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DC hopping photoconductivity via three-charge-state point defects in partially disordered semiconductors

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Abstract

The stationary (DC) hopping photoconductivity caused by the migration of electrons via intrinsic point *t*-defects of the same type with three charge states (−1, 0, and +1 in units of elementary charge) is theoretically studied. It is assumed that *t*-defects are randomly (Poissonian) distributed over a crystal and hops of single electrons occur only via *t*-defects in the charge states (−1), (0) and (0), (+1). Under the influence of intercenter illumination nonequilibrium charge states (−1) and (+1) of defects are generated due to photostimulated electron transitions between pairs of defects in the charge states (0). During the recombination of nonequilibrium charge states (−1) and (+1) of defects, pairs of defects in the charge states (0) are formed. It is assumed that illumination does not heat the crystal, i.e. does not increase the coefficient of thermal ionization of *t*-defects. The dependence of the ratio of photoconductivity to dark hopping electrical conductivity on the ratio of photoionization coefficient (γ) of neutral *t*-defects to coefficient of 'capture' (α) of an electron from a negatively charged to a positively charged *t*-defect is calculated. The calculations of hopping photoconductivity were carried out for the partially disordered silicon crystal with total concentration of *t*-defects of $3{\cdot}10^{19}$ cm^{-3}, compensated by shallow hydrogen-like donors. The ratios of donor concentration to *t*-defect concentration (compensation ratios) are 0.25, 0.5, and 0.75. It is taken into account that an electron localization radius on *t*-defect in the charge state (−1) is greater that on *t*-defect in the charge state (0). The calculated value of the dark hopping electrical conductivity is consistent with the known experimental data. A negative DC photoconduction at $\gamma > \alpha$ is predicted, due to a decrease in the concentration of electrons hopping via states (−1), (0) and (0), (+1).

1. Introduction

In the experimental study of germanium and silicon crystals moderately doped with hydrogen-like impurities in the temperature range of liquid helium, Dobrego and Ryvkin [1, 2] introduced the concept of hopping photoconductivity as a change in the magnitude of DC (stationary) hopping electrical conductivity under the influence of optical radiation. When the intrinsic absorption band of crystalline semiconductors is excited by light, 'free' electrons in the *c*-band and holes in the *v*-band are created as a result of interband transitions. Nonequilibrium electrons and holes are captured by donors and acceptors that are present in the semiconductor, which provide hopping migration of electrons and holes: the value of hopping electrical conductivity changes—hopping photoconductivity is observed. Somewhat later, the study of hopping photoconductivity under interband excitation of germanium crystals was carried out by Davis [3].

Note that even in early works on hopping conductivity [4] in lightly doped semiconductors the connection between conductivity and the degree of compensation of a majority (doping) impurity by a minority (compensating) impurity was mentioned. This dependence was considered as empirical. Later, this relationship was supported theoretically both for the ordinary (dark) hopping electrical conductivity [5] and for hopping photoconductivity [6].

A method for excitation of hopping photoconductivity, when there are several impurity energy levels in the band gap of the semiconductor and hopping migration of electrons (or holes) can be conducted via one of them (shallow, hydrogen-like) was proposed and experimentally implemented in [7]. With compensation corresponding to the absence of electrons (or holes) at the shallow energy level hopping conduction will not be observed. However, when the semiconductor is illuminated with a photon energy equal to the energy difference between the impurity levels, it is possible that carriers are transferred from the deeper level to the shallow one and hopping conduction occurs. In this case, hopping photoconductivity arises due to the excitation of interimpurity transitions of electrons by light.

Deep impurities in the crystal matrix tend to form precipitates as their concentration increases, and only irradiation-induced defects can be introduced in significant concentrations sufficient to realize hopping electrical conductivity at room temperature. To introduce three-charge-state *t*-defects into covalent semiconductors, they are irradiated with ionizing radiation (gamma rays, fast electrons, neutrons, etc.). In contrast to 'metallurgical' doping with impurities, the concentration of intrinsic radiation defects can be largely controlled by annealing [8]. In some crystals, e.g., in Si, GaAs, SiC, GaN, diamond, the Fermi level is pinned in the lower half of the band gap as the radiation fluence increases, i.e. with the accumulation of intrinsic irradiation-induced defects (atomic vacancies, interstitial atoms, and their associates) [9].

Previously, the photoconductivity of amorphous hydrogenated silicon (*a*-Si:H) films containing *t*-defects was considered due to nonequilibrium *c*-band electrons and *v*-band holes [10, 11], but the possibility of hopping migration of electrons via *t*-defects in these works was not taken into account.

A model of hopping photoconductivity in amorphous semiconductors when they are excited by long-wavelength infrared radiation was proposed in [12]. According to this model, stimulation of hopping photoconductivity by long-wavelength radiation implies an initial transition of the electron to a neighboring energetically higher localized state in the vicinity of the Fermi level. Subsequently, in most cases, a reverse transition occurs without affecting the electrical conductivity, however, some spatially separated localized states are associated with others, allowing the electron and hole to separate over a long distance. This is the only case where hopping photoconductivity is observed.

Hopping stationary photoconductivity via three-charge-state impurity atoms in the three-dimensional crystal was considered in [6], but the value of electrical conductivity was not calculated. In [13], for the first time, a Peltier element with hopping migration of electrons via intrinsic point defects randomly (Poissonian) distributed over the crystal matrix was proposed. However, in [13] hopping photoconductivity via three-charge-state point defects (defects of *t*-type) was not considered and was not calculated.

The dependence of hopping electrical conductivity on temperature in disordered semiconductors with point structural defects was studied earlier [14–18]. For example, in [14], hopping photoconductivity of *a*-Si:H films was measured before and after their irradiation with protons, and the data were interpreted according to the Mott model of hopping electrical conductivity [19]. In [15], the electrical conductivity of *a*-Si doped with donor phosphorus atoms with the concentration of $5.5{\cdot}10^{18}$ cm^{-3} was measured. The temperature dependence of hopping electrical conductivity in amorphous carbon films was also measured [20, 21]. To explain the dependences obtained, it was assumed in [20] that small polarons migrate in the variable range hopping (VRH) regime. (VRH regime is the regime of electron hopping via defects, when the hops with the lowest activation energy are realized primarily and the hops with the shortest hopping length are realized secondarily.) The interpretation of the experimental data in [21] on photo- and electrical conductivity was based on the parameterization of the Gaussian electronic density of states and the postulation of the temperature and energy dependence of the hopping mobility with fitting parameters without its theoretical justification. Moreover, in [14–21], hopping electrical conductivity via three-charge-state point defects could not be described without using fitting parameters (see also [22, 23]).

The purpose of this work is to calculate the change in the DC hopping photoconductivity of the semiconductor with point *t*-defects in the charge states (-1, 0 and $+1$) under the change in the illumination intensity, which stimulates electron transitions between *t*-defects in the charge states (0).

2. Hopping photoconductivity model

Let us consider a three-dimensional partially disordered crystalline semiconductor sample positioned between metal ohmic electrodes (M). The sample dimensions are much larger than the average distance between defects. The crystal contains point two-level defects in three charge states (*t*-defects) with their concentration sufficient to pin the Fermi level E_F in the energy band gap and to realize hopping conductivity via *t*-defects. Defects of *t*-type in the charge states (-1) and (0) form a $|1\rangle$-band with an average energy level E_1 and the ones in the charge states (0) and ($+1$) form a $|2\rangle$-band in the band gap (with an average energy level E_2), located closer to *v*-band than $|1\rangle$-band (figure 1). We assume that the thermal ionization energies of hydrogen-like donors $|d\rangle$ and

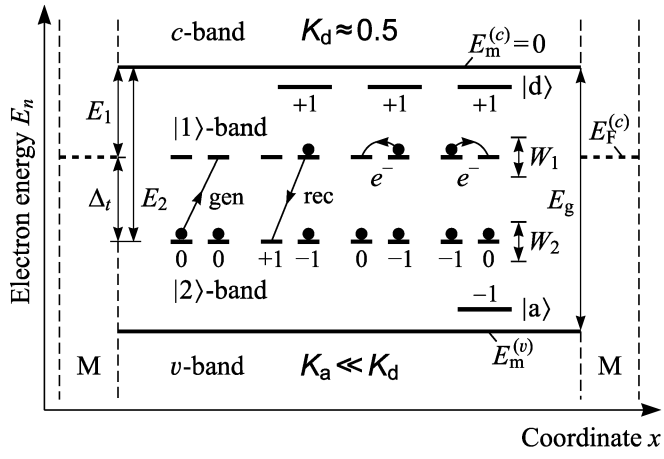

Figure 1. Single-electron energy E_n as function of x coordinate in semiconductor with two ohmic electrodes (M) in equilibrium: $E_m^{(c)} = 0$ and $E_m^{(v)}$ are the drift mobility edges for c-band electrons and v-band holes, $E_F^{(c)} < 0$ is the Fermi level, counted from the electron mobility edge ($E_m^{(c)} = 0$), $E_m^{(c)} - E_m^{(v)} = E_g$ is the width of the energy band gap of semiconductor, $\Delta_t = E_2 - E_1$ is the width of energy gap between $|1\rangle$- and $|2\rangle$-bands of point three-charge-state t-defects, W_1 and W_2 are the widths of $|1\rangle$- and $|2\rangle$-bands. Arrows indicate hops of single electrons e^- via $|1\rangle$-band as well as generation [gen: $2(0) \rightarrow (-1) + (+1)$] and recombination [rec: $(-1) + (+1) \rightarrow 2(0)$] electron transitions between $|1\rangle$- and $|2\rangle$-bands; $|d\rangle$ and $|a\rangle$ are the states of shallow hydrogen-like donors and acceptors in the charge states $(+1)$ and (-1), respectively; $K_d \approx 0.5$ and $K_a \ll K_d$ are the compensation ratios of t-defects by donors and acceptors (the position of the Fermi level $E_F^{(c)} < 0$ practically coincides with the energy level E_1). [Number of hops of single electrons from the charge states (0) to the charge states $(+1)$ of t-defects in $|2\rangle$-band is small and they are not shown.]

acceptors $|a\rangle$ are much less than E_1 and $E_g - E_2$, respectively. Note that typical shallow hydrogen-like impurity atoms contribute energy levels of about 40 meV deep in the energy gap of crystalline silicon. They can be introduced up to the Mott concentration (see, e.g., [24]).

Let us consider semiconductor under conditions of only hopping electron migration via immobile irradiation-induced defects (of t-type) in the charge states (-1) and (0), as well as in the charge states (0) and $(+1)$. The total concentration of t-defects is $N_t = N_{t,-1} + N_{t,0} + N_{t,+1} \equiv N_{-1} + N_0 + N_{+1}$ in the charge states $(-1, 0$ and $+1)$. We assume that the shallow hydrogen-like donors $|d\rangle$ and acceptors $|a\rangle$ are completely ionized and their concentrations in the charge states $(+1)$ and (-1) are $N_d < N_t$ and $N_a < N_t$, respectively.

The electrical neutrality condition for the partially disordered semiconductor with t-type defects, taking into account totally ionized hydrogen-like donors and acceptors with concentrations $N_d = K_d N_t$ and $N_a = K_a N_t$, has the form:

$$N_{+1} + K_d N_t = N_{-1} + K_a N_t, \tag{1}$$

where $0 \leqslant K_d < 1$ and $0 \leqslant K_a < 1$ are the compensation ratios of t-type irradiation-induced defects by hydrogen-like donors $|d\rangle$ and acceptors $|a\rangle$, respectively.

Note that for $K_d = 0.5$ and $K_a \ll K_d$ the Fermi level $E_F^{(c)}$ practically coincides with the top energy level E_1 (figure 1). If the Fermi level in metallic contacts coincides with the energy level E_1, then these contacts are ohmic, and in this case hopping conduction via t-defects in charge states (-1) and (0) dominates.

The average concentrations of ionized and neutral t-defects can be written as [25]:

$$N_Z = N_t \langle f_Z \rangle = N_t \iint_{-\infty}^{+\infty} f_Z \, G_1 G_2 \, \mathrm{d}\Delta_1 \mathrm{d}\Delta_2, \tag{2}$$

where f_Z is the probability that the defect is in the one of three possible charge states $Z = -1, 0, +1$ (in units of the elementary charge e).

If we neglect the excited states of t-defects, then the inverse distribution functions $1/f_Z$ of defects in $|1\rangle$- and $|2\rangle$-bands over charge states are [26, 27]:

$$\begin{aligned}
\frac{1}{f_{-1}} &= 1 + g_1 \exp\left(\frac{-(\Delta_1 + E_1 + E_F^{(c)})}{k_B T}\right) + \frac{g_1}{g_2} \exp\left(\frac{-(\Delta_1 + \Delta_2 + E_1 + E_2 + 2E_F^{(c)})}{k_B T}\right), \\
\frac{1}{f_0} &= 1 + \frac{1}{g_1} \exp\left(\frac{\Delta_1 + E_1 + E_F^{(c)}}{k_B T}\right) + \frac{1}{g_2} \exp\left(\frac{-(\Delta_2 + E_2 + E_F^{(c)})}{k_B T}\right), \\
\frac{1}{f_{+1}} &= 1 + g_2 \exp\left(\frac{\Delta_2 + E_2 + E_F^{(c)}}{k_B T}\right) + \frac{g_2}{g_1} \exp\left(\frac{\Delta_1 + \Delta_2 + E_1 + E_2 + 2E_F^{(c)}}{k_B T}\right),
\end{aligned} \tag{3}$$

where $E_F^{(c)}$ is the Fermi level (counted from the c-band electron mobility edge [28, 29]); $E_F^{(c)} < 0$ for the Fermi level in the band gap; $E_1 > 0$ is the average energy of the electron detachment from the negatively charged t-defect and its transition to the c-band mobility edge $E_m^{(c)} = 0$; $E_2 > 0$ is the average energy of electron detachment from t-defect in the charge state (0) and its transition to the c-band mobility edge $E_m^{(c)} = 0$; $\Delta_1 = \mathcal{E}_1 - E_1$ and $\Delta_2 = \mathcal{E}_2 - E_2$ are the differences between the t-defect energy level and the average t-defect energy level in $|1\rangle$-band and $|2\rangle$-band, respectively; k_B is the Boltzmann constant; T is the absolute temperature; $g_1 = g_0/g_{-1} \approx 1, g_2 = g_0/g_{+1} \approx 1$, where g_Z is the number of quantum states of t-defect in the charge state Z.

We assume that the energy levels $\mathcal{E}_1 = \Delta_1 + E_1$ and $\mathcal{E}_2 = \Delta_2 + E_2$ of t-defects in the band gap of semiconductor have a normal (Gaussian) distribution [25]:

$$G_1 = \frac{1}{\sqrt{2\pi}\,W_1}\exp\left[-\frac{1}{2}\left(\frac{\Delta_1}{W_1}\right)^2\right], \quad G_2 = \frac{1}{\sqrt{2\pi}\,W_2}\exp\left[-\frac{1}{2}\left(\frac{\Delta_2}{W_2}\right)^2\right], \tag{4}$$

where W_1 and W_2 are the effective widths of $|1\rangle$-band and $|2\rangle$-bands, respectively (figure 1).

With the total concentration of charged defects and impurity ions $N_{ch} = N_{-1} + N_{+1} + K_d N_t + K_a N_t$, randomly (Poissonian) distributed over the crystal, we have equal rms fluctuations of the electrostatic energy, i.e. the widths of $|1\rangle$- and $|2\rangle$-bands are [30]:

$$W_1 = W_2 = W = 2.64\frac{e^2 N_{ch}^{1/3}}{4\pi\varepsilon_r\varepsilon_0}, \tag{5}$$

where the Coulomb interaction of each charged defect is considered only with its nearest charged defect (ion); e is the elementary charge; $\varepsilon_r\varepsilon_0$ is the static dielectric permittivity; ε_r is the relative dielectric permittivity of partially disordered semiconductor, ε_0 is the electric constant.

In equation (5), taking into account equation (1), the concentration of ionized t-defects and shallow hydrogen-like impurity ions is $N_{ch} = 2(N_{+1} + K_d N_t) = 2(N_{-1} + K_a N_t)$. Further we consider the compensation of t-defects only by shallow hydrogen-like donors ($0.25 \leqslant K_d \leqslant 0.75$; $K_a = 0$). Thus, in the dark $N_{+1} \ll K_d N_t$, and the concentration of impurity ions is $N_{ch} \approx 2K_d N_t = 2N_{-1}$.

The hopping frequencies $\Gamma_{-1,0} = \Gamma_{-1,0}(r, \varepsilon_{-1,0})$ and $\Gamma_{0,+1} = \Gamma_{0,+1}(r, \varepsilon_{0,+1})$ of electrons via t-defects in the charge states (-1), (0) and (0), $(+1)$ are given by the relations (see, e.g., [23, 31, 32]):

$$\Gamma_{-1,0} = \nu_{lat}\exp\left[-\left(\frac{r}{a_{-1}} + \frac{\varepsilon_{-1,0} + |\varepsilon_{-1,0}|}{2k_B T}\right)\right], \quad \Gamma_{0,+1} = \nu_{lat}\exp\left[-\left(\frac{r}{a_0} + \frac{\varepsilon_{0,+1} + |\varepsilon_{0,+1}|}{2k_B T}\right)\right], \tag{6}$$

where r is the electron hopping length via t-defects in the charge states (-1), (0) and (0), $(+1)$; $\varepsilon_{-1,0}$ is the difference between the ionization energy of t-defect in the charge state (-1) and the electron affinity energy of another t-defect in the charge (0), between which the electron hops in $|1\rangle$-band; $\varepsilon_{0,+1}$ is the difference between the ionization energy of t-defect in the charge state (0) and the electron affinity energy of another t-defect in the charge $(+1)$, between which the electron hops in $|2\rangle$-band; ν_{lat} is the characteristic frequency of crystal matrix phonons; $a_{-1} \propto (m_1 E_1)^{-1/2}$ and $a_0 \propto (m_2 E_2)^{-1/2}$ are the radii of localization of an electron on a t-defect in the charge state (-1) in $|1\rangle$-band and in the charge state (0) in $|2\rangle$-band; $m_1 \approx m_2$ are the effective masses of an electron on a t-defect with average energy levels E_1 and E_2. In numerical calculations, we assumed $a_{-1} = d_{im}$ and $a_0 = a_{-1}(E_1/E_2)^{1/2}$, where $d_{im} = 2[4\pi(1 + K_d + K_a)N_t/3]^{-1/3}$ is the average diameter of a spherical region per one point defect (t-defect, donor or acceptor) in semiconductor; $a_{-1} > a_0$ since $E_2 > E_1$.

Note that the value $a_{-1} = d_{im}$ is a reasonable estimate (see, e.g., [33]), suitable for describing electron hopping via the excited state of a pair of t-defects in the charge states (-1) and (0). Our model is most applicable for the nearest neighbor hopping regime rather than for the variable range hopping regime, since the quantities $\varepsilon_{-1,0}$ and $\varepsilon_{0,+1}$ do not depend on the electron hopping length between t-defects.

The diffusion coefficients $D_{-1,0}$ and $D_{0,+1}$ of electrons hopping via t-defects in the covalent crystal matrix, in contrast to the classical definition [34], can be estimated by averaging over all probable hopping lengths r and quantities $\varepsilon_{-1,0}$ and $\varepsilon_{0,+1}$ (see, e.g., [35, 36]):

$$D_{-1,0} = \frac{1}{6}\langle r^2\Gamma_{-1,0}(r, \varepsilon_{-1,0})\rangle, \quad D_{0,+1} = \frac{1}{6}\langle r^2\Gamma_{0,+1}(r, \varepsilon_{0,+1})\rangle. \tag{7}$$

From equation (7), taking into account equation (6), we obtain

$$\begin{aligned} D_{-1,0} &= \frac{1}{6}\int_{-\infty}^{+\infty}\left(\int_0^{\infty} r^2\Gamma_{-1,0}(r, \varepsilon_{-1,0})P_{-1,0}(r)\,dr\right)G_{-1,0}(\varepsilon_{-1,0})\,d\varepsilon_{-1,0}, \\ D_{0,+1} &= \frac{1}{6}\int_{-\infty}^{+\infty}\left(\int_0^{\infty} r^2\Gamma_{0,+1}(r, \varepsilon_{0,+1})P_{0,+1}(r)\,dr\right)G_{0,+1}(\varepsilon_{0,+1})\,d\varepsilon_{0,+1}, \end{aligned} \tag{8}$$

where $P_{-1,0}(r)dr = 4\pi r^2(N_{-1} + N_0)\exp[-4\pi r^3(N_{-1} + N_0)/3]dr$ is the Poissonian probability density function that near t-defect in the charge state (-1) the mutually nearest t-defect in the charge state (0) is located in the

interval $(r, r + \mathrm{d}r)$; $P_{0,+1}(r)\mathrm{d}r = 4\pi r^2(N_0 + N_{+1})\exp\left[-4\pi r^3(N_0 + N_{+1})/3\right]\mathrm{d}r$ is the probability density function of mutually nearest t-defects in the charge states (0) and (+1) [30]; the Gaussian distribution of difference $\varepsilon_{-1,0}$ between the ionization energy of t-defect in the charge state (−1) and the electron affinity energy of another t-defect in the charge (0), between which the electron hops in $|1\rangle$-band, is (cf. equation (4)):

$$G_{-1,0}(\varepsilon_{-1,0}) = \frac{1}{\sqrt{2\pi}\,W}\exp\left[-\frac{1}{2}\left(\frac{\varepsilon_{-1,0}}{W}\right)^2\right];$$

the Gaussian distribution of difference $\varepsilon_{0,+1}$ between the ionization energy of t-defect in the charge state (0) and the electron affinity energy of another t-defect in the charge (+1), between which the electron hops in $|2\rangle$-band, is

$$G_{0,+1}(\varepsilon_{0,+1}) = \frac{1}{\sqrt{2\pi}\,W}\exp\left[-\frac{1}{2}\left(\frac{\varepsilon_{0,+1}}{W}\right)^2\right].$$

The normalization conditions for the Poissonian probability density functions $P_{-1,0}(r)$ and $P_{0,+1}(r)$ are satisfied:

$$\int_0^\infty P_{-1,0}(r)\,\mathrm{d}r = \int_0^\infty P_{0,+1}(r)\,\mathrm{d}r = 1. \tag{9}$$

Note that in the case of dependence of the hopping frequency $\Gamma_{-1,0}$ (or $\Gamma_{0,+1}$) on the variable hopping length r, according to [37] and equations (7) and (8), it is necessary to average their product $\langle r^2\Gamma_{-1,0}\rangle$ (or $\langle r^2\Gamma_{0,+1}\rangle$) in contrast to averaging separately $\langle r^2\rangle$ and $\langle\Gamma_{-1,0}\rangle$ (or separately $\langle r^2\rangle$ and $\langle\Gamma_{0,+1}\rangle$), as proposed in [38].

The drift hopping mobilities $M_{-1,0}$ and $M_{0,+1}$ of electrons hopping via point t-defects of the crystal matrix are related to the hopping diffusion coefficients $D_{-1,0}$ and $D_{0,+1}$ by the Nernst–Townsend–Einstein–Smoluchowski relation (cf. [27]):

$$\frac{D_{-1,0}}{M_{-1,0}} = \xi_{-1,0}\frac{k_\mathrm{B}T}{e}, \quad \frac{D_{0,+1}}{M_{0,+1}} = \xi_{0,+1}\frac{k_\mathrm{B}T}{e}, \tag{10}$$

$$\xi_{-1,0} = \frac{\langle f_{-1}\rangle\langle f_0\rangle}{[\langle f_{-1}\rangle + \langle f_0\rangle]\langle f_{-1}f_0\rangle + 2\langle f_0\rangle\langle f_{-1}f_{+1}\rangle - \langle f_{-1}\rangle\langle f_0f_{+1}\rangle},$$

$$\xi_{0,+1} = \frac{\langle f_0\rangle\langle f_{+1}\rangle}{[\langle f_0\rangle + \langle f_{+1}\rangle]\langle f_0f_{+1}\rangle + 2\langle f_0\rangle\langle f_{-1}f_{+1}\rangle - \langle f_{+1}\rangle\langle f_{-1}f_0\rangle},$$

where $\langle f_Z\rangle$ is given by equation (2) and the products $\langle f_Zf_Y\rangle = \langle f_Yf_Z\rangle$ for $Z \neq Y = -1, 0, +1$ are given by

$$\langle f_Zf_Y\rangle = \iint_{-\infty}^{+\infty} f_Z\,f_Y\,G_1G_2\,\mathrm{d}\Delta_1\mathrm{d}\Delta_2.$$

Dimensionless parameters $\xi_{-1,0} \geqslant 1$ and $\xi_{0,+1} \geqslant 1$ characterize the difference in the extent to which the diffusion coefficient and the mobility of electrons hopping in $|1\rangle$- and $|2\rangle$-bands are affected by fluctuations of the electrostatic potential energy in the crystal. Note that when obtaining equations (10) it was assumed that $W \propto N_\mathrm{ch}^{1/3}$ given by equation (5) and, hence, the (Gaussian) distributions G_1 and G_2 given by equations (4), or more exactly, the electronic densities of states in $|1\rangle$- and $|2\rangle$-bands, do not depend on the position of the Fermi level $E_\mathrm{F}^{(c)}$ (see, e.g., [39, 40]). In our case, this is accomplished at relatively high temperatures and moderate degrees of compensation of t-defects by shallow hydrogen-like donors (e.g., for $0.25 \leqslant K_\mathrm{d} \leqslant 0.75$).

The DC (stationary) hopping conductivities due to the migration of single electrons via immobile t-defects in the charge states (−1), (0) and (0), (+1) are $\sigma_{-1,0}$ and $\sigma_{0,+1}$, respectively. Thus, the total stationary hopping conductivity is

$$\sigma_\mathrm{h} = \sigma_{-1,0} + \sigma_{0,+1} = e(N_{-1,0}M_{-1,0} + N_{0,+1}M_{0,+1}), \tag{11}$$

where $N_{-1,0} = N_{-1}N_0/N_t$, $N_{0,+1} = N_0N_{+1}/N_t$ are the effective concentrations of single electrons hopping via t-defects in the charge states (−1), (0) and (0), (+1) (rather than pairs of electrons, or bipolarons); $M_{-1,0} = eD_{-1,0}/\xi_{-1,0}k_\mathrm{B}T$ is the drift mobility of electrons hopping via t-defects in the charge states (−1), (0); $M_{0,+1} = eD_{0,+1}/\xi_{0,+1}k_\mathrm{B}T$ is the drift mobility of electrons hopping via t-defects in the charge states (0), (+1).

Note that since for the electron localization radii on the t-defect in the charge state (−1) in $|1\rangle$-band (a_{-1}) and in the charge state (0) in $|2\rangle$-band (a_0) the relation $a_{-1} > a_0$ is satisfied, then the relation $\sigma_{-1,0} > \sigma_{0,+1}$ is valid for the electrical conductivities, other things being equal.

The uniform over the volume illumination of the partially disordered crystal, which causes electron transitions between two neutral t-defects [2(0) → (−1) + (+1)], changes the filling of $|1\rangle$- and $|2\rangle$-bands with electrons, acting as 'photogeneration' (figure 1). We assume that the irradiation does not result in the crystal heating and, hence, does not increase the coefficient $\beta = \alpha N_{-1}N_{+1}/(N_0)^2$, characterizing the thermal ionization of t-defects, where α is the coefficient characterizing the electron capture from the negatively charged to the positively charged t-defect [(−1) + (+1) → 2(0)]. Thus, the nonequilibrium values of the concentrations

$N_{-1}(\gamma)$, $N_0(\gamma)$ and $N_{+1}(\gamma)$ are determined from the relations [6]:

$$\begin{aligned} &\alpha\frac{N_{-1}(\gamma)N_{+1}(\gamma)}{[N_0(\gamma)]^2} = \beta + \gamma,\\ &N_t = N_{-1}(\gamma) + N_0(\gamma) + N_{+1}(\gamma),\\ &N_{-1}(\gamma) + K_\mathrm{a}N_t = N_{+1}(\gamma) + K_\mathrm{d}N_t, \end{aligned} \tag{12}$$

where γ is the photoionization coefficient of neutral t-defects, which is proportional to the intensity of illumination, which causes the electron transfer from $|2\rangle$- to $|1\rangle$-band.

From first equation in system (12) and $\beta = \alpha N_{-1}N_{+1}/(N_0)^2$ it follows that the concentrations of hopping electrons $N_{-1,0}(\gamma) = N_{-1}(\gamma)N_0(\gamma)/N_t$ and $N_{0,+1}(\gamma) = N_0(\gamma)N_{+1}(\gamma)/N_t$ under illumination ($\gamma > 0$) are determined by the concentrations of hopping electrons $N_{-1,0}$, $N_{0,+1}$ in the dark ($\gamma = 0$) and the ratio γ/α:

$$\frac{N_{-1,0}(\gamma)N_{0,+1}(\gamma)N_t^2}{[N_0(\gamma)]^4} = \frac{N_{-1,0}N_{0,+1}N_t^2}{(N_0)^4} + \frac{\gamma}{\alpha}. \tag{13}$$

Note that, for compensation ratios $0.25 \leqslant K_\mathrm{d} \leqslant 0.75$ and $K_\mathrm{a} = 0$, illumination has a little effect on the widths of $|1\rangle$- and $|2\rangle$-bands $W_1 = W_2 = W \propto N_\mathrm{ch}^{1/3}$, parameters $\xi_{-1,0}$, $\xi_{0,+1}$, and Fermi level $E_\mathrm{F}^{(c)}$. So, it is assumed that these quantities do not depend on γ. System (12) combines the balance of t-defect concentrations in the different charge states and the electrical neutrality equation under illumination conditions and does not explicitly depend on the Fermi level, but according to equation (13) depends only on γ/α ratio. Following [41], we neglect a weak dependence of the drift hopping mobilities $M_{-1,0}$ and $M_{0,+1}$ [compared to $N_{-1,0}(\gamma)$ and $N_{0,+1}(\gamma)$] on the photoionization coefficient γ of electrically neutral t-defects.

Thus, the stationary hopping photoconductivity is equal to

$$\sigma_\mathrm{h}(\gamma) = e[N_{-1,0}(\gamma)M_{-1,0} + N_{0,+1}(\gamma)M_{0,+1}], \tag{14}$$

where the concentrations of electrons hopping via t-defects $N_{-1,0}(\gamma)$ and $N_{0,+1}(\gamma)$ are determined by equations (12), and their drift mobilities $M_{-1,0}$ and $M_{0,+1}$ do not depend on illumination.

3. Calculation results and discussion

As an example, let us consider a partially disordered silicon crystal. For irradiation-induced t-defects in silicon we assume [42]: $E_1 = 400$ meV, $E_2 = E_1 + \Delta_t = 700$ meV, where $\Delta_t = 300$ meV is the difference between centers of $|1\rangle$- and $|2\rangle$-bands. The ratio of hopping photoconductivity to dark conductivity $\sigma_\mathrm{h}(\gamma)/\sigma_\mathrm{h}$ according to equations (11)–(14) was calculated numerically as a function of the decimal logarithm of the ratio γ/α of coefficient γ of the illumination stimulated transition of an electron between two t-defects in the charge states (0) to coefficient α of electron transition from t-defect in the charge state (−1) to t-defect in the charge state (+1). The value of the dark hopping electrical conductivity σ_h (in the absence of illumination, i.e. for $\gamma = 0$) was calculated according to equation (11) for the following parameter values: the characteristic frequency of crystal matrix phonons $\nu_\mathrm{lat} \approx 10$ THz [43]; the total concentration of t-defects $N_t = 3{\cdot}10^{19}$ cm^{-3} was chosen sufficiently high to realize hopping conductivity via t-defects and to pin the Fermi level in the energy band gap [9, 44–46]; the compensation ratios of t-defects by donors $K_\mathrm{d} = 0.25, 0.5, 0.75$ and acceptors $K_\mathrm{a} = 0$; the absolute temperature $T = 300$ K. The radius of electron localization on t-defect in the charge state (−1) is $a_{-1} = d_\mathrm{im}$, where $d_\mathrm{im} = 3.7$, 3.48, 3.31 nm for $K_\mathrm{d} = 0.25, 0.5, 0.75$, respectively; $d_\mathrm{im} = 1.24[(1 + K_\mathrm{d} + K_\mathrm{a})N_t]^{-1/3}$; $a_0 = 0.756a_{-1}$.

The Fermi level $E_\mathrm{F}^{(c)}$ in the absence of illumination ($\gamma = 0$) is found from the electrical neutrality condition (1), where concentrations of ionized t-defects N_{+1} and N_{-1} are calculated from equation (2), taking into account equations (3) and (4). The Fermi level $E_\mathrm{F}^{(c)}$ coincides with the energy level E_1 (half filled with electrons in the absence of illumination) for $K_\mathrm{d} = 0.5$ and $K_\mathrm{a} = 0$ (see figure 1).

Figure 2 shows the results of calculations according to equations (10) ratios of diffusion coefficients to drift mobilities $\xi_{-1,0} = eD_{-1,0}/M_{-1,0}k_\mathrm{B}T$ (blue line), $\xi_{0,+1} = eD_{0,+1}/M_{0,+1}k_\mathrm{B}T$ (red line), and $\xi_{-1,0} = \xi_{0,+1} = 1$ for $W \ll k_\mathrm{B}T$ (dashed line) as functions of the concentration of t-defects N_t for $K_\mathrm{d} = 0.5$ and $K_\mathrm{a} = 0$ at $T = 300$ K. It can be seen that the parameters $\xi_{-1,0}$ and $\xi_{0,+1}$ characterizing the ratio of the hopping diffusion coefficient to the drift hopping mobility increase with the concentration of t-defects N_t. Calculations in figure 2 find support in experiments [47] performed on a-Si:H films under conditions of photoconductivity by c-band electrons and v-band holes, in the sense that the parameters $\xi_{-1,0} \geqslant 1$ and $\xi_{0,+1} \geqslant 1$; for details of our calculations, see [48].

Figure 3 shows the results of calculations according to equations (12), taking into account equations (2) and (3), of the ratios of concentrations of t-defects in the different charge states: $N_{-1}(\gamma)$ (blue line), $N_0(\gamma)$ (black line), and $N_{+1}(\gamma)$ (red line), to total concentration N_t of t-defects depending on the ratio of photoionization coefficient γ of neutral t-defects, proportional to the illumination intensity, to coefficient of 'capture' α of electrons from $|1\rangle$- to $|2\rangle$-band. It can be seen that with an increase in γ/α, the concentrations $N_{-1}(\gamma)$ and $N_{+1}(\gamma)$ of t-defects in the charge states (−1) and (+1) increase, and their concentration $N_0(\gamma)$ in the charge states (0) decreases, due to

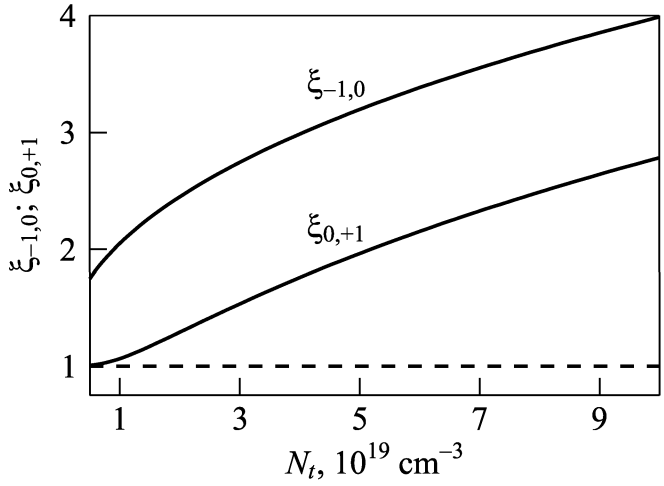

Figure 2. Dependences of the parameters $\xi_{-1,0}$ (blue line) and $\xi_{0,+1}$ (red line) at $T = 300$ K calculated by equation (10) on the concentration of t-defects N_t for $K_d = 0.5$ and $K_a = 0$; dashed line is $\xi_{-1,0} = \xi_{0,+1} = 1$ for $W \ll k_B T$.

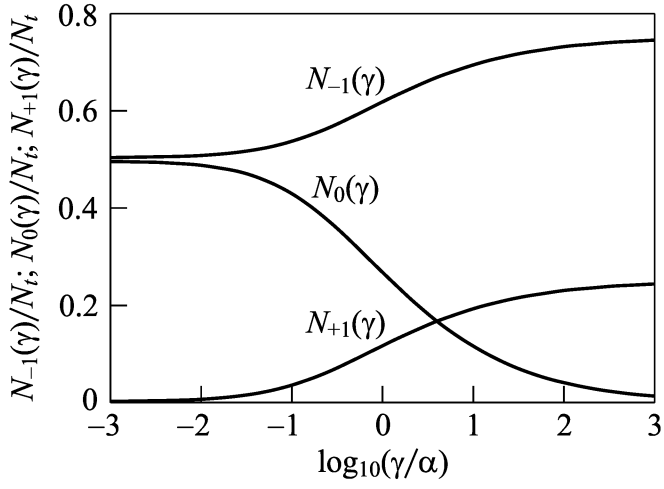

Figure 3. Dependences of the concentrations of t-defects in the different charge states (in units of N_t): $N_{-1}(\gamma)$ (blue line), $N_0(\gamma) = N_t - N_{-1}(\gamma) - N_{+1}(\gamma)$ (black line), and $N_{+1}(\gamma)$ (red line) calculated by equations (12), taking into account equations (2) and (3), on the decimal logarithm of the ratio γ/α of illumination intensity γ to recombination rate α of (-1) and $(+1)$ charge states, for $\varepsilon_r = 11.47$; $N_t = 3{\cdot}10^{19}$ cm^{-3}; $K_d = 0.5$ and $K_a = 0$ at $T = 300$ K.

electron transitions from neutral t-defects of $|2\rangle$-band to neutral t-defects of $|1\rangle$-band. These results can be useful for measuring the concentrations of t-defects by the electron spin resonance method.

Figure 4 shows the results of calculations according to equations (12), taking into account equations (2) and (3), of the ratios of concentrations of electrons hopping in $|1\rangle$-band $N_{-1,0}(\gamma) = N_{-1}(\gamma)N_0(\gamma)/N_t$ (curves *1*, *2*, *3*) and in $|2\rangle$-band $N_{0,+1}(\gamma) = N_0(\gamma)N_{+1}(\gamma)/N_t$ (curves *1′*, *2′*, *3′*) to total concentration N_t of t-defects depending on the ratio of photoionization coefficient γ of neutral t-defects, proportional to the illumination intensity, to coefficient of 'capture' α of electrons from $|1\rangle$- to $|2\rangle$-band. It can be seen that for $\gamma > \alpha$ the concentrations of hopping electrons $N_{-1,0}(\gamma)$ in $|1\rangle$-band and $N_{0,+1}(\gamma)$ in $|2\rangle$-band decrease due to electron transitions between neutral t-defects.

Figure 5 shows the results of calculations according to equations (11)–(14) of the ratio of hopping photoconductivity to dark conductivity $\sigma_h(\gamma)/\sigma_h$ depending on the ratio γ/α for $K_d = 0.25, 0.5, 0.75$ (curves *1*, *2*, *3*) at $T = 300$ K. It can be seen that as the illumination intensity increases, the photoconductivity $\sigma_h(\gamma) = \sigma_{-1,0}(\gamma) + \sigma_{0,+1}(\gamma)$ slightly increases and then decreases due to electron transitions from neutral t-defects of $|2\rangle$-band to neutral t-defects of $|1\rangle$-band, i.e. charge state transitions $2(0) \rightarrow (-1) + (+1)$. Figure 5 shows that at $\gamma > \alpha$ the value of photoconductivity $\sigma_h(\gamma)$ becomes less than the value of dark conductivity σ_h, i.e. there is a negative hopping photoconductivity due to a decrease in the concentration of hopping electrons with illumination intensity (see figure 4). Note that for compensation ratios $K_d = 0.25, 0.5, 0.75$ and $K_a = 0$ the nature of the dependence of hopping photoconductivity $\sigma_h(\gamma)$ is mainly determined by the change in the concentration

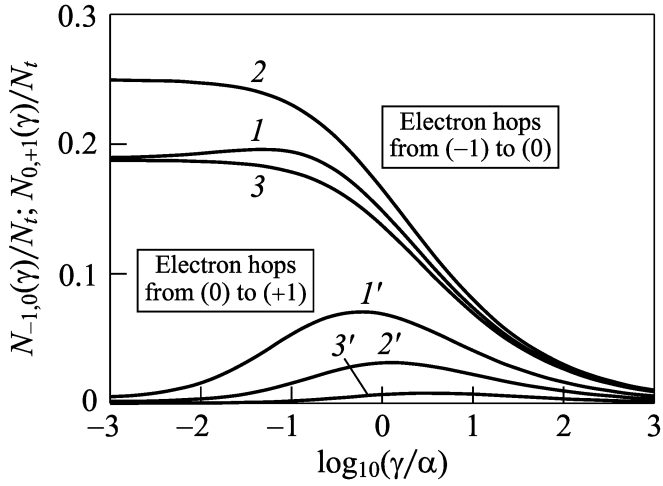

Figure 4. Dependences of the concentrations of electrons hopping via *t*-defects in partially disordered crystalline silicon (in units of N_t): $N_{-1,0}(\gamma)$ (in $|1\rangle$-band; curves *1*, *2*, *3*) and $N_{0,+1}(\gamma)$ (in $|2\rangle$-band; curves *1′*, *2′*, *3′*), calculated by equations (12), taking into account equations (2) and (3), on the decimal logarithm of the ratio γ/α of illumination intensity γ to recombination rate α of (−1) and (+1) charge states, for $\varepsilon_r = 11.47$; $N_t = 3{\cdot}10^{19}$ cm^{-3}; $K_d = 0.25$ (curves *1*, *1′*), 0.5 (curves *2*, *2′*), 0.75 (curves *3*, *3′*) and $K_a = 0$ at $T = 300$ K.

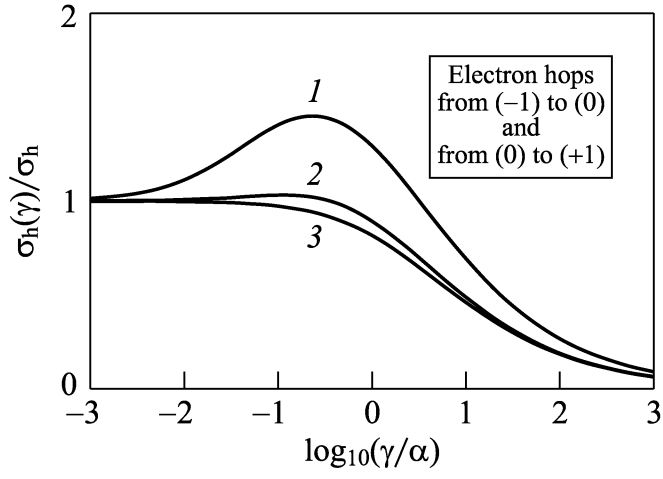

Figure 5. Dependence of the ratio of DC hopping photoconductivity $\sigma_h(\gamma)$ to its dark value σ_h, calculated by equations (11)–(14), on the decimal logarithm of the ratio γ/α of photoionization (γ) to recombination (α) coefficients, for $\varepsilon_r = 11.47$; $N_t = 3{\cdot}10^{19}$ cm^{-3}; $K_d = 0.25$ (curve *1*), 0.5 (*2*), 0.75 (*3*) and $K_a = 0$ at $T = 300$ K in partially disordered silicon.

of electrons hopping in $|1\rangle$-band $N_{-1,0}(\gamma)$ (figure 4, curves *1*, *2*, *3*), than of electrons hopping in $|2\rangle$-band $N_{0,+1}(\gamma)$ (figure 4, curves *1′*, *2′*, *3′*). For $N_t \approx 3{\cdot}10^{19}$ cm^{-3}, $K_d = 0.25, 0.5, 0.75$ and $K_a = 0$ at $T = 300$ K the values of DC dark electrical conductivity σ_h calculated according to equation (11) are ≈0.35, 0.33, 0.22 Ohm^{-1}·cm^{-1}, respectively; $W \approx 103$ meV for $K_d = 0.5$ and $K_a = 0$. The value of calculated dark electrical conductivity $\sigma_h \approx 0.32$ Ohm^{-1}·cm^{-1}, for $N_t \approx 1{\cdot}10^{19}$ cm^{-3}, $K_d = 0.5$, $K_a = 0$, and $T = 300$ K, is close in magnitude to the experimental values presented in [15] for partially disordered silicon.

Note that such a nonmonotonic character of the change in photoconductivity was described in [41] for hopping photoconductivity via shallow hydrogen-like acceptors and donors.

The above equations are also applicable for the compensation ratios $K_d = 0$ and $K_a = 0.5$, i.e. when the Fermi level $E_F^{(c)}$ coincides with the energy level E_2. In this case, the photoconductivity $\sigma_h(\gamma)$ will be mainly determined by the change in the concentration of holes $N_{0,+1}(\gamma)$ hopping via *t*-defects in the charge states (+1) and (0) in $|2\rangle$-band.

In this paper the photoconductivity is considered for the case of ohmic contact electrodes to a semiconductor sample, i.e. when $K_d = 0.5$ and $K_a = 0$ (or $K_d = 0$ and $K_a = 0.5$). In this case, the Fermi level $E_F^{(c)}$ in the metallic electrode coincides with the *t*-defect energy level E_1 (or E_2) in semiconductor. If $K_d = K_a$, an energy barrier $\Delta_t/2$ appears on the cathode for transitions of electrons from cathode to semiconductor, and the value of hopping conductivity will be limited by this barrier.

Note that in the calculation of hopping photoconductivity it was assumed that the sample is under isothermal conditions (at $T = 300$ K). However, it should be noted that under photogeneration of electrons from $|2\rangle$-band to $|1\rangle$-band [appearance of t-defects in the charge states (-1)] and electron vacancies in $|2\rangle$-band [appearance of t-defects in the charge states $(+1)$], for $K_d = 0.5$ and $K_a = 0$, the charge states $(+1)$ recombine at the cathode and heat is released (figure 1). For small photocurrents the thermoelectricity effects in such systems can be neglected (see also [13]).

4. Conclusion

A new model is proposed for the DC hopping photoconductivity in the partially disordered semiconductor with t-defects [three-charge-state $(-1, 0, +1)$ point defects with the concentration N_t]. Calculations for the case of compensation of t-defects by shallow hydrogen-like donors and acceptors with concentrations of N_d and N_a and compensation ratios $K_d = N_d/N_t = 0.5$, $K_a = N_a/N_t = 0$ show that the ratio of the hopping diffusion coefficient to drift mobility (parameters $\xi_{-1,0}$ and $\xi_{0,+1}$) increases with the concentration of t-defects. The photoconductivity was calculated for highly defective silicon crystal with the compensation ratios $K_d = 0.25, 0.5, 0.75$ and $K_a = 0$. It is shown that positive hopping photoconductivity increases with the intensity of intercenter illumination, when the photoionization coefficient γ of neutral t-defects is less than the coefficient α of electron 'capture' from a negatively to a positively charged t-defect. The photoconductivity increases due to electron transitions between neutral t-defects (from the bottom energy level $E_2 = 700$ meV to the top energy level $E_1 = 400$ meV), which generate charged states (-1) and $(+1)$. In this case, the concentration of neutral states is comparable with the concentration of (-1) states and illumination increases the concentration of $(+1)$ states. Negative photoconductivity is predicted, when γ becomes greater than α, due to a decrease in the concentration of neutral t-defects (up to total their extinction, when there are no places to hop). The value of the dark hopping electrical conductivity ≈ 0.32 Ohm^{-1}·cm^{-1} calculated for $N_t \approx 1 \cdot 10^{19}$ cm^{-3}, $K_d = 0.5$, $K_a = 0$, and the temperature $T = 300$ K is close in magnitude with the known experimental data. When calculating the diffusion coefficient of hopping electrons, we averaged over the energy and hopping length the product of the variable hopping length and the hopping frequency. The proposed model of positive and negative DC hopping photoconductivity via t-defects can be applied for the development of light-absorbing device structures.

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Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI:https://doi.org/10.17632/jmgrcgfrvs.

Conflict of interest

The authors declare no conflict of interest.

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