Band-offset determination and excitons in SiGe/Si(001) quantum wells

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We report both experimental and theoretical studies on $Si_{1-x}Ge_x/Si$ multiple quantum wells. A self-consistent calculation is employed to model the excitonic transition. It shows that, in the large conduction-band-offset region the Δ_2–heavy-hole (hh) exciton is the lowest transition, while in the small-offset region the Δ_4-hh exciton is the lower. From an analysis of the data, a type-II conduction-band-offset ratio of $30\pm3\%$ is concluded.

Silicon germanium/silicon heterostructures have attracted great attention in recent years for their potential application in the monolithic integration of Si-based optoelectronic devices.[1,2] Intensive research has been done to study the fundamental physical parameters of this system, such as effective masses, mobility, and in particular the band alignment.[3–5]

In previous studies of the band alignment of the SiGe/Si system, both type-I and type-II structures have been suggested by analyzing photoluminescence (PL) energy from quantum wells.[6–8] Recently, Houghton *et al.*,[9] have employed an externally applied uniaxial stress to probe the band alignment. A type-I structure was concluded based on the energy shift of the no-phonon PL under external uniaxial stresses in the [110] direction. By employing a similar technique but varying the excitation power of the laser, Thewalt *et al.*[10] have observed both type-I and type-II PL behavior at high ($I \geqslant 10^2 I_0$) and low ($I \leqslant 10^3 I_0$) laser power ($I_0 = 10$ W/cm^2). The type-I behavior was shown to result from charge transfer from the Si to the SiGe layer leading to substantial band bending. A type-II structure was demonstrated at low excitation power based on the observation of a red-shift of the PL energy under external stress. Due to the complications of the conduction band in this system, the band-offset ratio therefore is still not clear and it has recently been suggested theoretically that the ground state for excitons may have either a Δ_2–heavy-hole (hh) or Δ_4-hh character depending on the amount of type-II offset occurring for the SiGe Δ_4 level.[11] In this paper, we present both PL measurements and a theoretical treatment to study the band alignment of this system using multiple-quantum-well (MQW) structures. A self-consistent excitonic model taking into account the Coulomb interaction between electron and hole is used to analyze the PL energy. From the analysis of the ground-state transition, it is concluded that there is a relatively large type-II conduction-band-offset ratio of $30\pm3\%$.

The samples were grown on Si(001) substrate by hot-wall ultrahigh vacuum chemical vapor deposition (UHV-CVD) system and molecular beam epitaxy (MBE). The samples consist of a thick buffer layer (2000 Å) of Si, followed by a ten-period $Si_{1-x}Ge_x/Si$ multiple quantum well. The precise alloy composition was determined by high-resolution double-crystal x-ray diffraction measurement. The layers thickness were measured by cross-section transmission electron microscopy. The details of the growth conditions and sample characterization have been described by Chang *et al.*[12] A summary of the sample structure is listed in Table I.

Luminescence was excited by optic fiber using a diode laser at intensity levels of around 10 mW/cm^2, in the region where Thewalt *et al.* have observed low-intensity-limiting behavior.[10] The emission was collected by a fiber bundle and dispersed by using a 0.5 m spectrometer and a North Coast germanium detector. The measurements were performed at 4.2 K.

All three samples showed strong PL from both Si and SiGe quantum wells. The luminescence spectra of the narrower well samples N1 and N2 are shown in Fig. 1. Several PL lines can be seen in a wide energy range between 850 and 1200 meV. These features come from two groups of lines originating from the bulk Si and the $Si_{1-x}Ge_x$ quantum wells. On the high-energy side of the spectra, a family of Si-related transitions are observed at peak energies of 1155.9, 1136, and 1098.9 meV, corresponding to the no-phonon (NP), transverse acoustic (TA), and transverse optical (TO) mode phonon replicas. These are in good agreement with previous work.[13] In the low-energy regime, several strong QW features are also observed as marked by the solid arrows in the Fig. 1. These lines are assigned as the NP, TA, and TO transitions. The transition energies are summarized in Table I. In addition to the main features, the TO-phonon replica is broadened and split into several lines due to the different possible modes of the phonons, including mainly the Si-Si, Si-Ge, and Ge-Ge vibrations.[14,15] For the wider well width sample the quantum-well-related emissions are much weaker, indicating a degradation of the quality of the samples due to the onset of strain-induced dislocations. The strain, for the structures studied here, is almost all accommodated in the SiGe as biaxial compression, whereas the Si layers are not strained due to the lattice match with the buffer layer, although this will begin to break down as the number of quantum wells increases.

To quantitatively interpret the interband optical transition energies of the excitons, a self-consistent calculation of the excitonic energy level is performed. This model is in a similar spirit to the variational self-consistent treatments reported

TABLE I. Summary of sample structures and the transition energies of the no-phonon (NP), transverse acoustic (TA), and transverse optical (TO) lines. $\Delta_2-\Delta_4$ is the energy splitting of the two conduction bands. E_g is the band gap of bulk $Si_{1-x}Ge_x$ taken from Ref. 6.

Sample	Ge (%)	Well (barrier) (Å)	NP (meV)	TA (meV)	TO (meV)	$\Delta_2-\Delta_4$ (meV)	E_g (meV)
N1	16.3	46 (93)	1028.5	1010.8	969.8	107.7	1037.5
N2	23	52 (183)	961.6	-	902	152.2	988.9
N3	28	75 (85)	918.4	-	861.7	185.4	954.8

previously but with a Hermitian single-particle effective-mass equations for the electron and hole.[16,17] The details of this method will be the subject of a future publication. Here, we describe the characteristic of the model. The exciton Hamiltonian is written in cylindrical coordinates in the following form:[18]

$$H=\frac{-\hbar^2}{2\mu_\parallel}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\right]-\left[\frac{\hbar^2}{2m_{ez}}\frac{\partial^2}{\partial z_e^2}-V_e\right]-\left[\frac{\hbar^2}{2m_{hz}}\frac{\partial^2}{\partial z_h^2}-V_h\right]-\frac{e^2}{4\pi\epsilon[\rho^2+(z_e-z_h)^2]^{1/2}},\quad(1)$$

where m_{ez} (m_{hz}) is the effective masses of electrons (holes) along the quantum confinement direction (z) and $\mu_\parallel$ is the exciton reduced effective mass in the SL layer plane. V_e and V_h are the square-well potential for electrons and holes. The electron effective masses are taken from Ref. 11. The transverse and longitudinal mass of the heavy hole are derived from the Luttinger parameters using a linear interpolation between Si and Ge.[6]

There are two stages in solving Eq. (1), first the confined states in the growth direction is solved by using the ground-state wave function of $f_e(z_e)$ and $f_h(z_h)$. This gives the energy eigenstate of E_e (E_h) [the solution of the second and third brackets in Eq. (1)]. Second, three-dimensional exciton Hamiltonian is solved by the variational method using a wave function of $\phi=f_e(z_e)f_h(z_h)g(\alpha,\beta,\rho,z_e-z_h)$. g is the trial function chosen as the 1s-like hydrogenic function $\exp\{-\sqrt{\alpha^2[\rho^2+\beta^2(z_e-z_h)^2]}\}/a_B\}$ where α and β are the variational parameters and a_B is the effective Bohr radius.

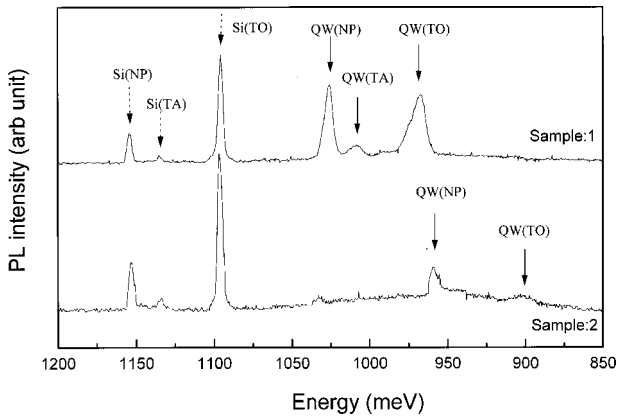

FIG. 1. Photoluminescence spectra of samples N1 and N2. Dotted arrows indicate the transition originating from Si. The solid arrows mark the transitions from the multiple quantum wells.

The total energy of the system (E) is obtained by minimizing the expectation value of the Hamiltonian with respect to the two variational parameters. Second, knowing E, the electron (hole) wave function f_e' (f_h'), under the influence of Coulomb interaction, can be obtained numerically by solving the following equation:

$$f_e'(z_e)=f_e(z_e)\times\sqrt{\int\int 2\pi d\rho dz_h|f_h(z_h)|^2 g(\alpha,\beta,\rho,z_e-z_h)^2}.\quad(2)$$

Given the f_e' (f_h'), the above two steps are repeated until the total energy converges to a chosen accuracy of 0.1 meV. The Rydberg energy (E_b, the Coulomb binding energy) is derived from the expectation value of the Coulomb interaction.

Before interpreting the data, we briefly describe the band structure of strained $Si_{1-x}Ge_x$ and discuss Coulomb effects in the SiGe/Si system. As discussed above, for the samples studied here the strain is present in the SiGe. This lifts the degeneracy of both the conduction (CB's) and valence bands (VB's). For the CB, the six Δ valleys split into Δ_2 and Δ_4 bands with the Δ_4 valleys having the lowest energy. The energy splitting is $\Xi_u e_T$, where Ξ_u is the deformation potential and e_T is the lattic mismatch[19] and is summarized in Table I. For the VB, the heavy hole (hh) rises above the light hole (lh). Including all of the above factors we find that the band gap of the strained SiGe is significantly larger than the NP lines seen in PL (see Table I), suggesting strongly that

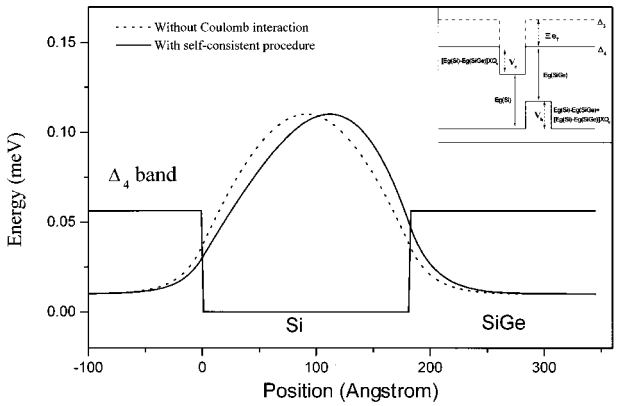

FIG. 2. Calculated carrier wave functions for a quantum-well system of SiGe/Si with a conduction- and valence-band offset of 56.2 meV and 237.2 meV, respectively, with and without the influence of Coulomb attraction. The inset shows a schematic diagram of the band alignment.

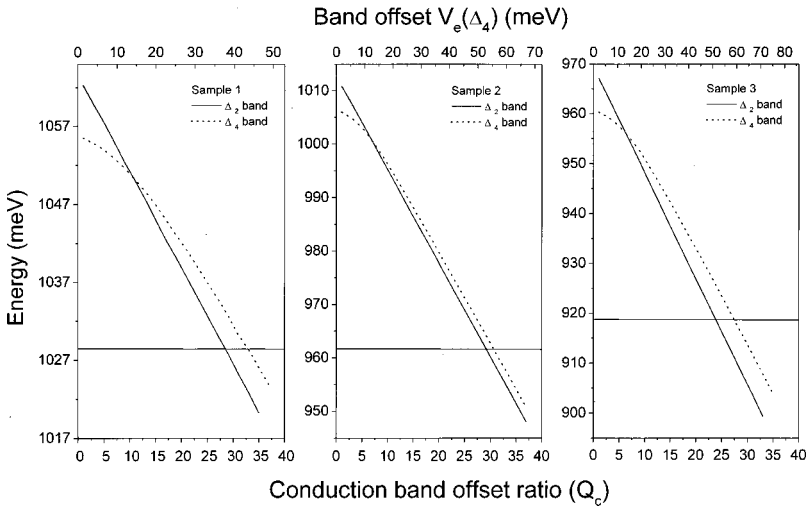

FIG. 3. Calculated interband transition energy for the Δ_2-hh (solid line) and Δ_4-hh (dotted line) emission for samples N1, N2, N3 as a function of the conduction-band-offset ratio. The experimental transition energies are shown for the three samples.

we require a type-II band alignment with the electrons confined in the unstrained Si layers. This will lead to the two lowest transitions from the Δ_2-hh and Δ_4-hh excitons being quite close in energy as the Δ_2 state has a higher effective mass but the Δ_4 state ''sees'' a lower barrier height in the SiGe. The Coulomb effects are illustrated using the sample structure of N2 with a type-II band alignment and the excitonic states for the Δ_4 valleys. The band profiles are set to $V_e(\Delta_4)=56.2$ and $V_h(\mathrm{hh})=237.2$ meV, corresponding to a conduction-band-offset ratio (Q_c) of 0.31, as defined below. Figure 2 shows that, without the self-consistent procedure, the electron wave function is distributed symmetrically in the region of the Si layer, as indicated by the dashed line. Including the Coluomb attraction, the wave functions (f_e') are modified and are pulled toward the Si/SiGe interface as plotted by the solid line. A similar behavior is also found for the hh state. The electron-hole wave-function overlap (oscillator strength) is thus enhanced and the binding energy increases (E_b shifts from 5.5 to 6.4 meV).

We now discuss the interband transition energies. For a type-II structure, the band offset is determined by the band gap of the two materials. The CB and VB offsets are $[E_g(\mathrm{Si})-E_g(\mathrm{SiGe})]Q_c$ and $[E_g(\mathrm{Si})-E_g(\mathrm{SiGe})](1+Q_c)$ as illustrated schematically in the inset of Fig. 2. $E_g(\mathrm{Si})$ and $E_g(\mathrm{SiGe})$ are the band gaps of Si and SiGe. Q_c is the conduction-band-offset ratio. In determining the strained bulk band gap of $Si_{1-x}Ge_x$, the main source of error is due to the differences in the strain coefficients that have been reported in the literature. In this report we have used the experimental values taken from Ref. 6. Knowing the potential profile, the interband transition energy is given by $E=E_g(\mathrm{SiGe})-[E_g(\mathrm{Si})-E_g(\mathrm{SiGe}))Q_c+E_e'+E_h'-E_b'$. To model the Δ_2-hh transition an energy of $\Xi_u e_T$ is added to obtain the potential for the Δ_2 band. The calculated transitions for the Δ_2-hh and Δ_4-hh excitons are plotted in Fig. 3 for all three samples. This shows that both transitions are strongly dependent on the band-offset ratio and decrease with increasing Q_c, reflecting a type-II band alignment. Note from the figure that the two transitions have very similar energies but cross over at a moderate conduction-band offset [$V_e(\Delta_4)\approx 14$ meV]. In the large conduction-band-offset region the Δ_2-hh exciton is the lowest transition while in the small-offset region the Δ_4-hh exciton is lower. This is attributed to the enhanced binding energy due to the small band offset for the Δ_4 valleys. Considering only the transition energies it is difficult to distinguish the two transitions but both require a values of $Q_c\approx 0.30\pm 3\%$ to fit the data from samples N1 and N2. The main uncertainty (beyond the linewidth) in the assignment of the offset value comes from the uncertainties in the input parameters. The higher Ge content (and thinner Si layer) sample N3 is better described by a value of $Q_c=0.25$ to fit the Δ_2 band, but this may be influenced by the onset of strain relaxation in this sample, which would lead to the presence of some strain in the Si layer.

In conclusion we can say that there is growing evidence for the assignment of a type-II band alignment in SiGe/Si quantum wells. In the study of Thewalt *et al.*,[10] PL measurements on a single quantum well suggested a weak type-II structure but with the lowest state due to Δ_2 electrons. By taking into account the Coulomb binding, Penn *et al.* have suggested that these single-well results can be reinterpreted as due to emission from the Δ_4-hh exciton with a relatively large type-II offset of order 40 meV for the specific sample studied.[11] In this study of MQW structures we are not able to distinguish which of the two valleys is lowest but data on a range of samples give a consistent value for the band offset independent of the valley assignment for several different alloy compositions. A conduction-band offset ratio of 30 $\pm 3\%$ is concluded, which is consistent with the value concluded by Penn *et al.*[11] for the single quantum well studied by Thewalt *et al.*[10]

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