Influence of Boundary Structure on a Light Absorption in Semiconductors

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Abstract

The phenomenological boundary conditions for the envelope wave function, which is applicable for contacts of semiconductors with a rather different crystal symmetry are proposed. It is shown that the boundary conditions are determined by the number of the real values, which are independent of the electron energy. The number of these parameters depends on the symmetry of the bordered materials as well as the symmetry of the boundary itself.

The proposed boundary conditions are used for the investigation of the light absorption at the indirect-band-gap semiconductor surface. It is shown that the possibility of the electron transitions with the momentum nonconservation could result in enhancement of the absorption. This is especially the case for the small crystallites, which size is about 50 Å, and where the share of the surface atoms is sufficiently large. The influence of the crystallite size as well as the structure of the interface on the absorption are investigated.

73.40.-c, 73.40.Qv, 78.66.-w, 79.60.Jv

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I. INTRODUCTION

The problem of the boundary conditions for the envelope wave function is widely discussed (see, for instance, and references therein). The main point of the problem is as follows. The electron behavior in the crystal subjected to the smooth field is usually described by means of the envelope wave function. This is more convenient than the Bloch wave function. The problem of their proper matching at the interface arises when two materials come to the close contact. The boundary conditions where the wave functions and their derivatives supposed to be equal at the interface are in common usage in the quantum mechanics. However, this procedure fails if the effective masses of the contacted materials are different, because it leads to nonconservation of the probability flux through the boundary. The most simple way to get around this difficulty has been proposed by Bastard. He has supposed that the envelopes and their derivatives divided to the corresponding effective mass should be matched at the interface. It is shown that these boundary conditions hold at the smooth interface. Nevertheless, they proved to be unacceptable in the simple models of the sharp boundary.

The problem becomes more complicated if the degeneration between the electron states from the different bands or valleys is present. In this case the intervalley conversion becomes possible at the interface. This problem has been considered numerically for the heterojunctions composed of the $\text{A}_{\text{III}}\text{B}_{\text{V}}$ semiconductors (GaAs/AlAs, HgTe/CdTe, GaSb/InAs). It is shown, that the Bastard boundary conditions are acceptable, if they relate the envelopes corresponded to the equivalent valleys from both sides of the contact. The parameters of the intervalley conversion were found to be small in these heterojunctions. Nevertheless, the physical reason for the Bastard boundary condition to be applicable in this case is not clear yet. It seems, that the symmetry equivalence of both contacted crystals is important. This makes possible to classify the wave functions in each material in the same way. The fact that both contacted materials are close chemically might be significant too.

Considerable recent attention has been focussed on the contacts of the rather different materials. First and foremost it concerns the surface of the many-valley semiconductors. The photoemission from the GaAs surface into vacuum has been considered in Ref. The quantum yield of the process was found to be quite less than anticipated. Besides, the energy distribution threshold of the emitted electrons suffered considerable downshift. It was shown, that both effects could be connected with the peculiarities of the boundary conditions in this case.

Currently considerably study is being given to the contacts of materials, which are rather different on the crystalline symmetry as well as on their chemical composition. This is especially true in regard to interfaces between the metal oxide semiconductors (TiO$_2$, Al$_2$O$_3$, ZrO$_2$) and the organic compounds. These structures are used for the solar energy cells. Because of this, the charge transfer from the organic compound to the conductivity band of the semiconductor is of main important. The metal oxide layers are composed of interconnected mesoscopic particles. That is why the study of the charge transfer between the nanocrystals as well as their optical properties are vigorously proceeding.

The modern technology allows to prepare the quantum dots, where the small semiconductor crystallites are arranged in the certain matrix. The latter could be crystalline or amorphous, organic or nonorganic. Their optical spectra was found to be quite sensitive
It seems improbable, that Bastard boundary conditions are applicable to these contacts. Besides, the simple boundary conditions do not allow to describe the intervalley conversion of the electrons at the interface. The boundary conditions, which are appropriate for the contacts of the materials with different crystal symmetry have been proposed in Ref. However, the \( k - p \) approximation adopted in this paper restrict its applicability to the semiconductor contacts with the small band offsets. The contact two-valley crystal–one valley crystal has been investigated in Ref. where the simple one-dimensional microscopeing model has been used to obtain the exact boundary conditions.

In this paper the phenomenological boundary conditions, which are applicable to the contacts of the material with the rather different band structures, are proposed. It is shown that the boundary conditions are determined by the certain array of the parameters. These parameters depend only on the contacted materials and on the technology of the contact preparing. They could be numerically calculated or measured in experiments. The magnitude of these parameters is estimated.

The proposed boundary conditions are used to investigate the light absorption at the surface of the indirect-band-gap semiconductors. It is well known that the light absorption near its edge in the indirect-band-gap semiconductors is much weaker than that in the direct-band-gap semiconductors. It happens because of the momentum conservation law. In order to satisfy it the third object has to be involved. It should carry out the extra momentum, which the electron obtains when it moves from the top of the valence band to the bottom of the conductive band. This momentum is large (of the order of \( \pi \hbar / a \), where \( a \) is the lattice constant) in comparison with the photon momentum. This third object may be either an impurity (it is important in the heavy doped semiconductors) or a short-wavelength phonon. The weakness of the interaction in both cases manifest itself in the additional small parameter, which has to appear in the theory.

It is clear that the momentum should not be conserved, if the absorption takes place at the sharp interface or at the surface. The surface becomes the above-mentioned third object in this case, and the proximity to it determines the small parameter araised in the problem. The ratio \( a / L \) (or more precisely, the certain degree of this ratio), where \( L \) is the absorption length is the parameter, which specifies the proximity. This value is too small when the light absorption in the bulk material is investigated. Nevertheless, it is not the case for the restricted semiconductors. Then \( L \) becomes the size of the semiconductor, so that the constant of the electron-phonon interaction may become comparable or even less then this parameter. This means, that the considerable increase of absorption could be observed in the small semiconductor object. The latter may be the quantum dots, wires, colloidal solutions of semiconductors, semiconductor polycrystals, or any other objects where the share of the surface atoms is sufficiently large.

This paper is organized as follows. In Sec. II the phenomenological boundary conditions for the envelope wave function are derived. The expressions for the parameters of the boundary conditions are presented and analyzed. In Sec. III the light absorption at the sharp semiconductor boundary is investigated. It is shown that its value as well as its behavior at the transparency edge is determined on the parameters of the boundary conditions. The results are discussed in Sec. IV and summarized in Sec. V. The units there \( \hbar = 1 \) are adopted.
II. BOUNDARY CONDITIONS FOR ENVELOPE WAVE FUNCTIONS AT SHARP INTERFACE OF MATERIALS WITH A DIFFERENT CRYSTAL SYMMETRY

The influence of the smooth external field on the electron in the crystalline lattice could be investigated in terms of the envelope wave function. In the one band approximation the envelope obeys the equation

\[ [\varepsilon_n(-i\nabla) + V(r)]F(r) = EF(r). \]  

(1)

Here \( \varepsilon_n(k) \) is the band spectra of an electron in the \( n \)-th band, \( V(r) \) is an external field, and \( F(r) \) is the envelope. It is assumed that the main scale where \( V(r) \) change is essentially larger than the lattice constant. The equation (1) holds in the bulk of crystal, but not at the interface. Therefore the certain boundary conditions have to be imposed to match the envelopes from both sides of the interface. The simplest boundary condition demands the envelope and its derivatives divided to the effective mass to be continued through the interface. The last condition ensures the probability flux conservation.

The problem becomes more complicated if the degeneration is present between the electron states from the different bands or valleys, i.e., if the equation \( \varepsilon_n(k) = E \) has a few solutions. This is possible if any nonintrinsic symmetry element (a screw axis or a glide plane) is present in the crystal. The operator corresponded to this element moves the electron from one valley to another. This operator should commutate with the Hamiltonian, so that the electron energy does not change. This is the reason for the degeneration. The nonintrinsic symmetry could not exist at the interface, so that the degeneration should be removed there. This means, that the certain relation between the wave functions from the different valleys should be fulfilled at the interface. This relation implies the additional boundary condition, which has to be aroused from the degeneracy.

Let \( M \) be the number of nonequivalent solutions of the equation \( \varepsilon_n(k) = E \) for the lefthand semiconductor and \( N \) be that for the righthand semiconductor. The solution of the Schrödinger equation is determined if the irradiation condition is specified at infinity. We can specify \( M \) solutions for the lefthand semiconductor. This means that \( M \) different plain waves could be incident on the contact from the left. In a similar manner \( N \) solutions could be specified for the righthand semiconductor. Thus, the boundary conditions should be specified by the system of \( M + N \) equations. If the effective mass approximation is applicable in both sides of the contact when it is sufficient to remain the quadratic term in the expansion of \( \varepsilon_n(-i\nabla) \). Then the boundary conditions should be represented by the system of \( M + N \) linear equations for the envelopes and their derivatives at the boundary.

Let us consider the contact between two materials 1 and 2 (Fig. 1). The plains \( S_1 \) and \( S_2 \) are parallel to the boundary \( z = 0 \) being removed from it so that the electron wave functions at these plains are Bloch. Nevertheless, the distance between \( S_1 \) and \( S_2 \) is much more less then any characteristic size of the envelope. Thus, the space becomes divided on three regions: the left region \((z < z_1)\), the right region \((z > z_2)\), and the interface region \((z_1 < z < z_2)\). Let \( G(r, r') \) be the Green function of the boundary problem. It obeys the equation

\[ [-\Delta + 2m_e(U(r) - E)]G(r, r') = \delta(r - r'). \]  

(2)
Here $U(r)$ is the potential energy of the electron. It is the periodical function in the left and in the right regions, but it is not periodical in the interface region.

Let complete the plains $S_1$ and $S_2$ with the spheres at infinity as it is represented with the dotted line in Fig. 1. We can use the Green’s theorem in order to connect the wave function at the surface $S_1$ to that at the plain $S_2$

$$
\psi(r_2) = \int_{S_1} \left[ G(r_2, r_1) \frac{\partial \psi(r_1)}{\partial z_1} - \psi(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] d^3r_1.\tag{3a}
$$

The wave function here is supposed to be vanished at the right infinity, so that the equation (3a) corresponds to the irradiation conditions where the plain wave is incident from the left. We can apply also the Green’s theorem to the surface $S_2$ to obtain the equation corresponded to the inverse irradiation conditions

$$
\psi(r_1) = \int_{S_2} \left[ G(r_1, r_2) \frac{\partial \psi(r_2)}{\partial z_2} - \psi(r_2) \frac{\partial G(r_1, r_2)}{\partial z_2} \right] d^3r_2.\tag{3b}
$$

We introduce the envelope wave functions as follows

$$
\psi(r) = \begin{cases}
\sum_{i=1}^{M} F_i^l(r) \varphi^l_{k_i}(r), & \text{if } z < z_1, \\
\sum_{i=1}^{N} F_i^r(r) \varphi^r_{k_i}(r), & \text{if } z > z_2.
\end{cases}\tag{4}
$$

Here $\varphi^l_{k_i}(r)$ are the Bloch wave function of the electron from the left and from the right regions and $F_i^l, r(r)$ are the envelopes. The subscript $i$ enumerates here nonequivalent values of the wave vector $k_i$ for that $\varepsilon(k_i) = 0$. The envelopes $F_i^l, r(r)$ are supposed to be smooth, so that the main size of their deviation considerably exceeds all other scales of the problem.

Substituting (4) in (3), multiplying the resulting equations by $\varphi^l_{k_j}$, and integrating them over the certain regions $\Omega_{1,2}$, we obtain

$$
\sum_{i=1}^{M} \int_{\Omega_1} F_i^l(r_1) \varphi^l_{k_i}(r_1) \varphi^{l*}_{k_j}(r_1) d^3r_1 = \sum_{i=1}^{M} \int_{\Omega_1} \int_{\Omega_2} \left\{ G(r_1, r_2) \frac{\partial}{\partial z_2} \left[ F_i^r(r_2) \varphi^r_{k_i}(r_2) \right] - F_i^l(r_2) \varphi^l_{k_i}(r_2) \frac{\partial G(r_1, r_2)}{\partial z_2} \right\} \varphi^{l*}_{k_j}(r_1) d^3r_2 d^3r_1, \quad j = 1, \ldots, M \tag{5}
$$

$$
\sum_{i=1}^{N} \int_{\Omega_2} F_i^r(r_2) \varphi^r_{k_i}(r_2) \varphi^{r*}_{k_j}(r_2) d^3r_2 = \sum_{i=1}^{M} \int_{\Omega_2} \int_{\Omega_1} \left\{ G(r_2, r_1) \frac{\partial}{\partial z_1} \left[ F_i^l(r_1) \varphi^l_{k_i}(r_1) \right] - F_i^r(r_1) \varphi^r_{k_i}(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right\} \varphi^{r*}_{k_j}(r_2) d^3r_1 d^3r_2, \quad j = 1, \ldots, N.
$$

Here $\Omega_{1,2}$ are the vicinities of the points $r_1$ and $r_2$. Their size is supposed to be large in comparison with the lattice constant, but it is small in comparison with the scale of envelope. In other words, $\Omega_{1,2}$ are large enough, so that the orthogonality conditions for the Bloch functions are satisfied, while the envelopes could be expanded in series at these
regions. Equations (4) specifies the $M+N$ boundary conditions for the envelopes. They are essentially nonlocal in agreement with (3). If the effective mass approximation is applicable in both semiconductors, then it is possible to retain only the quadratic term in (1) and the linear term in expansion of the envelopes in (3). We obtain

$$F_i^r + \tau_{i0}^r \frac{\partial F_i^r}{\partial x} + \tau_{i0}^y \frac{\partial F_i^r}{\partial y} + \tau_{i0}^z \frac{\partial F_i^r}{\partial z} = \sum_{j=1}^{M} \left( t_{ij}^r F_j^r + \tau_{ij}^r \frac{\partial F_j^r}{\partial x} + \tau_{ij}^y \frac{\partial F_j^r}{\partial y} + \tau_{ij}^z \frac{\partial F_j^r}{\partial z} \right) i = 1, \ldots, N,$$

$$F_i^l + \tau_{i0}^l \frac{\partial F_i^l}{\partial x} + \tau_{i0}^y \frac{\partial F_i^l}{\partial y} + \tau_{i0}^z \frac{\partial F_i^l}{\partial z} = \sum_{j=1}^{N} \left( t_{ij}^l F_j^l + \tau_{ij}^l \frac{\partial F_j^l}{\partial x} + \tau_{ij}^y \frac{\partial F_j^l}{\partial y} + \tau_{ij}^z \frac{\partial F_j^l}{\partial z} \right) i = 1, \ldots, M.$$

There

$$\tau_{i0}^{rx} = \frac{1}{v_0} \int_{S_0} \left[ x u_{ji}^l(r) u_{ji}^s(r) \right] d^3r, \quad \tau_{i0}^{ry} = \frac{1}{v_0} \int_{S_0} \left[ y u_{ji}^l(r) u_{ji}^s(r) \right] d^3r, \quad \tau_{i0}^{rz} = \frac{1}{v_0} \int_{S_0} \left[ z u_{ji}^l(r) u_{ji}^s(r) \right] d^3r,$$

$$\tau_{ij}^{rx} = \int_{S_1} \int_{S_2} \left( z_1 \varphi_{ji}^l(r_1) \right) - \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] \varphi_{ji}^s(r_2) d^2r_1 d^3r_2,$$

$$t_{ij}^l = \int_{S_1} \int_{S_2} \left( \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} - \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] \varphi_{ji}^s(r_2) d^2r_1 d^3r_2,$$

$$\tau_{ij}^{lx} = \int_{S_2} \int_{S_1} \left( y_1 - y_2 \right) \left( G(r_2, r_1) \frac{\partial \varphi_{ji}^l(r_1)}{\partial z_1} \right] - \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] \varphi_{ji}^s(r_2) d^2r_1 d^3r_2,$$

$$\tau_{ij}^{ly} = \int_{S_2} \int_{S_1} \left( \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] - \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] \varphi_{ji}^s(r_2) d^2r_1 d^3r_2,$$

$$\tau_{ij}^{lz} = \int_{S_2} \int_{S_1} \left( \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] - \varphi_{ji}^l(r_1) \frac{\partial G(r_2, r_1)}{\partial z_1} \right] \varphi_{ji}^s(r_2) d^2r_1 d^3r_2,$$

$$v_0$$ is the unit cell volume, and $u_{ji}^{lr}$ are the Bloch amplitudes. To determine $t_{ij}$ and $\tau_{ij}$ from Eq. (7) it is necessary to obtain the Green function $G(r_1, r_2)$ from Eq. (3). This is possible only if the potential $U(r)$ is known at the interface. Usually it is not the case. Nevertheless, the certain general conclusions could be done.

(a) If the points $k_i$ are the particular points of the Brillouin zone, then the Bloch functions $\varphi_{k_i}(r)$ could be chosen as real. Therefore the parameters $t_{ij}$ and $\tau_{ij}$ are real as well. Moreover, $t_{ij}$ and $\tau_{ij}$, if they belong to the equivalent valleys are equal too. In general, they should be complex conjugated.
Indeed, if we suppose the lattice constant to be vanished, then the potential $U(r)$ becomes independent of $x$ and $y$. It follows from Eq. (2) that $G(r_2, r_1) = G(|r_2 - r_1|)$ in this case. Then the integrals over the surfaces $S_1$ and $S_2$ in the expressions for $\tau^x$ and $\tau^y$ are vanished due to oddness of the integrands. In other words, the integrals (6) are determined by the regions, which size is of about the lattice constant. As regards $\tau^z$, it is small due to existence of the value $z_2 \sim w$ in the integrands.

(c) It is possible to make use of the fact, that the boundary is the short-range potential in comparison with the mean size of the envelope. That is why the scales of about $|r_2 - r_1| \sim w$ are significant in the integrands Eq. (7). Then it is possible to assume $E$ in Eq. (2) to be equal to the energy of the relevant valley edge $E_b$. Such substitution leads to the appreciable error in Green function at the distances of about $(2m|E - E_b|)^{-1/2} \gg w$. In other words the mean energy scale for $G(r_1, r_2)$ and so for the parameters $t_{ij}$ and $\tau_{ij}$ is $|E - E_b| \sim (2mw^2)^{-1}$, i.e., the bandwidth. So that the parameters $t_{ij}$ and $\tau_{ij}$ could be regarded as independent of energy.

(d) It seems that it is possible to omit the terms with the derivatives in Eq. (8). Really it is not the case. Indeed, if the determinant consisted from the coefficients at the envelopes $F^{l,r}$ is not vanished, then omitting of $\tau F'$ leads to the trivial result $F^{l,r}(0) = 0$. This means that the electron cannot even achieve the boundary. In fact $F^{l,r}$ is simply proportional to the small value in this case, $F(0) \sim w/\lambda$, so that each term in Eq. (8) becomes of the same order. It was shown that the existence of this small parameter is really leads to the significant suppression (of the order of $(w/\lambda)^2$) of the interface transparency. This suppression disappears at the structure resonance, then the above-mentioned determinant is vanished, i.e.,

$$
\begin{vmatrix}
E_{MM} & ||t_{ij}'|| \\
||t_{ij}'|| & E_{NN}
\end{vmatrix} = 0.
$$

(8)

Here $E_{MM}$ is the $M \times M$ identity matrix and $||t_{ij}'||$ are the matrixes composed from the parameters (7). In this case Eq. (8) could be represented as the system of $M + N - 1$ equations for the envelopes $F^{l,r}$ only and one equation for their derivatives $F'$. The latter equation does not contain the terms $t_{ij}F_j$ at the resonance and contains them with a small $t_{ij}$ nearby it.

There are $8MN + 3(M + N)$ parameters in Eq. (7). They are not independent because the probability flux should be continued through the interface. The number of nonvanished parameters could be essentially reduced if the boundary is symmetrical. This could be done by evolution of integrals (7) with the group-theoretical method. It follows from Eq. (2) that the Green function $G(r_1, r_2)$ is invariant under the symmetry transformations connected with the symmetry of potential $U(r)$. This is possible if both boarded material as well as the boundary itself are symmetrical, i.e., if any axis or a plain is perpendicular to the interface $z = 0$. Then the certain parameters $t_{ij}$, $\tau_{ij}$ in Eq. (4) becomes vanished. This means that the intervalley relation at the interface disappeared for such valleys.

It should be noted, that the nonintristic symmetry elements, which have been the origin for the intervalley degeneracy, could not exist at the interface. Indeed, a screw axis or a glide plane should distort the boundary shape or shift it in the distance of about the lattice
constant. In other words, they alter the potential $U(r)$ at the interface. Nevertheless, if such distortions have not essentially change $G(r_1, r_2)$, then the corresponding parameters $t_{ij}, \tau_{ij}$ become small. Two possibilities could be imagined in this way. Firstly, then the interface is smooth, i.e., if the periodic potential $U(r)$ from the leftside material change to that from the rightside material smoothly on the size, which is much larger than the lattice constant ($w \gg a$). In this case, the Bastard’s boundary conditions are applicable for each pair of the equivalent valleys. Secondly, if the bordered materials are not only crystallographically, but are chemically similar also. The pseudopotentials in both contacted materials are closely related in this case. So that the small deviation of the potential at the interface due to the nonintristic transformation should not appreciably affect $G(r_1, r_2)$. Such situation is really occur in the heterojunctions GaAs/AlAs. It is difficult to imagine why the intervalley relation could disappear in more general case.

The equation (5) allows to obtain the boundary conditions also if the effective mass approximation is unsufficial and the nonparabolicity of the band is essential. Then it is necessary to retain more terms in the expansion of Eq. (6). The received boundary conditions would contain the higher derivatives of the envelopes. The corresponding terms would be as small as $w/\lambda$.

III. LIGHT ABSORPTION AT SHARP BOUNDARY IN INDIRECT-BAND-GAP SEMICONDUCTOR

Let us consider the light absorption in the semiconductor, which band structure is presented in Fig. 2. We assume for simplicity that the valence band is not degenerate. There are two valleys in the conductive band: the central valley with the minima at the center of the Brillouin zone and the side valley at the edge of it ($\pm \pi/a, 0, 0$). Suppose, also, that the symmetry of the crystal makes it possible to divide the variables, so that the problem becomes one-dimensional.

The probability for the photon to be absorbed is determined by the squared module of the matrix element

$$M = \int \psi_f^* H_{int} \psi_i \, dV \quad (9)$$

Here

$$H_{int} = -\frac{i e}{mc} A_0 e^{-i(\omega t - \kappa_0 z)} \frac{\partial}{\partial z},$$

$A_0$ is the vector potential of the light field, $\omega$ and $\kappa_0$ are the frequency and the wave number of light, the electric field of the light is supposed to be directed along the $z$ axis, $\psi_i$ and $\psi_f$ are the wave functions of the electron before the excitation (in the valence band and after it (in the conductive band); $\psi_i$ is a superposition of the incident wave and the divergent scattered wave, whereas $\psi_f$ is a superposition of the reflected wave and the convergent scattered wave.\[8\]
We can write the wave functions as follows:

\[
\psi_i = \begin{cases} 
    u_v(z)e^{ipz} + Ru_v^*(z)e^{-ipz}, & z < 0, \\
    T_v e^{-\gamma vz}, & z > 0,
\end{cases}
\]  

(10)

\[
\psi_f = \begin{cases} 
    Au_{c0}(z)e^{\kappa z} + Bu_{cq}(z)e^{i(q-\hat{\pi})z} + u_{cq}(z)e^{-i(q-\hat{\pi})z}, & z < 0, \\
    T_c e^{-\gamma cz}, & z > 0.
\end{cases}
\]

Here \( u_v(z), u_{c0}, \) and \( u_{cq} \) are the Bloch amplitudes in the valent band, the central and side valleys of the conductive band, \( p, \kappa, \) and \( q \) are the wave numbers in these valleys. The wave function of the electron in the central valley is supposed to be decaying from the boundary. It should be noted that the decaying exponent might be not so large if the valley minima are close. The semiconductor occupies the region \( z < 0, \) so that the wave functions are decaying then \( z > 0. \) The coefficients \( R, T_v, A, B, T_c \) are determined by the boundary conditions (8). We have

\[
t_{11}^v(1 + R) + ip\tau_{11}^v(1 - R) = T_v(1 - \gamma_v \tau_{11}^v),
\]

\[
T_v(t_{21}^v - \gamma_v \tau_{21}^v) = 1 + R + ip\tau_{20}^v(1 - R),
\]

\[
(t_{11}^c + \kappa \tau_{11}^c)A + t_{12}^c(1 + B) + iq\tau_{12}^c(B - 1) = T_c(1 - \gamma_c \tau_{10}^c),
\]

\[
A(1 + \kappa \tau_{20}^c) = T_c(t_{21}^c - \gamma_c \tau_{21}^c),
\]

\[
1 + B + iq\tau_{30}^c(B - 1) = T_c(t_{31}^c - \gamma_c \tau_{31}^c).
\]

Hence

\[
R \approx -1 - \frac{2ip(t_{21}^v \tau_{11}^v - \tau_{20}^v)}{t_{11}^v t_{21}^v - 1 - ip(t_{21}^v \tau_{11}^v - \tau_{20}^v)},
\]

\[
A \approx -\frac{2iq t_{12}^c (\tau_{12}^c - t_{12}^c \tau_{30}^c)}{1 - t_{12}^c t_{31}^c - t_{11}^v t_{21}^v - iq(t_{31}^c \tau_{12}^c + t_{11}^v t_{21}^v \tau_{30}^c - \tau_{30}^c)},
\]

\[
B \approx -1 - \frac{2iq(t_{31}^c \tau_{12}^c + t_{11}^v t_{21}^v \tau_{30}^c - \tau_{30}^c)}{1 - t_{12}^c t_{31}^c - t_{11}^v t_{21}^v - iq(t_{31}^c \tau_{12}^c + t_{11}^v t_{21}^v \tau_{30}^c - \tau_{30}^c)}.
\]

Here \( t_{ij}^v, \tau_{ij}^c \) are the boundary parameters determined by Eq. (11). It is assumed that \( |k\tau| \ll 1 \) and \( |q\tau| \ll 1. \) The structure resonance conditions (8) in this case means that the denominators in Eq. (11) have vanished. It is clear from Eq. (11) that \( |R| = 1, |B| = 1. \) Thus apart from the resonance \( R = -1 \) and \( B = -1, \) whereas the conversion degree \( A \sim a/\lambda. \) If the resonance occurs for a valence band, then \( R = 1. \) For the resonance in conductive band \( B = 1 \) and \( A = 2t_{21}/t_{31}. \)

Let us determine the matrix element (3) with the wave functions (11, 12):

\[
M = \frac{-ie}{mc} A_0 Sc^{(e_v - e_w - \omega)} t \mathcal{P}_{vc}, \text{ then }
\]

\[
\mathcal{P}_{vc} = \int_{-\infty}^{0} \left[ A^* u_{c0}(z)e^{i\kappa z} + B^* u_{cq}(z)e^{-i(q-\hat{\pi})z} + \right. \\

\left. u_{cq}^*(z)e^{i(q-\hat{\pi})z} \right] \frac{\partial}{\partial z} \left[ u_v(z)e^{ipz} + Ru_v^*e^{-ipz} \right] dz.
\]

(12)
The wave number of light is assumed to be vanished in Eq. (12). We could take advantage of the periodicity of Bloch functions to evaluate the integral (12), then

$$\mathcal{P}_{vc} = A^* P_c \left( \frac{1}{\kappa + ip} + \frac{R}{\kappa - ip} \right) + \frac{a}{2} P_s (1 + B^*)(1 + R).$$

(13)

Here

$$P_c = \frac{1}{a} \int \! u_{c0}^* \frac{\partial u_v}{\partial z} \, dz, \quad P_s = \frac{1}{a} \int \! u_{eq}^* \frac{\partial u_w}{\partial z} \, dz.$$

Two terms in Eq. (13) could be interpreted as follows. The first one corresponds to the exitation of the electron to the surface state of the central valley subsequented by the conversion to the side valley. It could be prevailing if the valleys minima are close, so that $\kappa a \ll 1$. The second term in Eq. (13) corresponds to the immediate transition of the electron to the side valley at the interface (Fig. 2).

The absorption constant should be expressed as follows:

$$\alpha = \frac{2}{(2\pi)^2 Nv} \int |\mathcal{P}_{vc}|^2 \delta(\varepsilon_c - \varepsilon_v - \omega) \, d^3k$$

(14)

The magnitude of $\alpha$ substantially depends on presence or absence of the structure resonance in any band. If the resonance is absent in either band then $A \sim iq\tau$, $1 + R \sim ip\tau$, and $1 + B^* \sim iq\tau$. Then from (13, 14) $\mathcal{P}_{vc} \propto kq$ and so

$$\alpha \propto (\omega - \varepsilon_g)^4 \left( \frac{\pi a}{L} \right)^6 \left[ |P_s|^2 + \beta \frac{P_c^2}{(\kappa a)^2} \right],$$

(15a)

there $L$ is the absorption length, $\beta$ is the dimensionless parameter arisen from the first term in expression (13). If the resonance takes place in any band, then $\mathcal{P}_{vc} \propto k, q$, and

$$\alpha \propto (\omega - \varepsilon_g)^3 \left( \frac{\pi a}{L} \right)^4 \left[ |P_s|^2 + \beta \frac{P_c^2}{(\kappa a)^2} \right].$$

(15b)

For the resonant case in both bands

$$\alpha \propto (\omega - \varepsilon_g)^2 \left( \frac{\pi a}{L} \right)^2 \left[ |P_s|^2 + \beta \frac{P_c^2}{(\kappa a)^2} \right].$$

(15c)

It is clear that the absorption magnitude as well as its frequency dependence at the edge are determined by the conditions at the boundary.

**IV. DISCUSSION**

The boundary conditions for the envelope wave function proposed in this paper are applicable for the contacts of the materials with rather different band structures. They are suitable also if the degeneracy degrees in both bordered crystals are different. The present boundary conditions do not assume the band offsets to be small at the interface, i.e., they are appropriate not only for the heterojunctions, but also at the boundaries metal–semiconductor, metal–insulator, inorganic–organic contacts, and at the crystalline surface.
It is shown that the boundary conditions are defined as array of the linear equations for the envelopes and their derivatives. The coefficients at the derivatives there are shown to be small. However, they are important then the transport through the boundary as well as the contact phenomena are considered.

It is easy to understand why the coefficients at the derivatives are so small. At first, let consider the ordinary one-dimensional quantum mechanical problem for the electron in the potential wall. The same Schrödinger equation holds at both sides of the wall. So that, in order to define the solution of this equation it is necessary to define the wave function in any two points. Would we choose the distance between these points to be infinitesimal, then the wave function and its derivative become given at the point. This is the ordinary matching condition for the wave function. However, this is not the case for the envelope wave functions, which obeys the different equations at each side of the interface. Moreover, the equation (1) does not hold in the interface region. The Schrödinger equation with the proper interface potential has to be considered in this region. Its solution defines the wave functions, in which the lattice constant (it might be different at each side of the contact) is the particular parameter. As it has been shown in the exact solvleble models, this leads to the nonlocality of the boundary conditions. This is true in the general case as well. This means, that it is impossible to match the envelopes at the arbitrary points. So that the envelopes from each side have to be matched not at the same site, but at the different sites. The positions of these sites $r_i$ could be obtained from Eq. (6), if we suppose there $F(r_i) = F(0) + \tau \nabla F(0)$ for each envelope or expand the envelopes in Eq. (5) in these particular points, where $\nabla F(r_i) = 0$. The distances between these sites could not be chosen arbitrary, so that the simple relation for the derivatives is no longer exist. Nevertheless, it would appear reasonable that these distances should be of the order of the lattice constant $a$. Then $\tau \sim a$. These qualitative arguments are confirmed by the results of this paper.

It is shown that the structure resonance occurs not only in the simplest models, but in the general case as well. At first glance Eq. (8) is not practicable. Really, it is not the case. To understand the physical meaning of the structure resonance let us consider the electron scattering at the boundary. In the simplest cases of the one-valley and two-valley semiconductors the wave functions could be written as $\psi_i$ and $\psi_f$ in Eq. (10). The reflection coefficients ($R$ and $B$) for both cases are determined by Eq. (11). The resonant condition (8) is satisfied if the real parts of the denominators Eq. (11) are vanished. On the other hand, the poles of the reflection coefficients determine the positions of the surface levels. Thus, the structure resonance condition (8) means that the energy position of a surface level is close to the edge of the relevant band. As a rule such levels do exist at the semiconductor surface and they are responsible for the pinning of the Fermi level at the interface. If so, then the electron with Fermi energy in bulk should be in resonance then crossing the interface.

It is known, that the large amount of the surface states are existing in the gap of the amorphous semiconductors. So, the structure resonance could be expected at the interface with an amorphous semiconductor. This might manifest itself, in particular, as the difference of the optical spectra of the same semiconductor nanocrystal in the different (amorphous and crystalline) matrices. The effect might be associated with the difference of the quantization conditions for an electron at the resonance (at the interface with the amorphous matrix) and beyond from it. The envelope wave function of the electron could be assumed to be vanished at the boundary in the absence of the resonance. This is the quantization condition in this
However, it is not the case at the resonance. Then the crystallite effective size should increase, so that the electron could spend more time in the matrix. The possibility of the intervalley conversion also should affect the electron spectrum.

It is probable that the suppression of the boundary transparency apart from the structure resonance is responsible for the blue shift in the absorption spectra in TiO$_2$ observed in Ref. [3]. The blue shift there is associated with the electron confinement in the small (about the few nm) crystallites. This crystallites compose the thick (of the order the hundred nm) film, which has been prepared by the anode oxidative method. It is important that the conductance of the layer should be large enough to ensure the film growth. Thus, the layer should be conductive in order to the film growth, while the electrons could be confined in order to the blue shift becomes observable. To understand the phenomenon it should be emphasized that the boundary transparency is suppressed only for the long-wavelength electrons. The electrons moved by the light to the bottom of the conductive band are long-wavelength ($\lambda \sim L$, where $L$ is the crystallite size). So that the transparency factor $(a/\lambda)^2$ is small for them. This is not the case for the electrons moved to the conductive band from the outside. Thus, the quantum size effect concerns only the electrons excited by light, whereas the electrons with $\lambda \sim a$ maintain the current, which is necessary for the film growth.

It is shown that the boundary conditions at the sharp interface could be described by the parameters, which are independent of energy. Their number seems to be large for the many-valley semiconductors. Nevertheless, it could be significantly reduced if the bordered materials as well as the boundary itself are symmetrical. The group-theoretic method may be used for this purpose. The expressions for the parameters (11) are appropriate for this purpose. The boundary conditions parameters could be either calculated from the microscopic models or measured in the experiments. It is important, that the impurities as well as the structure imperfections would they exist at the interface should affect the parameters. Thus, the magnitude of the parameters for the interface should depend on the technology of its preparation. The latter factor hardly could be taken into account in the numerical simulations, but it should manifest itself in the experiments. The possible experimental ways for the determination of the boundary conditions parameters will be considered in the separate publication.

The boundary conditions obtained in the paper are applied for the investigation of the light absorption at the surface of the indirect-band-gap semiconductor. This is of particular importance in the restricted semiconductors where the share of the surface atoms is sufficiently large. It is shown that the enhancement of the effect has to take place. Firstly, it happens owing to the immediate electron transition to the side valley at the interface where the nonconservation of the electron momentum is possible. Secondly, it happens due to the conversion of the electron from the surface state at the central valley to the side one. The latter mechanism is essential if the energy positions of the valley minima ($\delta E$) are close. Such a situation occurs in Ge and in some semiconductors of A$_{III}$B$_{V}$ group, there $\delta E \sim 0.1$ eV, so that the effect has to increase in $(ka)^{-2} \sim 100$ times. Moreover, the valley minima possibly becomes closer in the nanocrystallites of the porous semiconductors (TiO$_2$, p-Si).

It is shown that the absorption value $\alpha$ as well as its dependence on the photon energy at the absorption edge are sensitive to the structure resonance whether it is present at the interface. The small parameter, to which the absorption is proportional, varied according to

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Eq. (15) from $(\pi a/L)^6$, if the resonance is absent in any band to $(\pi a/L)^2$ then it is present in both bands. It is easy to understand the reason. The wave function of the electron is small at the interface in the absence of the structure resonance, i.e., the electron spends too little time at the interface, where the light absorption without the momentum conservation is possible.

Let us estimate the minimal size of the crystallite, in which the mechanism of the light absorption proposed in Sec. IV is essential. We have to compare the small parameter aroused in Eq. (15) to that aroused in the phonon assisted light absorption. It is known, that the contribution of the latter mechanism to $\alpha$ is small in comparison with the contribution of the direct vertical interband electron transition as $10^{-2} - 10^{-3}$. $(\pi a/L)^6 \sim 10^{-3}$ then $L \sim 10a$, i.e., for the crystallite size of about $30 - 50$ Å. It has a very rapid increase then $L$ becomes less. It is quite possible, that the enhancement of the light absorption in the nanocrystalls, which has been observed in the experiments, could be connected with the mechanism considered in the paper.

The structure resonance in any or in both bands leads to the essential enhancement of the absorption. The latter could be possible in the amorfous semiconductors, where the density of the surface levels at both band extrema is high. The value $\alpha$ is determined by Eq. (15) in this case, so that $(\pi a/L)^2 \sim 10^{-3}$, then $L \sim 100a$. The significant (in 100 times) enhancement of the light absorption has been observed in the a-Si layers, which thickness is about $1\mu$m.

It follows from Eq. (15), that absorption should rapidly increase when the crystallite size becomes less. This means, that in the porous materials where the strong dispersion of the crystallite size occurs, the main contribution to the absorption comes from the smallest of them. Thus, the estimation of the crystallites size from the blue shift in the absorption spectra is really determines its lower bound.

V. SUMMARY

The boundary conditions for the envelope wave function, which are appropriate for the contacts of rather different materials have been proposed. It is shown that the boundary conditions are determined by the certain array of the parameters, depended only on the interface structure and the bordered materials themself. These parameters essentially identify all the properties of the interface, which can be described in terms of the envelope wave functions. The values of these parameters could be found numerically from the appropriate microscopeing models or measured in experiments.

It is shown that the electron behavior at the interface significantly depends on the structure resonance, whether it is occurring at the interface [Eq. (8)]. The absence of the resonance means that the electron wave function is small at the interface, so that all the physical phenomena governed by the boundary becomes suppressed.

The light absorption at the indirect-band-gap semiconductor interface is investigated. It is shown that the possibility of the nonconservation of the electron momentum at the interface made the significant enhancement of the absorption in the crystallites, which are as small as $30 - 50$ Å. The essential influence of the structure resonance at the interface on the absorption has been demonstrated.
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FIGURES

FIG. 1. The Cartesian coordinate system adopted in the problem. Two materials 1 and 2 are separated by the plain $z = 0$. The dotted lines indicate the extensions of the plains $S_1$ and $S_2$ at infinity.

FIG. 2. The two ways of the light absorption at the indirect-band-gap semiconductor surface: the immediate electron transition to the side valley $P_s$ and the vertical transition $P_c$ followed by the conversion to the side valley (dotted arrow).
