Deep acceptor states in asymmetric quantum-well systems in an electric field

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The strong effect of an electric field on the ionization energy of deep acceptors in asymmetric quantum-well systems is due to the field-dependence of the mixing of the states in the heavy- and light-hole subbands. The dependence of the ionization energy on the field and the position of impurities in the structure was calculated in the strongly localized potential model. © *1995 American Institute of Physics.*

1. In Ref. 1 the effect of the change produced in the ionization energy of a donor impurity in a system of quantum wells (QWs) by the relocation of the electronic envelope functions, occurring when an electric field is applied parallel to the growth axis of the heterostructure (HS), is studied and possible applications of this effect are indicated. An electric field also produces a relocation of the hole envelopes, but since the electron and hole effective masses in heterostructures such as $Al_xGa_{1-x}As$–GaAs are different, an effect similar to the one considered in Ref. 1 can occur only if the fields are very strong. Nonetheless, a large change in the ionization energy of deep centers in specially selected quantum-well systems can also occur in moderate fields, even in fields which are weaker than those required for effective relocation of the electronic envelopes.

A one-dimensional potential, which modulates the top of the valence band of a semiconductor heterostructure with quantum wells, not only removes the degeneracy of the valence band at the center of the Brillouin zone, but also produces specific interference effects in the system of heavy- and light-hole subbands. Such mixing of states[2] can, in separate cases, and especially in asymmetric quantum-well systems, substantially change the character of the hole dispersion in some subbands, and even change the sign of the effective mass. The nonparabolicity effects in the dispersion law can become very large even for relatively small transverse (with respect to the axis of the heterostructure) hole quasimomentum.

The mixing of states in, for example, the first light-hole subband (LH1) and the second heavy-hole subband (HH2) is strongest when the edges of these subbands lie close to one another. In asymmetric quantum-well systems, in contrast to heterostructures with a single square quantum well, the order of the LH1 and HH2 subbands depends strongly on the geometry of the heterostructure: For example, it is comparatively easy to cause these two bands to change places by changing the dimensions of the quantum wells and barriers or the depth of the quantum wells. It can be shown that this effect also occurs

in the case of a heterostructure in a longitudinal external electric field: In the case of heterostructures with close LH1 and HH2 subbands a unique inversion of the hole spectrum occurs even with a comparatively weak field. It is significant that the mixing of states is strongest near the critical field F_m, and the bottom subband in a given field $F \cong F_m$ exhibits anomalous dispersion, i.e., a negative effective mass. Near the so-called loop of extrema,[3] which is formed in this case, the density of states has a form that is characteristic of one-dimensional (1D) systems. In $Al_xGa_{1-x}As$–GaAs the bottom hole subband is the first heavy-hole subband (HH1), so that a radical change in the character of the dispersion in the HH2 subband must affect, for example, the binding energy of deep acceptor states which, by virtue of their symmetry, are split off from the heavy-hole band.

In the present paper we shall consider the dependence of the binding energy of such deep acceptors on the strength of the electric field and on the position of the acceptors in the quantum-well systems. We shall examine type-I heterostructures with several narrow, square (in the absence of a field) quantum wells and tunneling-transparent barriers with no constraints on the geometric parameters of the structure. The well-known method of envelope functions within the effective-mass approximation is used to investigate the hole states;[4] the conditions for the envelopes at the heteroboundaries are, as usual, a continuity of the envelopes and conservation of the probability flux calculated for such envelopes.[4]

2. An electric field applied perpendicular to the heteroboundaries introduces a slope in the potential well of the heteroboundary. All quantum-size states then become quasistationary.[5] We restrict the analysis to relatively weak fields, so that tunneling from the bottom quantum-well subbands through the last barrier of the heterostructure can be ignored:

$$F \ll \frac{m^{1/2}(V_0-E)^{3/2}}{\hbar e}.$$

Here m is the hole effective mass, V_0 is the height of the potential well for a hole in the heteroboundary, and E is the energy of the edge of the hole quantum-well subband. For the heterostructures $Al_xGa_{1-x}As$–GaAs with $x \leqslant 0.3$ we have $V_0 - E \approx 100$ meV for the bottom subbands; this leads to the inequality $F \ll 10^6$ V/cm. In studying such weak fields we shall therefore ignore the slope of the potential well in the last (semi-infinite) barrier layers which bound the system of quantum wells.

The energy spectrum of the holes in each subband for a given value of the field is determined from the condition that the system of 1D equations for the envelope functions within the quantum wells and barriers, which follows from the boundary conditions, has a solution. The procedure for determining the energy spectrum and the corresponding envelopes can be greatly simplified by taking into account the fact that the elements of the Luttinger Hamiltonian,[6] which are off-diagonal in the spinor indices and vanish as $k \to 0$, where $\mathbf{k}$ is the transverse quasimomentum of a hole, mix the heavy- and light-hole states. Since quasimomenta $ka \ll 1$, where a is the lattice constant, are important for the formation of the local states,[7] the contribution of the off-diagonal elements of the Hamiltonian can be taken into account by perturbation theory.

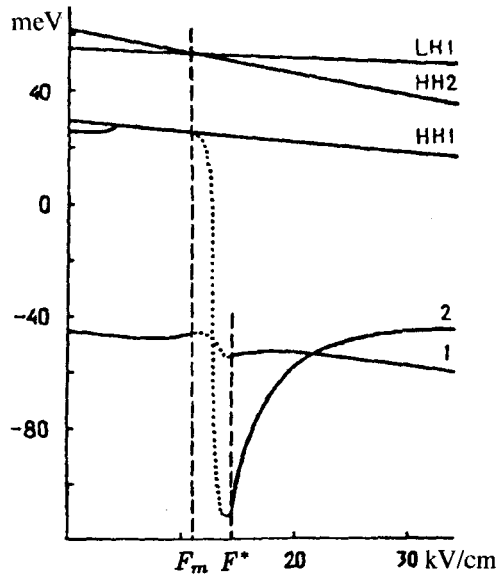

FIG. 1. Energies of 2D quantum-well subbands (HH1, HH2, and LH1) for $k=0$ as a function of the electric field strength. Curves *1* and *2* represent the binding energy of a deep acceptor located at the center of the widest quantum well and at the center of the narrowest quantum well, respectively, as a function of the electric field strength.

For example, the numerical solution for a heteroboundary with two quantum wells of widths 8a and 4a, separated by a barrier of width 4a (8–4–4 structure), shows that the LH1 and HH2 terms cross at $F_m \approx 10^4$ V/cm. Many asymmetric heterostructures with more than two quantum wells exhibit such behavior. As one can see from Fig. 1, which shows the displacement of the subband edges as a function of the field, the splitting $\Delta(F)$ between the edges of the LH1 and HH2 subbands is a virtually linear function of the field and therefore can be written as

$$\Delta(F)=\Delta_0\left(1-\frac{F}{F_m}\right), \tag{1}$$

where Δ_0 is the splitting between the edges of the LH1 and HH2 subbands with $F=0$. In the approximation adopted here the heavy- and light-hole states with $k=0$ do not mix, just as, correspondingly, there is no repulsion of levels with $F \approx F_m$.

3. The effective hole masses in the LH1 and HH2 subbands are actually determined by $\Delta(F)$. The effective masses $m_\lambda^{(0)}$, where the subscript λ labels the quantum-well subband, which were calculated in the zeroth approximation in the off-diagonal elements of the Luttinger Hamiltonian and which are expressed in terms of the Luttinger parameters γ_1 and γ_2, now participate partially in the penetration of the envelopes into the region of the barrier layers. In second-order perturbation theory the contribution proportional to k^2 in the dispersion law originates from the matrix element

$$\langle\lambda'|\hat{L}|\lambda\rangle=3^{1/2}(k_x-ik_y)\langle\lambda'|[\gamma_3(z),-i\partial/\partial z]_+|\lambda\rangle, \tag{2}$$

where γ_3 is the third Luttinger parameter, and $[\hat{A},\hat{B}]_+$ is the symmetrized product of the operators $\hat{A}$ and $\hat{B}$ which ensures that the operator $\hat{L}$, which depends on the coordinate z along the axis of growth of the heterostructure, is Hermitian. Since the LH1 and HH2 subbands are very close to one another, only the contribution of these subbands needs to be taken into account in determining the corrections to the energy. Since the effective mass is calculated in the limit $k\to 0$, for all F, except for a small neighborhood of the point F_m, the matrix element (2) is much smaller than $\Delta(F)$, so that the standard perturbation theory can be used to calculate the second correction to the energy for subsequent calculation of the effective mass.

Let A be the contribution of the matrix element (2) to the hole energy (in units of $\hbar^2/2m_0$, where m_0 is the mass of a free electron). The reciprocal of the effective mass in the λ subband can then be written as follows:

$$m_0/m_\lambda = m_0/m_\lambda^{(0)} \pm A/\Delta(F), \tag{3}$$

where the upper sign corresponds to $\lambda =$ HH2 and the lower sign corresponds to $\lambda =$ LH1. It follows from Eq. (3) that, in principle, there exist values $F_\pm$ of the field for which the reciprocals of the effective masses of the HH2 and LH1 holes, respectively, pass through zero. For the field F_m the effective masses of these holes themselves change sign. Taking into account the contribution of these subbands to the effective masses of the LH1 and HH2 holes does not change the character of the dependence (3); it merely leads to renormalization of the first term. Writing the hole dispersion relation in the λ subband up to fourth-order terms in the quasimomentum as

$$E_\lambda(k) = E_\lambda^{(0)} + \hbar^2 k^2/2m_\lambda + \hbar^2 b_\lambda^2 k^4/2m_0, \tag{4}$$

we can treat the effective masses of the LH1 and HH2 subbands as known functions of the electric field strength F. The parameters b_λ, which clearly take into account the nonparabolicity of the dispersion relation, also depend in principle on the field, but in contrast to the effective masses, this dependence evidently has no singular points. In what follows these quantities are thus treated as phenomenological parameters. It can be shown[2] that their typical values range from 10^{-7} cm to 10^{-6} cm. The dispersion relation for some subbands thus depends strongly on the external parameter F. By varying this parameter it is possible to make the corresponding inverse effective masses vanish and, therefore, effectively to lower the dimensionality of the system.[8]

For the hole dispersion relation in the bottom (HH1) subband, the effective mass m_1 depends weakly on the field, so that the standard parabolic approximation $E_1(k) = \hbar^2 k^2/2m_1$ is adequate (in what follows, the abbreviated notation $\lambda = 1, 2$ is used for the indices of the heavy-hole subbands HH1 and HH2). In connection with the approximation adopted here, it should be noted that for $m_2 < 0$ the effective masses and the parameter b_2 cannot be chosen independently of one another. Since $E_2(k) > E_1(k)$, we have the obvious inequality

$$|m_2| > \frac{m_1}{\sqrt{\left(\frac{2m_1 x_0}{m_0}\right)^2 + 1} - 1}, \tag{5}$$

where $x_0^2 = 2m_0 b_2^2 E_2^{(0)}/\hbar^2$. For $b_2 \approx 10^{-6}$ cm, $m_1 = 0.133 m_0$, and $E_2^{(0)} = 30$ meV, for example, the quantity $|m_2|$ cannot be less than approximately $0.09 m_0$. The range of fields $F_m < F < F^*$, which is indicated in the figure, in which the inequality (5) does not hold, therefore requires a special analysis.

4. In the limiting case of strong localization, a potential forming a deep acceptor state can be represented in the form

$$U(\mathbf{r}) = -U_0 a^3 \delta(\vec{\rho})\delta(z - z_0), \tag{6}$$

where z_0 is the z coordinate of the impurity in the heteroboundary, $\vec{\rho}$ is the transverse radius vector, and the lattice constant a appears in the definition (6) exclusively to preserve the standard dimension of the depth U_0 of the potential well. The Lifshitz equation,[9] which determines the energy levels of the localized states of a hole, can be written as

$$\frac{(U_0 a^3)}{(2\pi)^2} \sum_{\lambda} |f_\lambda(z_0; F)|^2 \int (E_\lambda(k) - E)^{-1} d^2k = 1, \tag{7}$$

where $f_\lambda(z; F)$ is the hole envelope function which depends on the electric field strength F in the λ subband; the integration extends over the two-dimensional (2D) Brillouin zone, and because of the assumption made above that the localized state is formed by the heavy-hole band, the integration extends only over the 2D heavy-hole subband. In the case of narrow quantum wells and barriers, only a small number of subbands needs to be taken into account. In what follows, only two subbands — HH1 and HH2 — are included in the calculation.

For a qualitative investigation of Eq. (7), the weak dependence of the relative position of the edges of the HH2 and HH1 subbands on the external field F can be ignored, and the field dependence of the binding energy of the acceptor state can be attributed completely to the F dependence of the effective mass of the HH2 subband and the envelope functions of the HH1 and HH2 subbands on F. For dispersion relation (4) the integrals in Eq. (7) can be expressed in terms of elementary functions. This makes it possible to easily determine by numerical methods the binding energy E_i as a function of F. This function is shown in Fig. 1.

We note that it is comparatively easy to indicate the heterostructures in which, in addition to the fields F_m and F_+, for which the effective masses of the LH1 and HH2 holes vanish (F_m) and the effective mass of the HH2 hole changes sign (passing through $\pm\infty$) (F_+), there exists a field F_-, in which the sign of the LH1-hole mass changes sign. Of course, a heterostructure with a different sequence of lower hole subbands with $F = 0$ can be chosen; i.e., instead of the sequence HH1, LH1, and HH2 for $F = 0$ we have a different sequence HH1, HH2, and LH1.

It is obvious that in the interval $F_- < F < F_m$ the effective mass of the LH1 hole is negative, while in the interval $F_m < F < F_+$ the effective mass of the HH2 hole is negative. An effective lowering of the dimension (2D⇒1D) for the corresponding hole states occurs in these intervals. Consequently, if the heavy- and light-hole subbands form deep acceptor states, then we should expect anomalous behavior of the binding energy as a function of the field when $F_- < F < F_+$.

The binding energy depends very strongly on the position z_0 of the deep center in the heterostructure. This can be seen directly from Eq. (7). For example, if a deep center occurs at the node of the envelope function of the HH2 subband, then the corresponding term obviously drops out of the sum in Eq. (7). In this case no anomalies therefore arise in the F-dependence of the binding energy. The effective decrease of the dimension of the hole states is most pronounced in the case where z_0 falls on the maximum of the HH2 envelope. Within certain limits, selective doping can therefore give the required energy of a state localized on a deep acceptor.

Many impurities, as well as impurity complexes, give deep acceptor states in GaAs.[10] For example, copper is a doubly charged acceptor. The first acceptor level (Cu^-) lies 0.14–0.15 eV above the top of the valence band and the second acceptor level lies 0.44 eV above the top of the valence band.[10] In a 8–4–4 structure the principal maximum of the HH2 envelope lies near the center of the narrowest quantum well: Near this point the ratio of the squared moduli of the HH2 and HH1 envelopes is very large (>400), and if the impurity lies in this vicinity (the parameters of Cu^- were used in the calculations), then the HH2 subband makes the determining contribution to the formation of the acceptor state. Conversely, if the impurity lies at the center of the widest quantum well, where the corresponding ratio of the squared moduli of the envelopes is less than 0.01, the acceptor state is formed mainly by the bottom subband. An electric field $F \sim F_m$ changes the envelope functions of the HH1 and HH2 subbands very little, since their effective relocation in the 8–4–4 structure starts in fields $F \geqslant 60$ kV/cm. Therefore, an electric field actually has no effect on the binding energy of an acceptor in a wide quantum well (curve *1* in Fig. 1), but it can lead to an exceptionally strong dependence of the binding energy on the field when the impurity lies in a narrow quantum well (curve *2*). Of course, for fields in the range $F_m < F < F^*$ the dispersion relation cannot be approximated by the simple expression (4) because of the restriction (5). By making the hole-spectrum model correspondingly more complicated, it can be shown that in this region curve *1* remains continuous and curve *2* quite rapidly approaches the bottom of the HH1 subband, as shown by the dashed lines in Fig. 1.

The indicated dependence is due solely to the rearrangement of the hole energy spectrum as a result of application of an electric field and is accompanied by the appearance of a singularity, which is typical of 1D systems, in the density of states. We note that the binding energy of a shallow acceptor is very sensitive to the appearance of 1D singularities in the hole density of states in asymmetric quantum-well systems.

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