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**OPTICAL CHARACTERISTICS OF  $\text{Hg}_3\text{In}_2\text{Te}_6$   
AS A MATERIAL FOR 1.55- $\mu\text{m}$  PHOTODIODES****L.A. KOSYACHENKO, I.I. GERMAN, S.YU. PARANCHYCH,  
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We consider a semiconductor compound  $\text{Hg}_3\text{In}_2\text{Te}_6$  as a material for photodiodes with optical characteristics optimal for quartz fibers. Based on the transmission and photosensitivity spectra of ITO- $\text{Hg}_3\text{In}_2\text{Te}_6$  diodes, we found the width of the forbidden band in the temperature range 248–353 K, while the reflection spectra of polarized light allowed us to obtain the curve of optical absorption in the range 0.4–1.7  $\mu\text{m}$ .  $\text{Hg}_3\text{In}_2\text{Te}_6$  and Ge photodiodes were compared from the viewpoint of their utilization in fiber-optics communication systems.

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**1. Introduction**

The improvement of the existing elements of fiber-optics communication systems as well as the development of new ones, in particular, high-sensitive fast-responding detectors of optical radiation represent an actual scientific and technical problem. For the long-distance communication, of special importance is the spectral region in the neighborhood of 1.55  $\mu\text{m}$ , which corresponds to the minimum losses in quartz, being commonly used in the production of optical fibers [1,2]. This spectral region lies beyond that of the fundamental absorption of silicon, as the wavelength corresponding to the width of its forbidden band  $\lambda_g = hc / E_g$  is lower than 1.55  $\mu\text{m}$  ( $E_{g\text{Si}}=1.12$  eV at 300 K,  $\lambda_g=1.1$   $\mu\text{m}$ ). The threshold wavelength of germanium  $\lambda_g = 1.88$   $\mu\text{m}$  ( $E_{g\text{Ge}}=0.66$  eV) exceeds 1.55  $\mu\text{m}$ , but the dark current of a germanium diode (and therefore its noise) is much higher than that of a silicon one. In addition, germanium which belongs to semiconductors with indirect interband transitions is characterized by a relatively low absorption coefficient at wavelengths near 1.55  $\mu\text{m}$ . Due to this fact, in order to achieve a proper efficiency of a photodiode,

the thickness of its active region should be sufficiently large, which results in the worsening of the operation speed of the device. That's why, for the production of photodetectors operating at a wavelength of 1.55  $\mu\text{m}$  (as well as at 1.3  $\mu\text{m}$  which is related to the minimum chromatic dispersion in quartz), one uses semiconductor solid solutions InGaAs, GaInAsP, and AlGaAsSb with the corresponding contents of the components [1–3].

A photodiode structure based on  $\text{Hg}_3\text{In}_2\text{Te}_6$  chemical compound, that provides a nearly hundred-percent internal photoelectric quantum efficiency in the discussed spectral region, was described for the first time in papers [4,5]. A specific peculiarity and the advantage of this material lie in a high concentration of electrically neutral cation vacancies, which causes a low sensitivity of its properties to many impurities as well as nuclear radiation resistance [6,7]. In paper [8], the electrical properties of Au- $\text{Hg}_3\text{In}_2\text{Te}_6$  Schottky diodes were described. However, the mechanisms of the processes that determine the photoelectric efficiency of both ITO- $\text{Hg}_3\text{In}_2\text{Te}_6$  and Au- $\text{Hg}_3\text{In}_2\text{Te}_6$  diodes are not investigated. Their description requires information on optical absorption and reflection of  $\text{Hg}_3\text{In}_2\text{Te}_6$  monocrystals in the region of fundamental absorption ( $h\nu > E_g$ ). Such data are absent in literature, and only those for the spectral region  $h\nu < E_g$  ( $\lambda > 1.7$   $\mu\text{m}$ ) are available [9–12].

In the given paper, we present the results of studies of the optical characteristics of  $\text{Hg}_3\text{In}_2\text{Te}_6$  in a wide spectral band of fundamental absorption and, on their basis, analyze the possibilities of the utilization of this

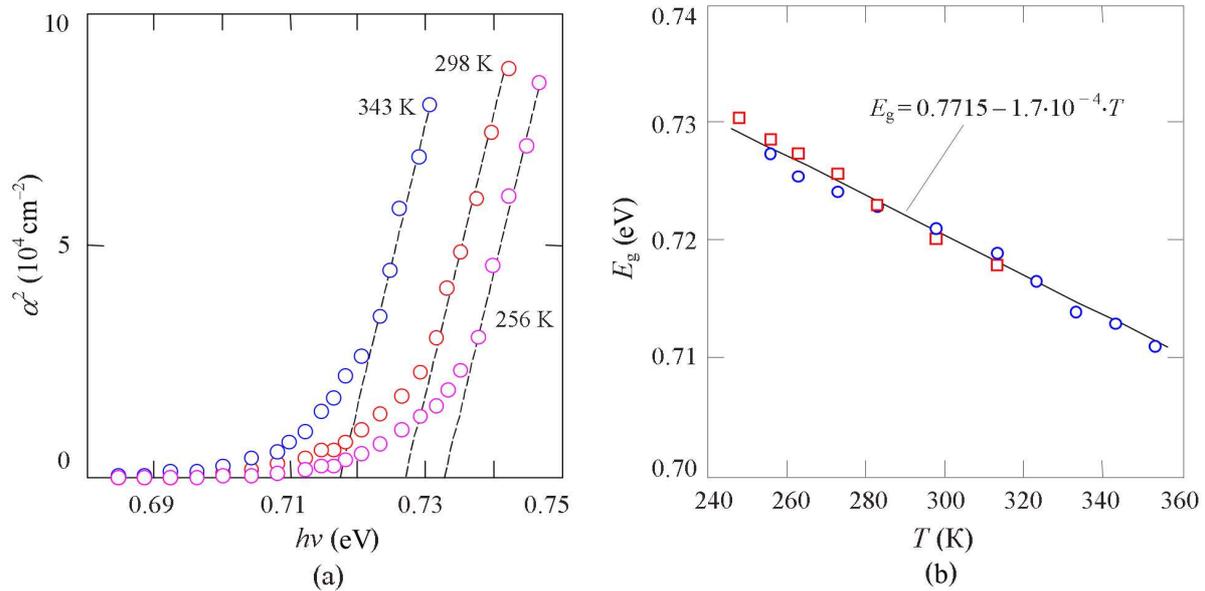


Fig. 1. *a* — Absorption curves of a  $\text{Hg}_3\text{In}_2\text{Te}_6$  crystal in the region  $h\nu \approx E_g$  at three temperatures; dashed lines — the linear approximation. *b* — Temperature dependence of the width of the  $\text{Hg}_3\text{In}_2\text{Te}_6$  forbidden band obtained from the absorption (circles) and photosensitivity (squares) curves of the ITO— $\text{Hg}_3\text{In}_2\text{Te}_6$  diode

material in photodiodes operating at a wavelength of  $1.55 \mu\text{m}$ .

## 2. Width of the Forbidden Band in $\text{Hg}_3\text{In}_2\text{Te}_6$ and Its Temperature Dependence

The width of the forbidden band of the investigated  $\text{Hg}_3\text{In}_2\text{Te}_6$  monocrystals was determined from the curves of optical transmission of thoroughly polished plates. In order to move forward to the region of high values of the absorption coefficient  $\alpha$ , the plates were polished up to a width lower than  $100 \mu\text{m}$ . The value of  $\alpha$  was determined by the formula, where the multiple reflection inside a sample was taken into account [13]:

$$\alpha = \frac{1}{d} \ln \left\{ \frac{(1-R)^2}{2T} + \left[ \frac{(1-R)^4}{4T^2} + R^2 \right]^{1/2} \right\}. \quad (1)$$

Here,  $d$  stands for the sample thickness,  $R$  is the coefficient of reflection from one crystal surface, and  $T$  is the optical transmission of the sample. Figure 1 shows the curves of optical absorption in the region of the long-wave edge of transmission, i.e. in the neighborhood of  $h\nu \approx E_g$ . As for a semiconductor with direct interband transitions, such as  $\text{Hg}_3\text{In}_2\text{Te}_6$  [14],

$$\alpha = \alpha_0 \sqrt{h\nu - E_g}, \quad (2)$$

( $\alpha_0$  is a quantity independent of  $h\nu$ ), the curves are given in the coordinates, in which a linear

dependence of  $\alpha^2$  on the photon energy  $h\nu$  is expected. As one can see from Fig.1, at high values of the absorption coefficient, the presented dependences for three temperatures chosen as an example can be well approximated with straight lines. The values of the cutoffs obtained in such a way on the energy axis in the temperature range 256–353 K are indicated in Fig.1 by circles.

The width of the forbidden band  $E_g$  can be also determined from the long-wavelength edge of the photosensitivity spectrum of a diode. In our experiments, we used a barrier structure obtained by the vacuum magnetron sputtering of an ITO ( $\text{SnO}_2 + \text{In}_2\text{O}_3$ ) layer. The ohmic contact on the substrate was produced by fusing In. Figure 2 depicts the spectra of the photoelectric quantum efficiency of the ITO/ $\text{Hg}_3\text{In}_2\text{Te}_6$  heterojunction measured at two temperatures.

The analysis of the photosensitivity curves of the photodiode at room temperature has demonstrated that the width of the forbidden band correlates with a high accuracy with the center of the rapidly increasing long-wavelength edge of the photosensitivity curve. This fact was used for the determination of the width of the  $\text{Hg}_3\text{In}_2\text{Te}_6$  forbidden band in the whole temperature range under investigation (248–313 K). The obtained results are indicated in Fig. 1 by squares.

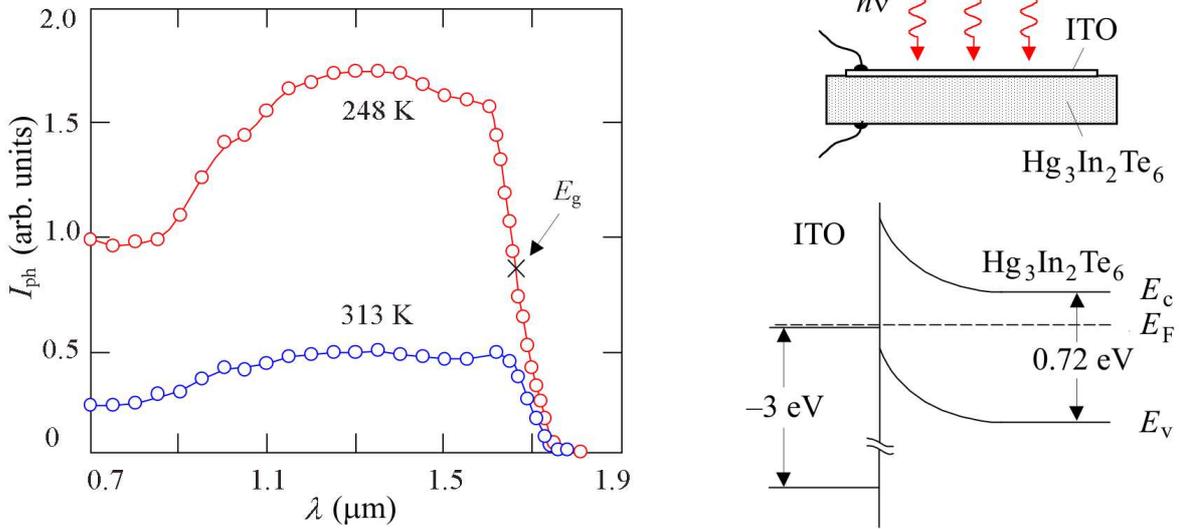


Fig. 2. Spectral curves of photosensitivity of the ITO–Hg<sub>3</sub>In<sub>2</sub>Te<sub>6</sub> diode at two temperatures. On the right – the diode cross-section and its energy diagram

As one can see from Fig. 1, the values of  $E_g$  obtained from the absorption and photosensitivity spectra agree to within an insignificant error that does not exceed 0.002 eV. Figure 1 shows the linear dependence  $E_g(T)$  that agrees with the obtained experimental results in the best way:

$$E_g(T) = 0.7715 - 1.7 \times 10^{-4}T, \quad (3)$$

i.e. the temperature dependence of the width of the Hg<sub>3</sub>In<sub>2</sub>Te<sub>6</sub> forbidden band can be approximated with the function  $E_g(T) = E_{g0} - \gamma \cdot T$ , where  $E_{g0} = 0.7715$  eV and  $\gamma = dE_g/dT$  is the temperature coefficient of variation of  $E_g$  that amounts to  $1.7 \times 10^{-4}$  eV·K<sup>-1</sup>. These parameters of Hg<sub>3</sub>In<sub>2</sub>Te<sub>6</sub> agree with the value  $E_g = 0.78$  eV obtained at 100 K in work [14], as well as with the value  $\gamma = 2 \times 10^{-4}$  eV·K<sup>-1</sup> obtained from photoelectric measurements carried out only at two temperatures — that of liquid nitrogen and room one. Thus, the temperature variation of the width of the forbidden zone in Hg<sub>3</sub>In<sub>2</sub>Te<sub>6</sub> is much weaker than that in germanium (the nearest substance as regards the magnitude of  $E_g$ ), for which  $\gamma = 4.4 \times 10^{-4}$  eV·K<sup>-1</sup> [15].

### 3. Absorption and Reflection Coefficients

In a wide range of fundamental absorption, the absorption coefficient  $\alpha$  was found by measuring the reflection of polarized light at various angles of incidence (the measurements of the optical transmission at high  $\alpha$  were complicated as they required too thin samples).

At the interface of two transparent materials characterized by the refractive indices  $n_1$  and  $n_2$ , the reflection of light polarized at right angle and in parallel to the plane of beam incidence is described by Fresnel formulas [16]

$$r_{\perp} = \frac{E_r}{E_i} = \frac{n_1 \cos \varphi - n_2 \cos \psi}{n_1 \cos \varphi + n_2 \cos \psi}, \quad (4)$$

$$r_{\parallel} = \frac{E_r}{E_i} = \frac{n_2 \cos \varphi - n_1 \cos \psi}{n_2 \cos \varphi + n_1 \cos \psi}, \quad (5)$$

where  $r_{\perp}$  and  $r_{\parallel}$  are the Fresnel coefficients defined as the ratio of the amplitude of the reflected wave  $E_r$  to that of the incident one  $E_i$  ( $\varphi$  and  $\psi$  signify the angles of incidence and refraction). In the case of an absorbing material, the refractive index is expressed through a complex number  $n - i\kappa$ , whose real part  $n$  represents the refractive index itself, while  $\kappa$  is the extinction (attenuation) coefficient connected with the absorption coefficient  $\alpha$  by the relation

$$\alpha = \frac{2\omega}{c} \kappa = \frac{4\pi}{\lambda} \kappa, \quad (6)$$

where  $\omega = 2\pi\nu$ , and  $c$  is the light velocity in vacuum.

The measured reflection coefficients  $R_{\perp}$  and  $R_{\parallel}$  amount to the ratio of the intensities of the reflected and incident waves, i.e. the squares of the Fresnel coefficients  $r_{\perp}^2$  and  $r_{\parallel}^2$ . Using the notations  $n_1 = 1$  for the first medium

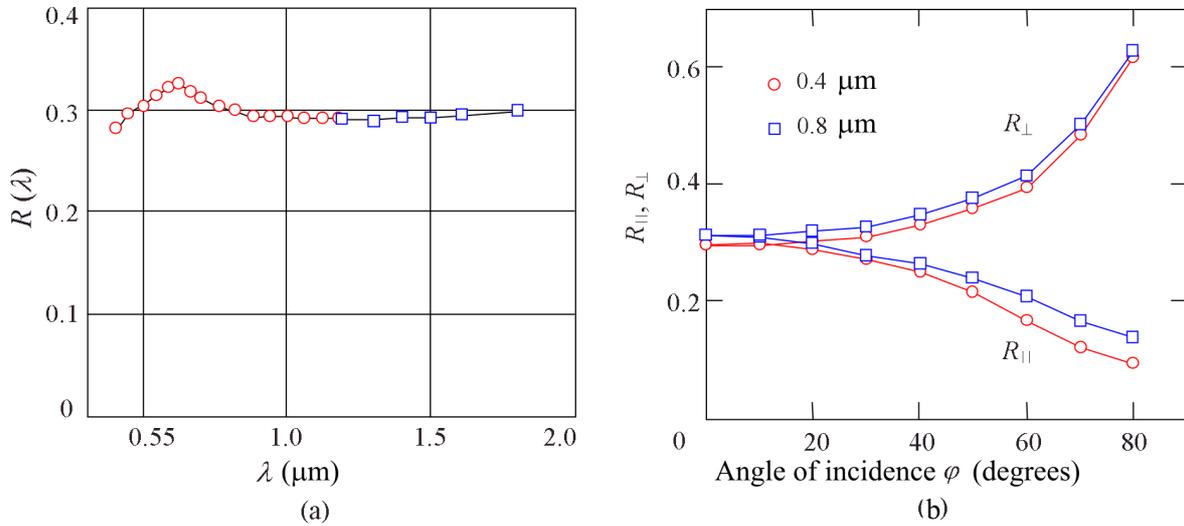


Fig. 3. *a* — Spectral dependence of the reflection coefficient  $R(\lambda)$  at normal incidence (300 K); *b* — Dependences of the reflection coefficient on the angle of incidence  $\varphi$  for light polarized in the plane of the incident beam,  $R_{\parallel}$ , and at right angle to it,  $R_{\perp}$

(air) and  $n_2 = n$  for the second one and eliminating the refraction angle  $\psi$  from (4) and (5) (by using the Snell relation  $n_1 \sin \varphi = n_2 \sin \psi$ , we obtain

$$R_{\perp} = \left| \frac{\cos \varphi - n \cos [\arcsin(\sin \varphi / n)]}{\cos \varphi + n \cos [\arcsin(\sin \varphi / n)]} \right|^2 = R_{\perp}(n, \kappa, \varphi), \quad (7)$$

$$R_{\parallel} = \left| \frac{n \cos \varphi - \cos [\arcsin(\sin \varphi / n)]}{n \cos \varphi + \cos [\arcsin(\sin \varphi / n)]} \right|^2 = R_{\parallel}(n, \kappa, \varphi). \quad (8)$$

In order to avoid dealing with the absolute values of reflection coefficients, one measures the ratio of  $R_{\parallel}$  to  $R_{\perp}$ . If the quantity  $R_{\parallel}/R_{\perp}$  is measured at two angles of incidence, the search for  $n$  and  $\kappa$  is reduced to solving two equations

$$\frac{R_{\parallel}(n, \kappa, \varphi_1)}{R_{\perp}(n, \kappa, \varphi_1)} = \xi_1, \quad (9)$$

$$\frac{R_{\parallel}(n, \kappa, \varphi_2)}{R_{\perp}(n, \kappa, \varphi_2)} = \xi_2, \quad (10)$$

where  $\xi_1$  and  $\xi_2$  are the experimentally obtained ratios  $R_{\parallel}/R_{\perp}$  at the angles of incidence  $\varphi_1$  and  $\varphi_2$ . When measuring  $R_{\parallel}$  and  $R_{\perp}$ , we used the technique of a spherical photometer with a polarize (Nicol prism) placed in front of its inlet [17].

In Fig. 3, *a*, we present the spectral dependences of the reflection coefficient  $R$  measured in the case of normal incidence of light, while Fig. 3, *b* demonstrates the reflection coefficients  $R_{\perp}$  and  $R_{\parallel}$  as functions of the angle of incidence (for two wavelengths). It is clear that, at  $\varphi = 0$ , the curves for  $R_{\perp}$  and  $R_{\parallel}$  coincide. At  $\varphi = 90^\circ$ , the both coefficients are equal to unity (the sample holder in the experimental setup did not allow us to take measurements for angles of incidence  $\varphi > 80^\circ$ ). The ratios  $\xi_1$  and  $\xi_2$  (the right-hand terms of Eqs. (9) and (10)) were obtained for the angles of beam incidence lying in the range  $40\text{--}70^\circ$ .

Equations (9) and (10) can be solved for  $n$  and  $\kappa$  (and, hence, for  $\alpha = 4\pi\kappa/\lambda$ ) using numerical, graphical, or computer methods. In Fig. 4, *a*, the circles indicate the results of the computer solution of these equations for  $\alpha$  for the spectral range  $\lambda < 1.7 \mu\text{m}$  (at  $\alpha > 10^3 \text{ cm}^{-1}$ , the multiple reflection in a sample  $0.5\text{--}1 \text{ mm}$  in thickness can be neglected). For the region  $\lambda > 1.7 \mu\text{m}$ , the value of  $\alpha$  is obtained from the transmission curve of the thin sample (squares). For the sake of comparison, Fig. 4 also demonstrates the curve of optical absorption of germanium [18]. One can see that the taken measurements allowed us to obtain the absorption curve for  $\text{Hg}_3\text{In}_2\text{Te}_6$  in a wide spectral region, and the values of  $\alpha$  obtained within different techniques coincide well in the range  $1.6\text{--}1.7 \mu\text{m}$ .

As for the operation of quartz-based fiber communication lines, a special attention should be paid to the spectral region in the neighborhood of  $\lambda \approx 1.55 \mu\text{m}$ .

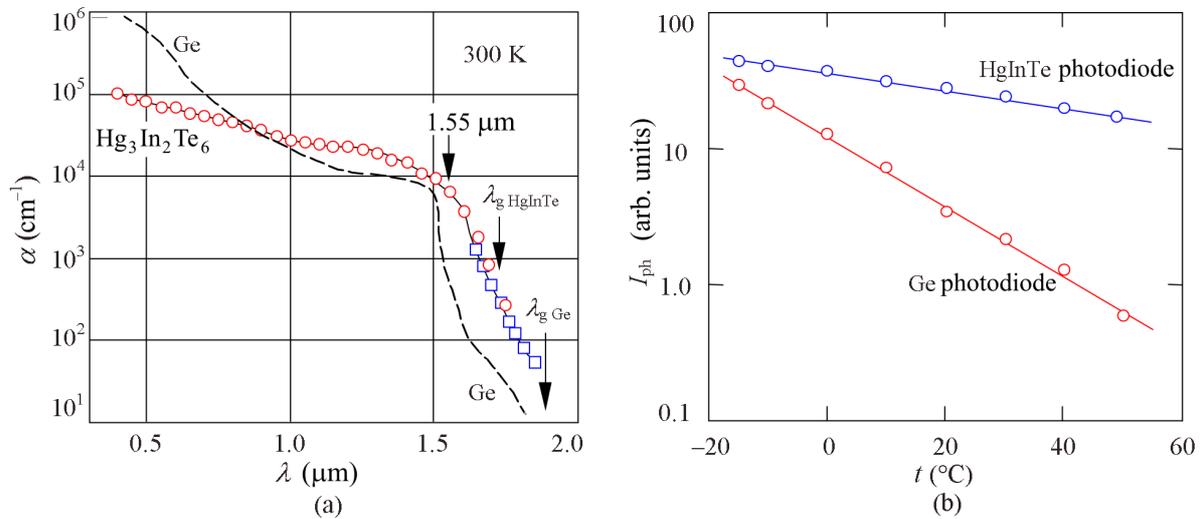


Fig. 4. *a* — Spectral dependence of the absorption coefficient  $\alpha(\lambda)$  for a  $\text{Hg}_3\text{In}_2\text{Te}_6$  monocrystal (the dashed line shows the absorption curve for germanium [18]); *b* — temperature dependences of photosensitivity of Ge and HgInTe diodes at a wavelength of  $1.55 \mu\text{m}$

As was already noted, in order to provide the efficient absorption of radiation, the threshold wavelength  $\lambda_g = hc / E_g$  for the semiconductor being used must exceed  $1.55 \mu\text{m}$  but not by a large amount, because narrowing the forbidden band results in the increase of the dark noise of a photodiode, with other conditions being equal. For  $\text{Hg}_3\text{In}_2\text{Te}_6$ , a wavelength of  $1.55 \mu\text{m}$  corresponds to the short-wave region of the rapid variation of the absorption coefficient, which evidently represents the optimal case. For Ge, the threshold wavelength  $\lambda_{g\text{Ge}}$  substantially differs from  $1.55 \mu\text{m}$  and corresponds to a much lower absorption coefficient, since the direct transitions in Ge are observed at  $\lambda < 1.5 \mu\text{m}$  [18]. Thus, from the viewpoint of the application in fiber-optics communication systems,  $\text{Hg}_3\text{In}_2\text{Te}_6$  represents undoubtedly a more preferable material for producing photodiodes than Ge.

At a wavelength of  $1.55 \mu\text{m}$ , the absorption coefficient for  $\text{Hg}_3\text{In}_2\text{Te}_6$  amounts to  $7000 \text{ cm}^{-1}$ , i.e. the effective depth of the radiation penetration  $\alpha^{-1}$  approximates to  $1.4 \mu\text{m}$ . This implies that nearly  $\sim 62\%$  of radiation is absorbed according to the formula  $1 - \exp(-\alpha d)$  in a layer  $d = 1.4 \mu\text{m}$  in thickness, and  $97-98\%$ , i.e. the nearly all radiation, is absorbed in a  $5-6 \mu\text{m}$  layer. In Ge, the absorption coefficient at the same wavelength is equal to  $460 \text{ cm}^{-1}$ , and a layer  $5-6 \mu\text{m}$  in thickness absorbs only  $20-24\%$  of radiation. The nearly total absorption of radiation ( $97-98\%$ ) at the wavelength of  $1.5 \mu\text{m}$  takes place in Ge at  $d > 80-90 \mu\text{m}$ .

As is known, the need for a substantially thick absorbing layer represents a serious difficulty for the introduction of both germanium and silicon photodiodes in fiber-optics communication systems. In order to overcome this problem, one has to complicate the diode construction arranging its thin active layer in a microresonator and using Bragg mirrors [19, 20]. Due to the spectral selectivity of the mirrors, the increase in the effectiveness and the operating speed in such a photodiode is accompanied with narrowing the spectral band of photosensitivity. But these positive features of a photodiode are achieved at the expense of the complication of the fabrication technology and a substantial rise in its price. A photodiode based on a direct band semiconductor (such as  $\text{Hg}_3\text{In}_2\text{Te}_6$ ) does not require such a complication.

Another advantage of a  $\text{Hg}_3\text{In}_2\text{Te}_6$  diode lies in a lower sensitivity of its parameters to the variation of the environment temperature (as compared to a germanium photodiode). As the wavelength of  $1.55 \mu\text{m}$  corresponds to the region of the rapid change in the absorption coefficient of germanium, the inessential temperature variation induces substantial variations of the photocurrent in the detector circuit conditioned by the temperature dependence of the forbidden zone width. For  $\text{Hg}_3\text{In}_2\text{Te}_6$ , the wavelength of  $1.55 \mu\text{m}$  corresponds to the region of a weaker variation of the absorption coefficient. That's why the influence of temperature variation on the photocurrent is less considerable. As one can see from the results of our measurements presented

in Fig. 4, *b*, with increase in temperature from  $-20$  to  $50$  °C, the photosensitivity of a Ge photodiode decreases almost by two orders of magnitude, while that of a  $\text{Hg}_3\text{In}_2\text{Te}_6$  photodiode — only by a factor of 2.5–3.

#### 4. Conclusions

From the optical transmission spectra, we have determined the width of the forbidden band of  $\text{Hg}_3\text{In}_2\text{Te}_6$  in the temperature range 248–353 K and the temperature coefficient of its variation  $dE_g/dt=1.7\times 10^{-4}\text{eV}\cdot\text{K}^{-4}$ . Taking measurements of the reflection coefficient of light polarized at right angle and in parallel to the plane of incidence, we obtained the absorption curve  $\alpha(\lambda)$  in the range  $\lambda=0.4\div 1.7$   $\mu\text{m}$  supplemented with the results of processing the transmission spectrum in the region  $\lambda \approx \lambda_g = hc/E_g$ .  $\text{Hg}_3\text{In}_2\text{Te}_6$  has evident advantages in comparison with Ge from the viewpoint of its utilization in fiber-optics communication systems. Indeed, in order to provide the almost total absorption of radiation with a wavelength of 1.55  $\mu\text{m}$ , the thickness of the active layer in a  $\text{Hg}_3\text{In}_2\text{Te}_6$  photodiode must exceed 5–6  $\mu\text{m}$ , while that in a Ge photodiode — 80–90  $\mu\text{m}$ . The temperature dependence of the photosensitivity of a  $\text{Hg}_3\text{In}_2\text{Te}_6$  photodiode at a wavelength of 1.55  $\mu\text{m}$  is much weaker than that in a Ge one.

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#### ОПТИЧНІ ХАРАКТЕРИСТИКИ $\text{Hg}_3\text{In}_2\text{Te}_6$ ЯК МАТЕРІАЛУ ДЛЯ ФОТОДІОДІВ НА 1,55 МКМ

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#### Резюме

Досліджено напівпровідникову сполуку  $\text{Hg}_3\text{In}_2\text{Te}_6$  як матеріал для фотодіодів з оптимальними для кварцового волокна оптичними характеристиками. Із спектрів пропускання та фоточутливості діодів ІТО– $\text{Hg}_3\text{In}_2\text{Te}_6$  знайдено ширину забороненої зони в інтервалі температур 248–353 К, а із спектрів відбиття поляризованого світла — криву оптичного поглинання в інтервалі 0,4–1,7 мкм. Проведено порівняльний аналіз  $\text{Hg}_3\text{In}_2\text{Te}_6$ - і Ge-фотодіодів з огляду на їхнє застосування у волоконно-оптичних лініях зв'язку.