Electron states at point defects in non-uniform semiconductor alloys

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Abstract. The broadening and shift of the electron localized states in non-uniform semi-conductor alloys are studied in the effective-mass approximation. The calculation of the density of states is carried out for the case of short-range and long-range (in comparison with the localized-state radius) inhomogeneities of the alloy composition. The path-integral method is used. The shape of the broadened peak of the density of localized states in the short-range case is Lorentz-like; however, in the case of long-range inhomogeneities it is Gaussian. The results for both cases are discussed, and compared with the experimental data.

1. Introduction

Numerous physical characteristics of both the monatomic or binary semiconductors and semiconductor alloys are determined by the parameters of the impurity states. These states in alloys have been widely studied during recent years (see e.g. [1–5] and references therein) for the cases of Coulombic and short-range potential defects. The latter case is typical for states localized on structure imperfections or on substitutional impurities. The theoretical treatment of these states is based on a zero-radius potential model. This consideration may be carried out within the Lucovsky model [6] for donors that are shallow enough in comparison with the gap (so that the effects of the multi-band structure of the deep levels, examined in [7], can be neglected). However, the examination of these states in inhomogeneous semiconductor alloys involves the consideration of the spatial variation of the band parameters, caused by the deviations in alloy composition (the electrical and optical characteristics of the alloys were discussed e.g. in [8–11]). In this paper we examine the effect of such inhomogeneities on the broadening and shift of the point defect energy levels in the gap.

   Our calculations are based on the model of the smooth (for the scale of distances of the order of the lattice constant, a) inhomogeneity of the composition x_r. The electron states which form the donors are treated within the framework of the effective-mass approximation. The position of the conduction-band edge and the effective-mass parameters are considered to change in correspondence with the change of the alloy composition. These changes of the parameters cause broadening of the deep levels, i.e. the δ-like density of states transforms into a form with a peak with a definite width and height. (We shall show later that the change of kinetic energy does not crucially influence the shallow impurity states.) The mechanism of this broadening is essentially different in the two limiting cases of the alloy inhomogeneity Δx having a correlation length l_c much greater and much smaller than the

localized-state radius r_0 (short- and long-range inhomogeneities). In the latter case we obtain inhomogeneous broadening of the peak, caused by the band-edge energy variations. In contrast, in the short-range case the random electric fields cause a shift and broadening of the donor level (though the average fields over the impurity volume are small).

Experimental studies of donors in semiconductor alloys have been carried out using photoconductivity (e.g. [12]) and capacitive (e.g. [2, 10, 13, 14]) methods. A semi-phenomenological theory of the defect broadening was worked out in e.g. [5, 15, 16]. It mainly concerned the random occupation of the sites near the defect by A and A′ atoms in the $A_x A'_{1-x} B$ alloy. The embedded-cluster method, with allowance made for the effects of the first- and second-neighbour disorder in the alloys, was worked out in [17–19]. In contrast, our examination will take into account the macroscopic inhomogeneity of the alloy composition (the correlation length l_c may be of the same order of magnitude as the localized-state radius r_0, and much greater than a). This approximation treats the level broadening in terms of small deviations of the alloy from the 'virtual-crystal' model [20]. The approach worked out here is based on a combination of the Slater–Koster model [21] and the path-integral method [22].

The background theoretical expressions are given in section 2 of this paper. They are applied to the cases of short-range and long-range inhomogeneities in sections 3 and 4 respectively. The discussion of the results obtained and a comparison with the experimental data are presented in the last section.

2. Theoretical background

The electronic states in semiconductor alloys with spatial inhomogeneity of the composition are described by the Hamiltonian

$$\hat{H} = \frac{1}{2}(\boldsymbol{p} \cdot m_r^{-1} \boldsymbol{p}) + U_r. \tag{1}$$

Here m_r and U_r are the inhomogeneous effective mass and the conduction-band-bottom energy. By adding into equation (1) the potential energy of the random ensemble of impurities, we get the equation for the Green's function of the electron:

$$\left[\hat{H} + \sum_{\alpha} u_0 \Delta(\boldsymbol{r} - \boldsymbol{R}_\alpha) - \varepsilon\right]\mathcal{G}_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{2}$$

Here $u_0 \Delta(\boldsymbol{r})$ is the potential energy of the impurity at the zero point of the coordinates ($\Delta(\boldsymbol{r})$ is a short-range δ-like function, localized in a volume whose magnitude is of the order of a^3), and $\boldsymbol{R}_\alpha$ is the random coordinate of the α-impurity. For the Green's function of the electron in the alloy (without impurities) we can write the equation

$$(\hat{H} - \varepsilon)G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{3}$$

With the use of equation (3) we may rewrite equation (2) in the integral form

$$\mathcal{G}_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') = G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') - u_0 \sum_{\alpha} \lim_{\boldsymbol{r}_1 \to \boldsymbol{R}_\alpha} G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}_1)\mathcal{G}_\varepsilon(\boldsymbol{r}_1, \boldsymbol{r}'). \tag{4}$$

The function $\mathcal{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{r}')$ in the right-hand side of equation (4) corresponds to a system of algebraic equations containing $G_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\beta)$. If the radius of the localized state examined is much smaller than the interdefect distance, then the contribution from $G_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\beta)$ in the

case where $\alpha \neq \beta$ is exponentially small, and these terms can be neglected. This yields

$$
\mathcal{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{r}') = \frac{G_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{r}')}{1 + u_0 \tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha)}
$$
$$
\tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha) = \lim_{\boldsymbol{r}, \boldsymbol{r}' \to \boldsymbol{R}_\alpha} G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}').
$$

(5)

This form corresponds to the Koster–Slater approximation [21]. The resulting Green's function for the ensemble of non-overlapping short-range impurities in the alloy is

$$
\mathcal{G}_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') = G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') - u_0 \sum_\alpha \frac{G_\varepsilon(\boldsymbol{r}, \boldsymbol{R}_\alpha) G_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{r}')}{1 + u_0 \tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha)}.
$$

(6)

Note that the Green's functions in equation (6) take the alloy's inhomogeneity into account exactly.

The general form for the density of states is

$$
\frac{2}{V} \, \mathrm{Im} \int \mathrm{d}\boldsymbol{r} \, \langle \mathcal{G}_\varepsilon(\boldsymbol{r}, \boldsymbol{r}) \rangle|_{\varepsilon \to E + \mathrm{i}0}
$$

where V is the normalizing volume. Therefore the contribution of the impurities to the density of states is

$$
\delta\rho_{im}(E) = -\frac{2u_0}{\pi V} \, \mathrm{Im} \int \mathrm{d}\boldsymbol{r} \, \left\langle \sum_\alpha \frac{G_\varepsilon(\boldsymbol{r}, \boldsymbol{R}_\alpha) G_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{r})}{1 + u_0 \tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha)} \right\rangle_{\varepsilon \to E + \mathrm{i}0}.
$$

(7)

Here $\langle \cdots \rangle$ means an average over the alloy's composition inhomogeneity. With the use of the exact expression for $G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')$ we obtain

$$
\int \mathrm{d}\boldsymbol{r} \, G_\varepsilon(\boldsymbol{r}, \boldsymbol{R}_\alpha) G_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{r}) = \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha).
$$

(8)

Therefore equation (7) can be transformed into

$$
\delta\rho_{im}(E) = -\frac{2}{\pi V} \, \mathrm{Im} \, \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left\langle \sum_\alpha \ln[1 + u_0 \tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha)] \right\rangle_{\varepsilon \to E + \mathrm{i}0}.
$$

(9)

In this way the impurity density of states is expressed in terms of the exact Green's function of the electrons in the inhomogeneous alloy, given by equation (3).

For the case of the homogeneous alloy we may substitute the free Green's function $g_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')$ into the expression for $\delta\rho_{im}$. After computation of the simple integrals we may express $u_0 g_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha)$ in terms of the 3D density of states $g(E)$. The result, proportional to the centre concentration n_{im}, can be written as

$$
\delta\rho_{im}(E) = -\frac{n_{im}}{\pi} \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \ln\left[1 + u_0 g(\xi_m) - \frac{u_0}{2} \pi g(|E|) + \mathrm{i}0 \right] = n_{im} \delta(E_0 - E).
$$

(10)

Here the energy of the level E_0 is determined by the equation

$$
1 + u_0 g(\xi_m) = u_0 \frac{\pi}{2} g(|E_0|).
$$

(11)

Here $\xi_m = (\hbar/a)^2 / 2m$ is the 'cutting' energy. The impurity levels near the conduction-band bottom exist in this approximation only if $|u_0| g(\xi_m)$ is of unity order.

3. The case of short-range inhomogeneities

The perturbation operator, linear in the alloy inhomogeneities δ_r, for the short-range case in equation (1), $\delta H_r^{(sr)}$, is

$$\delta H_r^{(sr)} = -\frac{\alpha}{2m}(\boldsymbol{p} \cdot \delta_r \boldsymbol{p}) + \Delta\varepsilon_c \, \delta_r. \tag{12}$$

Here α and $\Delta\varepsilon_c$ determine the rates of change of the effective mass and the conduction-band-bottom energy with the change of composition. The contribution of the first term in equation (12) can be estimated as $\bar{\delta}\alpha(\hbar/r_0)^2/2m$ ($\bar{\delta}$ is the average composition variance), while the energy $\Delta\varepsilon_c$ is of the order of the gap width. That is why the contribution of the kinetic energy inhomogeneities to equation (12) can be neglected, and the Green's function of the alloy can be expressed in terms of the ordinary path integral [22]:

$$G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') = \frac{i}{\hbar} \int_0^\infty dt \, \exp\left(\frac{i}{\hbar}\varepsilon t\right) \int_{\boldsymbol{x}_0=\boldsymbol{r}'}^{\boldsymbol{x}_t=\boldsymbol{r}} D\{\boldsymbol{x}_\tau\} \exp\left[\frac{i}{\hbar}\int_0^t d\tau \left(\frac{m\dot{\boldsymbol{x}}_\tau^2}{2} - \Delta\varepsilon_c \, \delta_{\boldsymbol{x}_\tau}\right)\right]. \tag{13}$$

After factoring out the inhomogeneous contribution to equation (13):

$$\delta G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') = G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') - \langle G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle \tag{14}$$

we can rewrite the average in equation (9) as

$$\left\langle \sum_\alpha \ln[1 + u_0 \tilde{G}_\varepsilon(\boldsymbol{R}_\alpha, \boldsymbol{R}_\alpha)]\right\rangle$$

$$\simeq n_{im}\left(\ln[1 + u_0\langle G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle]|_{\boldsymbol{r},\boldsymbol{r}'\to\boldsymbol{R}} - \frac{u_0^2}{2}\frac{\langle \delta G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\,\delta G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle}{[1 + u_0\langle G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle]^2}\bigg|_{\boldsymbol{r},\boldsymbol{r}'\to\boldsymbol{R}}\right). \tag{15}$$

The second term here corresponds to the small contribution to the density of states, estimated in the appendix. Therefore $\delta\rho_{im}$ can be expressed using the average Green's function equation (13) in the form

$$\delta\rho_{im}(E) = -\frac{2n_{im}}{\pi} \, \mathrm{Im} \, \frac{d}{d\varepsilon} \ln[1 + u_0\langle G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle]|_{\varepsilon\to E+i0;\boldsymbol{r},\boldsymbol{r}'\to\boldsymbol{R}} + \Delta\rho_{im}^{(1)}(E). \tag{16}$$

In order to calculate the average Green's function $\langle G_\varepsilon\rangle$ in equation (16) we use the common framework of [23–25] and the Gaussian correlator $\langle \delta_r, \delta_{r'}\rangle = \bar{\delta}^2 W(|\boldsymbol{r} - \boldsymbol{r}'|)$ with the correlation length l_c. Finally equation (13) can be rewritten as

$$\langle G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle = \frac{i}{\hbar} \int_0^\infty dt \, \exp\left(\frac{i}{\hbar}\varepsilon t\right) \int_{\boldsymbol{x}_0=\boldsymbol{r}'}^{\boldsymbol{x}_t=\boldsymbol{r}} D\{\boldsymbol{x}_\tau\} \exp\left[\frac{i}{\hbar}\int_0^t d\tau \, \frac{m\dot{\boldsymbol{x}}_\tau^2}{2}\right.$$
$$\left. - \frac{(\bar{\delta}\,\Delta\varepsilon_c)^2}{2\hbar^2}\int_0^t d\tau_1 \int_0^t d\tau_2 \, W(|\boldsymbol{x}_{\tau_1} - \boldsymbol{x}_{\tau_2}|)\right]. \tag{17}$$

In the case where $l_c \to 0$ the main contribution from the inhomogeneous potential is determined by the close times τ_1 and τ_2, so the expansion $|\boldsymbol{x}_{\tau_1} - \boldsymbol{x}_{\tau_2}| \simeq |\dot{\boldsymbol{x}}_{\tau_1}||\tau_1 - \tau_2|$ can be used in $W(|\boldsymbol{x}_{\tau_1} - \boldsymbol{x}_{\tau_2}|)$. After carrying out the integration over $\tau_1 - \tau_2$ taking into account the translation invariance of $\langle G_\varepsilon\rangle$, we examine the function

$$J_{\Delta r}(E) = \lim_{\varepsilon\to E+i0} \langle G_\varepsilon(\boldsymbol{r}, \boldsymbol{r}')\rangle \qquad \Delta r = |\boldsymbol{r} - \boldsymbol{r}'|. \tag{18}$$

The expression for this function takes the form

$$J_{\Delta r}(E) = \frac{i}{\hbar} \int_0^\infty dt \ \exp\left(\frac{i}{\hbar} Et\right) \int_{x_0=0}^{x_t=\Delta r} D\{x_\tau\} \ \exp\left[\frac{i}{\hbar} \int_0^t d\tau \ \frac{m \dot{x}_\tau^2}{2}\right.$$
$$\left. - \sqrt{\pi} \frac{\bar{\delta}^2 l_c \, \Delta \varepsilon_c^2}{2\hbar^2} \int_0^t \frac{d\tau}{|\dot{x}_\tau|}\right]. \tag{19}$$

Because the contribution from the slow path (when $|\dot{x}_\tau|$ is small) is damped rapidly, and the contribution of the fast path (when the velocity $|\dot{x}_\tau|$ is high) is small due to the rapid oscillations of the kinetic energy, equation (19) can be computed within the optimal-path method [25]. After factoring out the direct-line contribution to equation (19), $\Delta r \, \tau/t$, we can write the optimal path as a circle with radius R (see e.g. [24]). If we examine this circle in the XOY plane, then $R_\tau = R(\cos(2\pi\tau/t) - 1, \sin(2\pi\tau/t), 0)$ and the exponent in equation (19) contains contributions from factors of the following type:

$$Q(R) = \frac{i}{\hbar}\left[\frac{m \, \Delta r^2}{2t} + \frac{m(2\pi R)^2}{2t} - \sqrt{\pi}\frac{\bar{\delta}^2 l_c}{2\hbar}\frac{(\Delta \varepsilon_c t)^2}{2\pi R}\right]. \tag{20}$$

The optimal-path radius is determined by the condition $Q'(R_c) = 0$. Therefore the main contribution to the exponent in equation (19) contains

$$Q(R_c) = \frac{i}{\hbar}\frac{m \, \Delta r^2}{2t} - i \, e^{-i\pi/6}\frac{3t}{2\hbar^2}\frac{\bar{U}^{4/3}}{E_c^{1/3}}. \tag{21}$$

Here the characteristic energy $\bar{U} = \bar{\delta} \, \Delta \varepsilon_c$ and the energy, corresponding to the characteristic length l_c, $E_c = (\hbar/l_c)^2/2m$, is introduced. The energy $\bar{U}$ determines the order of the inhomogeneities of the potential energy U_r.

The estimation of the contribution from the paths close to the optimal one can be performed like in [24]. After neglecting these small terms, we can rewrite equation (18) in the form

$$J_{\Delta r}(E) = \frac{i}{\hbar} \int_0^\infty dt \ \left(\frac{m}{2\pi\hbar it}\right)^{3/2} \exp\left[\frac{im \, \Delta r^2}{2\hbar t} + \frac{i}{\hbar}(E + \gamma/\sqrt{3})t - \frac{\gamma t}{\hbar}\right]. \tag{22}$$

Here the characteristic energy for the level broadening, γ, is introduced as

$$\gamma = \pi^{1/3}\frac{3\sqrt{3}}{8}\frac{\bar{U}^{4/3}}{E_c^{1/3}}. \tag{23}$$

The integral over time in equation (22) can be calculated exactly. With account taken of the energy ξ_m being very large in comparison with all of the other energies being examined, we get

$$J_{\Delta r}(E) \simeq g(\xi_m) - \frac{\pi}{2} g\left(-E - \frac{\gamma}{\sqrt{3}} - i\gamma\right). \tag{24}$$

Therefore the energy density of the impurity level can be written as

$$\delta\rho_{im}(E) = -\frac{2n_{im}}{\pi} \text{Im} \frac{d}{d\varepsilon} \ln[1 + u_0 J_{\Delta r}(\varepsilon)]. \tag{25}$$

Taking into consideration the energy of the non-disturbed level E_0 from equation (11), we finally transform equation (25) into the expression

$$\delta\rho_{im}(E) = \frac{2n_{im}}{\pi} \frac{\gamma}{(\tilde{E}_0 - E)^2 + \gamma^2} \qquad \text{where } \tilde{E}_0 = E_0 + \frac{\gamma}{\sqrt{3}}. \tag{26}$$

Therefore the deep level in the short-range case is described by a broadened Lorentz-like peak, shifted with respect to the initial level position E_0. Note, that the broadening and shift of the level in the alloy in this case are described by the same characteristic energy, γ.

The shift of the level obtained is to be compared with the shift of the conduction-band bottom due to the short-range inhomogeneities. The density of the continuous spectrum states can be obtained from the self-consistent Dyson equation (see e.g. [23]). We get the approximate form

$$\Delta E_c = \Delta \varepsilon_c^2 \, W(0) \int_{\varepsilon_p < E_c} \frac{\mathrm{d}\boldsymbol{p}}{(2\pi\hbar)^2} \, (\varepsilon_p - \varepsilon)^{-1} \simeq \frac{\bar{U}^2}{2\sqrt{\pi} \, E_c}. \tag{27}$$

Taking account of the smallness of l_c, we get for this case $\gamma \gg \Delta E_c$. This means that the shift and broadening of the defect level are large in comparison with the shift of the conduction-band bottom.

4. The case of long-range inhomogeneities

In the case of inhomogeneities with long-range (lr) disorder (in comparison with the localized-state radius), the operator of the perturbation, $\delta H_{Rr}^{(lr)}$, can be written in the vicinity of the impurity (the point $\boldsymbol{R}$) as the expansion

$$\delta H_{Rr}^{(lr)} = U_R + \sum_{\alpha} \nabla_{\alpha} U_R \, r_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} (\nabla_{\alpha} \nabla_{\beta} U_R) r_{\alpha} r_{\beta}. \tag{28}$$

The contribution of the kinetic energy inhomogeneities is here small for the same reasons as were discussed in the previous section. With the use of equation (28) we can express the Green's function for the centre examined in terms of the path integral

$$G_{\varepsilon R}(\boldsymbol{r}, \boldsymbol{r}') = \frac{\mathrm{i}}{\hbar} \int_0^{\infty} \mathrm{d}t \, \exp\left(\frac{\mathrm{i}}{\hbar}\varepsilon t\right) \int_{\boldsymbol{x}_0 = \boldsymbol{r}'}^{\boldsymbol{x}_t = \boldsymbol{r}} \mathrm{D}\{\boldsymbol{x}_\tau\} \, \exp\left[\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}\tau \, \left(\frac{m\dot{\boldsymbol{x}}^2}{2} - \delta H_{R\boldsymbol{x}_\tau}^{(lr)}\right)\right]. \tag{29}$$

After substituting this equation into the general expression for the density of states (9), we can get for the case of non-overlapping centres with the concentration n_{im}

$$\delta\rho_{im}(E) = -\frac{2n_{im}}{\pi} \operatorname{Im} \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left\langle \ln[1 + u_0 J_{\Delta r, R}(\varepsilon)]\right\rangle\big|_{\varepsilon \to E + \mathrm{i}0}. \tag{30}$$

Here $J_{\Delta r, R}(\varepsilon) = G_{\varepsilon R}(\boldsymbol{r}, \boldsymbol{r}')|_{|r-r'| \to \Delta r}$, and the average is now calculated over the random potential energy U_R.

To exclude the terms in the exponent of equation (29) that are linear in the path $\boldsymbol{x}_\tau$, we make the substitution $\boldsymbol{x}_\tau \to \boldsymbol{u}_\tau + \boldsymbol{s}_\tau$. Here $\boldsymbol{s}_\tau$ is the new variable for the path integration, and the $\boldsymbol{u}_\tau$-function corresponds to the equation

$$\ddot{u}_\tau^{\alpha} + \sum_{\beta} \nabla_{\alpha} \nabla_{\beta} U_R \, u_\tau^{\beta} = -\frac{\nabla_{\alpha} U_R}{m} \tag{31}$$

with the boundary conditions $\boldsymbol{u}_{\tau=0} = 0$ and $\boldsymbol{u}_{\tau=t} = \Delta\boldsymbol{r}$. Therefore $J_{\Delta r, R}(E)$ can be written in terms of the path integral:

$$J_{\Delta r, R}(E) = \frac{\mathrm{i}}{\hbar} \int_0^{\infty} \mathrm{d}t \, \exp\left(\frac{\mathrm{i}}{\hbar} \int \mathrm{d}\tau \, \left[\varepsilon - U_R - \frac{1}{2}(\nabla U_R \cdot \boldsymbol{u}_\tau)\right]\right)$$
$$\times \oint \mathrm{D}\{\boldsymbol{s}_\tau\} \, \exp\left(\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}\tau \, \left[\frac{m\dot{\boldsymbol{s}}_\tau^2}{2} - U_R - \frac{m}{2} \sum_{\alpha\beta} (\nabla_{\alpha} \nabla_{\beta} U_R) s_\tau^{\alpha} s_\tau^{\beta}\right]\right). \tag{32}$$

This integral can be calculated by expanding the path s_τ into a Fourier series in the time interval $(0, t)$. The characteristic frequencies $\omega_{1,2,3}$ of the symmetric quadratic form in the exponent are determined by the equation

$$\det \|\nabla_\alpha \nabla_\beta U_R - \omega^2 \delta_{\alpha,\beta}\| = 0. \tag{33}$$

The computation of the Gaussian path integrals in equation (32) is carried out within the standard framework. The result for $J_{\Delta r, R}(E)$ depends now not only on the potential energy U_R, but also on the random frequencies $\omega_{1,2,3}$ and random electric field ∇U_R as well:

$$J_{\Delta r, R}(E) = \frac{i}{\hbar} \int_0^\infty dt \left(\frac{m}{2\pi \hbar i t}\right)^{3/2} \exp\left(\frac{i}{\hbar}\left[t(\varepsilon - U_R) + \frac{m \Delta r^2}{2t}\right]\right)$$
$$\times \exp\left[-\frac{i}{2\hbar} \int_0^t d\tau \, \nabla U_R \cdot u_\tau\right] \prod_{k=1-3} \frac{\omega_k t/2}{\sin \omega_k t/2}. \tag{34}$$

The case of large l_c corresponds to small oscillator strength, so the second term in equation (31) can now be neglected, and its solution can be written in the simple form $u_\tau = (\nabla U_R/2m)\tau(t-\tau)$. After substituting this solution into equation (34) and integrating over $d\tau$, taking into account the smallness of the frequencies $\omega_{1,2,3}$, determined from equation (33), we get

$$J_{\Delta r, R}(\varepsilon) \simeq \frac{i}{\hbar} \int_0^\infty dt \left(\frac{m}{2\pi \hbar i t}\right)^{3/2} \exp\left(\frac{i}{\hbar}\left[t(\varepsilon - U_R) + \frac{m \Delta r^2}{2t}\right]\right)$$
$$\times \exp\left(-\frac{it^3(\nabla U_R)^2}{24m\hbar}\right)\left[1 + \frac{t^2}{24}(\omega_1^2 + \omega_2^2 + \omega_3^2)\right]. \tag{35}$$

This integral can be calculated for the characteristic energies of order E_0. Later we use the estimation of the characteristic times contributing to the integral as $\hbar/E_0$, and we assume that $|\nabla U_R| \simeq \bar{U}/l_c$. Therefore the estimation for $\omega_{1,2,3}$ from equation (33) yields

$$\left(\frac{\omega_k t_m}{2}\right)^2 \sim \frac{E_c \bar{U}}{2E_0^2} \ll 1 \qquad E_c = \frac{(\hbar/l_c)^2}{2m}. \tag{36}$$

Here t_m is the characteristic time of order $\hbar/E_0$. Taking account of the large magnitude of l_c, after taking into consideration the inequality $\bar{U} \ll E_0$, we get

$$\frac{E_c \bar{U}^2}{12E_0^3} \ll 1. \tag{37}$$

After substituting all of these inequalities into equation (35), we can integrate it within the standard method of [22]. This gives

$$J_{\Delta r, R}(\varepsilon) \simeq g(\xi_m) - \frac{\pi}{2} g(|E| + U_R). \tag{38}$$

This expression differs from equation (10) only in the substitution of $|E| + U_R$ for $|E|$. This yields

$$\delta\rho_{im}(E) \simeq 2n_{im}\langle \delta(|E_0| + U_R - E)\rangle. \tag{39}$$

With the use of the standard technique of [24], we get the Gaussian form of the broadened unshifted peak in the case of long-range inhomogeneities:

$$\delta\rho_{im} = \frac{2n_{im}}{\sqrt{2\pi}\bar{U}} \exp\left(-\left[\frac{E_0 - E}{\sqrt{2}\bar{U}}\right]^2\right). \tag{40}$$

Note that the dependences of the level broadening on the energy $\bar{U}$ differ substantially in the two limiting cases of the short-range and long-range inhomogeneities. The shape of

the peak also differs substantially, being Lorentz-like in the first case and Gaussian in the second.

5. Discussion

In this work we have examined the influence of the semiconductor alloy composition inhomogeneities on donor states, localized near short-range defects. It has been shown that the mechanism of the defect line broadening in non-uniform alloys is essentially different in the two limiting cases of the correlation length l_c of the alloy inhomogeneity Δx being much greater and much smaller than the localized-state radius r_0 (short- and long-range inhomogeneities). In the case of long-range inhomogeneities we obtain ordinary Gaussian inhomogeneous broadening of the peak, caused by the band-edge energy variations. In contrast, as was shown in section 3 of this article, in the short-range case the random electric fields cause a shift and broadening of the donor level (though the average fields over the impurity volume are small).

The modification of the local density of states for the cases of short-range and long-range inhomogeneities is described by equations (26) and (40) respectively. We can see that the shape of the density peak transforms from Lorentz-like to Gaussian with the transition from the case of short-range inhomogeneities to that of long-range inhomogeneities. The half-width of the levels, described in these cases by equations (23) and (41) respectively, depends on the parameters for the inhomogeneities (i.e. on the amplitudes and correlation lengths of the inhomogeneities) and the characteristics of the centre in different ways. Moreover, in the case of short-range inhomogeneities a level shift takes place, while there is no such shift in the case of long-range inhomogeneities. Therefore the theory presented predicts an essential difference between the behaviour of centres in alloys with long-range inhomogeneities and that of centres in alloys with short-range inhomogeneities. However, discrimination between these two cases can only be achieved with the use of experimental data.

The centres in the alloys have been studied by photoelectrical and capacitance methods. We note that in all work based on deep-level transient spectroscopy (DLTS) analysis, the level shape is considered to be Gaussian (see [10]). On the other hand, the accuracy of the photoelectrical examinations (see e.g. [12]) is not sufficient for discriminating unambiguously between the Lorentz-like and Gaussian peaks. Therefore the most appropriate method for discriminating between the two experimental situations is that of examining the shifts of the donors in the alloys (these shifts are predicted above to occur for short-range inhomogeneities only). The case of long-range inhomogeneities was thought to be realized e.g. in $GaAs_{1-x}P_x$, in which the deep donor was studied in [14]. The ionization energy for this level remained practically constant: $E_0 = 0.340$ eV for the whole of the direct-gap composition range. This corresponds to the value $r_0 = 1.2 \times 10^{-7}$ cm (see [6]). The correlation length l_c in this case should be greater than r_0. It was shown in [14] that for $x = 0,4$ (the region of direct-gap composition) the half-width of the level $\sqrt{2\bar{U}}$ is 30–40 meV. Using the experimental value $\Delta\varepsilon_c = 1.3$ eV, these values for σ can be obtained, if $\bar{\delta} = 0.02$–0.03. This value of the composition variance seems to be a very realistic one. Moreover, from the simple binomial expression, $\bar{\delta}^2 \sim x(1-x)$—see e.g. [8]. This dependence was also obtained experimentally in [14]. We note that the same order of the values for the half-width of the E3-like deep donor with $E_0 = 0.23$ eV in $GaAs_{0.86}Sb_{0.14}$ was obtained in [10, 13], and for the half-width of the DX-related centres in silicon-doped $Al_xGa_{1-x}As$ in [2]. In contrast, in [9] the positions of the deep radiation-induced donor levels E1, E2, and E3 in $Al_xGa_{1-x}As$ were studied as functions of the Al fraction x. It

was shown there that generally donors do not follow strictly the conduction-band shift, the deviation being the greater, the deeper the centre. Therefore we can assume that the case of short-range inhomogeneities was realized there.

We note in conclusion that our theory was worked out making the following assumptions: (a) the effective-mass approximation; (b) the zero-radius potential model for the defect centres; (c) a small concentration of defects (the effect of overlap was neglected); (d) a Gaussian distribution of the composition inhomogeneities; (e) the optimal-path method can be used for the case of short-range inhomogeneities. However, we get a good correspondence of our numerical estimates for the two cases of long-range and short-range inhomogeneities with the experimental data for realistic values of the average variance and correlation length. Comparison with the available experimental data shows that these two cases can be realized in practice. This should be taken into consideration for the rigorous analysis of the DLTS data (not only the Gaussian, but also the Lorentz-like shape of the peak should be used to reconstruct the form of the signal properly). Generally the expressions obtained for the additional defect density of states in semiconductor alloys with non-uniform compositions can be widely used in the analysis of the various experimental data.

Appendix

The additional term in equation (16) can be rewritten as

$$\Delta\rho^1_{im}(E) = \frac{u_0^2}{\pi}n_{im}\,\text{Im}\,\frac{\text{d}}{\text{d}\varepsilon}\frac{\langle G_\varepsilon(r,r')G_\varepsilon(r,r')\rangle - \langle G_\varepsilon(r,r')\rangle^2}{[1+u_0\langle G_\varepsilon(r,r')\rangle]^2}\bigg|_{\varepsilon\to E+\text{i}0;r,r'\to 0}. \tag{A1}$$

Now we should estimate the difference in the numerator of the right-hand part of equation (A1). Using the standard procedure, followed in section 3 of this paper, in analogy with equation (17) we get

$$\langle G_\varepsilon(r,r')G_\varepsilon(r,r')\rangle = -\frac{1}{\hbar^2}\int_0^\infty \text{d}t_1\int_0^\infty \text{d}t_2\,\exp\left(\frac{\text{i}}{\hbar}\varepsilon(t_1+t_2)\right)$$

$$\times\int_{x_0=r'}^{x_{t_1}=r}\text{D}\{x_{\tau_1}\}\int_{y_0=r'}^{y_{t_2}=r}\text{D}\{y_{\tau_2}\}\,\exp\left\{\frac{\text{i}}{\hbar}\int_0^{t_1}\text{d}\tau_1\,\frac{m\dot{x}_{\tau_1}^2}{2}+\frac{\text{i}}{\hbar}\int_0^{t_2}\text{d}\tau_2\,\frac{m\dot{y}_{\tau_2}^2}{2}\right.$$

$$-\frac{(\bar{\delta}\,\Delta\varepsilon_c)^2}{2\hbar^2}\left[\int_0^{t_1}\text{d}\tau_1\int_0^{t_1}\text{d}\tau_2\,W(|x_{\tau_1}-x_{\tau_2}|)\right.$$

$$\left.\left.+\int_0^{t_2}\text{d}\tau_1\int_0^{t_2}\text{d}\tau_2\,W(|y_{\tau_1}-y_{\tau_2}|)+2\int_0^{t_1}\text{d}\tau_1\int_0^{t_2}\text{d}\tau_2\,W(|x_{\tau_1}-y_{\tau_2}|)\right]\right\}. \tag{A2}$$

This expression differs from that of $\langle G_\varepsilon(r,r')\rangle^2$ only in the last contribution in the exponent. This term can be computed by analogy with equations (19)–(21), using the circular optimal paths $R_{\tau_{1,2}} = R_{1,2}(\cos(2\pi\tau_{1,2}/t_{1,2}) - 1, \sin(2\pi\tau_{1,2}/t_{1,2}), 0)$. After substituting these paths into the last correlator in (A2), we can estimate their contribution to the exponent as

$$-\left(\frac{\bar{U}t_c}{\hbar}\right)^2\exp\left[-\left(\frac{R(t_c)}{l_c}\right)^2\right]. \tag{A3}$$

The characteristic time t_c is here determined by the scale of the energies under examination. The characteristic path radius $R(t_c)$ is determined by equation (20) for times $t_{1,2}$ of order t_c. Generally there are three scales of time for this problem: (a) the shortest time $\hbar/\xi_m$,

corresponding to the large energy of 'cutting'; (b) the medium time $\hbar/E_0$, corresponding to the energy of the defect level; and (c) the longest time $\hbar/\gamma$, corresponding to the damping of the level. For case (a) (short times) a value of order unity appears as the exponent in equation (A3), but the pre-exponential factor is small due to the large magnitude of ξ_m, and therefore the whole of equation (A3) is small. In case (b) the pre-exponential factor can be of unity order, but the exponent is small. The smallness of equation (A3) in case (c) needs the additional inequalities $E_c \gg E_0$ (the case of short-range inhomogeneities), and $E_0 \gg \bar{U}$ (no deep fluctuations of the potential). If these additional conditions are fulfilled, then the contribution (A3) is always small, and therefore the additional term in equation (16) can be neglected.

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