

Electronic properties of Si/Si_{1-x-y}Ge_xC_y heterojunctions

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We have used admittance spectroscopy and deep-level transient spectroscopy to characterize electronic properties of Si/Si_{1-x-y}Ge_xC_y heterostructures. Band offsets measured by admittance spectroscopy for compressively strained Si/Si_{1-x-y}Ge_xC_y heterojunctions indicate that incorporation of C into Si_{1-x-y}Ge_xC_y lowers both the valence- and conduction-band edges compared to those in Si_{1-x}Ge_x by an average of 107±6 meV/% C and 75±6 meV/% C, respectively. Combining these measurements indicates that the band alignment is type I for the compositions we have studied, and that these results are consistent with previously reported results on the energy band gap of Si_{1-x-y}Ge_xC_y and with measurements of conduction band offsets in Si/Si_{1-y}C_y heterojunctions. Several electron traps were observed using deep-level transient spectroscopy on two *n*-type heterostructures. Despite the presence of a significant amount of nonsubstitutional C (0.29–1.6 at. %), none of the peaks appear attributable to previously reported interstitial C levels. Possible sources for these levels are discussed. © 1998 American Vacuum Society. [S0734-211X(98)10003-3]

I. INTRODUCTION

Research on Si/Si_{1-x}Ge_x heterostructure materials and devices has led to dramatic improvements in performance and functionality of Si-based electronic and optoelectronic devices. For example, Si/Si_{1-x}Ge_x heterojunction bipolar transistors have been fabricated with a power gain cutoff frequency, f_{\max} , of 160 GHz¹ and with a current gain cutoff frequency, f_t , of 113 GHz.² Additionally, improvements in both the transconductances and the mobilities in both *p*-channel³ and *n*-channel⁴ heterojunction field-effect transistors with Si_{1-x}Ge_x based materials have been demonstrated. However, the 4.18% lattice mismatch between Si and Ge imposes significant restrictions on composition and layer thickness in Si/Si_{1-x}Ge_x heterostructures.

Recently, considerable progress has been made in the growth and characterization of Si_{1-x-y}Ge_xC_y alloys,⁵⁻¹⁰ which offer considerably greater flexibility, compared to that in the Si/Si_{1-x}Ge_x material system, to control strain and electronic properties in group IV heterostructures. In particular, the smaller C atom compensates for the compressive strain present in Si_{1-x}Ge_x, leading to the possibility of fabricating group IV heterostructures lattice matched to Si substrates.⁵⁻¹¹ Recent measurements of the total energy band gap for Si_{1-x-y}Ge_xC_y compressively strained to Si (001) indicate that incorporation of C into Si_{1-x-y}Ge_xC_y increases the band gap by 21–26 meV/% C.¹²⁻¹⁵ Effective design, fab-

rication, and characterization of such devices, however, additionally requires the accurate measurement of the energy band offsets in Si/Si_{1-x-y}Ge_xC_y heterojunctions. Moreover, determining the effects of nonsubstitutional C on the electronic structure of these alloys is another key step to realizing these devices.

Although measuring energy band offsets presents many challenges to the experimentalist, admittance spectroscopy has been used successfully on several material systems in the past.¹⁶⁻¹⁸ In this article we present admittance spectroscopy measurements of valence- and conduction-band offsets, ΔE_v and ΔE_c , respectively, in Si/Si_{1-x-y}Ge_xC_y heterostructures. A detailed description of the technique can be found elsewhere.¹⁹ Since many of the samples examined contain a substantial fraction of nonsubstitutional C (0.29–1.6 at. %), we also examined some of these samples using deep-level transient spectroscopy²⁰ in an effort to gain an understanding of the influence of nonsubstitutional C on the electronic structure of these alloys.

II. EXPERIMENT

Several multiple quantum well (MQW) samples were grown by solid-source molecular beam epitaxy (MBE) on Si (001) conducting substrates (see Table I). The epilayers consisted of a 2000 Å Si buffer layer, followed by 150–250 Å of Si_{1-x}Ge_x or Si_{1-x-y}Ge_xC_y alternating with 350 Å Si for ten periods with dopant concentrations of 7.4×10^{16} and 1×10^{17} cm⁻³, respectively. Either *p*-type (B-doped) or

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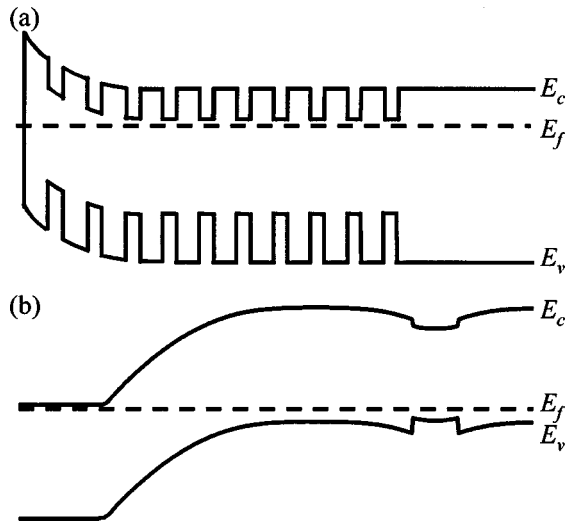


FIG. 1. (a) Schematic energy band diagram for an *n*-type MQW heterostructure grown by MBE. (b) Energy band diagram for a *p*-type SQW heterostructure grown by CVD.

n-type (Sb-doped) structures were used for measurement of, respectively, ΔE_v and ΔE_c . The heterostructures were grown at 450 °C, with some capped by an additional 2000 Å Si. Several samples were grown using Sb as a surfactant to improve structural quality.²¹ In all cases the thickness of the MQW structure was below the critical thickness for strain relaxation.²² X-ray diffraction (XRD), ion channeling, and, in some cases, transmission electron microscopy (TEM) were performed to confirm the high structural quality of the samples. The Ge concentration was determined using Rutherford backscattering, and the C concentration was then determined by applying a strain compensation ratio for Ge:C of 9.44:1, which is given by a linear interpolation of lattice constants between Si, Ge, and 3C-SiC, to the XRD patterns. In addition, secondary ion mass spectroscopy was used to determine the total C concentration.

Schottky barrier diodes required for the admittance measurements were formed by deposition of Cr/Au circular contacts 150–300 μm in diameter, followed by a mesa etch in a CF₄/O₂ plasma. A schematic energy band diagram for an

n-type Si/Si_{1-x-y}Ge_xC_y MQW structure is shown in Fig. 1(a). Al Ohmic contacts were then deposited on the back-sides of the samples.

In addition, several Si/Si_{1-x-y}Ge_xC_y heterostructures were grown by chemical vapor deposition (CVD) in a single wafer reactor on Si (001) conducting substrates. These samples consisted of a 500 Å *p*-type Si buffer layer, a 300 Å *p*-type Si_{1-x-y}Ge_xC_y single quantum well (SQW), a 2000 Å *p*-type Si spacer, and finally a 600 Å *n*-type Si cap [see the energy band diagram in Fig. 1(b)]. All the layers had dopant concentrations of approximately $1 \times 10^{17} \text{ cm}^{-3}$, except the cap which had a dopant concentration of $5 \times 10^{18} \text{ cm}^{-3}$. Extensive characterization of previous growths provided an accurate calibration of the Ge and C concentrations. Since a *pn* junction is used to perform the admittance spectroscopy on these samples, 300 μm diameter circular Al Ohmic contacts were deposited on the top sides of these samples followed by a mesa etch and an Al Ohmic backside contact.

III. RESULTS AND DISCUSSION

A. Admittance spectroscopy

We first examined several *p*-type Si/Si_{1-x}Ge_x heterostructures to verify the validity of the measurement technique (see samples MBE-1–3 in Table I). Valence-band (VB) offsets measured for these Si/Si_{1-x}Ge_x were found to be in excellent agreement with accepted values.^{23,24} Admittance measurements were then performed on various Si/Si_{1-x-y}Ge_xC_y heterostructures. Figure 2 shows the conductance and capacitance measured as functions of temperature for various frequencies for sample CVD-1. Conductance peaks and capacitance steps arising from temperature-dependent thermionic emission from the quantum well are clearly observed. The inset in Fig. 2 shows an Arrhenius plot of f and T_m , from which an activation energy of $68 \pm 19 \text{ meV}$ is obtained. The VB offset derived from this activation energy¹⁹ was found to be $88 \pm 20 \text{ meV}$.

Similar measurements were performed on the other heterostructures, and a summary of the results can be seen in Fig. 3 and Table I. As shown in Fig. 3, incorporation of C into Si_{1-x-y}Ge_xC_y lowers both the conduction-band- and the

TABLE I. Summary of results for Si/Si_{1-x}Ge_x and Si/Si_{1-x-y}Ge_xC_y heterostructures analyzed.

Sample No.	Type	Ge conc. (at. %)	Subst. C conc. (at. %)	Total C conc. (at. %)	Sb surf.?	Measured band offset (meV)
MBE-1	<i>p</i>	10.6%	0%	N/A	No	$\Delta E_v = 108 \pm 20$
MBE-2	<i>p</i>	17.9%	0%	N/A	No	$\Delta E_v = 160 \pm 20$
MBE-3	<i>p</i>	25.5%	0%	N/A	No	$\Delta E_v = 198 \pm 12$
MBE-4	<i>P</i>	20.6%	0.44%	0.48%	No	$\Delta E_v = 118 \pm 12$
MBE-5	<i>p</i>	39.4%	1.14%	?	Yes	$\Delta E_v = 223 \pm 20$
MBE-6	<i>n</i>	16.9%	1.14%	2.80%	Yes	$\Delta E_c = 100 \pm 15$
MBE-7	<i>n</i>	23.4%	2.21%	3.62%	Yes	$\Delta E_c = 275 \pm 23$
MBE-8	<i>n</i>	9.3%	0.81%	1.10%	Yes	No peaks
MBE-9	<i>n</i>	29.3%	2.37%	4.21%	Yes	$\Delta E_c = 149 \pm 21$
CVD-1	<i>p</i>	30%	1.50%	?	No	$\Delta E_v = 88 \pm 20$
CVD-2	<i>p</i>	25%	1.25%	?	No	$\Delta E_v = 59 \pm 17$
CVD-3	<i>p</i>	25%	1.50%	?	No	$\Delta E_v = 43 \pm 11$

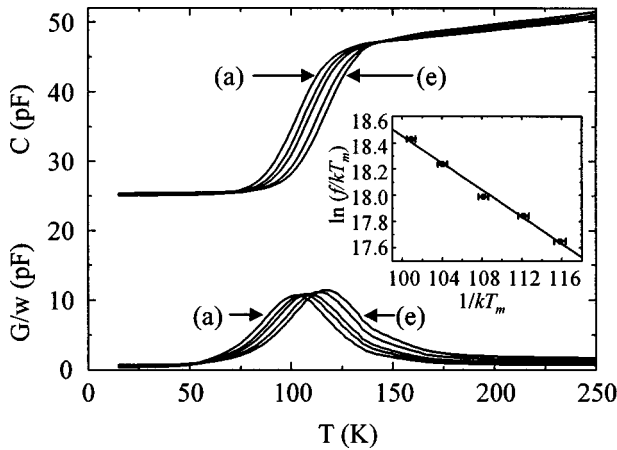


FIG. 2. Capacitance and conductance of a *p*-type Si/Si_{0.685}Ge_{0.30}C_{0.015} SQW structure (sample CVD-1) as functions of temperature for (a) 400 kHz, (b) 500 kHz, (c) 600 kHz, (d) 800 kHz, (e) 1 MHz. Inset: Arrhenius plot of frequency (f) and the peak temperature (T_m) at which the conductance peak is observed.

valence-band-edge energies compared to those for pure Si_{1-x}Ge_x, while slightly increasing the total band gap. Comparisons of our measured Si/Si_{1-x-y}Ge_xC_y band offset values with reported results for the change in total energy band gap, ΔE_g , of 21–26 meV/% C (substitutional C) for Si_{1-x-y}Ge_xC_y compressively strained to Si (001)^{12–15} indicates that the band alignment for our samples is type I. Fur-

thermore, these comparisons show that our band offset values are in quantitative agreement with reported values for ΔE_g over the range of compositions for which we have measured the band offsets. Combining our average change in ΔE_v , 107 ± 6 meV/% C, with our average change in ΔE_c , 75 ± 6 meV/% C, we obtain a value for the change in band gap, ΔE_g , of 32 ± 9 meV/% C (for substitutional C). One of the samples, MBE-7, exhibits a significantly stronger dependence of ΔE_c on C concentration than do the others. This sample, however, contains a large C concentration, 2.21 at. % substitutional and 3.63 at. % total, and this anomalous dependence may arise partly from the presence of a particularly high concentration of nonsubstitutional C.

We may extrapolate our measured band offsets to a wider range of Ge and C composition using the model-solid approach described by Van de Walle.²⁵ Using this approach, which systematically incorporates both the compositional or “alloy” contribution and the strain effect on the band offset, we have confirmed that our measured value of ΔE_c is in agreement with estimates of Si/Si_{1-y}C_y conduction-band offsets obtained from electrical and photoluminescence²⁶ measurements. *C*-*V* measurements²⁷ on Si/Si_{1-y}C_y metal-oxide-semiconductor field-effect transistor structures yielded $\Delta E_c = 40$ meV for Si/Si_{0.996}C_{0.004} and $\Delta E_c = 70$ meV for Si/Si_{0.992}C_{0.008}. In comparison, our measurements would indicate values of 52 ± 18 meV and 106 ± 22 meV, respectively. Hall measurements²⁸ on a Si/Si_{0.98}C_{0.02} QW suggest a lower bound on the CB offset of 150 meV; our results correspond to a CB offset of 261 ± 14 meV.

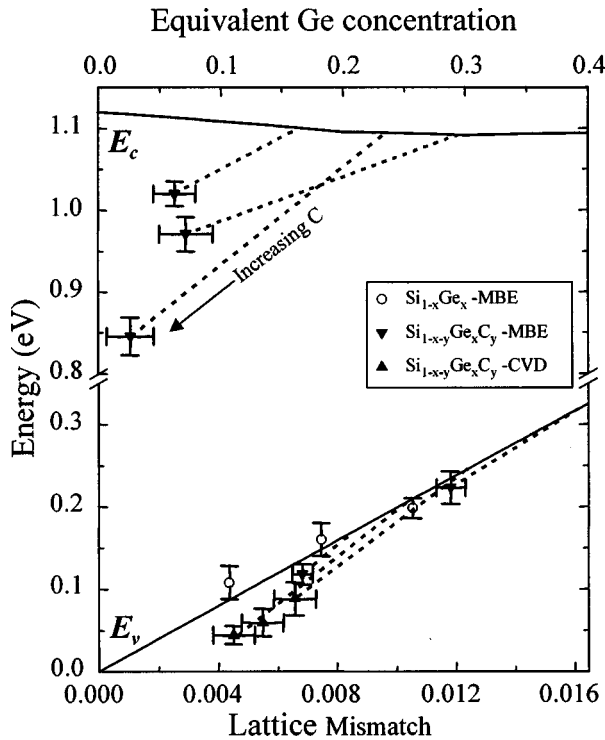


FIG. 3. Summary of measured valence- and conduction-band-edge energies measured as a function of lattice mismatch and equivalent Ge concentration for Si_{1-x}Ge_x (open circles) and Si_{1-x-y}Ge_xC_y (closed triangles). The solid lines represent interpolated band-edge energies for Si_{1-x}Ge_x, while the dotted lines indicate the effect of C incorporation into Si_{1-x-y}Ge_xC_y with fixed Ge concentration.

B. Deep-level transient spectroscopy

Using the notation $E(x)$ to denote an electron trap level at energy $E_c - x$ eV, C has been found to form several electron traps in Si, including an interstitial C_i level at $E(0.12)$ ²⁹ and a C_i -Si pair at $E(0.17)$.³⁰ As shown in Table I, many of the samples contain a significant fraction of C incorporated nonsubstitutionally. Deep-level transient spectroscopy (DLTS) was performed on several of the samples to assess the impact of this nonsubstitutional C on the electronic structure of Si_{1-x-y}Ge_xC_y alloys. Interpretation of the spectra is complicated by the presence of the quantum wells because, under certain measurement conditions, one would expect emission from the wells to display itself as a DLTS peak. For all of the measurement conditions we have used, there were no DLTS peaks in the admittance spectra, indicating that we are in fact observing deep-level traps. DLTS spectra from sample MBE-6 that was obtained for $V_{rev} = -1$ V, $V_{pulse} = -0.1$ V, a pulse width of 1 ms, and various rate windows is shown in Fig. 4. We observe three clear deep levels corresponding to electron traps at $E1(0.231 \pm 0.020)$, $E2(0.334 \pm 0.008)$, and $E3(0.405 \pm 0.012)$. The largest of these peaks corresponds to a trap concentration of approximately 2×10^{15} cm⁻³. There also appear to be several minor peaks within the spectrum, but accurate activation energies could not be extracted. In sample MBE-8, for which no peaks in the admittance spectra

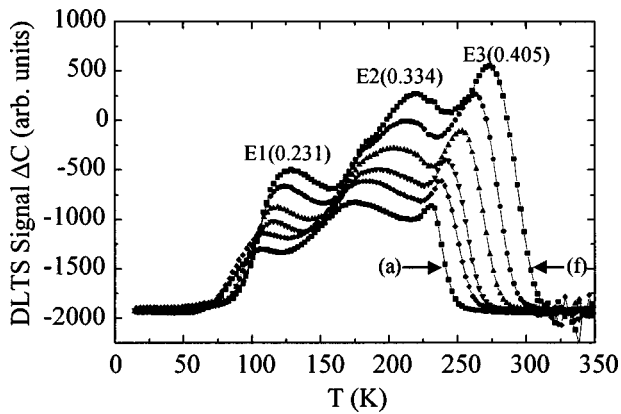


FIG. 4. DLTS spectra for a Si/Si_{0.82}Ge_{0.169}C_{0.011} MQW structure (sample MBE-6) taken at $V_{rev} = -1.0$ V, $V_{pulse} = -0.1$ V, a pulse width of 1 ms, and rate windows of 20, 50, 80, 200, 400, and 1000 Hz for (a)–(f), respectively.

were observed, we observed a single DLTS peak that corresponds to an electron trap at E4(0.356±0.023).

A large number of deep levels have been identified in Si and Si_{1-x}Ge_x by deliberately incorporating a known impurity,³¹ by deliberately damaging the sample using etching³² or radiation bombardment,³³ or by combining DLTS with other measurements, such as electron paramagnetic resonance.³⁴ Although additional measurements have not been performed on these samples, we have identified in the literature some possibilities for the sources of these traps. For Si_{1-x}Ge_x, previously reported measurements of the compositional behavior of the trap energy levels suggest that the energy levels are pinned to an absolute reference energy, thereby displaying a shift in measured activation energy equal in amount to the shift in the relevant band edge energy.^{35,36} Therefore, we have used the model-solid approach to shift our measured levels by the expected value for ΔE_c , which is 107±16 meV for MBE-6 and 72±11 meV for MBE-8. When this calculation is performed, we are left with deep-levels at E1(0.338±0.026), E2(0.441±0.018), and E3(0.512±0.020) for sample MBE-6 and E4(0.428±0.025) for sample MBE-8. The traps E2 and E4 in the two samples now appear to be due to the same defect level at 437±15 meV below the conduction-band edge of Si, a level that is consistent with a Sb vacancy pair level previously observed in Si_{1-x}Ge_x.³⁷ The E1 level may be due to an oxygen-related defect³⁸ or a dislocation kink site,³⁵ and the E3 level, which we have also observed in much lower densities ($< \sim 5 \times 10^{12}$ cm⁻³) in similar Si/Si_{1-x}Ge_x heterostructures, could be due to a Au-related defect³⁹ or to an unidentified midgap recombination-generation center.³⁵

Interestingly, the shallow interstitial C levels mentioned earlier are not observed at the expected temperatures (below 100 K) to a sensitivity of $\sim 2 \times 10^{13}$ cm⁻³ in samples MBE-6 and MBE-8, even though they contain, respectively, 1.7 at. % and 0.4 at. % nonsubstitutional C. If the levels remain fixed with respect an absolute reference energy, then we would not expect to observe them in the DLTS signal because the conduction-band edge itself is close to or below the E(0.12) and E(0.17) levels. It is possible in fact that the

nonsubstitutional C contributes additional states above the conduction-band edge of Si_{1-x-y}Ge_xC_y, thereby adding to the density of states within the quantum wells.

IV. CONCLUSION

Admittance spectroscopy and deep-level transient spectroscopy have been performed to elucidate the electronic structure of Si/Si_{1-x-y}Ge_xC_y heterostructures. Both the conduction- and valence-band offsets have been extracted from the admittance spectra, and both band-edge energies were observed to decrease, compared to those of pure Si_{1-x}Ge_x, with increasing substitutional C incorporation in Si_{1-x-y}Ge_xC_y. The resulting conduction-band offsets may allow Si/Si_{1-x-y}Ge_xC_y or Si/Si_{1-y}C_y heterojunctions to provide an attractive alternative to Si/Si_{1-x}Ge_x grown on strain-relaxed Si_{1-x}Ge_x buffer layers for fabrication of *n*-type heterostructure devices. DLTS measurements have revealed the presence of a number of deep electron traps in Si_{1-x-y}Ge_xC_y alloys. Previously reported interstitial C levels were not observed, despite the presence of a substantial fraction of nonsubstitutional C. Work is currently in progress to further characterize the effects of this nonsubstitutional C on the electronic structure of these alloys.

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