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1997 J. Phys.: Condens. Matter 9 5321

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Theory of incompletely isovalent δ -doped semiconductors

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Received 14 March 1997

Abstract. In order to calculate the dependence of the electronic structure of single δ -doped layers on the area concentration c of isovalent impurities, the averaged t -matrix approximation (ATA) is applied to the case of a few impurities within a layer, and generalized to the case of a few missing impurities in an otherwise completely filled layer. In this way, exact results for the limits $c \rightarrow 0$ and $c \rightarrow 1$ are obtained. An interpolation between these limits results in Green's functions which allow the calculation of c -dependent electronic properties. In the case of GaAs:In, the top of the heavy-hole subband is calculated for a short-range (δ -like) difference between the host atom (Ga) and the impurity (In) potentials on the basis of a parabolic host band structure as well as by applying a three-band Hamiltonian. The comparison with the results from a virtual-crystal approximation proves the latter to describe the subbands well, provided that single impurities do not bind charge carriers. The subband dispersion for heavy holes, calculated for AlAs:Ga on the basis of a realistic ten-band Hamiltonian, shows a camel-back structure caused by the warping of the host heavy-hole band. This structure is proved to result in a pronounced high-energy peak of the subband density of states, in contrast to its step-like behaviour in the case of parabolic bands.

1. Introduction

The question of under which circumstances a single isovalent impurity can bind an electron or hole was considered first by Faulkner [1], and later by Baldereschi and Hopfield [2] and by Baldereschi [3]. These authors found conditions on the short-range potential of the isovalent impurity for the existence of bound states. The only known system in which isovalent impurities act as electron traps is GaP doped with nitrogen at phosphorus sites (GaP:N_P), with a binding energy of about 10 meV [4]. GaP:Bi_P is the only system that has been observed to bind a hole [5]. No other isovalent substitutions in III–V semiconductors yield bound states.

The renewal of interest in isovalent doping is due to the development of modern growth technologies, providing the possibility of embedding single layers of impurities (also called monolayers or δ -layers) into a host material. A large number of experiments on various isovalent δ -doped semiconductors (GaAs:In_{Ga} [6–9], InP:As_P [10], GaAs:Al_{Ga} [11], and AlAs:Ga_{Al} [11]) have shown surprisingly intense and sharp photoluminescence lines as compared to those for the bulk host material.

Recently, submonolayers with only a partial filling of a layer with isovalent impurities have been studied experimentally [11–13]. Even one single monolayer with only 8% In impurities in GaAs was shown to result in remarkably different optical spectra compared with those of bulk GaAs [13].

Theoretical investigations by Mäder and Baldereschi [14, 15] for the case of a completely filled δ -layer proved that it will always bind an electron or a hole, regardless of the strength

of the short-range single-impurity potential. The isovalent monolayer introduces 2D bands within the forbidden gap of the host material, and the carriers in such a 2D band may subsequently attract carriers of opposite sign. Due to their short-range potential, isovalent impurities act as efficient scattering centres for excited electron–hole pairs, and enhance the external quantum efficiency of the system.

The electronic structure of isovalent monolayers is usually interpreted as that of the limiting case of a thin quantum well [7–9] or by describing the monolayer as a giant homogeneous planar impurity [16, 14, 17]. The fairly good results obtained by using the envelope function scheme [8, 9] are unexpected—because the potential induced by the isovalent impurity layer is not a slowly varying one—and they merit discussion. From this point of view, the tight-binding calculations of Mäder [14] and Wilke and Henning [17], made using a Green’s function theory, are more reliable. All of these theoretical concepts, however, neglect the effects of the structural disorder resulting from the random distribution of the impurities in an incompletely filled layer, and could be applied to the case of an incomplete filling only if the virtual-crystal approximation (VCA) were valid.

The object of the present paper is the calculation of the dependence of the electronic structure of isovalent δ -doped layers on the area concentration c of the isovalent impurities, on the basis of a multiple-scattering theory. Using the methods given in [18, 19] for the case of charged impurities, we obtain exact results in the limits of low ($c \rightarrow 0$) and high concentration (nearly complete filling, $c \rightarrow 1$).

The standard method for use when performing calculations at arbitrary c is the coherent potential approximation (CPA) [20, 21] or its simplified version, the Klauder-V approximation [22], in which so-called multiple-occupancy corrections are neglected. However, as shown in [19, 23, 24], the self-energy M in both approximations correctly reproduces the self-energy $M|_{c=0}$ in the limit of a vanishing impurity concentration c , but not its first derivative with respect to the concentration, $(dM/dc)|_{c=0}$, at energies near those of the bound states. The same is true in the limit $c \rightarrow 1$. Therefore, we will use an interpolation formula for the self-energy M , which reproduces correctly both the self-energy in the low-concentration ($c \rightarrow 0$) and high-concentration ($c \rightarrow 1$) limits, and also its first derivatives with respect to the concentration in both limits.

This interpolation formula does not account for impurity density fluctuations, however, and the densities of states of the impurity bands in this approximation show sharp cut-offs and no band tails. In this paper we do not attempt to calculate the band tails, but restrict ourselves to concentration-dependent effects without taking into account pair (and higher) correlations in the impurity distribution. As a consequence, the influence of possible island formation of the impurities on the electronic properties is neglected.

The essential input parameter within the theoretical framework used here is the potential difference between that of a host atom and that of an isovalent impurity. Following the work of [14, 17], we choose this short-range potential difference to be δ -like in Wannier space, with a magnitude given by the band offset of a corresponding heterojunction. Such a choice can be regarded as a first approximation only, and we cannot expect to obtain subband energies which reproduce experimental results without subsequent adjustment.

This is especially evident in the case of lattice-mismatched systems such as GaAs:In.

In section 2, we present the basic theory of the treatment of two-dimensional disorder, and calculate the subband self-energies in the low- and high-concentration limits. An interpolation formula that applies over the entire concentration range is also presented. In section 3, heavy-hole subbands are calculated on the basis of a parabolic host band structure as well as by applying a three-band model Hamiltonian. It is proved that a virtual-crystal approximation reproduces the results well, provided that single impurities do not give rise to

bound states. In section 4 a realistic calculation of the heavy-hole subband is performed for AIAs:Ga on the basis of a ten-band tight-binding band structure of the host semiconductor. It is shown that its dependence on the two-dimensional momentum in the layer shows a so-called camel-back structure, giving rise to a pronounced peak in the density of states. Conclusions are presented in the last section.

2. Theory

We consider the one-electron Hamiltonian

$$H = \sum_{n,l} E_n(l) a_n^+(l) a_n(l) + \sum_{n,ll'} W_n(l,l') a_n^+(l) a_n(l') \quad (1)$$

where l labels the atomic positions $\mathbf{R}(l)$, and $a_n(l)$ and $a_n^+(l)$ are the destruction and creation operators for an electron or a hole in the band n at site l . Our main assumption is that the $W_n(l,l')$ are independent of the potentials $E_n(l)$. This means that the band structures of the host semiconductor (e.g. GaAs) and of the semiconductor built up from the impurities (e.g. InAs) are approximated as being rigidly shifted. Possible lattice mismatches are neglected as well. The $E_n(l)$ are given by

$$E_n(l) = E_n + \Delta_n(l) \quad (2)$$

where the $\Delta_n(l)$ are short-range (δ -like in Wannier space) perturbations by the impurities at sites $\mathbf{R}(l)$. The corresponding potential matrix elements in \mathbf{k} -space are

$$\begin{aligned} \langle n\mathbf{k}|V|n'\mathbf{k}'\rangle &= \frac{1}{N} \sum_{\{l\}} \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}(l)] \int u_{n,\mathbf{k}}^*(\mathbf{r}) v(\mathbf{r}) u_{n',\mathbf{k}'}(\mathbf{r}) \\ &\quad \times \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] d\mathbf{r} \\ &= \rho(\mathbf{k} - \mathbf{k}') \Delta_n \delta_{n,n'}. \end{aligned} \quad (3)$$

The coupling of different bands of the host semiconductor by the impurity potentials is neglected. The approximation (3) is a slight generalization of the envelope function approximation; the potential matrix elements Δ_n are allowed to still depend on the band index n .

The case of a three-dimensional distribution of the impurities within the model given by (1)–(3) has been well studied (see e.g. [22, 25, 26]), and the basic framework can be extended easily to a two-dimensional impurity distribution within a doped layer. In this case, all of the impurities are confined within an (001)-oriented atomic monolayer, which is chosen to be at $z = 0$.

2.1. The low-concentration limit, $c \rightarrow 0$

Repeating the corresponding analysis—given e.g. in [25]—we obtain for the single-impurity t -matrix averaged over all of the configurations of the impurities within the doped layer

$$\langle t_n(m) \rangle = t_n = \frac{c \Delta_n}{1 - \Delta_n P_n(0)} \quad (4)$$

where c is the area concentration, and $P_n(0) = P_n(l, l)$ are the Green's functions of the bands n of the host semiconductor.

The well-known averaged t -matrix approximation (ATA) for the total T -matrix of many impurities then results in the self-energies

$$\bar{M}_n(\mathbf{k}, \mathbf{k}') = M_n(E) \delta(\mathbf{k}' - \mathbf{k}_2) = \frac{1}{N_z} \frac{c \Delta_n \delta(\mathbf{k}'_2 - \mathbf{k}_2)}{1 - (1 - c) \Delta_n P(0)} \quad (5)$$

valid for small c as well as for $c \equiv 1$.

Here we have used the notation $\mathbf{k} = (k_x, k_y, k_z) = (\mathbf{k}_2, k_z)$, where the z -axis is parallel to the normal of the doped layer. $\delta(\mathbf{k}'_2 - \mathbf{k}_2)$ is a two-dimensional δ -function ensuring momentum conservation within the layer, and N_z is the number of planes in the z -direction. We note that the self-energy is not proportional to $\delta(k_z - k'_z)$, and is independent of k_z and k'_z . Hence, it is related to the configuration-averaged Green's functions of (1) by the equation

$$\langle G_n(\mathbf{k}, \mathbf{k}') \rangle = P_n(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}') + P_n(\mathbf{k})\bar{M}_n(\mathbf{k}, \mathbf{k}') \sum_{k'_z} \langle G_n(\mathbf{k}'', \mathbf{k}') \rangle \quad (6)$$

and not by

$$\langle G_n(\mathbf{k}, \mathbf{k}') \rangle = \frac{1}{E - \varepsilon_n(\mathbf{k}) - M_n(E)} \quad (7)$$

as in the case of a three-dimensional impurity distribution.

2.2. The high-concentration limit, $c \rightarrow 1$

The case of a few missing impurities in an otherwise filled two-dimensional layer is not as obvious as the $c \rightarrow 0$ limit.

We need first the exact Green's functions for the completely filled monolayer in a three-dimensional crystal, and then we have to apply a modification of the ATA to the case of missing impurities.

The Green's functions for $c = 1$ are given formally by

$$L = P + PVP + \dots \quad (8)$$

The structure factors in (8) are given by

$$\rho(\mathbf{p}) = \frac{1}{N} \sum_{R(i) \in \text{layer}} e^{i\mathbf{p} \cdot R(i)} = \frac{1}{N_z} \delta(\mathbf{p}_2).$$

The expansion (8) then can be summed over, with the result

$$L_n(\mathbf{k}, \mathbf{k}') = P_n(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}') + P_n(\mathbf{k}) \left[\frac{1}{N_z} \Delta_n \delta(\mathbf{k}_2 - \mathbf{k}'_2) / \left(1 - \frac{1}{N_z} \Delta_n \sum_{q_z} P(\mathbf{k}'_2, q_z) \right) \right] P_n(\mathbf{k}'). \quad (9)$$

Additional poles to those of $P_n(\mathbf{k})$ are given by the solutions of the equations

$$1 = \frac{\Delta_n}{N_z} \sum_{k_z} P_n(\mathbf{k}'_2, k_z) = \frac{\Delta_n}{N_z} \sum_{k_z} \frac{1}{E - \varepsilon_n(\mathbf{k}_2, k_z)} = \Delta_n P_n(\mathbf{k}_2) \quad (10)$$

first derived by Mäder [14]. From (9) we get bound states for every \mathbf{k}_2 , resulting in the subband dispersion for each band n . As noted above, mixing of different bands due to the impurity potential is neglected. It could easily be included if the non-diagonal potential term $\Delta_{n,n'}$ were known.

The case of a few missing impurities in the monolayer (small $r = 1 - c$) can now be treated by generalizing the ATA, the potential of the missing impurities being just $-\Delta_n$.

The results for the self-energies corresponding to (5) are

$$\bar{W}_n(\mathbf{k}, \mathbf{k}') = \frac{1}{N_z} \frac{-r \Delta_n \delta(\mathbf{k}'_2 - \mathbf{k}_2)}{1 + (1 - r) \Delta_n L_n(0)} \quad (11)$$

with

$$L_n(0) = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} L_n(\mathbf{k}, \mathbf{k}') = \frac{1}{N_2} \sum_{\mathbf{k}_2} \frac{P_n(\mathbf{k}_2)}{1 - \Delta_n P_n(\mathbf{k}_2)} \quad (12)$$

where N_2 is given by $N = N_2 N_z$.

These self-energies \bar{W}_n allow the determination of the configurationally averaged Green's functions $\langle G_n(\mathbf{k}, \mathbf{k}') \rangle$ in terms of the $L_n(\mathbf{k}, \mathbf{k}')$:

$$\langle G \rangle = L + L\bar{V}L + \dots = L + L\bar{W}\langle G \rangle$$

where the \bar{V} are the potentials due to the missing impurities.

With the help of the expansion (8), we get after some algebra finally

$$\begin{aligned} \bar{M}_n(\mathbf{k}, \mathbf{k}') &= M_n(E, \mathbf{k}_2) \delta(\mathbf{k}'_2 - \mathbf{k}_2) \\ &= \frac{1}{N_z} \frac{c \Delta_n \delta(\mathbf{k}_2 - \mathbf{k}'_2)}{1 - \Delta_n P_n(\mathbf{k}_2)} \left[\frac{1 + \Delta_n L_n(0)}{1 + c \Delta_n L_n(0)} - \frac{\Delta_n P_n(\mathbf{k}_2)}{1 - (1 - c) \Delta_n P_n(0)} \right]. \end{aligned} \quad (13)$$

These self-energies are correct in the limit $c \rightarrow 1$, as well as at $c \equiv 0$.

For $c = 1$, the self-energies are simply

$$M_n(E, \mathbf{k}_2) = \frac{1}{N_z} \Delta_n \quad (14)$$

as expected.

As in the limit $c \rightarrow 0$, the $M_n(\mathbf{k}, \mathbf{k}')$ are proportional to $\delta(\mathbf{k}_2 - \mathbf{k}'_2)$, but not to $\delta(k_z - k'_z)$, leading to equation (6) instead of (7).

2.3. The interpolation formula

For the construction of a suitable interpolation formula, we use the fact that the two expressions (5) and (13) for the self-energies give the correct limits $c = 0$ and $c = 1$, as well as the exact first derivatives with respect to c :

$$M_n|_{c=0} = 0 \quad (15)$$

$$\left. \frac{dM_n}{dc} \right|_{c=0} = \frac{1}{N_z} \frac{\Delta_n}{1 - \Delta_n P_n(0)} \quad (16)$$

$$M_n|_{c=1} = \frac{1}{N_z} \Delta_n \quad (17)$$

$$\left. \frac{dM_n}{dc} \right|_{c=1} = \frac{1}{N_z} \Delta_n \left[1 + \frac{\Delta_n^2 P_n(k_2) P_n(0) - \Delta_n L_n(0)/(1 + \Delta_n L_n(0))}{1 - \Delta_n P_n(\mathbf{k}_2)} \right]. \quad (18)$$

A simple Padé approximation to the self-energies

$$M_n(c) = \frac{\alpha_n + \beta_n c + \gamma_n c^2}{1 + \eta_n c} \quad (19)$$

reproduces these limiting values if

$$\alpha_n = M_n|_{c=0} \quad (20)$$

$$\beta_n = \left. \frac{dM_n}{dc} \right|_{c=0} \quad (21)$$

$$\gamma_n = \left(- \left. \frac{dM_n}{dc} \right|_{c=0} + 2M_n|_{c=1} - \left. \frac{dM_n}{dc} \right|_{c=1} \right) / \left(\left. \frac{dM_n}{dc} \right|_{c=1} - M_n|_{c=1} \right) \quad (22)$$

$$\eta_n = \left((M_n|_{c=1})^2 - \left. \frac{dM_n}{dc} \right|_{c=0} \left. \frac{dM_n}{dc} \right|_{c=1} \right) / \left(\left. \frac{dM_n}{dc} \right|_{c=1} - M_n|_{c=1} \right). \quad (23)$$

This interpolation formula is identical to that derived in [24] in another way. It was proved there that (19) with (20)–(23) has all of the analytical properties required for a self-energy, and avoids some shortcomings of a CPA expression; see also [18] and [19].

3. Results

The self-energies obtained are related to the averaged Green's functions by equation (6). A one-dimensional Schrödinger equation with the Hamiltonian (1) would result in the equation

$$G_n(k_z, k'_z) = P_n(k_z)\delta(k_z - k'_z) + P_n(k_z) \frac{\Delta_n}{N_z} \sum_{k'_z} G_n(k'_z, k'_z) \quad (24)$$

which, multiplied by $\delta(k_2 - k'_2)$, is equivalent to (6).

Hence, the band structure of an isovalent δ -doped semiconductor can be obtained by solving a one-dimensional Schrödinger equation with the potential replaced by an effective E - and k_2 -dependent one. In the case of a full layer, this effective potential, according to (14), is just Δ_n/N_z , the monolayer being equivalent to one impurity in a one-dimensional Schrödinger equation. Hence, it results in a bound state (for each unperturbed band) for an arbitrarily small potential, as first observed by Mäder and Baldereschi [14, 15].

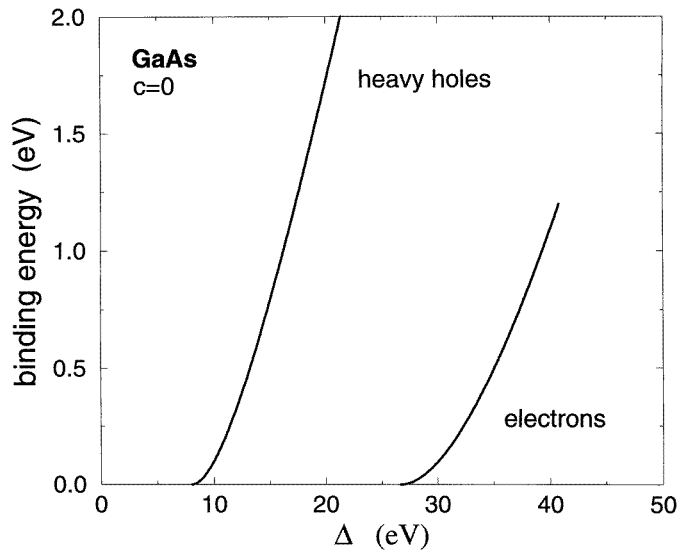


Figure 1. Binding energies of heavy holes and electrons in the low-concentration limit, $c = 0$, obtained using the approximation of parabolic bands of GaAs as the host material.

In the limiting case $c \rightarrow 0$, poles of the $\langle G_n(\mathbf{k}, \mathbf{k}') \rangle$ additional to those of $P_n(\mathbf{k})$ are given by

$$1 = \frac{\Delta_n}{N} \sum_{\mathbf{k}} \frac{1}{E - \varepsilon_n(\mathbf{k})} = \Delta_n P_n(0) \quad (25)$$

which is just the Koster–Slater equation [27] as expected. It results for III–V semiconductors in bound states only in the cases of GaP:N_P [4] and GaP:Bi_P [5]. We obtained the dependence of (25) on the strength of the impurity potential within the approximation of parabolic bands by integrating numerically over the Brillouin zone. Figure 1 shows the

results for heavy holes and electrons in the case of GaAs. There are no bound states for reasonable values of Δ_n ; in the case of the heavy-hole band, $\Delta_{hh} > 8$ eV would be required.

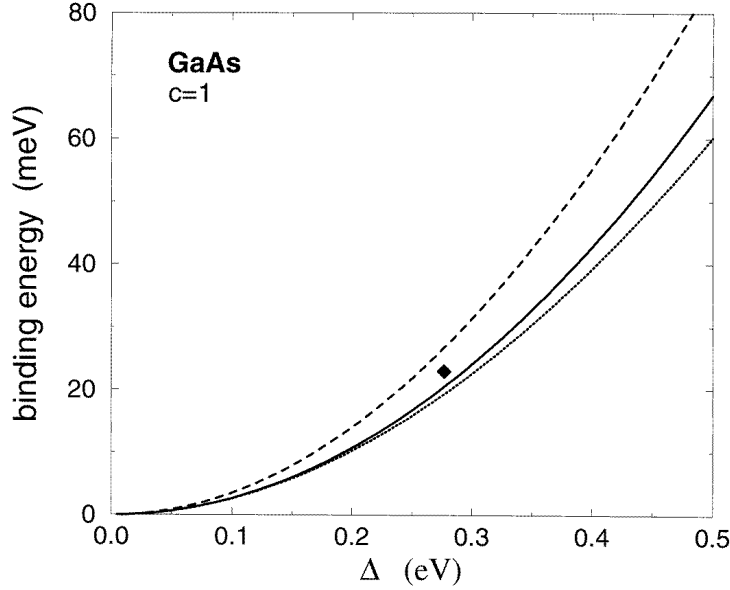


Figure 2. Binding energies of heavy holes in the high-concentration limit, $c = 1$, with different approximations for the band structure of the host material: the solid curve corresponds to a parabolic band with the integration extended to infinity; the dotted curve corresponds to a parabolic band with the integration within the Brillouin zone boundaries; and the dashed curve gives the results obtained by using a three-band model Hamiltonian. Closed diamond: see the text.

In the opposite case, $c = 1$, subbands can be obtained easily for the host semiconductor dispersion relation

$$\varepsilon(\mathbf{k}) = \varepsilon(\mathbf{k}_2) + \frac{\hbar^2 k_z^2}{2m^*}. \quad (26)$$

Equation (10) can be solved analytically, and we obtain, placing the zero of energy at the top of the valence band and extending the integration in

$$N_z^{-1} \sum_{k_z} = \frac{a}{4\pi} \int_{-2\pi/a}^{2\pi/a} dk_z$$

to infinity, for electrons for example

$$E_e = E_{gap} - \frac{2m^* a^2}{\hbar^2} \left(\frac{\Delta_e}{4} \right)^2 + \varepsilon_e(\mathbf{k}_2) \quad (27)$$

if Δ_e is negative, in accordance with the standard envelope function result

$$E = E_i + \frac{\hbar^2(k_x^2 + k_y^2)}{2m^*}. \quad (28)$$

The effective-mass approximation used, and the extension of the integration to infinity are not critical, as shown in figure 2. The solid line displays the result corresponding to (27) for holes. The dotted line corresponds to the parabolic band approximation, but integrating

(10) within the Brillouin zone boundaries. The dashed line was obtained using a three-band model Hamiltonian for the uppermost valence bands in a zinc-blende crystal [2], in which case (10) can be solved analytically for $k_2 = 0$. The single closed diamond refers to an experimental binding energy of $E_b = 23$ meV for heavy holes and an appropriate band offset for strained InAs/GaAs of $\Delta_{hh} = 0.277$ eV, as given in [9]. The agreement between the experimental and the theoretical results based on a crude approximation to the real band structure of the host material is astonishing.

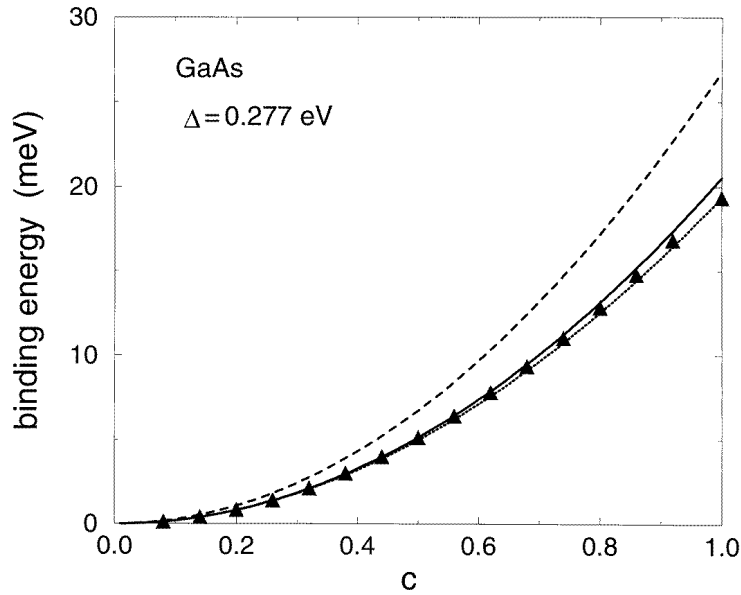


Figure 3. The dependence of the top of the heavy-hole subband in GaAs with the band offset of strained InAs/GaAs of 0.277 eV on the concentration calculated with the interpolation formula (19) (triangles). For comparison, the VCA results for the same approximations as in figure 2 (solid, dotted, and dashed curves) are also shown.

Figure 3 shows the dependence of the top of the heavy-hole subband on the impurity concentration c for GaAs:In and with $\Delta_{hh} = 0.277$ eV, as given above. The triangles are calculated using the interpolation formula (19) and integrating (10) within the Brillouin zone boundaries (using the parabolic band approximation). The solid, dotted, and dashed lines correspond to the same approximations for the band structure of the host crystal as were used to obtain the curves in figure 2, but scaling the strength of the potential Δ_{hh} with the help of the VCA ($\Delta_{hh} \rightarrow c\Delta_{hh}$).

The VCA and the interpolation formula for the self-energy give nearly the same results, except that at high concentrations a small deviation is found which vanishes at $c \equiv 1$. We conclude that the use of the numerically simple VCA is fully justified in cases in which single impurities ($c \rightarrow 0$) do not result in bound states. The E - and k_2 -dependences of the self-energies become important only as regards reproducing the impurity band formation from bound states of single impurities, as occurs in the case of charged impurities [18, 19].

The calculations resulting in figure 3 were performed with a real self-energy. Its imaginary part gives rise to finite lifetimes of the charge carriers in the subbands due to scattering processes which, of course, cannot be described when applying the VCA.

4. The camel-back structure of the heavy-hole subband dispersion

As shown above, in the case of the absence of bound states due to single impurities, the subband dispersions can be calculated to a good approximation by solving the VCA equation

$$1 = c\Delta_n \frac{a}{4\pi} \int_{-2\pi/a}^{2\pi/a} dk_z \frac{1}{E - \varepsilon_n(\mathbf{k}_2, k_z)}. \quad (29)$$

In the case of quadratic dispersion relations $\varepsilon_n(\mathbf{k}_2, k_z) \sim \mathbf{k}_2^2$, we obtain quadratic subband dispersions $E_n = E_n^0 + \sim \mathbf{k}_2^2$, and, hence, step-like densities of subband states.

The valence bands of the host III–V semiconductors, however, are not parabolic. They show a warping which can be calculated near the centre of the Brillouin zone, e.g. by the $\mathbf{k} \cdot \mathbf{p}$ method. But equation (29) requires integration over a full line of the Brillouin zone, for which the $\mathbf{k} \cdot \mathbf{p}$ approximation is not adequate.

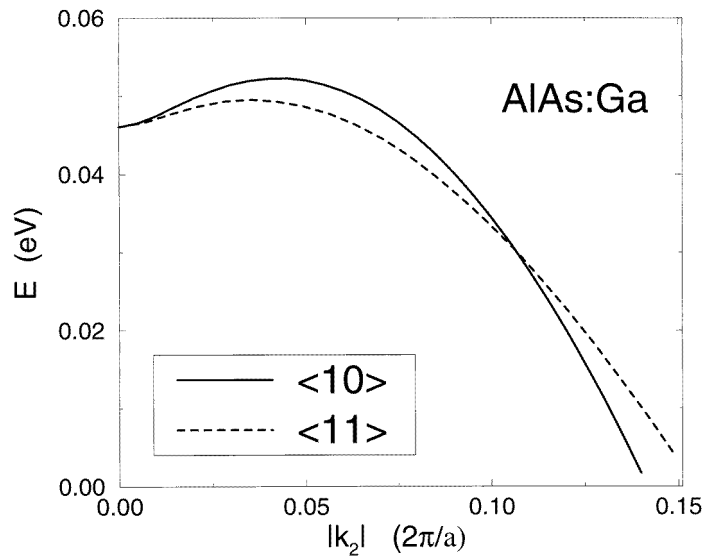


Figure 4. Heavy-hole subband dispersion in two different directions for a completely filled ($c = 1$) AlAs:Ga layer obtained from an sp^3s^* semiempirical tight-binding Hamiltonian with $\Delta_{hh} = 0.556$ eV.

To be specific, we choose the case of a (001)-oriented Ga monolayer in AlAs. This system was chosen because lattice mismatch can be neglected, and a realistic description in terms of the model Hamiltonian (1) is adequate. We put $c = 1$ and take $\Delta_{hh} = 0.556$ eV [14]. $\varepsilon_{hh}(\mathbf{k})$ is obtained from the ten-band effective tight-binding Hamiltonian [28]. Equation (29) is solved numerically, and the two-dimensional density of states of the heavy-hole subband is obtained by using a tetrahedron method [29, 30]. The results are shown in figures 4 and 5. Because along the whole k_z -line the band structure of the host heavy-hole band has a local minimum near $k_2 = 0$, the integration in (29) simply adds these structures, resulting in a similar behaviour of the subband dispersion. Such a two-dimensional camel-back structure gives rise, however, to a high-energy peak in the density of states instead of a step-like behaviour, as shown in figure 5. The occurrence of this peak can easily be understood, in general: for an arbitrary dispersion $E = E(|\mathbf{k}|)$ (neglecting the relatively

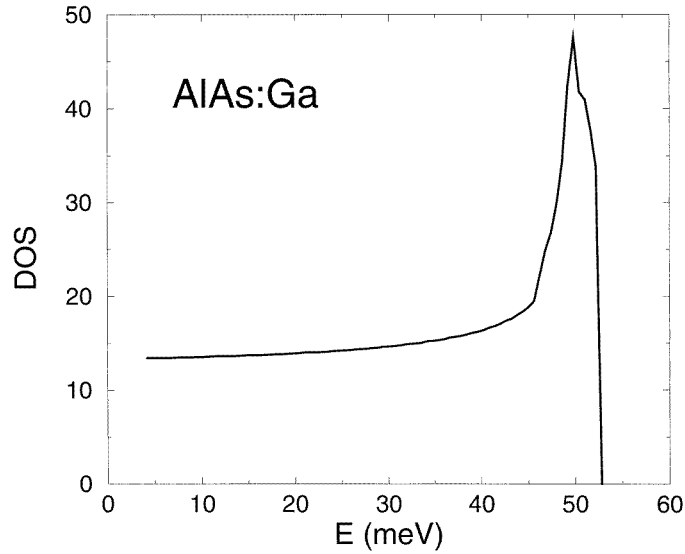


Figure 5. The two-dimensional density of states corresponding to figure 4 obtained from a two-dimensional Brillouin zone integration by using a tetrahedron method. Due to numerical uncertainties in the solution of equation (29), no values below 4 meV are displayed.

small directional dependence of k_2) with a maximum $E = E_0$ at $k = k_0 \neq 0$, we get in d dimensions by using $k^{d-1} dk \sim \rho(E) dE$ the density of states as follows:

$$\rho(E) = \alpha \frac{k^{d-1}}{dE/dk} = \alpha \frac{k^{d-1}}{E'(k)}.$$

With $E'(k_0) \approx E''(k_0)(k - k_0)$, we get

$$\rho(E) = \alpha \frac{k_0^{d-1}}{E''(k_0)(k - k_0)} \quad \text{for } E \lesssim E_0.$$

$E = E_0 - \beta(k - k_0)^2$ results in $\rho(E) = \delta/\sqrt{E_0 - E}$, which corresponds to a one-dimensional density of states, peaked at $E = E_0$.

The warping-induced camel-back structure of the subbands of the two-dimensional monolayer simulates a one-dimensional density of states. This result may explain the unexpectedly intense photoluminescence signals found experimentally even for small area concentrations c . This effect could be checked experimentally: in the case of (111)-oriented isovalent monolayers the integration in (29) has to be carried out along the $k_x = k_y = k_z$ -line of the Brillouin zone. At all points of this line, the heavy-hole bands of the host III-V semiconductors are maximal, and no camel-back structure and no peak in the subband density of states are expected. Assuming comparable dipole matrix elements for all \mathbf{k} -directions, a remarkable loss of photoluminescence intensity should be observed.

We remark, however, that we fully neglected valence band mixing due to non-diagonal impurity potential matrix elements. A mixing between light- and heavy-hole bands is known to result in a camel-back structure of subbands in the case of thick quantum wells, too [31, 32]. This type of camel-back structure was obtained by applying a Luttinger Hamiltonian that is not diagonal in the band indices, together with a diagonal potential, which is equivalent, in principle, to a generalization of our approach using a diagonal band

Hamiltonian with a non-diagonal potential. The Luttinger Hamiltonian approach, however, cannot be applied to thin quantum wells, which require the knowledge of the host band structure over the full Brillouin zone. On the other hand, band-mixing effects included into the theory developed above would increase the number of unknown parameters (non-diagonal potential matrix elements $\Delta_{nn'}$), and they would exceed the number of existing values known so far.

First-principles calculations of the subbands are the only possibility for taking into account the effects both of warping and of band mixing. We are not aware of any sufficiently accurate first-principle calculations that result in the expected effect: the accuracy required is of the order of some meV.

5. Conclusions

The electronic structure of quantum wells and of the limiting case of a filled monolayer as an ultrathin quantum well can be obtained in the envelope function approximation by solving a one-dimensional Schrödinger equation. We tried to treat the problem of completely or incompletely filled monolayers as far as possible exactly, in order to test the applicability of this method. The treatment was based on the following approximations.

(i) The short-range potential differences between the impurity and host atoms have been treated as δ -like functions in Wannier space. The corresponding matrix elements have been allowed to depend on the band index. Interband mixing was not taken into account, however.

(ii) The hopping matrix elements have been assumed not to depend on the occupation of the sites by host or by impurity atoms. In the case of thick quantum wells this assumption is certainly not correct; in the case of an incompletely filled monolayer we believe it to be tolerable.

(iii) Lattice mismatch has been neglected.

(iv) The multiple-scattering approach used does not account for band tailing. It therefore neglects, e.g., the influence of island formation within a partially filled δ -layer.

Under these suppositions, expressions for the subband self-energies have been derived which are, in general, E - and k_2 -dependent. The following results were obtained.

(i) In the case of weak single-impurity potentials, which are not able to bind charge carriers, the numerically simple VCA reproduces the results well. The energy and momentum dependence of the self-energy can be neglected in this case, if we are not interested in finite-lifetime effects.

(ii) The monolayer, however, binds charge carriers for arbitrarily small potentials, as stated for $c = 1$ by Mäder and Baldereschi [14, 15]. In the case of incompletely filled monolayers there is no threshold concentration for subband formation.

(iii) On the basis of a realistic ten-band tight-binding Hamiltonian describing the host semiconductor, a pronounced peak in the heavy-hole subband density of states is obtained for (001)-oriented δ -layers, which is due to the warping of the host semiconductor band structure, and not due to interband mixing.

The basic assumptions of our approach can be avoided only by making first-principles band-structure calculations and then performing configurational averaging. We are not aware of such calculations being available with the required numerical accuracy, of the order of some meV.

Acknowledgments

We gratefully acknowledge useful discussions with Professor Dr K Unger from the Leipzig University, and the help of Professor Dr P Vogl from the Technical University of Munich concerning the tight-binding calculations.

This work was supported by the Deutsche Forschungsgemeinschaft under Grant No Mo 673/1-1.

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