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ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

Extrinsic Conductivity of $Hg_3In_2Te_6$ Single Crystals

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Abstract—*n*-$Hg_3In_2Te_6$ single crystals with resistivity of 1–2 Ω cm used in photodiodes for the wavelength 1.55 μm are studied. It is shown that electrical conductivity of the material is controlled by donors of two types with ionization energies of 0.063 and 0.18 eV, while the mobility of charge carriers is predominantly controlled by scattering at charged centers. On the basis of the electroneutrality equation, a quantitative description of the observed temperature dependence of the electron concentration in the temperature range from 100 to 370 K is obtained.

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The development and improvement of fiber–optics communication systems presume the presence of high-efficiency and high-speed photodetectors. The spectral region $\lambda = 1.55$ μm is especially important for long-distance communication since losses in the optical fiber made of quartz glass are lowest (0.15–0.2 dB/km) in this region [1]. At present, epitaxial layers of a quaternary $In_xGa_{1-x}As_yP_{1-y}$ alloy (with $x = 0.57$ and $y = 0.95$) grown on InP substrates are used in fabrication of photodiodes for this spectral region [1]. It was shown previously [2, 3] that a good match of the band gap with the maximum in photosensitivity at a wavelength of 1.55 μm is attained for the semiconductor compound $Hg_3In_2Te_6$ (E_g = 0.72 eV) with practically 100% efficiency for a photodiode based on this compound (with antireflection coating).

The $Hg_3In_2Te_6$ compound crystallizes in the structure of zinc blend, in which case 1/3 of all sites in the cationic sublattice are vacant. The presence of these stoichiometric vacancies with a concentration of $\sim10^{21}$ cm^{-3} is responsible for the electrical indifference to defects and many impurities, and also for high resistance of the parameters to ionizing radiation. The radiation resistance of such semiconductors is at least two–three orders of magnitude higher than the resistance of Ge, CdTe, and ZnSe (see, for example, [4] and references therein). The problem of radiation resistance of materials (in particular, semiconductors) is very important in the context of the need for prolonged operation of measurement instrumentation under conditions of high doses and intensities of ionizing radiation, in nuclear reactors and storage pits of nuclear wastes, in commercial accelerators, and in the case of defect spectroscopy of metals and of the prolonged presence of instrumentation in outer space.

If special measures are not undertaken, the electrical conductivity of $Hg_3In_2Te_6$ is found to be close to the intrinsic conductivity, while the resistivity of this material at room temperature is equal to $(1–4) \times 10^3$ Ω cm [5]. The charge-carrier concentration in this material equals $(3–5) \times 10^{13}$ cm^{-3}; the mobility of charge carriers is in the range from 40–50 to 200–250 cm^2 V^{-1} s^{-1} and, in the majority of cases, changes only slightly as temperature is increased. Still, the electrical properties of $Hg_3In_2Te_6$ can be significantly changed by varying the conditions of single-crystal growth or by conducting the subsequent heat treatment of these crystals in vacuum or in the atmosphere of certain elements [6]. A semiconductor with intrinsic conductivity cannot be used in fabrication of photodiodes, since, in this case, any bending of the energy bands leads to enrichment of the layer with charge carriers rather than to depletion of this layer of the carriers. In this context, a material with extrinsic conductivity is of most interest.

In this paper, we report the results of experimental studies and physical interpretation of electrical properties of $Hg_3In_2Te_6$ single crystals used in the fabrication of photodiodes with pronounced *n*-type extrinsic conductivity. Obtained parameters of the material are needed for interpretation of charge-transport mechanisms and photoelectric characteristics of diode structures [7, 8].

We studied the $Hg_3In_2Te_6$ single crystals obtained by the modified Bridgman–Stockbarger method with subsequent annealing of the 0.8-mm-thick wafers cut from the ingot in mercury vapors for 700–800 h at temperatures of 190–220°C. At room temperature, the resistivity of the obtained *n*-type material was 1–2 Ω cm. According to the measurements of optical transmittance in the photon-energy region $h\nu \approx E_g$, there is no

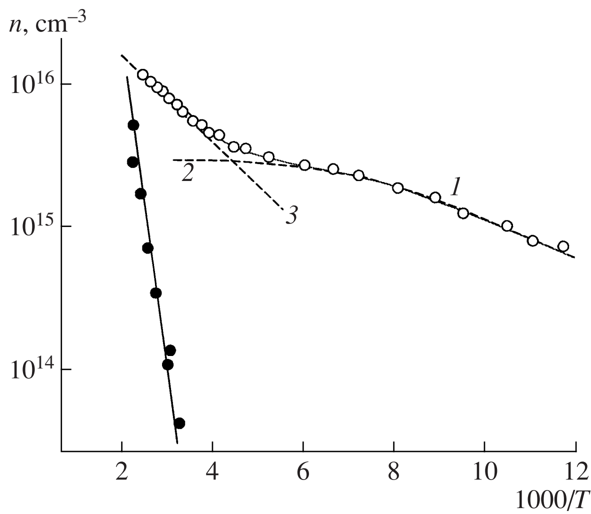

Fig. 1. Temperature dependence of the electron concentration in a $Hg_3In_2Te_6$ single crystal annealed in mercury vapors (open circles). The dashed line represents the electron concentration caused by shallow-level donors (the regions of freezing-off *1* and depletion *2* at low and elevated temperatures, respectively); dashed line *3* represents the electron concentration caused by deeper donors. The solid line corresponds to the calculated intrinsic electron concentration and close circles represent the charge-carrier concentration in an unannealed sample.

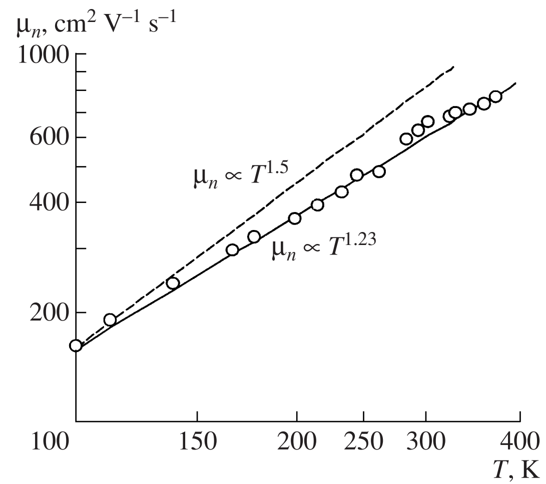

Fig. 2. Temperature dependence of electron mobility in a $Hg_3In_2Te_6$ single crystal annealed in mercury vapors.

appreciable variation in the band gap, while measurements of resistivity showed that electrical characteristics of the wafers annealed under identical conditions did not change. Test measurements of parameters of both single crystals and diode structures for a long time (longer than a year) showed that the studied $Hg_3In_2Te_6$ single crystals also feature a high temporal stability of properties (properties of the crystals that were not subjected to heat treatment are often unstable with time). Characteristics of the studied samples (both of single crystals and photodiodes on their basis) are reproduced to a high extent also in the case of multiple measurements in the range of 77–370 K.

The temperature dependence of the electron concentration n determined from measurements of the Hall coefficient R_H and electrical conductivity σ in the temperature range 80–370 K is shown in Fig. 1 (it was assumed that the Hall factor is equal to unity). The temperature dependence of the charge-carrier concentration in an unannealed sample is also shown in Fig. 1 by close circles for comparison; the solid line represents the intrinsic carrier concentration calculated using the formula $n_i = (N_c N_v)^{1/2}\exp(-E_g/2kT)$. The band gap E_g of the semiconductor was assumed to be equal to $0.7715–1.7 \times 10^{-4}T$; $N_c = 2(m_n kT/2\pi\hbar^2)^{3/2}$ and $N_v = 2(m_p kT/2\pi\hbar^2)^{3/2}$ are the effective densities of states in the conduction and valence bands, respectively [9]. The calculated dependence $n(T)$ coincides precisely with experimental results if the effective masses of electrons m_e and holes m_h are assumed to be equal to the electron mass in free space. As can be seen from Fig. 1, annealing in mercury vapors radically changes the electrical properties of the material. Even at the highest temperature under consideration (370 K), the electron concentration in an annealed sample is higher than the charge-carrier concentration in the initial material by more than an order of magnitude.

In Fig. 2, the temperature dependence of electron mobility μ_n in a sample annealed in mercury vapors is shown in log–log coordinates; the mobility was obtained as the product of electrical conductivity σ and the Hall coefficient R_H. It is worth noting that there is high mobility of charge carriers in the single crystals under study (approximately, 650 cm^2 V^{-1} s^{-1} at 300 K), which is indicative of a quite high quality of a semiconductor material in this class. The experimental dependence of electron mobility μ_n on temperature T can be adequately approximated using a power function $\mu_n \propto T^p$ with $p \approx 1.23$ (the solid line in Fig. 2). Taking into account a high electron concentration (and, consequently, a high concentration of ionized donors N_d), we may assume that scattering by ionized impurities is the dominant mechanism determining the charge-carrier mobility in the single crystals under study. In this case, the following well-known Conwell–Weisskopf (Brooks–Herring) formula for the electron mobility can be used [10]:

$$\mu_n = \frac{8\varepsilon^2\sqrt{2}(kT)^{3/2}}{N_d e^3\sqrt{m_n\pi^3}\ln(24 m_n kT r_0^2/\hbar^2)}. \quad (1)$$

Here, ε is the relative permittivity, k is the Boltzmann constant, e is the elementary charge, and r_0 is the screening length (equal in a nondegenerate semiconductor to $(\varepsilon\varepsilon_0 kT/e^2 n)^{1/2}$). Substituting (for estimation) ε = 10–15 and $N_d = n = 10^{15}$–10^{16} cm^{-3} into formula (1), we can verify that the logarithmic factor in the denomina-

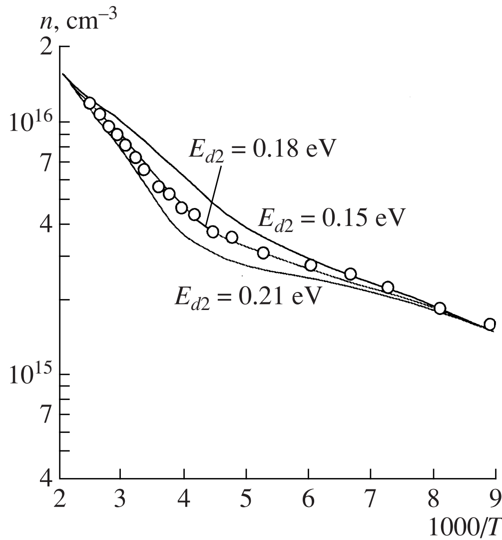

Fig. 3. Comparison of experimental temperature dependence of the electron concentration n with calculated values of n for various ionization energies of deep-level donors.

tor does not affect significantly the run of the dependence $\mu_n(T)$. Therefore, a deviation of the temperature dependence $\mu_n(T)$ from $\mu_n \propto T^{3/2}$ (dashed line in Fig. 2) can be accounted for by the effect of another mechanism of scattering; most likely, this mechanism is independent of the temperature of scattering by neutral centers (the latter are represented by stoichiometric vacancies).

Starting the discussion of temperature dependence of the electron concentration n, we should at once exclude the contribution of intrinsic charge carriers; i.e., we should assume that electrical conductivity in $Hg_3In_2Te_6$ single crystals annealed in mercury vapors is due to an extrinsic mechanism. The observed specific shape of the curve $n(T)$ makes it possible to assume that two types of donor impurities are involved in the electrical conductivity of single crystals under study: shallow-level donors are involved in conductivity at low temperatures, while deep-level donors are most important at elevated temperatures. At $T < 110$–120 K, the shallow-level impurities are partially ionized (the freezing-off region *1*) and are completely ionized at elevated temperatures (the depletion region *2*), which is shown conventionally by the dashed line in Fig. 1. In the case of temperatures increased still higher (higher than 170–180 K), ionization of deeper donor impurities sets in, which manifests itself in an abrupt (almost exponential) increase in n with temperature (dashed straight line *3* in Fig. 1).

Let us denote the ionization energy of the shallow-level donor by E_{d1}, the corresponding energy for a donor with a deeper level by E_{d2}, and the energy distance between the Fermi level and the conduction-band bottom by $\Delta\mu$. The concentration of holes at shallow and deeper donors (p_{d1} and p_{d2}, respectively) can be expressed by the formulas

$$p_{d1} = \frac{N_{d1}}{\exp\left(\frac{E_{d1} - \Delta\mu}{kT}\right) + 1}, \qquad (2)$$

$$p_{d2} = \frac{N_{d2}}{\exp\left(\frac{E_{d2} - \Delta\mu}{kT}\right) + 1}, \qquad (3)$$

where N_{d1} and N_{d2} are the concentrations of shallow and deeper donors, respectively (the degeneracy factors for impurity levels were assumed to be equal to unity).

In the case of thermodynamic equilibrium, the condition for electroneutrality implies that the electron concentration in the conduction band

$$n = \frac{N_c}{\exp\left(\frac{\Delta\mu}{kT}\right) + 1} \qquad (4)$$

is equal to the sum of concentrations of holes at both donors (since we consider a low-resistivity n-type semiconductor, we can disregard the involvement of holes in the valence band in electrical conductivity); i.e.,

$$n = p_{d1} + p_{d2}. \qquad (5)$$

When solving the equation of electroneutrality (5) with respect to $\Delta\mu$, we should first take into account that the electron concentration n in the conduction band is governed only by shallow-level donors in the temperature range $T < 170$–180 K (Fig. 1). Taking this fact into consideration, it is not difficult to choose the values of the ionization energy E_{d1} and concentration N_{d1} for which the dependence $\Delta\mu(T)$ (and, correspondingly, $n(T)$) best describes the experimental data in this temperature region (in this case, $E_{d1} = 0.063$ eV and $N_{d1} = 2.6 \times 10^{15}$ cm^{-3}).

The ionization energy of the deeper donor E_{d2} can be determined from the slope of the high-temperature portion ($T > 250$–260 K) of the curve in Fig. 1; however, the result is only approximate, since the contribution of shallow-level donors is still appreciable in this region (Fig. 1). Varying simultaneously the quantities E_{d2} and N_{d2} in order to obtain the values of n that coincide with experimental data on n at high temperatures, we can get a different run of $n(T)$ in the temperature region $T > 120$–130 K. The result of these procedures is shown in Fig. 3. As can be seen, a comparison of the results of calculations of $n(T)$ with the experimental curve makes it possible to determine rather precisely the values of the ionization energy and concentration of deeper donors (in the case under consideration, $E_{d2} = 0.18$ eV and $N_{d2} = 1.0 \times 10^{16}$ cm^{-3}).

In Fig. 3, the solid line represents the results of calculations of the electron concentration in the conduction band using formula (4) and the values of $\Delta\mu$ deter-

mined from solution of the electroneutrality equation. As can be seen, we attain very good agreement between the results of calculations and experimental data (circles) in the entire temperature range.

Thus, electrical conductivity of the $Hg_3In_2Te_6$ single crystals under study is governed by donors of two types with the ionization energies E_{d1} = 0.063 eV and E_{d2} = 0.18 eV. Interaction with charged donors is the dominant mechanism of scattering that governs the electron mobility. It is worth noting that the electron concentration 10^{15}–10^{16} cm^{-3} is lower (by five or six orders of magnitude) than the concentration of electrically neutral stoichiometric vacancies.

Elucidation of the nature of donors controlling the electrical characteristics of the $Hg_3In_2Te_6$ single crystals under study was not the aim of this study. Still, we may assume that, as a result of annealing of these single crystals, diatomic mercury molecules occupy interstices and act as single- and double-charged donors with lower and higher ionization energy, respectively. It cannot be excluded that mercury atoms (in combination with vacancies) form complexes that manifest themselves as donor-type impurities in electrical characteristics of the material.

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