4.5 SiGe heterojunctions and band offsets

C.G. Van de Walle

June 1999

A INTRODUCTION AND NOTATION

When two semiconductors are joined at a heterojunction, discontinuities occur in the valence bands and in the conduction bands. For an atomically abrupt interface, these discontinuities are sharp on an atomic length scale (i.e. on the order of a few atomic distances). This is in contrast with band-bending effects, which are associated with depletion layers, and which occur on much larger length scales (hundreds of Å, up to several μm). The band discontinuities actually enter as boundary conditions in the solution of Poisson's equation, which would produce the band bending.

In the absence of strain, i.e. for a lattice-matched interface, the band lineup problem simply consists of determining how the band structures of the two materials line up at the interface; the lineup then produces values for the valence-band discontinuity ΔE_v, and the conduction-band discontinuity, ΔE_c. When the materials are strained, the strains will produce additional shifts (due to hydrostatic strain) and splittings (due to uniaxial strain) of the bands; these changes in the positions of valence and conduction bands will, of course, affect the band discontinuities.

If the heterostructure exhibits a lattice mismatch (such as the case of Si/Ge, or interfaces with $Si_{1-x}Ge_x$ alloys), the band discontinuities are well defined only if the interface is pseudomorphic, i.e. one or both of the materials has to be appropriately strained so that the in-plane lattice constant is continuous across the interface. Strain in epitaxial structures is discussed in Datareview 1.2; the effect of strain on the band structure is discussed in Datareviews 4.2 and 4.3. Since strain has significant effects on the band structure, the problem of band offsets will be intimately coupled with the strain effects.

The treatment of strains in Datareviews 4.2 and 4.3 actually allows for a straightforward separation between the 'lineup' problem and the 'strain' problem. The effect of strain on the bands is a bulk issue, i.e. once the strain tensor is known, the individual shifts of the valence band and the conduction band can be determined, as well as the splitting of these bands. In Datareviews 4.2 and 4.3, these shifts and splittings were expressed with reference to the average band positions, $e_{v,av}$ and $E_{c,av}$. The strain problem can therefore be handled completely on the basis of Datareviews 4.2 and 4.3. The lineup problem then consists of determining the proper offset between $E_{v,av}$ (or $E_{c,av}$) on either side of the interface, which really amounts to determining the lineup between the unstrained materials.

A note on notation: in Datareviews 4.2 and 4.3, the notation Δ was used to denote the shift in the band position due to strain; e.g. $\Delta E_{v,av}$ was the shift in the average valence-band position, within a specific material, due to hydrostatic strain. In the present Datareview, the notation Δ is used to denote band offsets, i.e. energy differences between two bands in different materials, across an interface; e.g. $\Delta E_{v,av}$ would refer to the offset between the average valence bands in the two materials that make up the heterojunction. The difference between these two uses of the same symbol should be clear from the context, but to avoid any possible confusion, we only use Δ in this Datareview to refer to a band offset.

This approach to the band offset problem is the most rigorous, as well as elegant, from the theoretical point of view. Theoretical values for the band offset, $\Delta E_{v,av}$ will be given in Section B. From an

experimental point of view, the problem is more complicated. Experimental measurements usually provide information only about the discontinuity in the highest-lying valence band in each material (or similarly, the lowest-lying conduction band). A single measurement does not provide information about how to separate the offset into a lineup and a strain part. Fortunately, virtually all experimental results have turned out to be consistent with the theoretical predictions, so that theory can provide a reliable framework. Experiments will be discussed in Section C.

B THEORY

The most direct way to predict values for $E_{v,av}$ in Si and Ge is provided by the model solid theory [1]. This approach treats the band offsets as linear quantities, which can be obtained as differences between reference values which have been calculated once and for all for each semiconductor. The reference potential for each material is determined for a 'model solid', which consists of a superposition of neutral atomic charge densities. The nature of these neutral-atom building blocks renders the electrostatic potential independent of the details of the surface (or interface) structure, producing a reference level which can be used for a lineup procedure. Details are given in [1]. The values derived in [1] were $E_{v,av} = -7.03$ eV for Si, and $E_{v,av} = -6.35$ eV for Ge. Note that the absolute values do not carry physical meaning; only differences between values are relevant. These values lead to $\Delta E^0_{v,av} = 0.68$ eV between Si and Ge, where the superscript 0 refers to an offset between unstrained materials. The error bar on model-solid theory predictions was estimated to be ±0.2 eV. The model-solid values have a tendency to overestimate the offset, by about 0.1 eV for the pure materials. Comparison with other theoretical work [2,3] and with experiment (discussed in Section C) indeed indicates that better agreement can be obtained by assuming an unstrained valence-band offset of $\Delta E^0_{v,av} = 0.58$ eV. We will use this value to derive band offsets for a variety of SiGe-based heterostructures.

Let us illustrate how this value, combined with the strain treatment of Datareviews 4.2 and 4.3, produces values for the actual band lineups. Theoretical values for the deformation potentials will be used (see TABLE 1 of Datareview 4.2 and TABLE 1 of Datareview 4.3); the use of experimental values would produce only minor changes. As an example we choose the lineup between a pseudomorphically strained Ge overlayer and a Si(001) substrate. The procedure is illustrated in FIGURE 1. On the Si side, there is no strain. However, we still have to keep in mind that the position of the highest-lying valence band (which is degenerate at Γ, consisting of light and heavy hole bands) differs from $E_{v,av}$ because of spin-orbit splitting. In Si, we have:

$$E_{v,1,2} = E_{v,av} + 1/3\ \Delta_0 = 0 + 1/3\ 0.04 = 0.01\ \text{eV} \qquad (1)$$

where we have set $E_{v,av}$ on the Si side equal to zero; i.e. this level is chosen as a reference. Δ_0 is the spin-orbit splitting, and the subscripts 1 and 2 on E_v refer to the light and heavy hole bands; this notation is discussed in Datareview 4.2.

The Ge side of the junction is pseudomorphically strained. Using the notation for strains established in Datareview 4.2, and elastic theory, we obtain $\varepsilon_{||} = -0.039$ and $\varepsilon_{\perp} = 0.029$ (we use lattice constants and elastic constants as listed in [1]). We then obtain

$$E_{v,av} = E^0_{v,av} + a_v \frac{\Delta V}{V} = 0.58 + 1.24\,(2\times(-0.039) + 0.029) = 0.52\,\text{eV} \qquad (2)$$

where $E^0_{v,av}$ refers to the value in unstrained material, which is $\Delta E^0_{v,av} = 0.58$ eV higher in energy than $E_{v,av}$ in Si (the reference level). The offset between the average valence bands in Si and strained Ge is

therefore $\Delta E_{v,av} = 0.52$ eV. Note that this offset does not contain the effects of uniaxial strain or spin-orbit coupling.

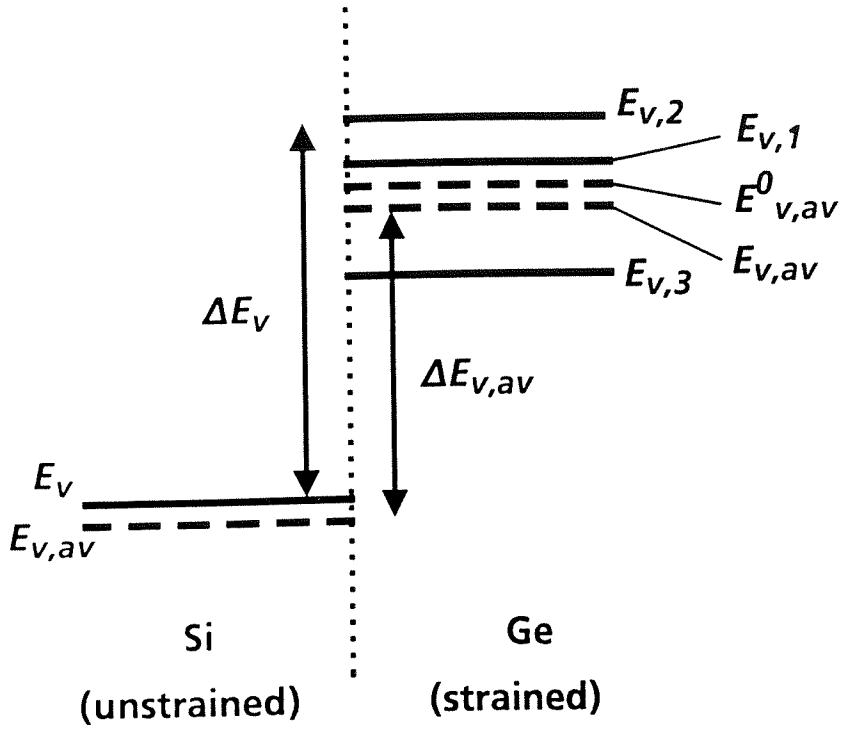


FIGURE 1 Theoretical valence-band lineups at an interface between unstrained Si and strained Ge (not to scale). The discontinuity in the average valence bands, $\Delta E_{v,av}$, is obtained from the model-solid theory. Strain shifts and splittings are obtained as described in the text, based upon the expressions in Datareviews 4.2 and 4.3.

Finally, the splitting of the Ge valence bands has to be determined, based on EQNS (5)–(7) in Datareview 4.2; the shifts in $E_{v,1}$, $E_{v,2}$ and $E_{v,3}$ are, respectively, 0.12 eV, 0.27 eV and –0.39 eV. Note that these three values add up to zero; indeed, these values should only express the splitting of the bands with respect to the average $E_{v,av}$, and not introduce any shift of the average.

The highest-lying valence band on the Ge side is therefore at $E_{v,av} + 0.27 = 0.79$ eV, resulting in a valence-band discontinuity: $\Delta E_v = 0.79 - 0.01 = 0.78$ eV. This result compares favourably with values of 0.84 eV [4], 0.86 eV [2], and 0.74 eV [3], obtained from full first-principles calculations, which do not make the approximations involved in the model-solid approach.

Similar arguments for Si/Ge structure grown on Ge(001) lead to $\Delta E_{v,av} = 0.58 - 0.12 = 0.46$ eV, and $\Delta E_v = 0.22$ eV. The latter value may be compared with the following values obtained from full first-principles interface calculations: 0.31 eV [4], 0.20 eV [2] and 0.20 eV [3].

When determining offsets for systems involving $Si_{1-x}Ge_x$ alloys, the strain effects in the individual materials can be assessed using linear interpolation, as described in Datareviews 4.2 and 4.3. It is also a good approximation to apply linear interpolation to obtain the band offset between average valence bands, based upon the band lineups between pure Si and pure Ge. Linear interpolation would, of course, not apply to the conduction bands, since it is known that the bandgap in the alloys exhibits substantial bowing. As described in Datareview 4.1, the Δ conduction band minimum (near the X point) exhibits bowing that can be described with a bowing parameter b = 0.206 eV (from [5]). Once

the valence band lineup is known, this experimental information about the bandgap in unstrained alloys can be combined with deformation-potential theory to obtain the conduction band lineup. The positions of Δ and L conduction band minima in the unstrained materials are taken from [4].

We can put together all aspects of this procedure and calculate the band offsets for a variety of heterojunctions; the results are shown in FIGURES 2–4. We focus on the (001) orientation, which is technologically most relevant. FIGURE 2(a) depicts band positions, and FIGURE 2(b) band offsets, for a $Si_{1-xs}Ge_{xs}$/Si (001) heterojunction. We use the following notation: for a heterojunction A/B, we consider A to be the substrate and B to be the overlayer. The term substrate can also refer to a thick, relaxed layer of a material with a given alloy composition x_s. The substrate A is always considered to be unstrained, whereas the overlayer B is pseudomorphically strained to match the in-plane lattice constant of the substrate.

For the band positions (FIGURE 2(a)) we (arbitrarily) choose the average valence band in the substrate as the zero of energy. Average valence bands are indicated by dashed lines, and bands in the substrate are indicated by dotted lines. The bands are labelled as follows: for valence bands, we use the notation v_1, v_2 and v_3 defined in Section C of Datareview 4.2; we use these labels rather than light hole, heavy hole, and spin-orbit split-off bands, since strain induces mixing of the bands. For conduction bands, the labels Δ_2 and Δ_4 refer to the two-fold and four-fold degenerate conduction band minima near the X point.

For band offsets, depicted in FIGURE 2(b), the band offset between a particular type of band is defined to be positive if that band in material B is higher in energy than in material A. The band offsets depicted in FIGURE 2(b) are defined as follows: for each valence band, the energy difference is taken with the corresponding band in the substrate, i.e. by taking the differences between corresponding curves in FIGURE 2(a). The dashed line corresponds to $\Delta E_{v,av}$, the offset between the average valence-band position. For clarity, the conduction-band offsets are shifted by an energy equal to the bandgap of the substrate for $x_s = 0$.

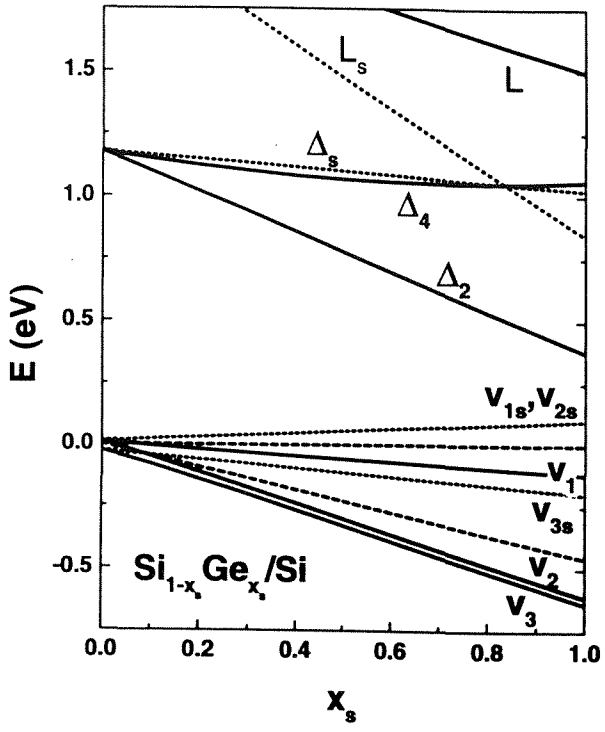
As an illustration of how to use FIGURE 2(b), consider the band offsets for strained Si on a Ge substrate that were calculated above. A Ge substrate corresponds to $x_s = 1$, for which FIGURE 2(b) shows a valence-band offset between the highest-lying valence bands of –0.22 eV; the minus sign indicates that the valence band in the strained Si overlayer lies below that of the unstrained Ge substrate, and the value agrees with our explicit derivation above.

FIGURE 3 depicts bands and offsets for a $Si_{1-xs}Ge_{xs}$/Ge(001) heterojunction, i.e. for strained Ge on a relaxed $Si_{1-xs}Ge_{xs}$ substrate. The situation $x_s = 0$ corresponds to strained Ge on a Si substrate for which we find an offset between the highest-lying valence bands of 0.78 eV, as derived above. FIGURES 2(a) and 2(b) are similar to Figures 5 and 6 of reference [6]; that reference contains further discussion of how such figures can be used for analysing heterostructures.

FIGURE 4, finally, depicts the band offsets at a $Si/Si_{1-x}Ge_x$ heterojunction, where now the alloy overlayer (with composition x) is strained to match a Si substrate.

As a final note, it has been shown that interface interdiffusion has a negligible influence on the band offset: Hybertsen [7] modelled the effect of a non-abrupt interface by including an interface layer of $Si_{0.5}Ge_{0.5}$, and found a change in the valence-band offset of less than 0.01 eV. This result is consistent with the notion that exchange of atoms across this interface between isovalent semiconductors does not generate any additional dipoles, as can be concluded from linear response theory [8].

(a)



(b)

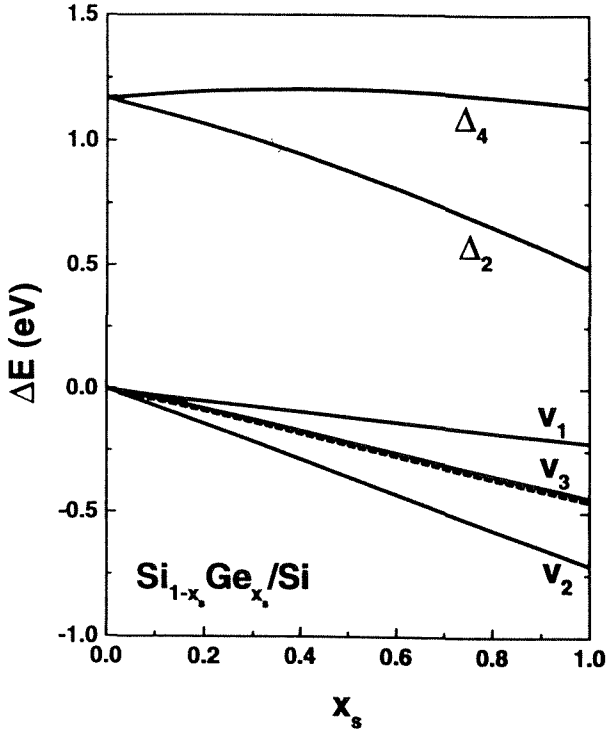
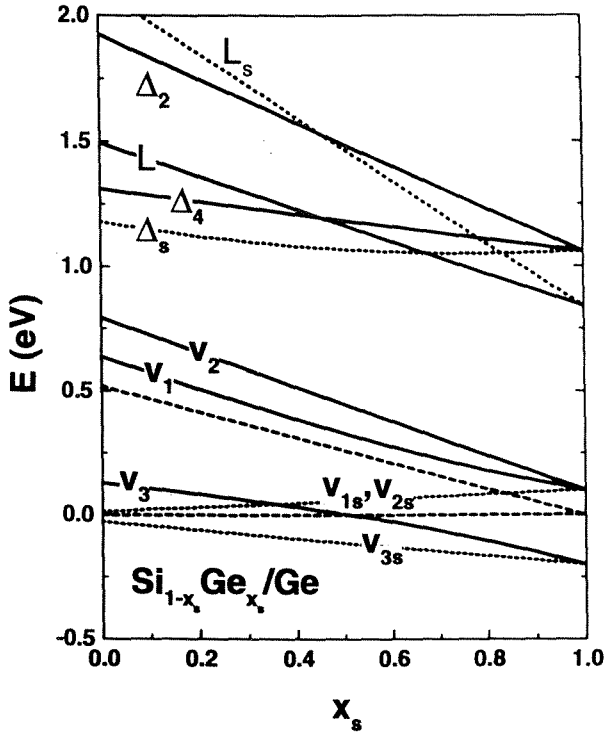


FIGURE 2 (a) Band positions for a pseudomorphic $Si_{1-xs}Ge_{xs}/Si$ heterojunction, as a function of alloy composition x_s in the substrate. Bands in the strained Si overlayer are indicated by solid lines, and bands in the $Si_{1-xs}Ge_{xs}$ substrate by dotted lines. The average valence band in the substrate is chosen as the zero of energy. Average valence bands are indicated by dashed lines. (b) Band offsets for this heterojunction.

(a)



(b)

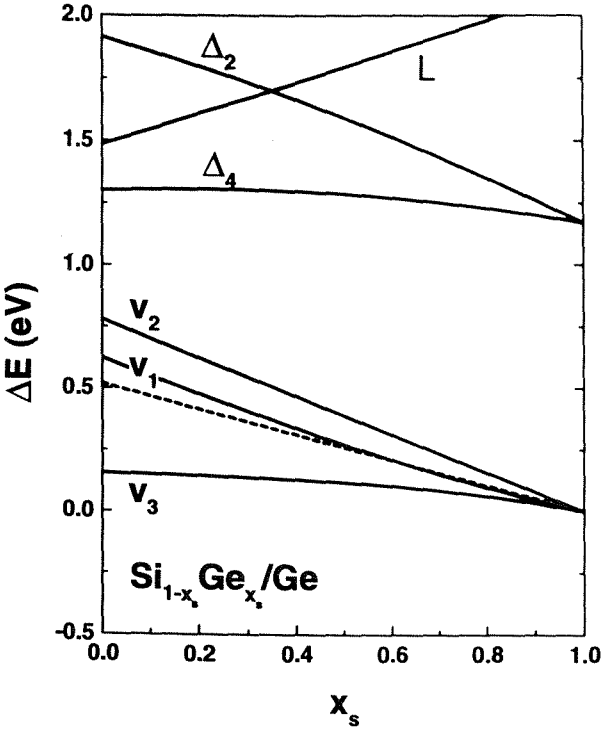
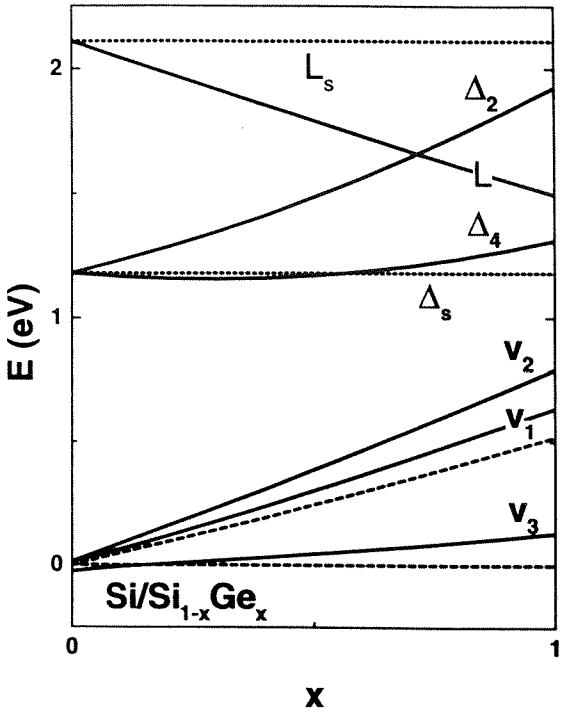


FIGURE 3 (a) Band positions for a pseudomorphic $Si_{1-xs}Ge_{xs}$/Ge heterojunction, as a function of alloy composition x_s in the substrate. Bands in the strained Ge overlayer are indicated by solid lines, and bands in the $Si_{1-xs}Ge_{xs}$ substrate by dotted lines. The average valence band in the substrate is chosen as the zero of energy. Average valence bands are indicated by dashed lines. (b) Band offsets for this heterojunction.

(a)



(b)

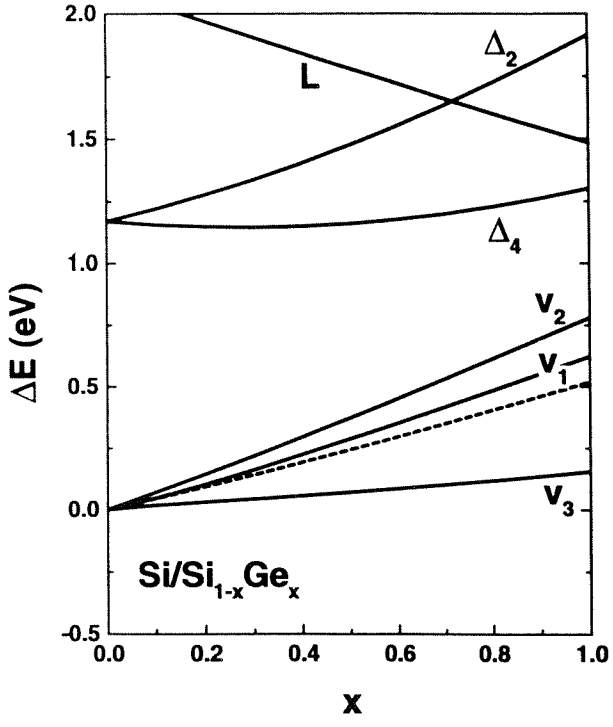


FIGURE 4 (a) Band positions for a pseudomorphic $Si/Si_{1-x}Ge_x$ heterojunction, as a function of alloy composition x in the overlayer. Bands in the strained $Si_{1-x}Ge_x$ overlayer are indicated by solid lines, and bands in the Si substrate by dotted lines. The average valence band in the substrate is chosen as the zero of energy. Average valence bands are indicated by dashed lines. (b) Band offsets for this heterojunction.

C EXPERIMENT

As pointed out above, experiments can yield a specific offset value for a specific structure, but this offset value is influenced by a number of parameters (the unstrained lineup, and the hydrostatic and uniaxial deformation potentials). To our knowledge, no experiments have been carried out aimed at systematically determining these various components. Our approach in this section will therefore be to show that the theoretical values discussed in Section B provide a reliable and accurate description of the band lineups in this system, by comparing the theoretical predictions with a number of experimental values for specific systems. We only discuss experiments on pseudomorphic interfaces, in which the strain state of the heterostructure was accurately known.

Schwartz et al [9] carried out core-level photoemission measurements on Si/Ge interfaces on Si(001) and on Ge(001) substrates. Their data, combined with calculated core-valence-band deformation potentials and uniaxial deformation potentials, lead to $\Delta E_v = 0.74 \pm 0.13$ eV in the case of the Si substrate, and $\Delta E_v = 0.17 \pm 0.13$ eV in the case of the Ge substrate. The theoretical values, calculated above, were 0.78 eV and 0.22 eV.

Yu et al [10] used X-ray photoelectron spectroscopy not only to obtain the core level lineups across the heterojunction, but also to measure the strain effect on the energy difference between core level and valence band. They obtained $\Delta E_v = 0.83 \pm 0.11$ eV for strained Ge on Si(001), and $\Delta E_v = 0.22 \pm 0.13$ eV for strained Si on Ge(001).

Ni and Hansson [11,12] also used X-ray photoelectron spectroscopy to obtain core level lineups, as well as to measure the band positions in strained materials. Their results are all in good agreement with the theoretical predictions; for instance, for a $Si/Si_{0.52}Ge_{0.48}$ interface on a Si(001) substrate they found $\Delta E_v = 0.36 \pm 0.6$ eV; the theoretical value is also 0.36 eV (see FIGURE 4(b)).

Vescan et al [13] have studied $Si_{0.7}Ge_{0.3}/Si$ single and multiple quantum wells grown by low-pressure chemical vapour deposition on a Si(001) substrate; they obtained $\Delta E_v = 0.27$ eV. The same group [14] has also performed DLTS measurements to obtain the valence-band offset at a $Si/Si_{0.7}Ge_{0.3}$ heterojunction grown on a Si substrate, leading to $\Delta E_v = 0.22 \pm 0.02$ eV. The theoretical value from FIGURE 4(b) is 0.22 eV for this structure.

Nauka et al [15] have used admittance spectroscopy to measure the valence-band offset in $Si/Si_{1-x}Ge_x$ heterojunctions ($0 < x < 0.45$) grown by chemical vapour deposition on Si(001). Within the model-solid approach it is possible to derive an analytic expression for the valence-band offset for such structures as a function of the composition x, keeping only terms linear in x. For $x < 0.5$, the theoretical prediction is $\Delta E_v = 0.75x$ (see also FIGURE 4(b)). The values reported in [15] agree with this prediction to within 0.03 eV, as long as $x < 0.4$. As pointed out in [15] higher values of x lead to the breakdown of the assumption of a pseudomorphic interface. Nauka et al also found a conduction-band discontinuity close to zero, in good agreement with the results predicted in FIGURE 4(b).

Brighten et al [16] determined the valence-band offsets in $Si/Si_{1-x}Ge_x$ heterostructures with $x < 0.14$ using CV measurements. Their results are in excellent agreement with $\Delta E_v = 0.75x$.

Rodrigues et al [17] have performed photoreflectance measurements on $Ge_{0.7}Si_{0.3}/Ge$ superlattices grown on Ge(001). Their analysis leads to $\Delta E_{v,av} = 0.14 \pm 0.03$ eV. This value still includes the contribution from hydrostatic strain. To compare with theory, we proceed as follows: the unstrained lineup for this structure would be $\Delta E^0_{v,av} = 0.58 \times 0.3 = 0.17$ eV. Linear elastic theory [1] predicts a

hydrostatic deformation in the $Ge_{0.7}Si_{0.3}$ layer of $\Delta V/V = 0.015$. The linearly interpolated absolute deformation potential for the valence band (see Datareview 4.2) is $a_v = 1.61$ eV, leading to a final lineup of $\Delta E_{v,av} = 0.17 - 0.02 = 0.15$ eV, consistent with the experimental value.

Similar arguments for a strained layer of pure Si grown on Ge(001) would lead to $\Delta E_{v,av} = 0.46$ eV (see FIGURE 2(b)). Comparing this value with the value of $\Delta E_{v,av} = 0.52$ eV which we previously obtained for a strained Ge layer grown on Si(001), we note that the offsets between the average valence bands are quite similar, and relatively unaffected by the specific strain situation. This point has been made already in [4] based on full first-principles calculations for these interfaces.

Finally, Morar et al [18] derived an unstrained valence-band offset between pure Si and Ge, based on spatially resolved electron-energy-loss spectroscopy in SiGe alloys, and the assumption that core level positions in the alloy can serve as references for determining the band lineup. They found $\Delta E^0_v = 0.78$ eV, where we use the superscript zero to denote the absence of strain. The theoretical value would be 0.67 eV (note that, even though strain is absent, spin-orbit splitting has to be taken into account in determining the position of the top of the valence band).

D CONCLUSION

The band offsets at interfaces between Si, Ge, and/or SiGe alloys are strongly influenced by strain effects, which depend on alloy composition. Rather than list individual values for specific heterostructures we have provided a comprehensive formalism that allows the determination of the band offsets for any heterojunction. The theoretical approach for the band lineup was inspired by the model solid theory [1]; we used a band offset between the average valence bands in unstrained Si and Ge of $\Delta E^0_{v,av} = 0.58$ eV. Figures are presented from which the band positions and band offsets for various pseudomorphically strained heterostructures can be immediately read off.

REFERENCES

[1] C.G. Van de Walle [*Phys. Rev. B (USA)* vol.39 (1989) p.1871]
[2] M. Ikeda, K. Terakura, T. Oguchi [*Phys. Rev. B (USA)* vol.48 (1993) p.1571]
[3] L. Colombo, R. Resta, S. Baroni [*Phys. Rev. B. (USA)* vol.44 (1991) p.5572]
[4] C.G. Van de Walle, R.M. Martin [*Phys. Rev. B (USA)* vol.34 (1986) p.5621]
[5] J. Weber, M.I. Alonso [*Phys. Rev. B (USA)* vol.40 (1989) p.5683
[6] F. Schaffler [*Semicond. Sci. Technol. (UK)* vol.12 (1997) p.1515]
[7] M.S. Hybertsen [in *Chemistry and Defects in Semiconductor Heterostructures* Eds. M. Kawabe, T.D. Sands, E.R. Weber, R.S. Williams (Materials Research Society, Pittsburgh, 1989) vol.148 p.329]
[8] S. Baroni, R. Resta, A. Baldereschi, M. Peressi [in *Spectroscopy of Semiconductor Microstructures* Eds. G. Fasol, A. Fasolino, P. Lugi (Plenum, London, 1989) p.251]
[9] G.P. Schwartz et al [*Phys. Rev. B (USA)* vol.39 (1989) p.1235]
[10] E.T. Yu, E.T. Croke, T.C. McGill, R.H. Miles [*Appl. Phys. Lett. (USA)* vol.56 (1990) p.569]
[11] W.-X. Ni, J. Knall, G.V. Hansson [*Phys. Rev. B (USA)* vol.36 (1987) p.7744]
[12] W.-X. Ni, G.V. Hansson [*Phys. Rev. B (USA)* vol.42 (1990) p.3030]
[13] L. Vescan et al [*Appl. Phys. Lett. (USA)* vol.60 (1992) p.2183]
[14] L. Vescan, R. Apetz, H. Luth [*J. Appl. Phys. (USA)* vol.73 (1993) p.7427]
[15] K. Nauka et al [*Appl. Phys. Lett. (USA)* vol.60 (1992) p.195]
[16] J.C. Brighten et al [*Semicond. Sci. Technol. (UK)* vol.8 (1993) p.1487]
[17] P.A.M. Rodrigues, F. Cerdeira, J.C. Bean [*Phys. Rev. B (USA)* vol.46 (1992) p.15263]
[18] J.F. Morar, P.E. Batson, J. Tersoff [*Phys. Rev. B (USA)* vol.47 (1993) p.4107]