Ab initio calculation of electronic properties of periodically Si-δ-doped GaAs

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We report an *ab initio* calculation of periodically Si-δ-doped GaAs, solving the Schrödinger equation in a three-dimensional system. We show, in the regime of high donor concentration, that the subband δ, even for small period ($p = 45$ Å), exhibits small dispersion as does a 2D system. Also, we discuss the stability of the Si sheet in the bulk, and the electronic properties of the clustering Si_{Ga}-Si_{As}.

Several works on low-dimensional systems have been devoted to the so-called δ doping, or sheet doping,[1] which was originally proposed by Wood *et al.*[2] Today the idea of δ doping of GaAs by silicon impurities during the growth by molecular beam epitaxy or metal-organic vapor phase epitaxy is very well established, but some important questions remain, particularly in the regime of high donor concentrations. In this paper we will discuss questions related to (i) the diffusion of the Si atoms in δ doping of GaAs, (ii) the decrease of carrier concentration when the Si δ doping increases higher than 10^{13} cm^{-2}, and (iii) the transition from two dimensions to three dimensions in the multi δ doping. Recently Liu *et al.*[3] have observed Si δ in GaAs by high resolution transmission electron microscopy in very high donor concentration of Si, higher than 10^{14} cm^{-2}. It was found that the diffusion of the Si atoms is limited to only about 3 ML. In high density doses, when the Si concentration exceeds $\sim 10^{13}$ cm^{-2}, the carrier density decreases abruptly.[4] The reason for this behavior is yet an open question.

Optical analysis such as absorption, or luminescence spectroscopy, of a single δ-doping layer is complicated due to the very low overlap between hole and electron wave functions which means a very low radiative recombination probability. This problem can be avoided if instead of a single δ, we consider a multi-δ-doped layer. Then in a periodically δ-doped structure, the overlap of the carrier wave function from adjacent layers gives rise to the formation of minibands whose bandwidths depend on the separation of the layer (period) and consequently an enhancement of the recombination rate is expected.[5-9]

All theoretical approaches in these systems were done on the basis of the effective-mass theory (EMT),[10,11] where the three-dimensional (3D) problem is reduced to the simple one-dimensional Schrödinger equation

$$\left[-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} + V_{H,\mathrm{xc}}(z) \right] \Psi_{n,k_z}(z) = \epsilon_n \Psi_{n,k_z}(z), \qquad (1)$$

where m^* is the effective mass at the botton of the conduction band and $V_{H,\mathrm{xc}}$ is the Hartree potential plus exchange-correlation potential from the free-electron gas.[12] n and k_z are the miniband index and the wave vector in the z direction, respectively.

In the high electron (donor) concentration regime, Eq. (1) is probably not efficacious because the δ potential becomes very deep. If we have a multi-δ doping with a small period (< 100 Å) in high concentration ($> 10^{14}$ cm^{-2}) a treatment beyond the effective-mass theory is necessary, particularly in the study of the 2D to 3D transition.

This work presents a microscopic model based on an *ab initio* theoretical calculation of multi-δ doping addressing the above mentioned questions. We solved the Schrödinger equation in a real 3D system. Our calculations were carried out using a tetragonal supercell, within the local density approximation using an *ab initio* nonlocal pseudopotential[13] with up to $l = 2$ and a plane-wave expansion up to 12 Ry in kinetic energy in the Kleinman-Bylander[14] formulation. The Kohn-Sham equations are solved in the Car-Parrinello scheme.[15] The total energy and the total charge were calculated with an Evarestov-Smirnov[16] special set of two k points ($\frac{1}{4}$ 0 $\frac{1}{4}$) and ($\frac{1}{4}$ $\frac{1}{2}$ $\frac{1}{4}$), with the same weighting factors, appropriated for tetragonal crystal lattice. In Fig. 1 we represent a schematic structure of the three-dimensional unit cell of GaAs:δ Si superlattice as grown along the $\langle 001 \rangle$ direction.

In this calculation we study four distinct cases related to concentration (n) and doping period (p): (i) $n = 6.25 \times 10^{14}$ cm^{-2}, $p = 45$ Å; (ii) $n = 3.12 \times 10^{14}$ cm^{-2}, $p = 45$ Å; (iii) $n = 6.25 \times 10^{14}$ cm^{-2}, $p = 22$ Å; and (iv) $n = 3.12 \times 10^{14}$ cm^{-2}, $p = 22$ Å. These situations correspond to 1 ML and 0.5 ML if the Si atoms occupy the Ga sites in the crystal lattice without spread.

In Fig. 2 we show our results for the multi-δ-doping band structure along the k_z direction (in units of the lattice parameter of each unit cell). We have plotted the δ energy level dispersion (δ band) for two periods $p = 45$ Å
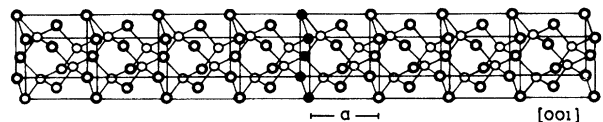

FIG. 1. Three-dimensional unit cell of a GaAs/Si δ/GaAs superlattice. Larger circles represent Ga atoms, smaller empty and full circles represent As and Si atoms, respectively; a is the bulk lattice parameter.
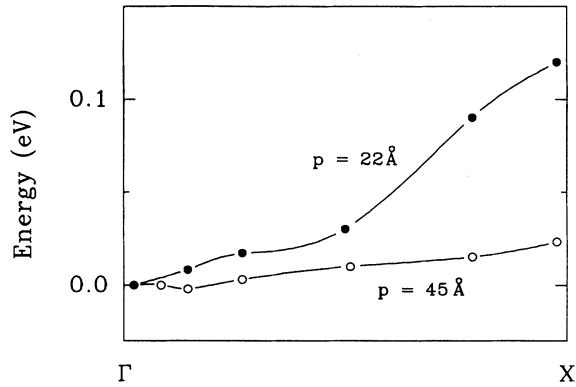
FIG. 2. Calculated electronic dispersion for δ doped in GaAs along K_z ($\langle 001 \rangle$ direction). The empty circles and full circles represent the δ band for $p = 45$ Å and $p = 22$ Å, respectively, and a Si concentration of 3.12×10^{14} cm^{-2}.

FIG. 4. Calculated electronic dispersion for δ doped in GaAs along $K_{x,y}$ ($\langle 100 \rangle$ direction). The triangles represent the top of the valence band (VB) and the conduction band (CB) and the full circles represent the Si δ level for $p = 45$ Å and $n = 3.12 \times 10^{14}$ cm^{-2}.

and $p = 22$ Å, both cases with $n = 3.12 \times 10^{14}$ cm^{-2}. The δ level presents a dispersion around 120 meV for $p = 22$ Å and a small dispersion, 23 meV, for $p = 45$ Å. As expected, when the period decreases, for the same donor concentration, the subband width must increase because of the coupling between adjacent δ wells.

The confinement on multiple δ of the two-dimensional gas is shown clearly in Fig. 3. We have plotted the charge density for (a) the conduction band, (b) the δ band, and (c) the valence band (the levels correspond to the case of $p = 45$ Å and $n = 3.12 \times 10^{14}$ cm^{-2}). For the conduction band and valence band there are big delocalizations in charge; however, for the δ band (at the Γ point), we have a very strong charge confinement in the layer.
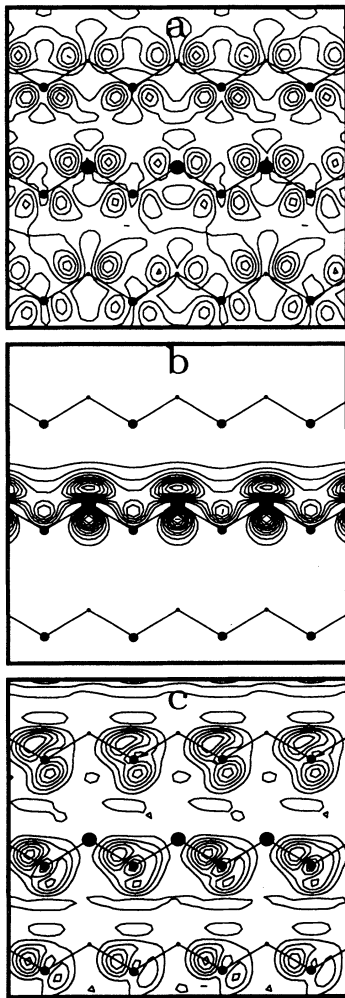
From our calculations it is also possible to analyze the

FIG. 3. Calculated squared single-particle wave functions at the Γ point for $p = 45$ Å and $n = 3.12 \times 10^{14}$ cm^{-2}: (a) bottom of the conduction band, (b) Si δ band, and (c) top of the valence band. The larger full circles represent the Si atoms in the Ga site, on a $\langle 110 \rangle$ plane.
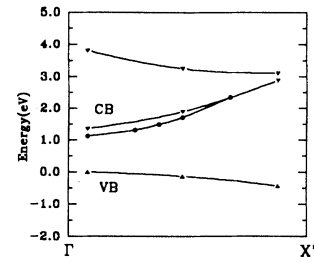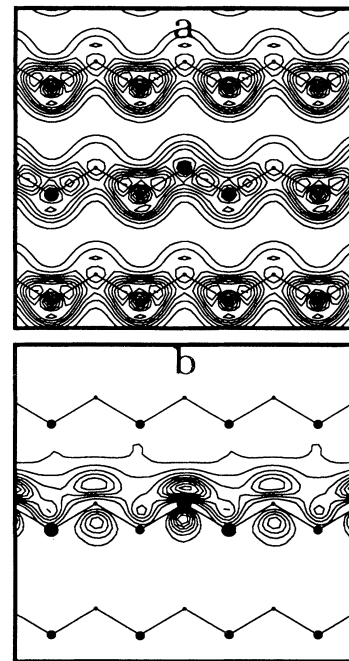

FIG. 5. Results for complex configuration Si$_{Ga}$-Si$_{As}$: (a) the total valence band charge density and (b) the squared single-particle wave function for the unoccupied Si δ level at the Γ point. The larger full circles are the Si atoms.

band structure in the $k_{x,y}$ directions. In Fig. 4 we have plotted the energy bands only around the Γ point[17] as a function of $k_{x,y}$ for $p = 45$ Å and $n = 3.12 \times 10^{14}$ cm^{-2}. As we can see, the δ band has a parabolic form, which is expected if the electrons behave like a free-electron gas in the x-y plane. The effective mass calculated via the parabolic fitting is 0.065 m_e, which is in very good agreement with the experimental value for the conduction band of GaAs.

Very interesting works have been done about the transition from 2D to 3D behavior in the low concentration donor regime[9,10,18] for multi-δ doping. These works show that for a period lower than 100 Å we get a 3D behavior. From our *ab initio* calculation we see that even when the period is very small (45 Å) we have a 2D behavior if we have a very high donor concentration. The reason is that in the high concentration regime, we have a very deep δ potential which provides high localized states. These results can be also obtained qualitatively by EMT. We solve Eq. (1) using $p = 45$ Å and $n = 6.25 \times 10^{14}$ cm^{-2} and we obtain 10 meV for the δ-band width and a very deep potential. The 2D to 3D crossover is related to the stronger overlap between the wave function of the Si δ of adjacent layers, as we can see in the large bandwidth, 120 meV, for a period of 22 Å.

Our total energy calculation, for single neutral Si defects in GaAs with the Si atom in the tetrahedral Ga site, shows a small inward relaxation of the nearest-neighbor As atoms ($\sim$1% of the bond length).[19] In the case of Si δ doping in GaAs for high donor concentration, we obtain a very small dislocation of the As atoms, neighbors of the Si atoms, outward of the doped plane ($\sim$2% of the bond length). We conclude that the sheet of Si atoms in the Ga site is a stable configuration. To understand the decrease of the carrier density at donor concentrations higher than 10^{13} cm^{-2},[4] we consider the possibility of the Si atom occupying also the As site (Si$_{As}$) in a doping period of $p = 45$ Å with 2 ML (Ga and As planes) half occupied. From our calculation we obtain for this complex configuration (Si$_{Ga}$-Si$_{As}$) no electronic levels in the gap, leaving the center electrically inactive. In Fig. 5(a) we plot the total charge distribution for the Si$_{Ga}$-Si$_{As}$ system. It is interesting to observe a strong chemical bond between the two Si atoms confined. The electronic charge distribution over the two Si atoms is almost the same, giving a dipole moment close to zero. In Fig. 5(b) we show the unoccupied impurity level for the Si$_{Ga}$-Si$_{As}$ pair. The squared single-particle wave function is very similar to the single Si δ [Si$_{Ga}$, see Fig. 3(b)], as we expected.

In summary we have performed an *ab initio* calculation for multi-δ Si doped in GaAs showing that (i) the 2D-3D transition does not occur even for a small period ($p = 45$ Å) in high donor concentration and presents a small dispersion for the δ band, 23 meV; (ii) the sheet of Si atoms in the Ga site is a stable configuration; and (iii) the Si$_{Ga}$-Si$_{As}$ clustering is an electrically inactive center, showing a very small dipole moment. This clustering is one possible cause for the decreasing in the carrier density in the high donor concentration regime.

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