1}cm^2$ was obtained.
To estimate the value of compensation degree of the grown n-$Hg_2MnInTe_6$ single crystals, the temperature dependence of their resistivity $\rho = \rho$ (T) was measured (Fig. 5).

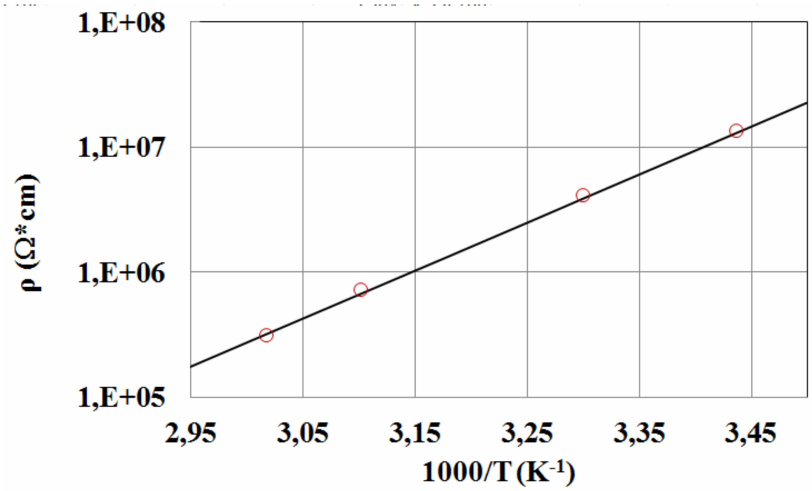

Fig. 5. Temperature dependence of resistivity for In/n-$Hg_2MnInTe_6$/In. Activation energy was ≈ 0.76 eV.

The dependence $\rho = \rho$ (T) is equal to:

$$\rho = \frac{1}{q(n\mu_n + p\mu_p)}, \tag{4}$$

From dependence (4) we define $\Delta\mu$:

$$\Delta\mu = E_g + kT\ln\left(\frac{1+\sqrt{1-4q^2\rho^2\mu_n\mu_p N_v N_c \exp\left(-\frac{E_g}{kT}\right)}}{2q\rho\mu_n N_c}\right), \tag{5}$$

where n, p and μ_n, μ_p are the concentration and mobility of electrons and holes, respectively, N_d and N_a are the concentration of donors and acceptors, $N_c= 2(m_nk/2\pi\hbar)^{3/2}$and $N_v= 2(m_pk/2\ \pi\hbar)^{3/2}$ are the densities of states in the respective bands, m_n, m_p are the effective masses of electrons and holes. The solution of the electroneutrality equation (6) was performed by the numerical method:

$$p + \frac{N_d}{1+\exp\left(\frac{\Delta\mu - E_d}{kT}\right)} = n + \frac{N_a}{1+\exp\left(\frac{E_a - \Delta\mu}{kT}\right)}, \tag{6}$$

To do this, we used the temperature dependence of the band-gap E_g(T), μ_n, and μ_p, which can be represented as:

$$E_g(T) = 1.27 - 4.2\times10^{-4}T \tag{7}$$

$$\mu_n = 1.0\times10^6 T^{-3/2} \tag{8}$$

$$\mu_p = 4.4\times10^5 T^{-3/2} \tag{9}$$

The effective masses of electrons m_n and holes m_p are equal to $0.43m_o$ and $0.35m_o$ [9], respectively, where m_o is the mass of electron in vacuum. As shown in [10, 11], the electroneutrality equation has two solutions, which correspond to strong and weak compensation of the semiconductor material. You can choose the desired solution by measuring the temperature dependence of V_o(T). If V_o depends on the temperature, then we have a highly compensated material, if not, it is poorly compensated. Fig. 6 shows the temperature dependence of V_o (T).
Thus, from Figs. 3 and 6 we see that V_o depends on temperature. It should be noted that the temperature dependence $\Delta\mu(T)$, found using the experimental temperature dependence $\rho(T)$, can be obtained only with a single combination of E_d and N_a/N_d. The coincidence of calculation and experiment was obtained at $E_d \sim 0.37$-0.4 eV and $N_a/N_d \approx 0.99$.

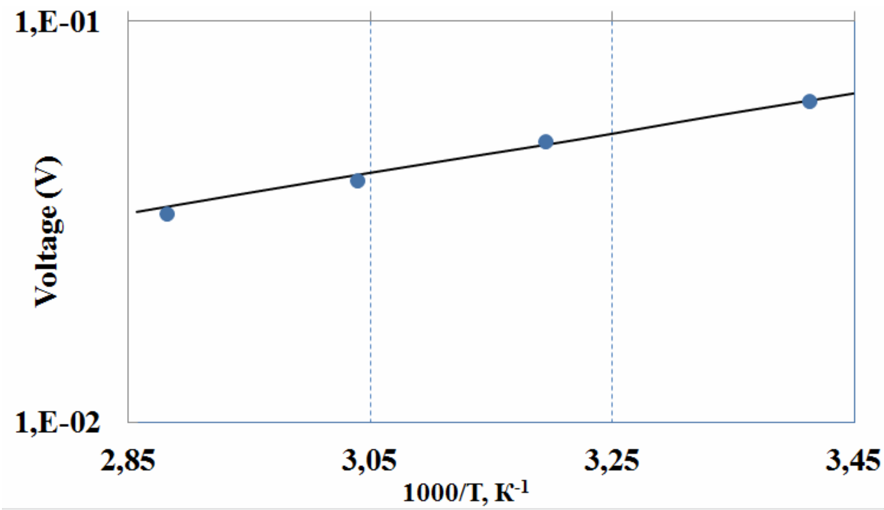

Fig. 6. Temperature dependence of the transition voltage from the *I-V* section, where Ohm's law is fulfilled to SCLC. Activation energy $\Delta E \approx 0.1$ eV.

4.CONCLUSIONS

The n-type $Hg_2MnInTe_6$ single crystals were grown by the modified zone melting method. From the measurements of the optical transmission of $Hg_2MnInTe_6$ single crystals, the band-gap E_g = 1.15 eV (293 K) was determined. From *I-V* measurements for In/*n*-$Hg_2MnInTe_6$/In structure with two ohmic contacts, the resistivity of single crystals $\rho \approx 5\times10^6$ Ohm-cm (293 K) was measured. The compensation degree (~0.99) of n-$Hg_2MnInTe_6$/In single crystal and the energy position of the deep level E_d (~ 0.37-0.4 eV), responsible for the dark conductivity, were determined. Complex studies of the temperature dependences of resistivity ρ and transition voltage V_o from the *I-V* ohmic section to the SCLC, with the solution of an electroneutrality equation, were performed by a numerical method. Both structures with two ohmic contacts - In/*n*-$Hg_2MnInTe_6$/In and structures with a rectifying contact - Au/*n*-$Hg_2MnInTe_6$/In were fabricated. The product $(\mu\tau)_n \approx (1.7\text{-}3.4)\times10^{-4}$ $V^{-1}cm^2$ was determined. $Hg_2MnInTe_6$ semiconductor single crystals are characterized by a high radiation resistance of the electrical and photoelectric parameters, and they can be used both for the manufacture of radiation-resistant photodiodes in the optical range and for ionizing radiation detectors in the X- and gamma-ray energy range.

REFERENCES

[1] V. M. Koshkin, I. N. Volovichev, Yu. G. Gurevich, L. P. Gal'chinetskiy, I. M. Rarenko, Materials and devices with giant radiation resources. Kharkov, 2006.

[2] V. M. Koshkin, Yu. Dmitriev, Chemistry and Physics of Compounds with Loose Crystal Structure, Harwood Acad. Publishers. Ser. Chem. Rev., England – Switzerland, 1994. v. 2, part. 2, 138 p.

[3] I. Rarenko, D. Korbutyak, V. Koshkin, B. Danilchenko, L. Kosyachenko, P. Fochuk, V. Sklyarchuk, Z. Zakharuk, S. Dremlyuzhenko, A. Rarenko, Y. Nikonyuk, V. Kladko, L. Demchyna, S. Budzulyak, N. Vakhnyak, A. Medvid, E. Dauksta, Materials and photosensor devices with high radiation stability. Advanced Materials Research, 1117, p. 107-113 (2015).

[4] Sklyarchuk, V. M., Gnatyuk, V. A., Pecharapa, W., Low leakage current Ni/CdZnTe/In diodes for X/γ-ray detectors, Nucl. Instr. and Meth. in Phys. Res., A, A879, p. 101-105 (2018).

[5] Patent 108138. Ukraine. IPC HO1L 21/66. Method of determining the band gap of semiconductor materials / V. P. Makhniy, V. M. Sklyarchuk. - № u2015 11247; publ. 11.07.2016, Bull. №13.

[6] V. P. Makhniy, Yu. V. Vorobiev, V. M. Sklyarchuk, and J. González-Hernández. Improvement in optical band gap determination for cadmium telluride and related compounds // Telecommunications and Radio Engineering, 75(15), p. 1369-1376 (2016).

[7] A. E. Bolotnikov, G. S. Camarda, E. Chen, R. Gul, V. Dedic, G. DeGeronimo, J. Fried, A. Hossain, J. M. MacKenzie, L. Ocampo, P. Sellin, S. Taherion, E. Vernon,G. Yang, U. El-Hanany, and R. B. James, Use of the drift-time method to measure the electron lifetime in long-drift-length CdZnTe detectors // J. Appl. Phys. – 2016. – Vol. 120. – P. 104507; doi: 10.1063/1.4962540.

[8] V. M. Sklyarchuk, P. M. Fochuk. Patent № 87411, “Method for determining the charge transport parameters in semi-insulating materials based on CdTe and its solid solutions”. 2014.
[9] G. G. Grushka, Z. M. Grushka, N. P. Gavaleshko. Ukrayins’kyy fizychnyy zhurnal, 30(2), p. 304 (1985).
[10] G. G. Roberts, F.W. Smidlin. Interpretation of Thermal Activation Energies in Wide Band-Gap Materials // Phys. Rev. 180, 785 (1969).
[11] A. V. Malovichko, S. V. Svechnikov, K. P. Shul’ga, Ukrayins’kyy fizychnyy zhurnal, 20(2) (1975).