Confinement and interwell coupling effects in Ge double quantum wells pseudomorphic to a Si (001) substrate

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We present a theoretical study of the electronic properties of two coupled Ge quantum wells separated by a variable number of Si monolayers, epitaxially grown on a Si (001) substrate. We adopt the real space decimation-renormalization method and a $sp^3d^5s^*$ nearest neighbors tight binding Hamiltonian for the description of the electronic states of bulk Si and Ge crystals. Strain, band offsets and spin-orbit interactions are properly taken into account. From the Green's function of the multilayer structure considered, the energy spectrum and partial and total densities of states projected on each layer and orbital are obtained. This has allowed us to investigate the nature of the valence and conduction confined states and the effect of interwell coupling on the optical properties. In particular we show that position and red shift with Ge width of the experimental no phonon luminescence line of these structures are well interpreted by the present calculation and that additional luminescence lines are predicted.

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I. INTRODUCTION

During the last two decades a continuous interest has been devoted to the electronic properties of Si/Ge quantum wells (QWs) and superlattices due to the task of fabricating efficient light emitting devices exploiting the Si-based integrated circuit technology.[1–4] The lattice mismatch between pure Si and Ge is about 4% and pseudomorphic multilayer deposition of SiGe structures on Si or Ge substrates has been possible if a maximal thickness of the structure was not exceeded so that the mismatch could be completely accommodated by uniform lattice strain.

For pure Ge on Si (001), the case we discuss in this paper, this critical thickness is about six Ge monolayers[5] but it can increase significantly in the case of SiGe alloys on Si substrate[6] or by surfactant mediated growth.[7] Due to this limitation only a few experimental studies have been dedicated to pure Ge QWs,[8,9] while the main effort has been devoted to SiGe alloys QWs (see, e.g., Refs. 1–4 and 10). Ge on Si buffer undergoes biaxial compressive stress in the growth plane and its bulk electronic structure is consequently distorted: The fundamental indirect energy gap (i.e., the distance between the bottom of the conduction band at Δ and the top of valence band at Γ) of strained Ge is reduced (see, for instance, Refs. 1, 11, and 12) and cubic degeneracies of eigenvalues are tetragonally resolved.[13–16] Besides strain, also confinement of the electronic states in the created Si and Ge QWs contributes to modify the band offsets and thus the energy gaps, leading to a great variety of effects on optical and electronic properties of these structures with large possibilities in band engineering.

In this paper we have analyzed theoretically the electronic states of double Ge QWs separated by a variable thickness of Si, epitaxially grown on a Si (001) substrate. Our approach is based on the tight binding formalism and exploits the decimation-renormalization procedure[17] to reduce the original multilayer structure into an equivalent quasi one dimensional manageable chain system. The Green's function is then the main tool for the determination of eigenvalues and densities of states. Spin-orbit interactions, strain effects, band offsets are properly taken into account. We are thus able to interpret luminescence experimental data obtained for such structures and to control the effect of coupling of Ge wells on the optical properties.

From the results here reported we evidence the great potentiality of the tight-binding renormalization method to solve with high accuracy the Schrödinger equation of multilayer systems of arbitrary length and composition. The method has been applied here to group IV devices but it can be easily implemented to handle structures with different atoms in the "anion" and "cation" positions. The importance of exploiting very accurate one-electron microscopic Hamiltonians which incorporate spin-orbit, alloy and strain effects is evidenced. We are thus able to provide a detailed description in real and k space of the states of the device in a wide energy range, overcoming limitations typical of the envelope function formalism (see for instance the discussion in Ref. 18).

In Sec. II we present the geometry of the multilayer structures studied and the essential lines of the theoretical method. Section III contains the results for double QWs of Ge and a comparison with the experiments. The conclusions are reported in Sec. IV.

II. SYSTEM AND METHOD DETAILS

We have studied the electronic properties of samples composed by two QWs of Ge pseudomorphic to Si (001) substrate separated by a variable number of monolayers of pure Si. Luminescence properties for such systems have been experimentally investigated as function of the Ge wells thickness (2, 3, or 4 monolayers) with interwell separation of 17 or 20 Si monolayers.[8,9] For these samples two main luminescence lines have been identified: A no-phonon (NP) fundamental line and a TO-phonon replica.

To study theoretically the electronic states of isolated double QWs, we have constructed an ideal long period superlattice with primitive cell, in the growth direction, made by the two Ge QWs embracing a number of Si layers ranging from 5 to 80, followed by a thick region of pure Si (we have inserted up to 1000 monolayers) which isolates the double QW structure from the neighboring ones. We have thus investigated a system which is perfectly periodic both in the growth direction and in the orthogonal planes: This has allowed us to exploit the tight-binding renormalization approach which has proven very efficient for the study of periodic multilayer structures of arbitrary length.[19,20]

The first ingredient of the calculation is the bulk electronic band structures of the isolated Si and Ge crystals; for this we have adopted the $sp^3d^5s^*$ tight binding semiempirical Hamiltonian, $H(\mathbf{k})$, introduced by Jancu *et al.*[21] This nearest neighbors parametrized Hamiltonian includes spin-orbit interaction and well describes the valence and the conduction electronic eigenvalues and densities of states of the bulk semiconductors in a wide energy range around the fundamental gap. Moreover $H(\mathbf{k})$ can be easily modified to include hydrostatic and uni-axial strain effects through appropriate scaling laws of the parameters[21] and modifications of the geometrical phase factors which are linked to the spatial positions of the atoms in the crystal lattice.

The Si substrate remains in the cubic structure with lattice constant $a_{\mathrm{Si}}=5.43$ Å; the unstrained (cubic) lattice constant of Ge is $a_{\mathrm{Ge}}=5.65$ Å. In the (001) Si-Ge structure considered, the Ge regions are lattice matched to the substrate in the planes (001) (i.e., $a_{xy}(\mathrm{Si})=a_{xy}(\mathrm{Ge})=5.43$ Å) while the macroscopic lattice constant along the growth direction expands due to Poisson effect.[22]

In addition to the chemical difference between Si and Ge, the macroscopic strain is essential for the evaluation of the energy bands lineups at the Si-Ge interface. We have taken from the literature[23] the valence band offset (VBO) value of 0.74 eV at the interface between pure Si and pure strained Ge: Within this result we also qualitatively account for charge redistribution at the interface. Only the valence band offset is considered as fixed external parameter; all the other energies in the bands profile result from the tight binding parametrization and the corresponding scaling laws. In Fig. 1 we report the schematic profile of the potential experienced by the carriers at the Γ point of the two dimensional Brillouin zone. The resulting type II confinement shows that electrons and holes are confined in spatially separated regions. We have also verified that type I alignment is obtained with QWs made by Ge rich SiGe alloys on SiGe substrates.[12]

The superlattice so obtained has then been treated as a multilayer structure in the (001) direction expanding the Hamiltonian $H(\mathbf{k})$ on the basis of two dimensional Bloch sums as shown in Refs. 24 and 25: For each two dimensional wave vector $\mathbf{q}$ the original system is thus mapped exactly into an equivalent linear chain structure with on site matrix energies and nearest neighbors matrix interactions. The dimension N of the tight binding Hamiltonian is given by the number of atomic orbitals within each layer in the primitive cell (20 orbitals per layer, including spin) multiplied by the total numbers of layers, thus reaching the value $N\sim 10^4$ or more.

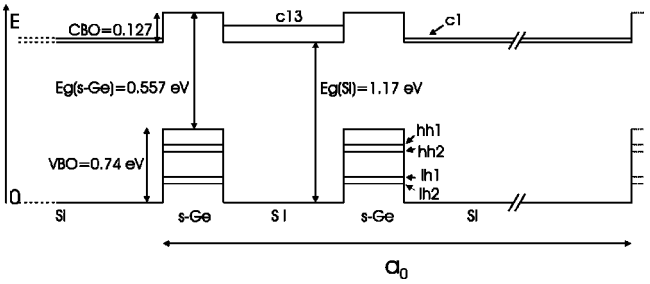

FIG. 1. Schematic band structure potential of the Si/Ge superlattice. a_0 is the length of the primitive cell in the growth direction: It contains two Ge QWs 2–10 monolayer thick, embracing a Si region of 5–80 monolayers, and a long Si spacer region thick enough to make isolated the double QWs structure. $E_g=1.17$ eV is the energy gap for the silicon slab and 0.557 eV is the energy gap of the strained Ge crystal. The meaning of the confined c_1 and c_{13} conduction levels is specified in the text. Energies are not in scale.

On the chain model system so obtained the iterative real-space renormalization procedure can be applied, and the Green's function of the superlattice is then evaluated. From it the energy spectrum and the densities of states projected on each orbital in each layer of the system are obtained. The process we adopt consists in the recursive decimation of each internal layer of the primitive cell; at each step the decimation of a generic layer gives rise to appropriate self energies for the adjacent surviving layers and to a new effective interaction between them. This procedure is iterated until all the layers in the cell are exausted, but the first one, and this eventally provides the matrix Green's function of the superlattice. Projected densities of states are available from partial traces of the Green's functions of each layer. It is worth noticing that the numerical code we have implemented, exploiting nearest neighbor interactions, is able to perform the decimation-renormalization process considering a single layer at time, and to handle even or odd number of layers in the geometrical configuration of the system.

III. RESULTS

Figure 2 shows the electronic band structure around the two dimensional Brillouin zone center, for the superlattice composed by 4 monolayers thick double QWs of Ge embracing 20 monolayers of Si. We have verified that a spacer of 200 Si monolayers is sufficient to make the double wells structure not affected by the periodicity of the superlattice.

We see in particular that four energy bands of the superlattice are confined in the Ge regions (as shown schematically also in Fig. 1); on the other side for a single Ge QW on Si (001) we have obtained that only two levels are confined, originated from the Ge heavy hole (hh) and light hole (lh) bands, respectively. In the present geometry made by double QWs, the confined levels are doubled (hh1, hh2 and lh1, lh2) due to the tunneling interaction between the adjacent Ge wells. This can be verified plotting the energy separation of each doublet (hh1-hh2 and lh1-lh2) as a function of the number of Si layers interposed between the wells. If the above interpretation of the two doublets is correct we expect that

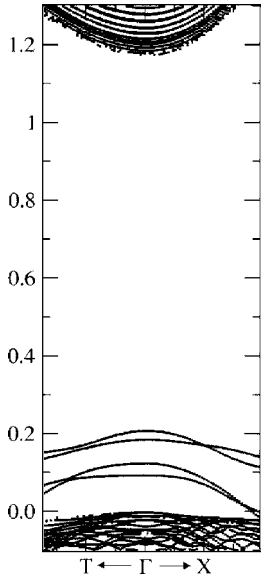

FIG. 2. Valence and conduction band structure of the Ge/Si superlattice presented in Fig. 1, around the two-dimensional Brillouin zone center. The 10% of the segments Γ-*X* and Γ-*T* are reported.

this separation vanishes in the limit of large number of interwell Si layers. This is exactly what happens as shown in Fig. 3. The insets suggest that an exponential law satisfactorily describes the doublet separation energy decay in agreement with the tunneling interaction hypothesis.

A deeper understanding of the valence states confined in the two Ge QWs, can be obtained from the solution of the single particle Schrödinger equation with appropriate effective masses $m^*(z)$ for the wells (Ge) and the barriers (Si) zones. For this, we have first evaluated numerically the energies of the heavy and the light hole bands in Si and strained Ge around the center of the Brillouin zone and we have

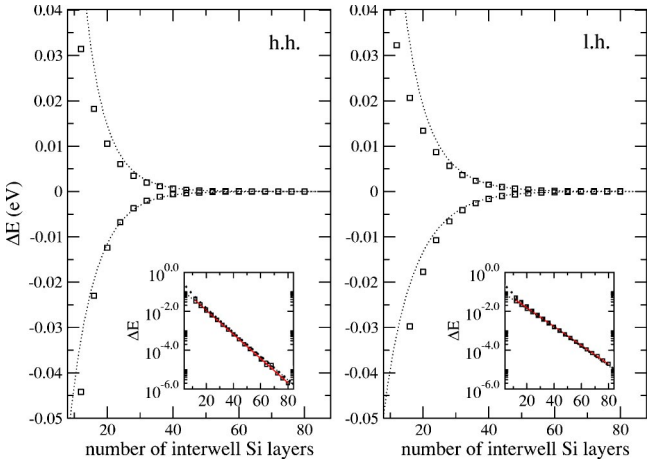

FIG. 3. hh1-hh2 (left) and lh1-lh2 (right) doublets energy separation as function of the Si monolayers between the Ge four monolayers thick QWs. The logarithmic energy scale in the insets shows the exponential behavior of these separations as function of interwell Si width. Dotted lines indicate the results obtained from the analytic model, see text.

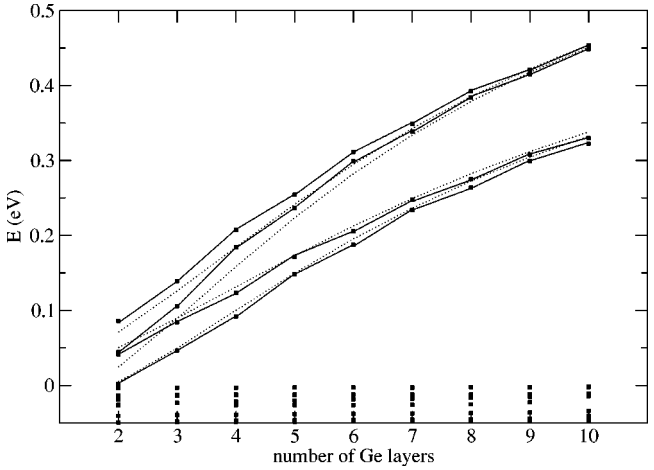

FIG. 4. hh and lh doublets separation as function of the Ge well width. Solid lines are the numerical results, dotted lines are the solution of the analytic model, see text. The interwell separation is of 20 Si monolayers. The square symbols below $E=0$ are the continuum of valence states, also reported in Fig. 2, at Γ point.

interpolated the results with a quadratic fitting in an interval of 0.4 eV. We have found that in the two zones the effective masses are quite similar, with values $m^*(\mathrm{hh})=2.02m_0$ and $m^*(\mathrm{lh})=2.06m_0$.[26] We have then studied the confinement of the states in a single, isolated square QW of width given by the number of Ge layers. For the hh states the bottom of the well is at $E=E_{VBO}$ while for the lh states the bottom is at $E=E_{VBO}-\Delta$ where $\Delta=0.1501$ eV is the energy separation between the hh and the lh bands of strained Ge at the Γ point. We have found that if the well width is narrower than 10 Ge monolayers, only the lowest ($n=1$) hh and lh states are confined in the well, while the higher ones merge in the continuum of valence states (see Fig. 2). The Schrödinger equation, for the double well model, can be solved as outlined by Bastard.[27] One finds that the ground-state eigenvalue E splits into two levels $E_{1,2}$, due to the interaction between the two adjacent wells

$$E_{1,2}=E\pm\frac{t}{1\pm r}+\frac{s}{1\pm r}, \tag{1}$$

where $r=\langle\chi_1(z)|\chi_2(z)\rangle$, $s=\langle\chi_2(z)|V_1(z)|\chi_2(z)\rangle$, and $t=\langle\chi_1(z)|V_1(z)|\chi_2(z)\rangle$; $\chi_i(z)$ are the eigenstates of the *isolated* well i, and $V_1(z)$ is the potential profile of the well 1. The results for the double well model are represented by dotted lines both in Fig. 3 for several separations of the Ge wells, and in Fig. 4 for different well widths and fixed interwell separation. For comparison the results obtained by the complete numerical calculation on the real system are reported in the same figures by solid lines.

From Figs. 3 and 4 we can see that the analytic model correctly reproduces splittings and trends of the confined valence states, mainly if the two wells are not too close. In fact this splitting is evaluated by means of a perturbative approach on the isolated QWs. We also notice that the monotonic trend of the plots in Fig. 4 is explained considering that

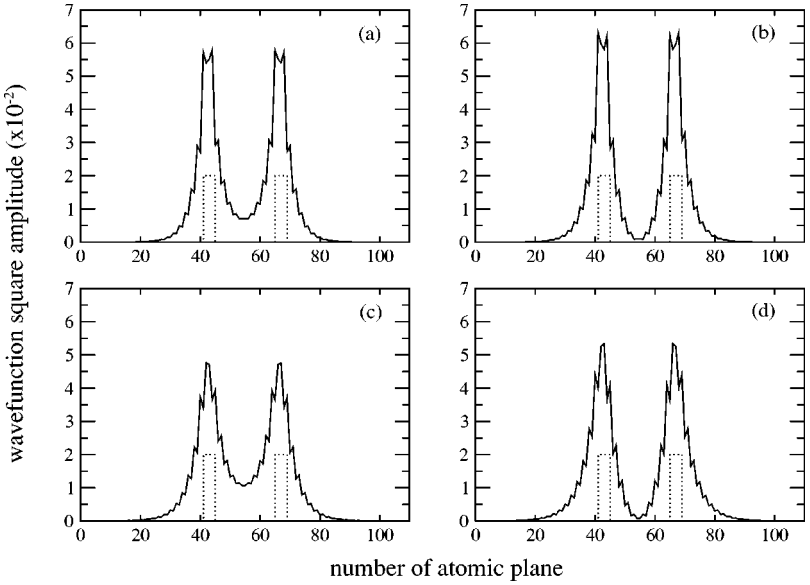

FIG. 5. Total square amplitude of the hh1 (a), hh2 (b), lh1 (c), and lh2 (d) wave functions on different atomic layers in the primitive cell of the superlattice. The Ge quantum wells profiles are reported with dotted lines.

increasing the number of Ge layers (for fixed interwell separation), the confinement energies decrease and then the bound states rise in energy.

We show in Fig. 5 the total square magnitude of the hh1, hh2, lh1, and lh2 superlattice wave functions projected on the layers of the primitive cell, calculated with the renormalization method for the case of QWs composed by 4 Ge monolayers, separated by 20 Si monolayers. The spatial confinement of these states is evident, moreover, the overlap of the wave functions confirms a tunneling interaction between the wells.

The corresponding analysis of layer and orbital resolved density of states reported in Figs. 6 and 7 allows us to appreciate with high numerical precision, the invariance of the results under $x \leftrightarrow y$ transformation. In particular we can conclude that the bound states in the Ge QWs are mainly composed by p_x and p_y orbitals with smaller contribution from d_{yz} and d_{xz} orbitals.

The comparison with the NP luminescence lines experimentally detected,[9] involves also the evaluation of the conduction states of the superlattice. As schematically shown in Fig. 1 the lowest conduction band is at $E=1.17$ eV in the large Si spacer region while higher energy confined conduction states in the Si region between the Ge QWs are expected due to the conduction band offset. We report in Fig. 8 the superlattice wave function components amplitude projected on the layers of the primitive cell, corresponding to the lowest 16 conduction bands eigenvalues at the Γ points (see Fig. 2). As already noticed[25] the presence of doublet states with oscillations characterized by a period of about three atomic

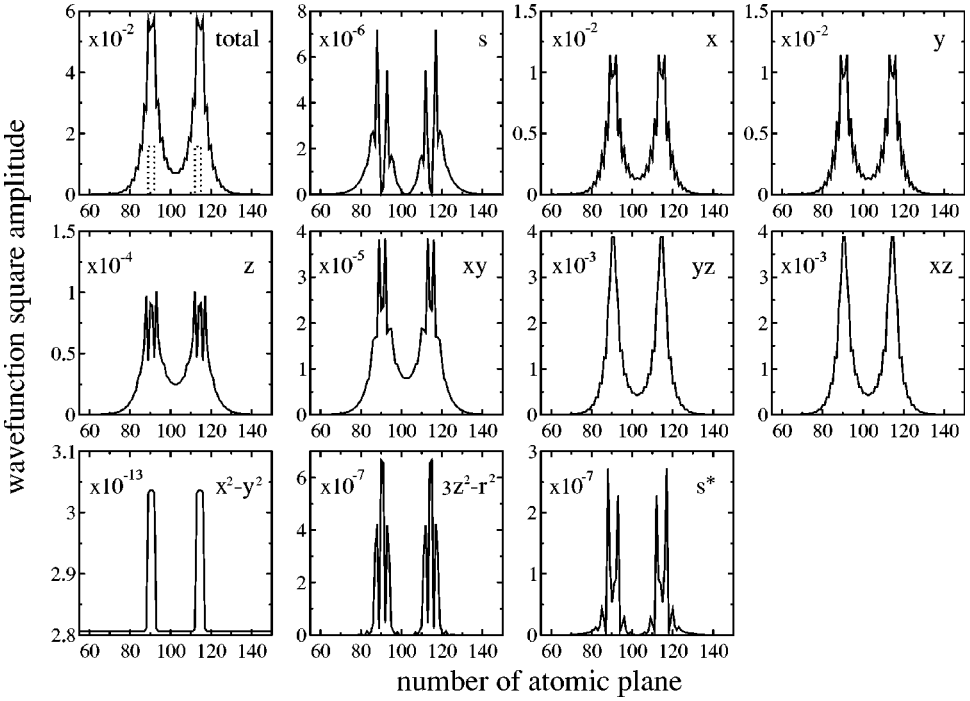

FIG. 6. Square amplitude of the hh1 wave function on different atomic layers in the primitive cell of the superlattice, projected on the basis orbitals. The Ge quantum wells profiles are reported with dotted lines.

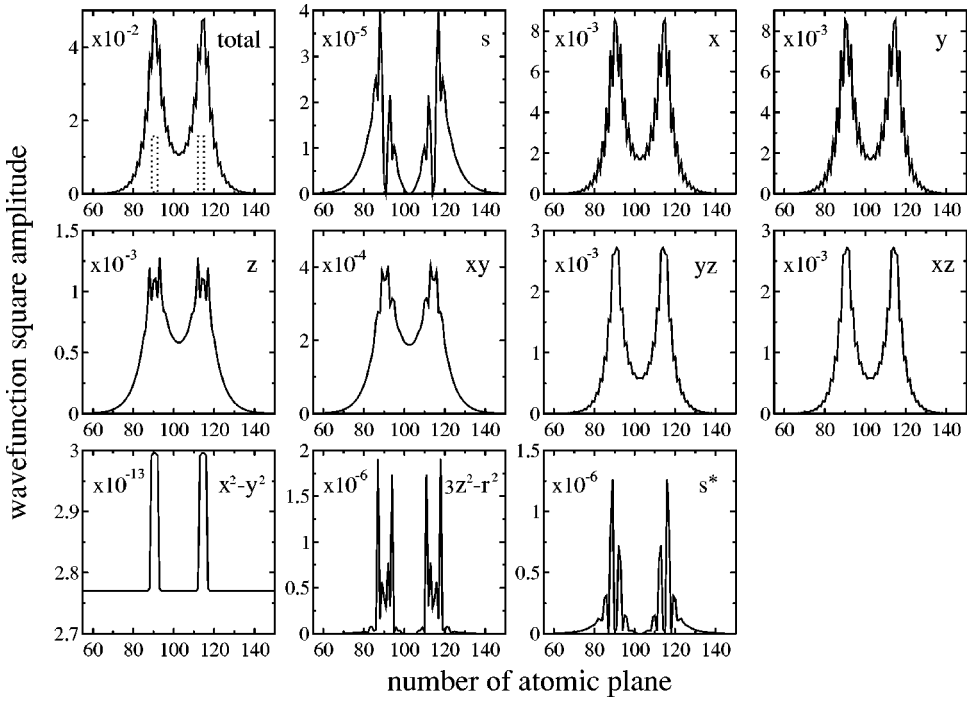

FIG. 7. Square amplitude of the lh1 wave function on different atomic layers in the primitive cell of the superlattice, projected on the basis orbitals. The Ge quantum wells profiles are reported with dotted lines.

layers is evidence of the interference of Bloch eigenfunctions corresponding to the equivalent valleys at $\pm 0.85\, 2\pi/a$. We notice that the lowest conduction states (the couples $c1$ and $c2$) are located in the large Si spacer region and do not penetrate the region between the Ge QWs. The next couple of eigenvalues ($c3$ and $c4$) can be interpreted, from its nodes, as the first excited state of the large Si spacer well, and so on. At higher energies these excited states start penetrating in the region within the two Ge wells. The thirteenth conduction state is almost completely confined in region between the two Ge wells and can be interpreted as the fundamental eigenstate of the Si quantum well defined by the Ge conduction band potential profiles.

This can be confirmed also comparing the numerical values of the conduction eigenvalues reported in Fig. 2 with the eigenvalues obtained from a model calculation for a *single* quantum well whose width is given by the width of the Si spacer region 1 or by the width of the Si interwell region 2. With the longitudinal effective mass $m^*_{\mathrm{Si}}=0.63m_0$ evaluated from the energy fitting of the bulk crystal electronic structure around Δ_{min}, in the z direction, we obtain $E_1=1.1705$ eV and $E_2=1.2039$ eV for the lowest energy states in the regions 1 and 2, respectively, in excellent agreement with the values $(E_{c1}+E_{c2})/2=1.1704$ eV and $E_{c13}=1.2050$ eV. The comparison can be further extended; we cite, for example, the first excited state in the region 1 which is found at 1.1733 eV, to

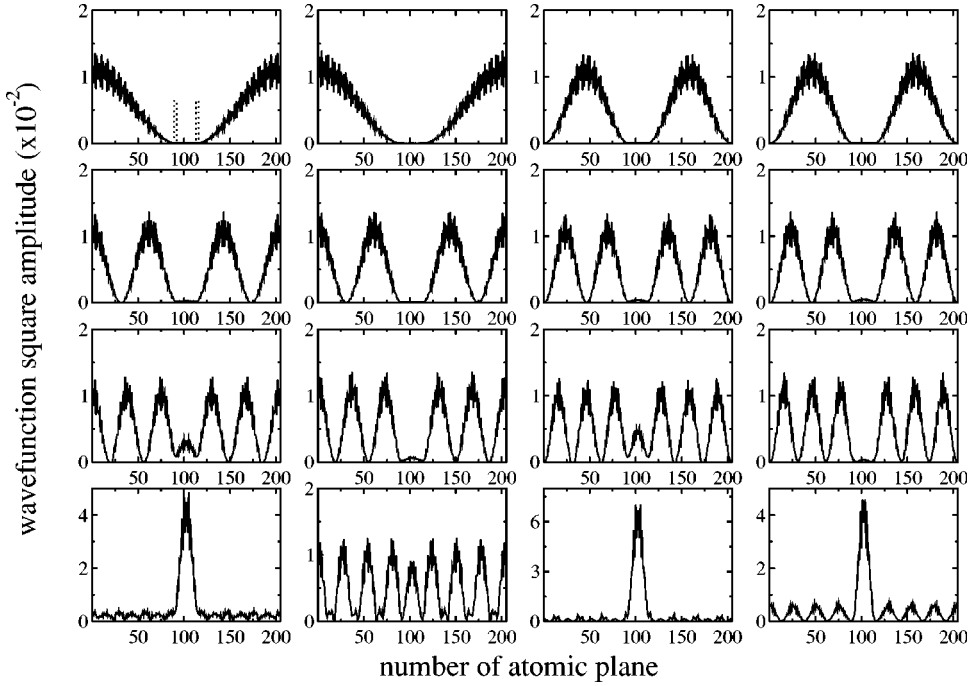

FIG. 8. Total square amplitude of the conduction band wave functions on different atomic layers in the primitive cell of the superlattice, corresponding to the lowest 16 conduction bands eigenvalues at Γ (see Fig. 2) from top left (c_1) to bottom right (c_{16}). For sake of clarity the conduction potential profile is superimposed to the plot in the top left figure.

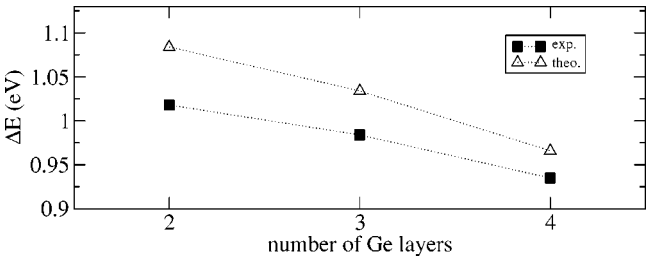

FIG. 9. $E_c - E_{\mathrm{hh1}}$ energy transition as function of the Ge QW width. Empty (full) symbols indicate theoretical (experimental) results. The interwell separation is 20 Si monolayers.

be compared with the numerical value $(E_{c3}+E_{c4})/2 = 1.1730$ eV reported in Fig. 2.

Finally, Fig. 9 shows the experimental NP luminescence line position and the energy difference between the lowest conduction band (c_1 level) confined in the Si region 1 and the highest hh1 valence localized levels in the Ge wells. Our calculations correctly reproduce the red shift trend of the luminescence line with the Ge QWs width. In addition to the fundamental NP luminescence line reported in Fig. 9, the energy levels obtained in this paper suggest possible interpretations of other transitions between conduction and valence states. In particular, the transition between the lowest c_1 conduction band and the hh2 band, split from the hh1 by the interwell interaction, is almost 50 meV higher in energy than the NP fundamental one; while the c_1-lh1 transition is almost 0.1 eV higher than the NP line. Both merge just into energy regions where transitions are experimentally detected and interpreted as originating from the Si substrate and the SiGe cap layers which clad the QWs structure in the experimental device.

IV. CONCLUSIONS

A theoretical study of the electronic properties of two interacting Ge QWs, separated by a variable number of Si monolayers, pseudomorphic to a Si (001) substrate, has been presented. We have exploited a tight binding nearest neighbor Hamiltonian with an orthogonal $sp^3d^5s^*$ set of orbitals with appropriate scaling laws for spatial dependance of the interaction parameters. The multilayer system considered has then been processed by iterative renormalization methods which allow to evaluate the Green's function of structures of arbitrary length. From it we have determined the energy spectrum and partial and total densities of states. For pure Ge wells grown on Si (001) the band alignment is of type II and we have evaluated the confinement energies of valence states in the Ge wells and of the conduction states in the Si regions. Analytic models based on the solution of the Schrödinger equation confirm the numerical results of the real system. A good agreement with the experimental measure of the fundamental no phonon luminescence line ($E_{c1} - E_{\mathrm{hh1}}$) has been found and the existence of other transitions between the evaluated conduction and valence states have been suggested.

ACKNOWLEDGMENTS

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