The effect of optical phonons on the quenching of photoluminescence of mercury vacancies in narrow-band solid solutions of CdHgTe with increasing temperature

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The capture times of holes to the ground level of the neutral mercury vacancy in a solid solution of $Hg_{1-x}Cd_xTe$ during the emission of an optical phonon are calculated. The calculation showed that this process can compete with the capture of holes into small excited states of vacancy centers with the emission of acoustic phonons. Such competition can lead to quenching of lines in the spectrum of vacancy photoluminescence of $Hg_{1-x}Cd_xTe$ layers with increasing temperature.

Keywords: mercury vacancy, optical phonon, non - radiative transition.

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1. Introduction

Solid solutions $Hg_{1-x}Cd_xTe$ of mercury cadmium telluride (MCT) were studied for about six decades [1,2]. Interest in such structures is caused by the possibility of changing the width of forbidden band of the material by selecting the composition of the solid solution: from 1.6 eV in pure CdTe to 0 in a solid solution with Cd concentration $< 16.5\%$. This fundamental property of MCT solid solutions makes such materials promising for far infrared optoelectronics [3]. One of the main problems in the creation of interband detectors and sources designed for the long-wavelength range is the carrier lifetime decreasing due to recombination by the Shockley–Reed–Hall (SRH) mechanism through impurity-defect centers.

The most common defect in HgCdTe is a mercury vacancy, which appears in these materials due to the weakness of the mercury–tellurium chemical bond. The mercury vacancy is a doubly charged or double acceptor. Such acceptor can be in three charge states: a neutral A_2^0-center, to which two holes are bound, and one-time ionized A_2^{-1}-center, to which one hole is bound, and, finally, a fully ionized A_2^{-2}-center free of holes. Although mercury vacancies are always formed in HgCdTe solid solutions, their energy spectrum is still insufficiently studied. Relative consensus was reached only that the vacancy is a double acceptor and the ionization energy of the A_2^0-center is ~ 10 meV for $x \sim 0.2$ [4–6] and 14 meV for $x \sim 0.3$ [7–9].

Determining the energy spectrum of vacancy is of considerable interest, since they can play a significant role in recombination via the SRH mechanism. Such recombination is a competing process with respect to both interband radiative recombination and nonradiative Auger recombination. Usually, the capture of carriers at centers in the forbidden band during recombination by the SRH mechanism is nonradiative: electrons and holes give up their energy to phonons during capture. However, in some cases the capture process is accompanied by intracenter transitions with the emission of photons. Thus, the SRH process may turn out to be partially radiative. These radiative processes were observed in studies of photoluminescence (PL) of a number of semiconductors and low-dimensional heterostructures [10,11].

For the first time, long-wavelength PL in the far infrared (IR) range associated with acceptor states in bulk MCT epitaxial layers and HgTe/CdHgTe heterostructures with quantum wells was observed in papers [12,13]. Lines were found in the PL spectra near quantum energies of 10 and 20 meV (the latter value is close to the ionization energy A_2^{-1}-center). A distinctive feature of such „impurity" lines is that, in contrast to the line of interband transitions, they do not shift to shorter wavelengths with temperature increasing, which leads to increase in the width of forbidden band [1].

The PL studies in the paper [13] were carried out on a structure with electronic type of conduction, in which all acceptor centers were completely ionized. In this case, all mercury vacancies in the absence of illumination were in the A_2^{-2} charge state, and A_2^{-1}-centers, due to which the longest wavelength PL is observed, appeared because of the capture of holes excited by illumination from the valence band to mercury vacancies. In the paper [14] it was shown that the PL spectrum is formed by hole transitions between localized states. Note that in the paper [14] it was sufficient to take into account only spontaneous processes associated with acoustic phonons, the intensity

of which weakly depends on temperature. To describe the mechanism of thermal quenching of the PL signal observed in [13], it is also necessary to take into account the stimulated emission of phonons, as well as the optical phonons effect on the dynamics of non-equilibrium carriers. The purpose of this paper is to calculate the intensity of nonradiative transitions of holes from the valence band to localized states of mercury vacancies with the emission of optical phonons and discuss the effect of these processes on intracenter photoluminescence.

2. Calculation method

Let us consider transitions of holes from the valence band to localized states of a neutral mercury vacancy upon emission of an optical phonon. During transitions of carriers with the emission of phonons, the law of conservation of energy must be satisfied, i.e., the energy lost by the carrier must be equal to the energy of the emitted phonon. In the case under study, the energy of optical phonons turns out to be greater than the ionization energy of the neutral center. This circumstance imposes a low limit on the initial energy of hole participating in the transition. This energy cannot be less than $\hbar\omega_{\text{ph}}-E_i$, where ω_{ph} is the phonon frequency, and E_i is the ionization energy of the localized state to which the hole passes. Note that optical phonons in the MCT solid solution can be HgTe-like and CdTe-like, while HgTe-like ones have a much lower energy [15]. The minimum energy of HgTe-like longitudinal optical phonon, which is reached at the edge of the Brillouin zone, is ~ 15 meV [15]. In this article we will consider transitions of holes with the emission of HgTe-like phonons. Then, since the ionization energy of the neutral mercury vacancy is $\sim 10-11$ meV, hole in the valence band needs additional $4-5$ meV of kinetic energy to make the transition to the ground state with the emission of optical phonon possible. For transitions to excited levels, this additional energy must be even greater. At temperatures other than zero, some of the holes may have an energy exceeding the indicated value due to the thermal distribution of holes over states in the valence band. The article will also consider such transitions with the emission of optical phonons that are possible for the largest number of holes, i.e., transitions to the ground state of acceptor center.

The intensity of hole transitions from the valence band to the ground state of neutral mercury vacancy upon optical phonon emission was calculated based on the Fermi golden rule. Phonons cause displacements of atoms and thereby distort the ideal periodic potential of the lattice. Let us denote the correction to the crystal potential due to lattice vibrations as δV. The potential δV can be decomposed into an electrostatic macrofield $\delta\bar{V}$ and a deformation microfield $\delta\tilde{V}$, $\delta V = \delta\bar{V} + \delta\tilde{V}$ [16]. A macrofield arises only in polar semiconductors, in which polarization occurs when atoms of the lattice are displaced. It was shown in [16] that in polar semiconductors the interaction of carriers with the macrofield usually turns out to be more significant than with the deformation potential, so we will take into account scattering only by the macrofield.

According to [16], the probability of emission of transverse optical phonon is 0, and for a longitudinal phonon the probability of emission per unit of time when hole passes from the valence band to the acceptor ground state takes the form

$$W_{i\to f} = \int\left[\frac{16\pi^{\varepsilon}a^{\varepsilon}}{\mu\omega_{\text{LO}}(q)}\right]\frac{e^2\gamma^2}{q^2}\,|\langle\Psi_{\text{cont}}|e^{i\mathbf{qr}}|\Psi_0\rangle|^2 \times\big(N_{\text{ph}}(q)+1\big)\delta\big(\varepsilon_{\text{cont}}-\hbar\omega_{\text{LO}}(q)-\varepsilon_0\big)d^3\mathbf{q}, \quad (1)$$

where $N_{\text{ph}}(q)$ are the occupation numbers of phonon states,

$$\mu = \frac{m_{\text{Hg}}m_{\text{Te}}}{m_{\text{Hg}}+m_{\text{Te}}}$$

— reduced mass of lattice cell atoms (tellurium and mercury atoms) $\mathbf{q}$ — phonon wave vector, $\omega_{\text{LO}}(q)$ is the frequency of the longitudinal optical phonon, a — the lattice constant of the solid solution $Hg_{1-x}Cd_xTe$, Ψ_{cont}, Ψ_0, $\varepsilon_{\text{cont},0}$ — wave functions and energies of states of the continuous spectrum and the main localized acceptor level (neutral mercury vacancy). According to paper [16], the coefficient γ for longitudinal optical phonons has the form

$$\gamma = \sqrt{\frac{1}{4\pi}\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_0}\right)\frac{\mu}{a^3}}\,\omega_{\text{LO}}(0),$$

where $\kappa_{\infty,0}$ is the high-frequency and static permittivity of the MCT solid solution, respectively, $\omega_{\text{LO}}(0)$ is the frequency of the longitudinal optical phonon at $\mathbf{q}=0$. The solid solution permittivity values were calculated as a linear interpolation between values for HgTe and CdTe taken from [17]. $\omega_{\text{LO}}(0) = 7.21\cdot 10^{13}$ Hz, according to [15]. The frequency of the longitudinal optical phonon, according to [18], varies from 17.5 meV at $\mathbf{q}=0$ to 15 meV at the edge of the Brillouin zone. The calculations considered the dependence of the optical phonon frequency on the quasiwave vector $\mathbf{q}$. This dependency was taken from [18]. To find the value a, we used a linear interpolation between the values of the lattice constants for HgTe (6.46 Å) and CdTe (6.48 Å) [19]. The energies and wave functions were calculated by the method described in [20]: the Schrodinger equation for the envelope wave functions was solved, including the Kane Hamiltonian, the acceptor ion potential, and the central cell potential (CCP) describing the chemical shift. The wave functions of the states of the continuous spectrum were calculated outside the Born approximation, taking into account the potential of the impurity center.

The hole capture frequency (inverse capture time) from the continuous spectrum can be obtained from expression (1) by integrating over the states of the continuous spectrum in the valence band, taking into account the hole

Characteristics of the ground state of neutral mercury vacancy in the $Hg_{0.81}Cd_{0.19}Te$ layer and three odd excited states

State	E_i, meV	τ_1	τ_2
$1\Gamma_8^+$ (basic)	–		
$2\Gamma_8^-$	3.8	9 ns	1.4 ns
$1\Gamma_7^-$	3.0	1.6 ns	0.7 ns
$3\Gamma_7^-$	0.42	1.5 ns	2 ns

distribution function:

$$\frac{1}{\tau} = \sum_{\text{cont}} W_{\text{cont}\to f}\, f. \tag{2}$$

The thermalization time of holes in the valence band is much shorter than the lifetime of carriers in this band, which reaches a few microseconds at low temperatures [21]. Therefore, the distribution function f can be considered quasi-equilibrium:

$$f = \frac{1}{1+\exp\left(\frac{\varepsilon_{\text{cont}}-\text{F}}{T}\right)}. \tag{3}$$

where F is the Fermi quasi-level, the position of which depends on the concentration of holes in the valence band and temperature, according to the expression

$$p = \frac{2}{(2\pi)^3}\left(\int \frac{d^3\mathbf{k}}{1+\exp\left(\frac{E_V+\frac{\hbar^2k^2}{2m_{hh}}-\text{F}}{T}\right)} + \int \frac{d^3\mathbf{k}}{1+\exp\left(\frac{E_V+\frac{\hbar^2k^2}{2m_{lh}}-\text{F}}{T}\right)}\right). \tag{4}$$

Here m_{hh} and m_{lh} are the effective masses of heavy and light holes in the MCT solid solution, respectively. Note that the mass of light holes is by order of magnitude smaller than the mass of heavy holes. Therefore, the second term in expression (4) turns out to be much less than the first, and it can be neglected. The calculated position of the Fermi level was used to calculate the frequency of hole capture from the valence band according to expression (2).

3. Results and discussion

The signal intensity of the long-wavelength (corresponding to photon energy from 3 to 11 meV) PL band of the MCT structure with cadmium fraction in the solid solution of 19% decreases with temperature increasing from 20 to 40 K by a factor of 3 [13]. This quenching of the PL signal can be associated with increase in the role of nonradiative transitions with the emission of acoustic phonons when holes are captured by the states of mercury vacancy. The intensity of such transitions increases with increasing of phonon occupation numbers.

The Table shows the energies of the ground and three p-like levels of the mercury neutral vacancy, optical transitions from which to the ground state, according to [18], have a large matrix element. As mentioned above, the mercury vacancy is a doubly charged acceptor, and neutral center appears when two holes are bound to a mercury vacancy. Note that the levels in the Table are classified according to the states of the particle at the excited level (the second particle is at the state $1\Gamma_8^+$, since otherwise the energy of the two-particle state falls into the continuous spectrum [22]). The third column of the Table shows the times of nonradiative transitions of holes during spontaneous emission of acoustic phonons from the states presented in the first column to all the lowest levels, i.e., the times of nonradiative depletion of these states. The fourth column shows the times of nonradiative transitions of holes during the emission of acoustic phonons to these states from the highest levels and from the continuous spectrum —times of nonradiative population of the levels.

The times of nonradiative depletion and filling of level with energy E_0 were calculated as

$$\frac{1}{\tau_1} = \sum_{E<E_0} \frac{1}{\tau(E)}$$

— depletion time and

$$\frac{1}{\tau_2} = \sum_{E>E_0} \frac{1}{\tau(E)}$$

— fill time. Here $\tau(E)$ is the time of holes transition between states with energies E and E_0 during the emission of acoustic phonons, calculated by the method from the paper [14].

It can be seen that for the three described states, the spontaneous nonradiative population times are shorter than the depletion times, which should lead to the holes accumulation at these levels and the appearance of PL signal during radiative transitions of holes to the ground state. However, as the temperature rises, the time of nonradiative depletion and filling of the states should decrease.

Fig. 1 shows how this time varies for the three odd states presented in the Table. For the $2\Gamma_8^-$ state, as the temperature rises from 20 to 40 K, the time decreases by a factor of 1.4, and for the $1\Gamma_7^-$ and $3\Gamma_7^-$ — states 1.9 times (see Fig. 1). The states filling time should also decrease with temperature increasing. However, even if this decreasing is not taken into account, it still remains at temperatures up to 40 K significantly below the nonradiative depletion time (see the Table). Thus, upon the temperature increasing the accumulation of carriers in the states $2\Gamma_8^-$, $1\Gamma_7^-$, and $3\Gamma_7^-$ is retained, and the conditions for the PL signal appearance are preserved. The rate increasing of nonradiative transitions by a factor of 2 should lead to proportional decreasing of the PL intensity, while in the experiment the PL signal

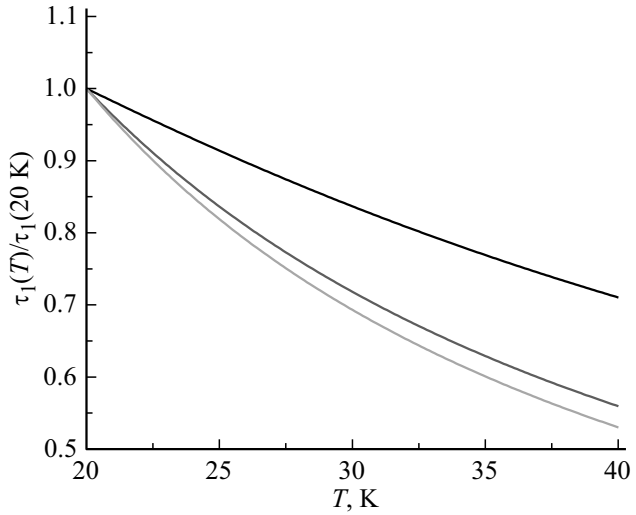

Figure 1. Change in the time of nonradiative, with the emission of acoustic phonons, depletion of three excited states of neutral mercury vacancy in $Hg_{0.81}Cd_{0.19}Te$ solid solution. Black line — change in the depletion time of the state $2\Gamma_8^-$. Gray line — change in the depletion time of the state $1\Gamma_7^-$. Light gray line — change in the depletion time of the state $3\Gamma_7^-$.

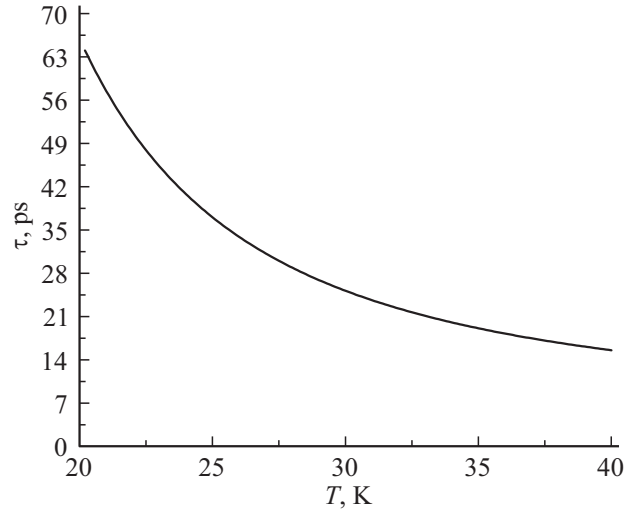

Figure 2. Time of emission of optical phonons during hole transitions from the valence band to the ground state of neutral mercury vacancy in the $Hg_{0.81}Cd_{0.19}Te$ layer vs. temperature. The concentration of free carriers in the zone is $5 \cdot 10^{14}\ \mathrm{cm}^{-3}$.

decreases by a factor of 3 as the temperature increases from 20 to 40 K. Therefore, it is necessary to consider other mechanisms of nonradiative transitions of carriers, in particular, transitions with the emission of optical phonons.

Optical transitions from excited states to the ground level form the long-wavelength band of vacancy PL observed in [13]. Second column — ionization energy of states. Third column — τ_1 — time of non-radiative depletion of states. Fourth column τ_2 — time of nonradiative filling of the states with holes. The times are calculated using the hole capture rates in the emission of acoustic phonons, obtained by the method from [14]. The CCP parameters for calculating the states of double acceptor are taken from [19].

The energy of optical longitudinal HgTe-like phonon lies in the range from 15 to 17.5 meV, which is noticeably higher than the ionization energy of neutral mercury vacancy. This means that carriers that find themselves near the edge of the valence band cannot pass to the localized states of such a vacancy due to the difference between the energies of the initial and final states being insufficient compared to the energy of the emitted phonon. However, at a temperature other than zero, there is a certain amount of carriers with energy sufficient to emit optical phonon upon transition to a localized state. The number of such carriers grows with temperature rise due to changes in the distribution function. This change in the number of high-energy carriers leads to the emission intensity increasing of optical phonons.

Fig. 2 shows the calculated temperature dependence of time of holes transition with emission of optical phonons from the valence band to the ground state of neutral mercury vacancy in the HgCdTe layer. It can be seen that the time of the hole transition from the continuum with the emission of optical phonon decreases with temperature increasing. Thus, as the temperature rises from 20 to 40 K, the time of emission of optical phonon decreases from 64 to 16 ps. The first value of the carrier capture time considerably exceeds the time of hole capture by shallow excited states during the acoustic phonons emission, and in this case the process involving optical phonon has little effect on the capture process. As the temperature rises to 40 K, the transition of the carrier to the ground state, which competes with the capture of holes to shallow acceptor states, becomes more significant. The carriers capture to shallow levels upon the acoustic phonons emission leads to PL due to radiative transitions between localized states, while the transition to the ground level with optical phonon emission does not contribute to PL. The competition between these two processes leads to the quenching of the PL signal with temperature increasing.

4. Conclusion

The times of holes capture by the ground level of the neutral mercury vacancy in the $Hg_{1-x}Cd_xTe$ solid solution upon emission of optical phonon are calculated. The calculation showed that, at low temperatures the carrier capture time upon emission of optical phonon significantly exceeds the times of hole capture by shallow excited states upon emission of acoustic phonons, and in this case, the process involving optical phonon turns out to be insignificant. However, as the temperature rises, these two processes become comparable in intensity and compete. Such competition can lead to lines quenching in the photoluminescence spectrum of mercury vacancies in the $Hg_{1-x}Cd_xTe$ solid solution with temperature increasing.

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Conflict of interest

The authors declare that they have no conflict of interest.

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