Nonrectangular quantum wells as a basis for studying the band offsets at GaAs-$Ga_{1-x}Al_x$ As interfaces

W. Pötz and D. K. Ferry
Center for Solid State Electronics Research, Arizona State University, Tempe, Arizona 85287
(Received 25 March 1985; revised manuscript received 10 June 1985)

Using the envelope-function formalism we calculate interband-transition energies for various shapes of effective quantum-well potentials generated by layers of GaAs and $Ga_{1-x}Al_xAs$. The sensitivity of these experimentally accessible energies to variations in the band-offset parameter Q_e is studied for rectangular, parabolic, triangular, and somewhat more complicated potential profiles. We show that this sensitivity may vary strongly for different profiles. Upon consideration of our numerical results as well as fabricational aspects we suggest that a triangular rather than a parabolic or rectangular quantum well should be used to determine Q_e.

I. INTRODUCTION

For over a decade the question of how conduction and valence bands match at an interface of intrinsic GaAs and direct-energy-gap $Ga_{1-x}Al_xAs$ has been investigated by both theorists and experimentalists, yet it is still an unsolved problem. Dingle[1] measured interband-transition energies of a single quantum well consisting of a layer of GaAs embedded in $Ga_{0.8}Al_{0.2}As$ and found Q_e, the ratio of the conduction-band offset to the difference in the main energy gaps of the alloy and GaAs, to be 0.85, by comparing his data to the results of a simple theoretical model. However, more recently a novel structure of multiple quantum wells (MQW's) that simulates a macroscopically parabolic potential profile between the confining $Ga_{1-x}Al_xAs$ layers has been used to study how the difference in the main energy gap is shared among conduction and valence bands. From these structures, Miller *et al.*[2,3] extracted a value of $Q_e=0.51$, and later 0.57 from both rectangular and parabolic potential wells. Dawson *et al.*[4] reported $Q_e=0.75$ for narrow rectangular quantum wells. Also, recent transport measurements indicate that Q_e is around 0.65.[5–7] A recent theoretical study resolved the origin of the large spread in values for Q_e obtained from photoluminescence data.[8,9] Optical interband-transition energies associated with rectangular wells are very insensitive to variations in Q_e. Taking into account fabricational uncertainties, no unique value exists for Q_e that can fully explain the experimental data. Parabolic wells were shown to have higher sensitivity to Q_e and given that the estimated error bars for the structure parameters are realistic, $Q_e=0.85$ can be ruled out in favor of a value between 0.5 and 0.65.

Here, we investigate the sensitivity of the optical interband-transition energies associated with different effective potentials simulated in between confining layers of $Ga_{1-x}Al_xAs$ with respect to variations in Q_e. We try to find an optimal, yet simple, form for the potential to reveal the band offsets. In Sec. II, we discuss the requirements made upon such an ideal potential. By simple physical arguments, which, for instance, explain why a parabolic well is superior to a rectangular well, we are led toward favorable potential shapes. The basis of our calculations is an (eight-band) envelope-function model (EFM). It is described in detail elsewhere.[8] We investigate rectangular, double-rectangular, parabolic, triangular, and $|z|-cz^2$ potential profiles. They can be developed by thin, alternating layers of GaAs and $Ga_{1-x}Al_xAs$ of varying thickness, in the same way as parabolic MQW's. A comparison of the results and a discussion is given in Sec. III, while summary and conclusions are deferred to Sec. IV.

II. SELECTION OF POTENTIAL WELLS

The band-offset parameter Q_e is an input parameter in EFM's which is adjusted to obtain optimal agreement with experimental data on quantum-well structures. Both results of transport measurements as well as photoluminescence experiments on such systems may be used. Here we are interested in optical measurements, which can provide us with intersubband transition energies E_{nmi} between conduction- and valence-band associated subband levels.[1–4,10] n and m denote the indices of the conduction- and valence-band associated levels, respectively. The third index i indicates whether a heavy- or light-hole level is involved in the transition ($i=h$ or l). Such experiments have been reported for both rectangular and quasiparabolic quantum wells for n and m typically smaller than 5. Unfortunately, no measured values for transition energies for subband levels associated with one and the same band seem to be available. Consequently, an accurate determination of the value for Q_e from these data requires that the interband-transition energies (for *low* subband levels) depend sensitively on Q_e. It is obviously not sufficient that the subband levels shift noticeably with varying Q_e as the shifts of these levels associated with different bands may largely cancel out in E_{nmi}. Furthermore, it is important that these shifts occur relative to the bottom of the quantum-well potentials, i.e., relative to the band edges of GaAs, in order to lead to changes in E_{nmi}. From the point of view of fabrication, the potentials simulated by layered structures should be

relatively simple functions of space in order to avoid high uncertainties in the structure parameters such as Al concentration x and sample length L_z.

It is easy to understand how the exciton spectrum of single quantum wells can conceal the band offsets so successfully. If the center layer is not too thin, such structures simulate a rectangular potential hole for the carriers. For the lowest bound states of a (deep) rectangular potential of width L_z and effective particle mass m^*, the binding energies can be approximated by

$$E_n=\frac{\hbar^2\pi^2}{2m^*L_z^2}n^2 , \tag{1}$$

where n is the level index. The corresponding wave functions are trigonometric functions that vanish at the potential walls, and quite remarkably, are independent of the particle mass m^*. Equation (1) shows that a change in the value for Q_e, corresponding to a change in the barrier height, will have little effect on the position of strongly bound levels with respect to the band edge. This can also be seen from first-order perturbation theory. For energy levels well below the potential edge, the wave function is basically confined within the well. It will hardly feel a change in the potential which, relative to the band edge, will only occur *outside* the well if Q_e is changed. In addition, as the energy gaps are constants, an increase of the barrier height for electrons must be accompanied by a decrease of the barrier height for holes by the same amount of energy. The wave functions are (nearly) independent of the effective mass, so that, within first-order perturbation theory, electron- and hole-associated sub-band levels will shift by the same amount of energy and the optical transition energies will remain unchanged. Only for excited levels, close to the edge of the well, can the levels be expected to respond noticeably to modest variations in Q_e.

For a parabolic well of diameter L_z and barrier height H, the lowest eigenvalues can be approximated by

$$E_n=2(n-\tfrac{1}{2})\frac{\hbar}{L_z}\left[\frac{2H}{m^*}\right]^{1/2} . \tag{2}$$

Even for the lowest levels, E_n is proportional to $H^{1/2}$. In the picture of first-order perturbation theory, a change in the band offset Q_e, i.e., H, will change the potential profile everywhere inside the well and the levels will respond with a shift in energy. Additionally, compared to the rectangular potential well, the sensitivity to variations in the values for m^* and L_z is reduced from $1/m^*$ and $1/L_z^2$ to $(1/m^*)^{1/2}$ and $1/L_z$, respectively.

Further increases in sensitivity with respect to Q_e can be achieved with potential profiles of the form $|z|^s$, where $0<s<2$. For $s=1$, the position of the lowest energy levels with respect to the band edge can be approximated by

$$E_n=\left[\frac{\hbar^2}{2m^*}\right]^{1/3}\left[\frac{H}{L_z}\right]^{2/3}\xi_n , \tag{3}$$

where ξ_n are well-known constants.[11] Equation (3) shows that the eigenvalues are proportional to $H^{2/3}$, yet, they are less sensitive to variations in L_z and m^* compared to both rectangular and parabolic potential profiles. At least in principle, with s approaching zero, the sensitivity could be further increased. Simultaneously, however, the number of bound states would decrease. Consequently, a smaller and smaller number of observable interband transitions would be available to fit Q_e. Also fabricational uncertainties will set a limit to reducing s below 1. For $0<s<1$, the potential has a sharp cusp at $z=0$ which would be hard to fabricate accurately, especially in regions that are important for the lowest levels. It appears that a triangular well comes close to the optimal choice for a potential well with levels sensitive to Q_e. Therefore, we rather study a potential of the form

$$f(z)=\begin{cases}(4H/L_z)(|z|-z^2/L_z) & \text{for } |z|\leq L_z/2\\ H & \text{for } |z|\geq L_z/2 ,\end{cases} \tag{4}$$

which has the advantage that it increases twice as rapidly around $z=0$ as the triangular potential for same L_z and H. Finally, we also investigate double wells upon their usefulness in revealing Q_e.

III. RESULTS AND DISCUSSION

Led by these simple physical arguments we calculated the subband energy levels for rectangular, parabolic, triangular, and type-(4) potential profiles created by layered structures of GaAs and $Ga_{1-x}Al_xAs$. We utilize our eight-band envelope-function approach that has been used before to compare theoretical values for interband-transition energies in quantum wells to their experimental exciton spectra. As this model and a comparison with previously published (simplified) envelope-function models is presented elsewhere, it is only described briefly.[8] A linear combination of eight Γ-point Bloch functions (six from the valence bands and two from the lowest conduction band) is used as a basis to expand the wave functions of the localized states introduced by the MQW structure. Remote-band effects are included in second-order perturbation theory. This allows a consistent representation of the host's band structure around the Γ point. The basis is chosen such that it diagonalizes the spin-orbit interaction at the Γ point. This procedure leads to an eigenvalue problem in form of a set of coupled differential equations for the envelope functions $f_j(z)$ which can be decoupled if terms higher than second order in d/dz are neglected. z denotes the direction normal to the interface. The differential equations have to be solved (we use a finite-difference method) self-consistently in the eigenvalues E. The direct energy gap E_g in $Ga_{1-x}Al_xAs$ is assumed to vary linearly with x. This is a good approximation for $x<0.5$.[12] Then the z-dependent band edges $E_{cd}(z)$, $E_h(z)$, and $E_l(z)$, relative to the valence-band edge in GaAs, can be written as

$$E_{cd}(z)=E_{cd}(\text{GaAs})+\left[\frac{Q_e}{Q_e+1}\right]\Delta E_g x(z) \tag{5}$$

and

$$E_h(z)=E_l(z)=-\frac{1}{Q_e+1}\Delta E_g x(z) , \tag{6}$$

TABLE I. Subband levels of the conduction (cd), heavy-hole (h), and light-hole (l) band calculated for various potential profiles. Energies are in meV. L_z is the total sample length and Q_e is the band-offset parameter.

	Rectangular $L_z=250$ Å		Rectangular $L_z=507$ Å		Parabolic $L_z=507$ Å		Triangular $L_z=507$ Å		$\|z\|-cz^2$ $L_z=507$ Å	
Q_e	0.51	0.85	0.51	0.85	0.51	0.85	0.51	0.85	0.51	0.85
E_{cd1}	1526.0	1527.0	1521.0	1521.1	1531.1	1534.8	1548.1	1559.8	1562.5	1580.5
E_{cd2}	1547.0	1549.0	1527.2	1527.4	1555.0	1565.8	1584.9	1611.5	1612.5	1652.7
E_{cd3}	1581.0	1585.0	1537.2	1537.7	1578.8	1596.1	1609.9	1646.5	1641.3	1695.8
E_{cd4}	1623.0	1632.0	1551.0	1551.9	1601.9	1625.8	1632.5	1678.2	1663.5	1731.2
E_{h1}	−1.2	−1.1	−0.3	−0.3	−4.5	−2.5	−14.7	−6.7	−22.6	−10.1
E_{h2}	−4.6	−4.4	−1.2	−1.1	−13.4	−7.4	−33.7	−15.3	−50.8	−22.4
E_{h3}	−10.7	−9.8	−2.6	−2.5	−22.3	−12.3	−46.8	−21.2	−68.8	−29.8
E_{h4}	−19.0	−17.3	−4.7	−4.5	−31.2	−17.2	−58.8	−26.6	−84.7	−36.1
E_{l1}	−5.3	−4.4	−1.4	−1.3	−10.1	−5.6	−25.32	−11.5	−38.1	−16.9
E_{l2}	−21.0	−17.4	−5.6	−5.2	−30.0	−16.6	−57.4	−26.0	−82.5	−35.3
E_{l3}	−46.2	−36.2	−12.6	−11.5	−49.6	−27.4	−79.2	−35.9	−100.9	−44.3
E_{l4}	−79.0		−22.2	−20.1	−68.9	−37.7	−99.1	−44.2	−129.9	

where cd, h, and l stands for conduction, heavy-hole, and light-hole band, respectively. ΔE_g is the increase in E_g per unit x. The different potential profiles enter via the z-dependent Al concentration $x(z)$. Q_e is assumed to be independent of x. The host properties, such as band structures and effective masses are taken from experiment,[10,12,13] leaving Q_e the only adjustable input parameter.

A rectangular potential can be realized by a (moderately thin) layer of GaAs embedded in $Ga_{1-x}Al_xAs$. The other profiles can be achieved by MQW's with varying layer thicknesses as demonstrated by Petroff *et al.*[14] and Gossard *et al.*,[15] or, at least in principle, by varying the alloy concentration $x(z)$ continuously. Previous studies on parabolic potential profiles have shown that the energies of the subband levels are practically the same whether the potential corresponding to the layered structure or the corresponding continuous potential is used.[8,9] Therefore, only continuous $x(z)$ are studied here. As we want to compare different profiles, we keep L_z and the maximum Al concentration x constant for all different profiles. Results for the lowest four subband-level energies attached to cd, h, and l bands are given in Table I using $L_z=507$ Å and $x=0.25$. The calculations were performed for $Q_e=0.51$ and 0.85, which represent the boundaries for values of the band offsets discussed in the literature. For $Q_e=0.51$ and 0.85, we obtain the conduction-band offsets as 0.158 and 0.264 eV; the valence-band offsets are 0.152 and 0.046 eV, respectively.

We first discuss absolute shifts of the four lowest levels associated with each band as a function of Q_e. For the rectangular well with $L_z=507$ Å, the cd- and l-associated levels never shift more than 2 meV, and h-associated levels remain practically unshifted. For the parabolic well, cd- and l-associated levels shift by up to 30 meV, whereas the h-associated levels shift by up to about 15 meV. For the triangular profile a further improvement is obtained. The four lowest cd and l levels shift between 12 and 50 meV; h-subband levels shift by up to about 32 meV. For the potential (4), shifts from 18 up to 56 meV are calculated for cd and l levels. Only three l bound states are obtained above the valence-band edge of the alloy. The h-subband levels shift by up to 50 meV. These findings clearly show the trends predicted in Sec. II.

In Table II, we show the resulting transition energies E_{nmi} for various profiles (no effort was made to include exciton effects). It reveals the striking insensitivity of these energies for the rectangular well when compared to the parabolic well, as noticed before.[8,9] However, further improvement can be achieved with a triangular potential profile and potential (4). For the triangular well in Table II, the sensitivity increases by a factor of 2, and for the latter by a factor of 3 relative to the parabolic well. As the nonrectangular structures investigated here produce lowest levels that are generally more localized than the equivalent ones for the rectangular well of the same total

TABLE II. Calculated interband-transition energies (in eV) for various potential profiles versus Q_e. $L_z=507$ Å and $x=0.25$.

	Rectangular $L_z=250$ Å		Rectangular $L_z=507$ Å		Parabolic $L_z=507$ Å		Triangular $L_z=507$ Å		$\|z\|-cz^2$ $L_z=507$ Å	
Q_e	0.51	0.85	0.51	0.85	0.51	0.85	0.51	0.85	0.51	0.85
E_{11h}	1.527	1.528	1.5213	1.5214	1.5356	1.5373	1.5628	1.5665	1.5851	1.5906
E_{13h}	1.537	1.537	1.5236	1.5236	1.5534	1.5471	1.5949	1.5810	1.6313	1.6103
E_{22h}	1.552	1.553	1.5284	1.5285	1.5684	1.5732	1.6186	1.6268	1.6633	1.6751
E_{24h}	1.566	1.566	1.5319	1.5319	1.5862	1.5830	1.6437	1.6381	1.6972	1.6888
E_{33h}	1.592	1.595	1.5398	1.5402	1.6011	1.6084	1.6567	1.6677	1.7101	1.7256
E_{44h}	1.642	1.649	1.5557	1.5564	1.6331	1.6430	1.6913	1.7048	1.7482	1.7673
E_{11l}	1.531	1.531	1.5224	1.5224	1.5412	1.5404	1.5734	1.5713	1.6006	1.5974
E_{22l}	1.568	1.566	1.5328	1.5326	1.5850	1.5824	1.6423	1.6375	1.6950	1.6880

length L_{z_3} the results for a rectangular well of width $L_z = 250$ Å are also displayed in Tables I and II. A comparison with the results for $L_z = 507$ Å demonstrates again how insensitive interband-transition energies are with respect to variations in the band offsets for this type of well. The cd- and l-subband levels shift between 1 and 10 meV, h-subband levels shift by up to 2 meV, but only for transitions involving higher h levels are noticeable effects on E_{nmh} seen to occur. For $Q_e = 0.85$, only three l levels are obtained.

We also investigated the sensitivity of double barriers with respect to variations in Q_e. We studied Dingle's double well[1] with well diameters of 50 Å and a well separation of 12.6 Å. We found that variations in Q_e between 0.5 and 0.85 cause changes in the interband transition energies that are of the same order of magnitude as those caused by variations of the distance between the wells by only one monolayer. Therefore, we conclude that a reliable value for Q_e from optical excitation spectra of double wells can only be obtained if the number of atomic layers is known exactly.

The sensitivity with respect to uncertainties in the total length L_z of the potential well was investigated for the different profiles. Obviously, the suggested nonrectangular structures are only a real improvement if they do not show equally increased sensitivity to uncertainties in structure parameters. We studied this in a quantitative way by increasing the sample thickness from 507 to 550 Å. Q_e was varied between 0.51 and 0.85. Changes in the lowest three optical interband transitions involving h levels were calculated. These energies are usually resolved in optical spectra. Averaging over these three values, we obtained the ratio $\Delta E_{nh}(L_z)/\Delta E_{nh}(Q_e)$ to be 6.5, 0.83, 0.66, and 0.60 for the rectangular, parabolic, triangular, and type-(4) potential, respectively. $\Delta E_{nh}(L_z)$ and $\Delta E_{nh}(Q_e)$ denote the changes in the transition energies E_{nnh} with L_z and Q_e, respectively. This confirms the trends expected from the analytic expressions given for infinitely deep wells. The most dramatic change occurs when one goes from rectangular to parabolic profiles, whereas the relative sensitivity to uncertainties in L_z decreases still by about another 20% in going from parabolic to triangular profiles. The same trend holds if relative sensitivities in the values for the effective masses are studied.

An increase in sensitivity to Q_e is unavoidably connected with an increase in sensitivity to uncertainties in the alloy parameter x. Both parameters determine the individual barrier heights. However, a change in x will modify the barrier heights for both electrons and holes in the same fashion, whereas a change in the value for Q_e will raise one barrier and lower the other. This shows that it is valuable to investigate *subband level splittings*. If, for example, the experimentally determined splittings are too large for both electron and hole subband levels, as compared to theory, the assumed value for x was too small and (or) the actual sample length remained under its estimated value. If, however, one set of levels is split too much and the other too little a wrong choice for the value of Q_e is indicated.

Finally, a further advantage of these nonrectangular structures is that optical transitions for $n =$ even to $m =$ even (or $n =$ odd to $m =$ odd) but $n \neq m$ are suppressed less than for a rectangular well. In particular, nonsymmetric profiles (e.g., a nonsymmetric triangular well) should be used to study transitions with $n =$ even to $m =$ odd (or $n =$ odd and $m =$ even), allowing a more detailed study of the level structure which is valuable for extracting the band offsets. This avoids the condition of having only a few observable transition energies sensitive to Q_e, as is the case for very thin single QW's.[4]

IV. SUMMARY AND CONCLUSIONS

We have performed a systematic theoretical study of various profiles of multiple quantum wells with respect to the sensitivity of their optical interband-transition energies as a function of the band-offset parameter Q_e. These profiles may be created by layered structures of GaAs and $Ga_{1-x}Al_xAs$ or continuous spatial variation of the alloy parameter x in $Ga_{1-x}Al_xAs$. We show that this sensitivity is significantly influenced by the choice of the structure. In particular for a triangular well, it increases approximately by a factor of 2 over that of a comparable parabolic well; however, the relative sensitivity with respect to uncertainties in the sample length and the effective masses decreases. These trends can be understood by simple physical arguments which also allow the prediction of profiles that exceed the sensitivity of a triangular potential. However, taking into account the relative simplicity of a triangular potential profile with respect to both fabrication and theoretical investigation, we suggest that this profile be used to attempt a determination of the band offsets at GaAs-$Ga_{1-x}Al_xAs$ interfaces.

ACKNOWLEDGMENTS

The authors would like to thank A. C. Gossard, F. Capasso, W. Porod, and U. Ravaioli for helpful communication. This work was supported by the U.S. Army Research Office.

[1]R. Dingle, in *Festkörperprobleme (Advances in Solid State Physics)*, edited by H. J. Queisser (Vieweg, Braunschweig, 1975), Vol. XV, p. 21.

[2]R. C. Miller, A. C. Gossard, D. A. Kleinman, and O. Munteanu, Phys. Rev. B 29, 3740 (1984).

[3]R. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B 29, 7085 (1984).

[4]P. Dawson, G. Duggan, H. I. Ralph, K. Woodbridge, and G. W. 't Hooft, Superlattices Microstruct. 1, 231 (1984).

[5]H. Kroemer, Appl. Phys. Lett. 46, 504 (1985).

[6]K. Hirakawa, H. Sasaki, and J. Yoshino, Appl. Phys. Lett. 45, 253 (1984).

[7]W. I. Wang, E. E. Mendez, and F. Stern, Appl. Phys. Lett. 45, 639 (1984).

[8]W. Pötz, W. Porod, and D. K. Ferry, following paper, Phys. Rev. B **32**, 3868 (1985).

[9]W. Porod, W. Pötz, and D. K. Ferry, J. Vac. Sci. Technol. (to be published).

[10]Z. Y. Xu, V. G. Kreismanis, and C. L. Tang, Appl. Phys. Lett. **43**, 415 (1983).

[11]F. Crowne, T. L. Reinecke, and B. V. Shanabrook, Solid State Commun. **50**, 875 (1984).

[12]R. Dingle, R. A. Logan, and J. R. Arthur Jr., *Gallium Arsenide and Related Compounds, Edinburg, 1976,* edited by C. Hilsum (IOP, London, 1977), Vol. 33a, p. 210.

[13]M. Cardona, in *Physics of Group IV Elements and III-V Compounds,* Vol. 17a of *Landolt-Börnstein,* edited by K. H. Hellwege (Springer, Berlin, 1981). See also Ref. 8.

[14]P. Petroff, A. C. Gossard, W. Wiegmann, and A. Savage, J. Cryst. Growth **44**, 5 (1978).

[15]A. C. Gossard, W. Brown, C. L. Allyn, and W. Wiegmann, J. Vac. Sci. Technol. **20**, 694 (1982).