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Extraction of large valence-band energy offsets and comparison to theoretical values for strained-Si/strained-Ge type-II heterostructures on relaxed SiGe substrates

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I. INTRODUCTION

The electronic band structure of tetrahedral semiconductors can be referred to a common energy scale from which the band offsets in the heterostructures can be derived, including those involving alloys of these materials. In the case of Si and Ge, earlier ab initio calculations indicated that in this common energy scale the “natural” valence-band offset between Si and Ge is about 500–600 meV, with the Ge valence band higher in energy. Starting from these values, the band lineups at specific heterojunctions can be predicted by performing appropriate strain corrections, which can be conveniently done by expressing the strain tensor as the sum of a hydrostatic contribution and a traceless shear component. People and Bean proposed the following widely used expression, based on Van de Walle and Martin’s 1985 theoretical work:

$$ \Delta E_v (\text{in meV}) \text{ for strained-Si/strained-Ge on (100) Si}_{1-x}\text{Ge}_x = 740 - 530x_s, $$ (1)

where $x_s$ is the Ge fraction of the relaxed substrate and $\Delta E_v$ is the valence-band offset between strained-Si (s-Si) and strained-Ge (s-Ge) in millielectron volts. Rieger and Vogl introduced an expression for the average valence-band offset between s-Si and s-Ge:

$$ \Delta E_{v,av} (\text{in meV}) \text{ for strained-Si}_{1-x}\text{Ge}_x \text{ on (100) Si}_{1-x}\text{Ge}_x = (470 - 60x_s)(x - x_s), $$ (2)

where $\Delta E_{v,av}$ is the offset between the average valence-band energy of s-Si$_{1-x}$Ge$_x$ on a relaxed Si$_{1-x}$Ge$_x$ virtual substrate. The average energy of the top three valence bands ($E_{v,av}$) is unaffected by the shear component of the strain or by the spin-orbit interaction. The predictions from Eqs. (1) and (2) are quite similar. For the s-Ge/unstrained-Si interface, for example, Eq. (2) leads to $\Delta E_v = 700$ meV when valence-band splitting is taken into account, which is close to the value $\Delta E_v = 740$ meV from Eq. (1).

Despite their widespread use, the validity of Eqs. (1) and (2) for the prediction of the band lineups of Si-Ge heterostructures is not firmly established. This is remarkable in view of the intense scrutiny on this material system for over 40 years; however, the Si-Ge heterostructure is particularly difficult from the standpoint of band offset theory not just because of the large lattice mismatch but also because the conduction-band minima in Si and Ge are located at different points away from the Brillouin zone center. The calculation of the effect of strain on such states requires the use of several deformation potentials, which are not well known for both materials because most experimental probes provide values associated with the conduction-band minimum. A known (but not widely acknowledged) discrepancy between theory and experiment is the band alignment at s-Si$_{1-x}$Ge$_x$/unstrained-Si interfaces. Using Eqs. (1) and (2), or similar expressions, combined with experimental band gaps and reasonable choices for the strain deformation potentials, it can be shown that the band alignment is type I for s-Si$_{1-x}$Ge$_x$/unstrained-Si (valence-band maximum and conduction-band minimum both in the s-Si$_{1-x}$Ge$_x$ layer) for $x < 0.7$ (Refs. 6 and 10), whereas experimental results for s-Si$_{0.70}$Ge$_{0.30}$/unstrained-Si clearly show that the alignment is type II (lower conduction-band edge in Si). Rieger and Vogl do predict a type-II alignment for s-Si$_{0.70}$Ge$_{0.30}$/unstrained-Si, but they use theoretical hydrostatic deformation potentials for the $\Delta$-minimum indirect band gap that differ from experimental values. Their theoretical deformation potential for Si is much larger and for Ge is of the opposite sign compared to experimental values. Interest in quantitatively understanding the type-II staggered band alignment of tensile strained-Si on compressively strained-Ge grown on relaxed SiGe [shown in...
dielectric (6 nm)

high-
boron at approximately 5 × 10^{16} cm^{-3}. To create a high-quality SiGe virtual substrate, the Ge alloy percentage of the initial SiGe layer was linearly graded from 2 to 35% over 4 μm of SiGe growth. Next, 1 μm of undoped relaxed 35% SiGe was grown on top of the graded buffer layer. Subsequently, approximately 6 nm of undoped compressively strained-Ge followed by 6 nm of undoped tensile strained-Si was grown on the surface of the SiGe virtual substrate. Similar growth procedures were used to also create s-Si/s-Ge heterostructures on 42 and 52% SiGe virtual substrates.

The epitaxial wafers underwent a modified RCA clean immediately before the high-κ dielectric deposition in an atomic layer deposition (ALD) system. A modified RCA clean was used to remove any contaminants while limiting removal of the thin s-Si layer, and it consisted of four key steps: (1) H_{2}SO_{4}:H_{2}O_{2} (3:1) piranha clean, (2) diluted HF dip, (3) HCl:H_{2}O_{2}:H_{2}O (1:1:5) clean, and (4) diluted HF dip. The last HF dip removed any native SiO_{2} that formed during the chemical cleaning. MOS capacitors were created by heating the sample to 250 °C in the ALD chamber and initially flowing 20% ozone in situ for 5 min. This was followed by the deposition of 6 nm of Al_{2}O_{3} dielectric using trimethylaluminium (TMA) and water as precursors. These steps were followed by ALD of 10 nm of tungsten nitride (WN). Sputtered aluminum was used to create contacts at the top and bottom surfaces of the samples. The devices were patterned using typical photolithographic techniques to create MOS capacitors of various sizes. A final forming gas anneal was performed at 450 °C for 30 min, which dramatically lowered the density of interface traps at the Si/dielectric interface.

The Ge molar fraction in the relaxed buffer layer was measured by secondary ion mass spectrometry (SIMS) and micro-Raman spectroscopy using 514-nm excitation. The measured Ge content derived from each technique is listed in Table I. Whereas SIMS measures the Ge chemical concentration, Raman spectroscopy measures the shift in the vibrational frequencies of the atomic bonds of the crystal. Due to anharmonic and mass substitution effects, these frequencies are dependent on the strain state and Ge fraction of the SiGe alloy. The shift (Δω) of the alloy Si-Si Raman peak relative to the bulk Si Raman frequency is related to the Ge fraction by

\[
xs = -0.015 \cdot \Delta \omega.
\]

This expression assumes that the SiGe layer is fully relaxed. Therefore, the excellent agreement between SIMS data and Raman-extracted Ge fraction indicates that the SiGe is nearly completely relaxed, as expected based upon the growth conditions. It should be noted that the Si and Ge layers are too thin for accurate measurements of strain using 514-nm excitation.

Ni Chleirigh performed an experimental analysis on the valence-band offset of the related s-Si/s-Si_{1-x}Ge_{x} heterostructure system; however, her work only covered s-Si_{1-x}Ge_{x} layers with up to 70% Ge. This paper expands that work by providing extraction of the band alignments for s-Si/s-Ge heterostructures on relaxed SiGe substrates of different Ge fractions, i.e., with different levels of biaxial strain in the heterostructure. Also, in contrast with the previous work, the present work employs a full-band quantum-mechanical simulator for the capacitance-voltage (CV) simulations.

**III. PHYSICS OF THE CV EXTRACTION TECHNIQUE**

A quasi-static CV (QSCV) measured from one of our samples is shown in Fig. 2. The band alignment extraction procedure originally developed by Kroemer et al. for Schottky and p-n junction devices was expanded by Voinigescu et al. to low-frequency CV measurements on high-quality MOS structures. Voinigescu found that the low-frequency CV curve of a Si/SiGe heterostructure MOS capacitor produces a distinctive plateau region (see region II of Fig. 2), which can be
TABLE I. Extracted and theoretical values for s-Si/s-Ge heterojunctions on different relaxed SiGe substrates. The experimental values were extracted by fitting quantum-mechanical simulations to experimental QSCV measurements. The theoretical values were calculated using an average valence-band offset of $\Delta E_{v,av} = 800$ meV between s-Si and s-Ge using the method described in Section VII: Unified Theoretical Description of the Si-Ge section.

<table>
<thead>
<tr>
<th>Name</th>
<th>Measured Ge fraction of SiGe layer</th>
<th>$\Delta E_v$ (meV)</th>
<th>Band alignments between s-Si/s-Ge layers</th>
<th>s-Si cap thickness (Å)</th>
<th>Measured (Exp.)</th>
<th>Raman (this work)</th>
<th>Theory (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“35% SiGe”</td>
<td>35.5%</td>
<td>770 ± 25</td>
<td>Exp. 190 ± 50</td>
<td>38 Å</td>
<td>190 ± 50</td>
<td>137</td>
<td>960 ± 50</td>
</tr>
<tr>
<td>“42% SiGe”</td>
<td>42.6%</td>
<td>760 ± 25</td>
<td>Exp. 185 ± 50</td>
<td>49 Å</td>
<td>185 ± 50</td>
<td>122</td>
<td>950 ± 50</td>
</tr>
<tr>
<td>“52% SiGe”</td>
<td>52.7%</td>
<td>670 ± 25</td>
<td>Exp. 190 ± 50</td>
<td>50 Å</td>
<td>190 ± 50</td>
<td>101</td>
<td>860 ± 50</td>
</tr>
</tbody>
</table>

used to extract the valence-band offset of the heterostructure. The valence-band offset extraction requires the material with a lower valence-band energy (in this case Si) to be at the surface of the heterostructure, thus producing a well for holes separated from the oxide/semiconductor surface.

The CV curve of the s-Si/s-Ge heterostructure MOS capacitor has four distinct regions illustrated in Figs. 2 and 3: hole accumulation in the Si and Ge layers (I), hole accumulation in the Ge layer (II), depletion of holes (III), and electron inversion in the Si layer (IV). The maximum capacitance of regions I and IV allow fitting of the dielectric thickness to an equivalent oxide (SiO$_2$) thickness (EOT), while region II, which we call the plateau region, allows for determination of the small effective band gap ($E_{G,eff} = E_{c,si} - E_{v,Ge}$) of the s-Si/s-Ge heterostructure.

In a p-type s-Si/s-Ge heterostructure MOS capacitor, represented in Figs. 2 and 3, as the gate voltage is swept from positive to negative, holes are first accumulated in the buried s-Ge quantum well (region II) and then eventually at the s-Si/dielectric interface as a more negative gate bias is applied (region I). The plateau width in region II is directly related to the valence-band offset. As the valence-band offset increases, increased negative gate voltage is required to bend the Si valence bands toward the Fermi level in order to accumulate the Si layer with holes, and this causes an increase in the plateau width (region II) of the CV curve. The plateau width of the simulated CV data is fit to the experimental data by varying the s-Si/s-Ge valence-band offset of the simulation.

The capacitance of the plateau region (region II) is approximately given by the series combination of the oxide and Si layer capacitances because the unpopulated Si layer acts as a dielectric. During the transition from region II to region I, as the gate bias is swept to more negative voltages, holes begin to populate the Si layer as the Si valence bands bend toward the Fermi level. The Si layer no longer acts as a dielectric, and the capacitance increases toward the oxide capacitance due to the decrease of the effective dielectric thickness.

Region III of the CV curve provides information about effective band gap, $E_{G,eff}$, at the s-Si/s-Ge heterojunction.

![FIG. 2. (Color online) Experimental and simulated QSCV curves for s-Si/s-Ge on a relaxed 35% SiGe substrate. The following parameters were used to produce the simulated CV curve: 38 Å EOT, 49 Å s-Si cap thickness, $\Delta E_v = 770$ meV, and $E_{G,eff} = 190$ meV. The CV analysis does not provide significant sensitivity to other parameters. Voltage regions of distinct carrier distributions are identified by Roman numerals and described in the text and shown schematically in Fig. 3.](image-url)

![FIG. 3. (Color online) Depiction of the heterostructure band diagrams and carrier populations (not drawn to scale) under the different regimes labeled in Fig. 2.](image-url)
which is given by

\[
E_{G,\text{eff}} = E_{c,\text{Si}} - E_{v,\text{Ge}},
\]

(4a)

\[
= E_{G,\text{Si}} - \Delta E_v,
\]

(4b)

where \(E_{c,\text{Si}}\) is the conduction-band-edge energy of s-Si, \(E_{v,\text{Ge}}\) is the valence-band-edge energy of s-Ge, \(E_{G,\text{Si}}\) is the band gap of s-Si, and \(\Delta E_v\) is the valence-band offset at the s-Si/s-Ge heterojunction. For a given s-Si band gap, an increase in \(\Delta E_v\) suggests a decrease in \(E_{G,\text{eff}}\) by the same amount.

Due to the small effective band gap of the heterostructure, electrons begin to collect in the Si conduction band before holes are fully depleted from the structure. Thus, the width of region III is very narrow, and the capacitance of region III does not decrease to the low values typically measured in Si homostructure MOS capacitors in depletion. \(E_{G,\text{eff}}\) is directly related to the width and capacitance of region III, and \(E_{G,\text{Si}}\) (the sum of \(\Delta E_v\) and \(E_{G,\text{eff}}\)) is directly related to the total width of regions II and III. The band alignment of s-Si/s-Ge can be extracted by varying \(\Delta E_v\) and \(E_{G,\text{eff}}\) of the simulation structure until a good fit is found between simulated and experimental CV. Because \(\Delta E_v\) and \(E_{G,\text{eff}}\) affect different regions of the CV curve, their values can be extracted independently.

IV. MEASUREMENT AND EXPERIMENTAL DETAILS

The CV curves were measured using a quasistatic method. For this technique, an Agilent 4156C Parameter Analyzer was used to apply a dc bias across the device. The parameter analyzer steps the voltage and integrates the current to determine the change in charge, \(\Delta Q\), that occurred over the voltage step, \(\Delta V\). The equipment also applies some basic algorithms to mitigate the effect of integrating oxide leakage current. A detailed description of the technique is given in Ref. 29. The QSCV method has the advantage that it emulates the quasistatic simulation technique and is able to probe the inversion regime of the CV curve. The inversion regime is difficult to measure with low-frequency CV due to the long carrier lifetimes attributed to the high quality of the epitaxial layers and 1/f noise that becomes substantial at frequencies less than 1 kHz.

The measurements shown in this paper were made using the QSCV technique on unpackaged samples in a dark, electromagnetically shielded probe station at room temperature. Voltage steps of 24 mV were used, with 500 ms of quasistatic integration time and 100 ms of leakage current integration time (which the 4156 algorithm uses to remove the effects of gate leakage). Devices were screened to ensure low dc gate leakage and high-quality dielectric. The dc leakage current through the dielectric of the MOS capacitors was measured to be less than 1 nA/cm² in the voltage range from −2 to 2.75 V. There was good agreement between low-frequency and QSCV measurements for ac frequencies less than 500 Hz. Alternating-current CV measurements at frequencies higher than 500 Hz showed a decrease in the inversion capacitance due to long carrier lifetimes in the high-quality material. The observed hysteresis between positive- and negative-directed voltage sweeps was less than 20 mV, indicating a high-quality dielectric.

A requirement for obtaining clean QSCV data reflecting only the semiconductor band structure is that the dielectric-semiconductor interface be of high quality. In our laboratory, significant work has been conducted on the deposition of high quality Al₂O₃ on Si and s-Si/s-Ge heterostructures with minimal density of interface traps \(D_{it}\) and mobile oxide charge that causes hysteresis.30-33 In the present work, the \(D_{it}\) of a Si control wafer with the same Al₂O₃ procedure as used for the heterostructure wafers was measured to be \(\sim 10^{13} \text{ cm}^{-2}\text{eV}^{-1}\) at midgap by using the conductance method.34,35 Simulations incorporating \(D_{it}\) (not shown in this paper) suggest that at values determined from the Si control wafer, there is minimal impact on the valence-band extraction method. Though the \(D_{it}\) of the Si control wafer may be considered a lower bound for the expected \(D_{it}\) of the heterostructure wafers, other features of the measured CV curves of the heterostructure devices also suggest a low \(D_{it}\). After accounting for series resistance, a capacitance offset, which would suggest the presence of \(D_{it}\), does not appear between the high- and low-frequency CV curves when transitioning from accumulation to depletion. Furthermore, a large \(D_{it}\) would stretch out the CV curve, yielding a larger value for the valence-band offset and for the s-Si band gap. However, the extracted s-Si band gap, shown in Fig. 7(a), is slightly lower than expected based on previous experiments and theory, which signifies a small \(D_{it}\) that has minimal impact on the extraction technique. Moreover, the slope of the experimental CV curve at the point where holes begin to accumulate in the s-Si layer (transitioning from region II to region I in Fig. 2) would also be stretched out by a large \(D_{it}\). But the simulation without \(D_{it}\) matches the experimental data well as shown in Fig. 2, which is consistent with a small \(D_{it}\).

Although a large hole barrier (i.e., the valence-band offset) exists between the s-Si and s-Ge (shown in region I of Fig. 3), limiting the rate at which holes can populate the s-Si layer, the slow voltage sweep rate of the quasistatic measurement method allows enough time for the carriers to respond so that quasiequilibrium can be reached between each voltage step. Ultimately, the path that the holes take (whether through thermionic emission or tunneling through the large valence-band barrier) to populate either of the quantum wells does not impact the QSCV measurement. What is important is that the carriers reach quasiequilibrium between each voltage step so that the change in charge in each quantum well is representative of the quasiequilibrium simulations.

V. RESULTS AND SIMULATIONS

The simulated QSCV capacitance curve was calculated by taking the numerical derivative of the change of integrated charge density in the semiconductor layers divided by the voltage step \(C = dQ/dV\). An advanced simulation tool that accounts for quantum-mechanical effects and band splitting due to strain is necessary to properly model the charge density at different voltages. Whereas Ni Chleirigh6 used a single-band simulator with a density gradient model for quantum corrections and a modified valence-band density of states \(N_v\) to account for strain,37 this work uses nextnano³ (Ref. 38 and 39), a full-band quantum-mechanical simulator. With nextnano³, we model multiple valence bands with a
The strain Hamiltonian mixes the light and split-off band. Uses the terms is quoted as the difference in the band edges. While the figure includes the effects of quantization, but only the band-edge difference is quoted in order to provide information about the band lineup that is independent of the quantum well thicknesses.

A comparison of the measured and fitted simulation QSCV is shown in Fig. 2 for s-Si/s-Ge on a relaxed 35% SiGe substrate. The extracted valence-band offset and effective band gap for the sample are $\Delta E_v = 770 \pm 25$ meV and $E_{G,\text{eff}} = 190 \pm 50$ meV, respectively. The quoted uncertainty reflects the range of these parameter values that yields a qualitatively good fit between simulation and experimental data. The extracted EOT and s-Si cap thicknesses are $38 \pm 2$ Å and $49 \pm 2$ Å, respectively, in agreement with values expected from the fabrication processes used.

In this paper we use the standard definition of valence-band offset: the energy difference between the valence-band maxima at both sides of a heterojunction between two semi-infinite materials. In the case of a Si/Ge heterostructure strained to SiGe, this definition corresponds to the difference between the s-Ge heavy-hole valence-band edge and the s-Si light-hole valence-band edge, as shown in Fig. 4. The simulation includes the effects of quantization, but the valence-band offset is quoted as the difference in the band edges. While the figure uses the terms heavy hole (hh) and light hole (lh) to identify the split valence bands, it should be noted that even at $k = 0$, the strain Hamiltonian mixes the light and split-off band.

In general, good agreement is obtained between experimental and simulated CV curves, with high sensitivity to small changes in the s-Si cap thickness, which allows the physical thickness to be extracted with low uncertainty ($\pm 2$ Å).

A change in $\Delta E_v$ produces a 90-mV change in the plateau width.

The sensitivity of the extraction method to changes in $\Delta E_v$ is illustrated in Fig. 6 for a 35% SiGe substrate. For these structures, a small change in the valence-band offset produces a four times larger change in the width of the plateau region (e.g., a 50-meV increase in $\Delta E_v$ produces a ~200-mV enlargement of the plateau width). The extracted values for the

FIG. 4. (Color online) Valence-band diagram of the s-Si/s-Ge/relaxed SiGe heterostructure. The heavy hole (hh) and light hole (lh) valence bands in s-Si and s-Ge split due to tensile and compressive strain, respectively. The valence-band offset quoted in this paper is the difference between the top valence-band edges of s-Ge and s-Si. The simulation models quantization effects, but only the band-edge difference is quoted in order to provide information about the band lineup that is independent of the quantum well thicknesses.

FIG. 5. (Color online) Measured and simulated CV curves illustrating the high sensitivity of the simulation to $\Delta E_v$. A 25-meV change in $\Delta E_v$ produces about a 90-mV change in the plateau width. A change in $\Delta E_v$ only impacts the portion of the CV curve shown here.
The dotted line is a linear relationship derived from updated calculations in Van de Walle and Martin’s 1986 paper. The valence-band offsets extracted in this work are about 100 meV larger than the linear relationship derived from experimental data extracted using a MOS CV technique for the band gap from Ref. 7 with values extracted in this work as a function of substrate Ge fraction. People and Bean calculate a linear relation from theoretical work by Van de Walle and Martin in 1985 (Ref. 8). The dotted line is a linear relationship derived from updated calculations in Van de Walle and Martin’s 1986 paper. The valence-band offsets extracted in this work are about 100 meV larger than the linear relationship derived from theoretical values of Ref. 6.

The movement of the s-Si conduction band and the s-Ge valence band moves lower in energy with increasing strain. The net result is that both the s-Si conduction band and the s-Ge valence band move lower in energy with increasing strain, whereas decreasing strain in s-Ge causes the germanium valence and conduction bands to move toward one another. Increasing strain in s-Si increases the effective band gap of s-Si decreases as biaxial strain in the silicon is increased (increasing xs), and the values are in reasonable agreement with People and Bean’s calculated values. However, Fig. 7(b) shows that the extracted valence-band offset between s-Si/s-Ge is about 200 meV greater than Eq. (1) and 100 meV greater than a linear relationship derived from Van de Walle and Martin’s updated 1986 theoretical values (Ref. 6).

Because ΔEv is roughly 100 meV larger than reported calculated values, we find EG,sil to be significantly smaller than previously expected [EG,sil ~190 meV versus 300–400 meV based on Eqs. (1) and (2)]. Interestingly, EG,sil remains relatively constant as a function of the substrate Ge fraction, xs, as shown in Table I. As xs increases, biaxial tensile strain in the s-Si increases and biaxial compressive strain in the s-Ge decreases. Increasing strain in s-Si causes the silicon valence and conduction bands to move toward one another, whereas decreasing strain in s-Ge causes the germanium valence and conduction bands to move apart. The net result is that both the s-Si conduction band and the s-Ge valence band move lower in energy with increasing xs so that EG,sil remains relatively constant. The same effect causes ΔEv to decrease with increasing xs. The movement of the bands with strain is shown schematically in Fig. 8.

The valence-band offset extracted in this work is compared to previous experimental work on s-Si/s-Ge alloys are interpolated following Ref. 41. The average energy Ev,av is a convenient reference because it is unaffected by either the shear component of the strain or the spin-orbit interaction. When a strained heterojunction is formed, only the hydrostatic component of the strain affects the interaction. When a strained heterojunction is formed, only the hydrostatic component of the strain affects the band lineup of Si/Ge was calculated to be between 500 and 700 meV. Using the deformation potentials in Table II, which are justified in the Appendix, we adjusted the value of ΔEv,av to reproduce the 40-meV type-II band is in good agreement with the extrapolated value from Ni Chleirigh’s data.

VI. DISCUSSION

Figure 7(a) compares the theoretical values of the s-Si band gap from Ref. 7 with values extracted in this work as a function of substrate Ge fraction (xs). Also plotted are Welser’s experimental data extracted using a MOS CV technique for s-Si grown directly on relaxed SiGe. The data show that the band gap of s-Si decreases as biaxial strain in the silicon is increased (increasing xs), and the values are in reasonable agreement with People and Bean’s calculated values. However, Fig. 7(b) shows that the extracted valence-band offset between s-Si/s-Ge is about 200 meV greater than Eq. (1) and 100 meV greater than a linear relationship derived from Van de Walle and Martin’s updated 1986 theoretical values (Ref. 6).

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The valence-band offset extracted in this work is compared to previous experimental work on s-Si/s-Ge heterojunction grown on relaxed Si1-xGex in Fig. 9, and the valence extracted in this work for s-Si/s-Ge on ~40% SiGe substrate

VII. UNIFIED THEORETICAL DESCRIPTION OF THE Si-Ge SYSTEM

The calculation of band lineups based on common reference levels is described in detail by Van de Walle. The starting point is the average energy Ev,av of the top three valence bands of each bulk, unstrained semiconductor. For elemental and binary compounds, these averages can be predicted theoretically on a common energy scale. The corresponding energies for alloys are interpolated following Ref. 41. The average energy Ev,av is a convenient reference because it is unaffected by either the shear component of the strain or the spin-orbit interaction. When a strained heterojunction is formed, only the hydrostatic component of the strain affects the Ev,av energies. The corresponding shifts can be calculated using the absolute valence-band deformation potentials, Ev,av, for each material. The shear strain and the spin-orbit interaction split the electronic bands in ways that can be computed using standard deformation-potential theory. For the case of unstrained Si/Ge, ΔEv,av between Si and Ge was calculated to be between 500 and 700 meV. Using the deformation potentials in Table II, which are justified in the Appendix, we adjusted the value of ΔEv,av to reproduce the 40-meV type-II band

FIG. 7. (Color online) (a) Calculations by People and Bean of the band gap of s-Si for different Ge fractions of the relaxed Si1−xsGexs substrate compared to values extracted from CV analysis in this work. The experimental data from Welser is also included for comparison. (b) Valence-band offset, ΔEv,s as a function of Ge fraction in the substrate. People and Bean calculate a linear relationship derived from theoretical work by Van de Walle and Martin in 1985 (Ref. 8). The dotted line is a linear relationship derived from updated calculations in Van de Walle and Martin’s 1986 paper. The valence-band offsets extracted in this work are about 100 meV larger than the linear relationship derived from theoretical values of Ref. 6.

FIG. 8. (Color online) Illustration of the changes in the band edges with increased Ge fraction in the substrate (s-s).
Chleirigh36 extracted the valence-band offset using a CV technique heterostructure band diagram highlighting the valence-band offset. Ni and Bean7 calculate a linear relation from Van de Walle and Martin’s relations derived from theory by Van de Walle and Martin. People similar to this work. Both calculations shown in the plot are linear.

\[ \Delta E_{v,av} = \frac{2.24}{\Delta 1E_{v,av}} \]

We obtain an exact fit using an offset at the Si0.70Ge0.30/Si, as observed by Thewalt et al.11 We obtain an exact fit using \( \Delta E_{v,av} = 800 \text{ meV} \). Using this value without any other adjustments, we then calculate the band offsets and effective band gaps in our three samples using standard deformation-potential theory. These are shown as the theoretical entries in Table I.

Representative band lineups calculated with standard deformation-potential theory are shown in Fig. 10. We find a remarkable agreement of the theoretical predictions with the experimental data, particularly when one takes into account that we are assuming linear elasticity and deformation-potential theory in the presence of very large biaxial strains of up to 2% in Si and 2.7% in Ge. The extracted and theoretical valence-band offsets are well within experimental error for two samples and marginally outside experimental error for the sample with the largest strain on the Si layer, whereas the effective band gaps are just below the lower end of the experimental error bar. These effective band gaps, as mentioned above, are more difficult to extract from the data, and their theoretical values are also more sensitive to the exact values of the deformation potentials. Had we computed the sample shown in Fig. 10 using \( \Delta E_{v,av} = 600 \text{ meV} \), a value considered until now to be consistent with experiment, we would have obtained \( \Delta E_v = 550 \text{ meV} \) and \( E_G,eff = 320 \text{ meV} \), in strong disagreement with our experimental results. It is also worth noting that the calculations reproduce the weaker dependence of the effective band gap on the substrate composition.

Our results imply a band offset \( \Delta E_v = 910 \text{ meV} \) for the s-Ge/Si interface, much larger than expected from Eq. (1). It is instructive to compare our results with core-level spectroscopy measurements of the band offsets. In these experiments, the band edges are measured relative to core levels. The band offsets follow immediately from the data if the core levels are independent of the volume (i.e., if their absolute hydrostatic deformation potential is zero). This, however, is not necessarily the case. Schwartz and coworkers45 find \( \Delta E_v = 740 \pm 130 \text{ meV} \) for s-Ge on Si, in agreement with Eq. (1), using theoretical Si 2p and Ge 3d deformation potentials, which are not known independently, so that the accuracy of their result is difficult to assess. Morar et al.46 introduced a very elegant transmission electron energy loss method that yields \( \Delta E_{v,av} \) between Ge and Si directly from measurements of the Si 2p conduction-band absorption edge in relaxed Si1−xGex alloys. They find \( \Delta E_{v,av} = 690 \text{ meV} \). However, in their estimate of the correction to the assumption of a constant Si 2p level, they compute a volume deformation potential of 2 eV for the 2p level. More detailed calculations by Franceschetti et al.,44 give \( -0.1 \text{ eV} \) for the same deformation potential. If we

![Graph showing valence-band offset for s-Si/s-Si1−xGe−x grown on relaxed SiGe substrate.](image)

**FIG. 9.** (Color online) Valence-band offset for s-Si/s-Si1−xGe−x grown on a relaxed SiGe substrate with ~40% Ge, as a function of Ge fraction in the s-Si1−xGe−x layer. The inset shows a depiction of the heterostructure band diagram highlighting the valence-band offset. Ni Chleirigh36 extracted the valence-band offset using a CV technique similar to this work. Both calculations shown in the plot are linear relations derived from theory by Van de Walle and Martin. People and Bean7 calculate a linear relation from Van de Walle and Martin’s 1985 paper,8 while the purple (dark gray) data point is calculated potential theory in the presence of very large biaxial strains that we are assuming linear elasticity and deformation-potential theory are shown in Fig. 10. We find standard deformation-potential theory. These are shown as the value without any other adjustments, we then calculate the band edges are measured relative to core levels. The band offsets follow immediately from the data if the core levels are independent of the volume (i.e., if their absolute hydrostatic deformation potential is zero). This, however, is not necessarily the case. Schwartz and coworkers45 find \( \Delta E_v = 740 \pm 130 \text{ meV} \) for s-Ge on Si, in agreement with Eq. (1), using theoretical Si 2p and Ge 3d deformation potentials, which are not known independently, so that the accuracy of their result is difficult to assess. Morar et al.46 introduced a very elegant transmission electron energy loss method that yields \( \Delta E_{v,av} \) between Ge and Si directly from measurements of the Si 2p conduction-band absorption edge in relaxed Si1−xGex alloys. They find \( \Delta E_{v,av} = 690 \text{ meV} \). However, in their estimate of the correction to the assumption of a constant Si 2p level, they compute a volume deformation potential of 2 eV for the 2p level. More detailed calculations by Franceschetti et al.,44 give \( -0.1 \text{ eV} \) for the same deformation potential. If we

![Graph showing calculated band lineups.](image)

**FIG. 10.** (Color online) Calculated band lineups of the (a) s-Si/s-Ge heterostructure pseudomorphic to 42% SiGe and (b) s-Si0.70Ge0.30/Si heterostructure pseudomorphic to Si using standard deformation potential theory. The calculations assume that the average valence-band offset between Si and Ge is \( \Delta E_{v,av} = 800 \text{ meV} \).

| Table II: Selected deformation potentials for Si and Ge in eV. The notation is as in Ref. 4, and the values are explained in the Appendix. For alloys, the deformation potentials are linearly interpolated. |
|---|---|---|---|
| Valence-band absolute deformation potential, \( a_v \) | Valence-band shear deformation potential, \( b \) | Hydrostatic deformation potential, \( \frac{1}{3}E_d + (\frac{2}{3}a_v + a_d) \Delta \) | Conduction-band shear deformation potential, \( E_{u,d}^{\Delta} \) |
| Si | 2.24 | -1.73 | 1.47 | 8.70 |
| Ge | 2.10 | -1.88 | 1.80 | 8.95 |

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recompute Morar’s results using the Franceschetti deformation potential, we find that their measurements imply $\Delta E_{v,av} = 770$ meV, in much better agreement with our results. Moreover, the most recent \textit{ab initio} calculations of band offsets\textsuperscript{45} yield $\Delta E_{v,av} = 750$ meV for the Si-Ge system, which is also closer to our results than previous \textit{ab initio} predictions.

VIII. SUMMARY

The valence-band offsets for s-Si/s-Ge heterojunctions pseudomorphic to various relaxed SiGe substrates were extracted by fitting full-band quantum-mechanical simulations to experimental QSCV measurements on MOS capacitors. Good agreement was found between simulated and measured CV curves with high sensitivity to the valence-band offset of the s-Si/s-Ge heterostructure. Values of $\Delta E_v$ were found for 770, 760, and 670 meV for 35, 42, and 52% Ge fraction SiGe substrates, respectively. The effective band gap was found to be about 190 meV, irrespective of the substrate Ge fraction.

The large valence-band offsets measured in this paper as well as the observation of type-II alignment in s-Si$_{1-x}$Ge$_x$/Si heterojunctions by Thewalt \textit{et al.} can be simultaneously explained by assuming an average valence-band offset, $\Delta E_{v,av} = 800$ meV between Si and Ge. This value is much larger than usually assumed in simulations of the s-Si-Ge system.

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APPENDIX

As indicated in the introduction, the use of several deformation potentials with different degrees of uncertainty is unavoidable when analyzing Si-Ge heterostructures. The most important parameters that affect our calculations are given in Table II. It should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II, should be stressed, however, that our main conclusion, namely that the Si-Ge valence-band offset is given in Table II.

We briefly summarize how they were obtained.

For the absolute deformation potentials, we start with the deformation potentials from Van de Walle\textsuperscript{4} and following the same procedure used above, we fit the offset that reproduces Thewalt’s photoluminescence results\textsuperscript{11} is $\Delta E_{v,av} = 720$ meV, which is also very large. When applied to our s-Si/s-Ge heterostructure, this model gives somewhat better effective band gaps and somewhat worse band offsets. Nevertheless, we believe that the deformation potentials presented in Table II represent a better choice, and we briefly summarize how they were obtained.

For the absolute deformation potentials, we start with the experimental pressure dependence of the direct band gap $E_0$ in Ge, as measured by Goñi \textit{et al.}\textsuperscript{46} They find that the resulting volume dependence of the band-gap energy is not exactly linear, so we fit a linear expression over the range of volume changes ($\sim 0$ to 2.5%) likely to be found in epitaxially strained systems. We obtain a band-gap volume deformation potential, $a_v - a_c = -9.47$ eV. Here we express the band-gap deformation potential in terms of the absolute deformation potentials for the conduction and valence bands at the $\Gamma$-point of the Brillouin zone, $a_c$ and $a_v$. These have been calculated theoretically by several groups. We use values from Li \textit{et al.}\textsuperscript{47} who obtain $a_c = -7.83$ eV and $a_v = 2.23$ eV, in good agreement with Ge band-gap data ($a_c - a_v = -10.06$ eV).

We correct for the residual small deviation by multiplying the theoretical values by a factor 9.47/10.06 = 0.94 to match the band-gap data exactly. This gives the value listed in Table II, $a_v = 2.10$. For Si, there are no pressure dependence studies of $E_0$. Therefore, we take the value of $a_v$ from Ref. 44 and “renormalize” with the same factor used for Ge. The resulting absolute deformation potentials in Table II are in excellent agreement with the values needed to fit the hole mobilities in Si and Ge.\textsuperscript{38}

From the pressure dependence of the fundamental band gap of Si\textsuperscript{49} we obtain the hydrostatic deformation potential $(\Xi_0 + \frac{1}{3} \Xi_u - a_u)^\Delta = 1.47$ eV for Si. The pressure dependence of the indirect gap associated with the $\Delta$-valley in Ge has been measured by Ahmad and Adams,\textsuperscript{13} and from their measurements, we obtain $(\Xi_u + \frac{1}{3} \Xi_u - a_u)^\Delta = 1.80$ eV for Ge.

The shear deformation potentials that give the splitting of bands due to the traceless component of the strain tensor are traditionally measured in uniaxial stress experiments, which potentially suffer from stress calibration issues, as suggested by the fact that Raman phonon Grüneisen parameters obtained from such experiments do not agree very well with direct hydrostatic pressure measurements in diamond anvil cells.\textsuperscript{30–33}

In the case of the valence-band shear deformation potential, Liu \textit{et al.}\textsuperscript{54} recently determined $b = 1.88$ eV for Ge using strained-layer Ge films in which the strain was measured with high-resolution x-ray diffraction. It is interesting to point out that the hydrostatic deformation potential obtained by these authors agrees exactly with the value obtained from Goñi \textit{et al.}\textsuperscript{46} when the data from the latter is fit over the same volume change range. We use Liu’s value for Ge, and for Si, we take the

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{fig11}
  \caption{Experimental $\Delta$-like absorption edges of strained Si$_{1-x}$Ge$_x$ alloys on relaxed Si substrates from Lang \textit{et al.} (circles; Ref. 57), and our calculation of these edges (lines) using the experimental compositional dependence of the band gap in relaxed Si$_{1-x}$Ge$_x$ alloys from Ref. 58 and the deformation potentials in Table II.}
\end{figure}
Ge value for $b$ and multiply times the theoretically predicted ratio of this quantity for Si and Ge. Finally, for the shear deformation potential for Si associated with the $\Delta$-minimum of the conduction band, we use the value measured by Laude et al., $\Xi_a = 8.7$ eV. There are no equivalent measurements for Ge, but most theoretical calculations give values slightly larger than similar calculations for Si that are in good agreement with the experimental data. Accordingly, we use $\Xi_a = 8.95$ eV for Ge, which follows from multiplying the Si value from Laude and the theoretical ratio for $\Xi_a$ for Ge and Si. Assuming linear interpolation of the deformation potentials for $Si_{1-x}Ge_x$, the predicted dependence of the split indirect band gaps in $Si_{1-x}Ge_x$ alloys pseudomorphic to Si substrates is compared with experimental data in Fig. 11.

As a final comment, we point out that in 1991, Li and coworkers introduced a capacitance method from which the shear deformation potential $\Xi_a$ can be obtained quite straightforwardly from samples under uniaxial stress. They find $\Xi_a = 11.3$ eV for Si, significantly larger than the value above from Laude and they present a very thorough discussion of the errors associated with different experiments. We suspect that the discrepancies between different authors are due in part to differences in the calibration of their stress apparatuses, as suggested above. In the case of Laude, the hydrostatic deformation potentials deduced from their experiment agree very well with the direct hydrostatic pressure measurements in Ref. 48, suggesting small stress calibration errors. No corresponding hydrostatic data comparison is presented by Li. Moreover, if we use Li’s value for $\Xi_a$, the agreement between theory and experiment in Fig. 11 worsens, so we prefer to use Laude’s value until Li’s shear-deformation-potential value is confirmed by new experiments.

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