Shallow donors in multiple-well GaAs-$Ga_{1-x}Al_xAs$ heterostructures

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The effects of finite-width barriers upon the binding energies and probability distributions of shallow donor states in GaAs-$Ga_{1-x}Al_xAs$ heterostructures are reported. We have performed calculations for the ground and low-lying excited states for donor positions within a GaAs well or a $Ga_{1-x}Al_xAs$ barrier. Although the binding energy of the ground state of a donor located at the center of a well is typically not strongly affected by barriers wider than an effective Bohr radius, those of the excited states are reduced significantly for the on-center case. All states considered show significant effects due to the neighboring wells if the donor is located near the edge of a well or within a barrier.

INTRODUCTION

It has become possible to grow systems of alternating layers of two different lattice-matched semiconductors with controlled thicknesses and sharp interfaces through the use of crystal-growth techniques such as molecular-beam epitaxy and metal-organic chemical vapor deposition. These alternating, ultrathin layers form a one-dimensional periodic structure called a superlattice. One of the most widely studied semiconductor superlattices is GaAs-$Ga_{1-x}Al_xAs$.

There have been many theoretical calculations of the electronic properties of shallow donors in GaAs-$Ga_{1-x}Al_xAs$ heterostructures. The model used in these studies[1-4] has been that of a hydrogenic impurity center located in a single GaAs quantum well sandwiched between two semi-infinitely wide $Ga_{1-x}Al_xAs$ barriers. One of the pioneers in the area is Bastard,[1] who used the model stated above with an infinite barrier height to calculate the energy of the ground state of a hydrogenic donor associated with the lowest electron subband level. He used a variational approach to calculate the energy as a function of the GaAs well size and the impurity-ion position. The infinitely high barrier assumption was removed by several subsequent calculations.[2-4]

To the best of our knowledge, the only attempt to use more than a single quantum well was done by Chaudhuri,[5] who used three quantum wells in his variational calculation of the ground-state energy of the donor electron with respect to the lowest subband level. Chaudhuri considered the case of the donor atom at the center of the center well with various well widths and barrier thicknesses.

In this paper we report calculations of the binding energies for the ground state ($1s$-like) and low-lying excited states ($2p\pm$-like) of a hydrogenic donor associated with the first subband level. Our model consists of a donor atom placed in a periodic square-well potential. The subband energy levels are those of the periodic square well. Results have been obtained for various values of the quantum well width and potential barrier width and height. We have considered the cases of the impurity ion located at the center of a GaAs well, at the center of a $Ga_{1-x}Al_xAs$ barrier, and at several locations in between, including the barrier-well interface. A variational approach was used in which the trial wave functions were expanded in terms of Gaussian basis sets.

The final results show that the finite-width square-well model can give significantly smaller binding energies than the single quantum well model. The largest differences occur for the case of the impurity ion located at the barrier-well interface.

GENERAL THEORY

Using the effective-mass approximation, the Hamiltonian of a hydrogenic donor in a GaAs-$Ga_{1-x}Al_xAs$ heterostructure can be expressed as

$$H=\frac{p^2}{2m_e^*}-\frac{e^2}{\epsilon r}+V_B(z)\ , \tag{1}$$

where m_e^* is the effective mass of the electron, ϵ is the static dielectric constant, and $V_B(z)$ is the periodic square-well potential.

The lowest subband of the GaAs-$Ga_{1-x}Al_xAs$ superlattice will likely possess an anisotropic effective mass whose value along the growth direction (z axis) is intermediate between that in GaAs and $Ga_{1-x}Al_xAs$. Since the probability of finding the electron in the GaAs wells is much higher than in the $Ga_{1-x}Al_xAs$ barriers, we believe that the effective mass in the superlattice will be close to that in GaAs. Consequently, for the results to be presented, we have taken the effective mass to be equal to the bulk GaAs value ($0.067m_e$) throughout the material. To check the sensitivity of the binding energies to this choice, and for comparison to previous isolated well calculations, we have made similar calculations with a spatially varying effective mass of $m^*=0.067m_e$ in GaAs, and $m^*=(0.67+0.083x)m_e$ in $Ga_{1-x}Al_xAs$, with matching conditions of $f(z)$ and $(1/m^*)(\partial f/\partial z)$ continuous at the interfaces. The binding energies differ by 1% or less with the donor at the center of the well, and by about 4% with the donor at the edge of the well, for the well and barrier widths investigated.

The electron's position relative to the impurity is given by $r=[\rho^2+(z-z_I)^2]^{1/2}$, where ρ is the distance in the x-y plane and z_I is the position of the impurity atom. The square-well potential is written as

$$V_B(z)=\begin{cases}0, & -\frac{L}{2}+n(L+b)<z<\frac{L}{2}+n(L+b)\ ,\\ V_0, & \frac{L}{2}+n(L+n)<z<-\frac{L}{2}+(n+1)(L+b)\ ,\end{cases} \tag{2}$$

where L is the well width, b is the barrier width, and n is

any integer. The barrier height is given by $V_0 = 0.6\Delta E_g$, based on recent experiments.[6-9] The total band-gap difference between the two bulk semiconductors is obtained from $\Delta E_g = 1.155x + 0.37x^2$ eV.[10]

Since this system exhibits cylindrical symmetry, a dimensionless form of the Hamiltonian in cylindrical coordinates can be written as

$$H = -\frac{1}{m^*}\nabla^2 - \frac{2}{r} + V_B'(z) \ . \tag{3}$$

The effective Bohr radius in GaAs, $a_0^* = \hbar^2\epsilon/m^*e^2$, is used as the unit of length and the effective Rydberg, $R^* = e^2/2\epsilon a_0^*$, is the unit of energy. V_B' and m^* are dimensionless forms for V_B and m_e^*. Using the GaAs values for the effective mass and the dielectric constant, $a_0^* = 98.7$ Å and $R^* = 5.83$ meV.

For the values of x and L used, the barrier height is much larger than the effective Rydberg, so that the Coulomb binding energy will be small compared to the subband energy. Therefore, it is helpful to explicitly factor the lowest-energy solution to the periodic square well, $f(z)$, out of the donor variational wave function ψ:

$$\psi(\rho,z,\phi) = f(z)G(\rho,z,\phi) \ . \tag{4}$$

$G(\rho,z,\phi)$ describes the internal states of the donor. The (unnormalized) lowest-energy solution to the periodic square-well problem is given by

$$f(z) = \begin{cases} \cos(kz), & -L/2 < z < L/2 \ , \\ Ae^{\kappa z} + Be^{-\kappa z}, & L/2 < z < L/2 + b \ , \end{cases} \tag{5}$$

extended with period $L + b$ in z. The parameters k, κ, A, and B are determined by the matching conditions at the interfaces.

Since the Hamiltonian has cylindrical symmetry, the z component of the angular momentum is a good quantum number, so that the ϕ dependence of the wave function has the form $\exp(im\phi)$, where m is an integer. As in the work of Greene and Bajaj,[4] the function $G(\rho,z,\phi)$ is written as

$$G(\rho,z,\phi) = \rho^{|m|}e^{im\phi}\sum_{i,j} A_{ij}G_{ij}(\rho,z) \ , \tag{6}$$

when the donor is located at the center of the well. The basis functions $G_{ij}(\rho,z)$ are given by Gaussian functions:

$$G_{ij}(\rho,z) = \exp(-\alpha_i\rho^2 - \alpha_j z^2) \ . \tag{7}$$

For the off-center case z is replaced by $z - z_I$ in the G_{ij} functions, where z_I is the position of the donor impurity ion. For the case of the donor at an edge of a GaAs well, $z_I = \pm L/2$.

The parameters α_i are taken from the results of Huzinaga,[11] who did a detailed study of the use of Gaussian basis functions in the calculations of hydrogen atom energy levels. The set of α_i (13.4, 2.01, 0.454, 0.123, 0.0267) used gives energies for the $1s$, $2s$, and $2p$ free hydrogen states accurate to within 0.002 Ry. Note that although the $G_{ij}(\rho,z)$ functions are separable in ρ and z, $G(\rho,z,\phi)$ of Eq. (6) is not.

The eigenvalues of the Hamiltonian were calculated following a variational approach. Thirteen terms were included in the expansion of Eq. (6), as in Greene and Bajaj.[4] The binding energy for each state is obtained by subtracting the corresponding eigenvalue from the lowest subband energy of the periodic square well.

RESULTS AND DISCUSSION

In the energy calculations for the periodic square- and single-well models, the GaAs values were used for the effective mass and dielectric constant. Various values of L (well width) and b (barrier width) were considered for two values of x ($x = 0.15$ and $x = 0.30$).

Figures 1 and 2 display the variation of the binding energy of the ground state and the lowest $m = \pm 1$ excited states as a function of the donor position, z_I/L. ($z_I/L = 0.0$ corresponds to the donor impurity at the center of a well, while $z_I/L = 0.5$ represents the case in which the impurity is located at a GaAs-$Ga_{1-x}Al_xAs$ interface.) Figure 1 shows the binding energy of the ground state for three different values of the width of the $Ga_{1-x}Al_xAs$ barrier (b), an aluminum fraction $x = 0.3$, and a GaAs well width of $L = 1.0a_0^*$. For $b = 2L$ the ground-state binding energy is not much different from that of the isolated well ($b \rightarrow \infty$), so long as the donor is located at or near the center of the well. A similar result was found by Chaudhuri.[5] However, for donors near the interface, or within the barrier itself, the difference becomes more substantial, exceeding 25% of the isolated well result. The $b = L$ case shows significant differences from the single well for all values of z_I. Curiously, the difference is smallest for $z_I = 1.0$, which for $b = L$ corresponds to a donor site at the center of a barrier. The slope of the curve is zero for this value of z_I, which should lead to a second peak in the photoluminescence spectra for a heterostructure with a uniform distribution of donors.[12] The $B = 2L$ case also exhibits the same characteristic, but the center of its barrier ($z_I/L = 1.5$) is not shown in Fig. 1.

As expected, the excited states show much larger percent differences between the finite and infinite barrier width cases. This is indicated in Fig. 2, again for $x = 0.3$ and $L = 1.0a_0^*$. As for the ground state, the largest relative

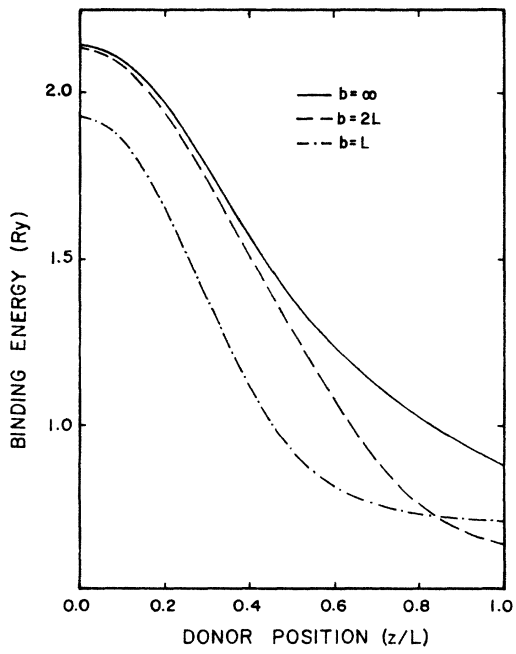

FIG. 1. Binding energy of the ground state of a shallow donor in a $Ga_{1-x}Al_xAs$ well as a function of donor position. The aluminum fraction is $x = 0.3$ and $L = 1.0a_0^*$.

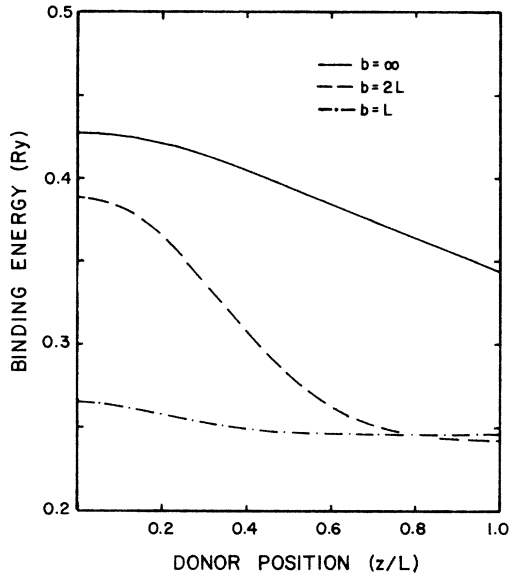

FIG. 2. Binding energy of the lowest $m = \pm 1$ excited states of a shallow donor in a $Ga_{1-x}Al_xAs$ well as a function of donor position. The aluminum fraction is $x = 0.3$ and $L = 1.0a_0^*$.

differences typically occur for donor impurities near the interface or within the $Ga_{1-x}Al_xAs$ layer. For example, for a donor impurity located at the GaAs-$Ga_{1-x}Al_xAs$ interface the binding energy for the isolated well case is approximately 43% (60%) larger than for the multiple well, $b = 2L$ ($b = L$) case. The $b = L$ case of Fig. 2 is unusual in that it also shows very large effects for donors located at the center of a well. This is apparently due to the fact that the centers of the GaAs wells are separated by two effective Bohr radii, the characteristic size of the $n = 2$ hydrogenic levels.

The ground state (Fig. 1) shows a stronger dependence of the binding energy upon the impurity position than do the excited states of Fig. 2. This is primarily due to the different symmetries of the states with the impurity located at the center of a well ("on center") and the corresponding states of an impurity located, for example, at an interface ("on edge"). The on-center ground state of Fig. 1 is $1s$-like, in that as L is increased it approaches a hydrogenic $1s$ state. The on-edge ground state, on the other hand, has a lot of p_0 character. As the well width and barrier height approach infinity, it approaches a single lobe of a $2p_0$ hydrogenic function. In these limits the on-center binding energy is four times that of the on edge. The excited states also undergo a symmetry change—from $2p$- to $3d$-like for the $m = \pm 1$ states. However, for these states the relative change in binding energies in the infinite barrier height and well width limit is only about half that for the ground state. This behavior is maintained for the finite barrier height and well width of Figs. 1 and 2, although the relative differences between the on-center and on-edge cases is not so large.

We have found qualitatively similar effects for other values of the well width and barrier height and width. As expected, the differences between the single- and multiple-well cases are more pronounced for smaller values of L and b, and for $x = 0.15$ (smaller barrier height) than for the cases shown in Figs. 1 and 2. Larger L and b values show significantly smaller effects. However, for the excited states with $L = a_0^*$, differences of 10% or more persist to barrier widths of $b = 4a_0^*$.

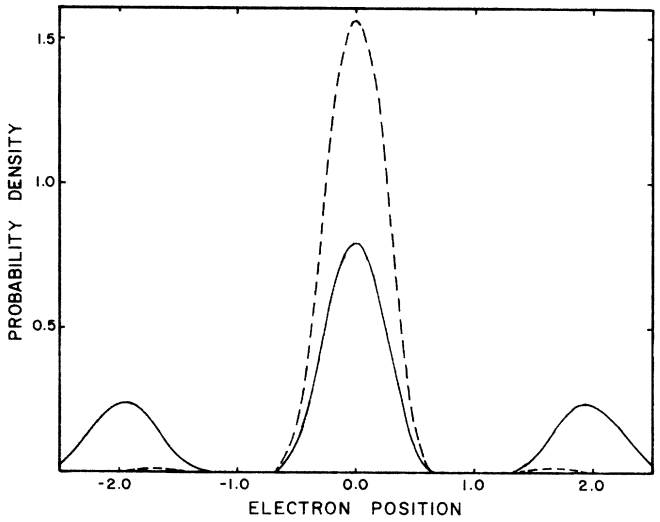

FIG. 3. Probability density of the ground state (dashed line) and lowest $m = \pm 1$ states (solid line) for the donor impurity at the center of a GaAs well.

The relatively large differences in binding energies between the single- and multiple-well systems is due to spillover of the wave function into neighboring wells. This is clearly illustrated in Figs. 3 and 4, where we have plotted a probability density obtained by integrating the square of the effective-mass envelope function [Eq. (5)] over ρ and ϕ. With the donor impurity at the center of the well (Fig. 3), there is little probability of finding a ground-state electron in the neighboring wells. The $m = \pm 1$ states, however, have relatively large probability in the neighboring wells. Figure 4 illustrates the situation of the impurity at an interface between GaAs and $Ga_{1-x}Al_xAs$ ($z = 0.5$ in the figure). The major effects on the excited states are a decrease in the central peak and a corresponding increase in the peak associated with the well centered at $z = 2.0$. The probability density of the ground state is more strongly affected by the

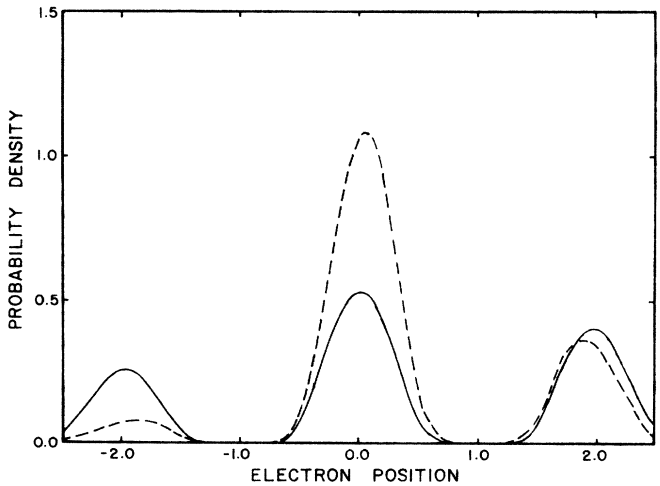

FIG. 4. Probability density of the ground state (dashed line) and lowest $m = \pm 1$ states (solid line) for the donor impurity at an edge of a GaAs well.

interfacial position of the impurity. The probability of the electron being found in the $1.5 < z < 2.5$ well is nearly as large as that for the $m = \pm 1$ excited state. More surprisingly, there is a significant probability associated with the $-2.5 < z < -1.5$ well. This is a manifestation of the p_0-like symmetry of the on-edge ground state, as discussed earlier.

Probability densities for heterostructures with small wells and barriers show larger effects, of course. For example, for $L = b = 0.5a_0^*$, significant peaks arise in the next-nearest wells.

SUMMARY

In summary, we have found that the binding energies of shallow donors in GaAs-$Ga_{1-x}Al_xAs$ heterostructures can be significantly affected by the width of the barrier regions for typical structures. For the ground state, the strongest effects occur for donor atoms near the semiconductor interfaces or within the barrier regions. The lowest $m = \pm 1$ excited states, on the other hand, can show relatively large effects due to neighboring wells for all donor locations. Plots of the electron probability density show that these effects are due to spillover of the wave function into neighboring wells.

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