Measurement of band offsets in $Si/Si_{1-x}Ge_x$ and $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions

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Realization of group IV heterostructure devices requires the accurate measurement of the energy band offsets in $Si/Si_{1-x}Ge_x$ and $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions. Using admittance spectroscopy, we have measured valence-band offsets in $Si/Si_{1-x}Ge_x$ heterostructures and conduction-band and valence-band offsets in $Si/Si_{1-x-y}Ge_xC_y$ heterostructures grown by solid-source molecular-beam epitaxy. Measured $Si/Si_{1-x}Ge_x$ valence-band offsets were in excellent agreement with previously reported values. For $Si/Si_{1-x-y}Ge_xC_y$ our measurements yielded a conduction-band offset of 100 ± 11 meV for a *n*-type $Si/Si_{0.82}Ge_{0.169}C_{0.011}$ heterojunction and valence-band offsets of 118 ± 12 meV for a *p*-type $Si/Si_{0.79}Ge_{0.206}C_{0.004}$ heterojunction and 223 ± 20 meV for a *p*-type $Si/Si_{0.595}Ge_{0.394}C_{0.011}$ heterojunction. Comparison of our measured band offsets with previously reported measurements of energy band gaps in $Si_{1-x-y}Ge_xC_y$ and $Si_{1-y}C_y$ alloy layers indicates that the band alignment is type I for the compositions we have studied and that our measured band offsets are in quantitative agreement with these previously reported results. © *1997 American Vacuum Society.* [S0734-211X(97)07204-1]

I. INTRODUCTION

Extensive research on $Si/Si_{1-x}Ge_x$ heterostructure materials and devices has yielded impressive gains in the functionality and the performance of Si-based electronic and optoelectronic devices. 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.[1–5] $Si_{1-x-y}Ge_xC_y$ offers considerably greater flexibility, compared to that available 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 heterostructure devices lattice matched to Si.[1–6] 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.[7–10] Effective design, fabrication, 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.

II. EXPERIMENT

We have used admittance spectroscopy to measure both conduction-band and valence-band offsets, ΔE_c and ΔE_v, respectively, in $Si/Si_{1-x}Ge_x$ and $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions. Multiple quantum well (MQW) samples consisting of 150–250 Å $Si_{1-x}Ge_x$ or $Si_{1-x-y}Ge_xC_y$ alternating with 350 Å Si for ten periods with dopant concentrations of approximately $7.4\times10^{16}-1\times10^{17}$ cm^{-3}, respectively, were grown by solid-source molecular-beam epitaxy on Si(100) conducting substrates. *N*-type (Sb doped) and *p*-type (B doped) structures were used for measurement of, respectively, ΔE_c and ΔE_v. These heterostructures were grown at 450 °C on 2000 Å Si buffer layers, and the *p*-type $Si/Si_{0.79}Ge_{0.206}C_{0.004}$ heterostructure was capped by an additional 2000 Å Si layer. In addition, the *p*-type $Si/Si_{0.595}Ge_{0.394}C_{0.011}$ heterostructure and the *n*-type $Si/Si_{0.82}Ge_{0.169}C_{0.011}$ heterostructure were grown using Sb as a surfactant to improve structural quality.[11] In all cases, the thickness of the MQW structure was below the critical thickness for strain relaxation.[12] X-ray diffraction (XRD), ion channeling, and transmission electron microscopy (TEM) were performed on these samples to confirm their high structural quality. 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 SiC, to the XRD patterns. In addition, secondary ion mass spectroscopy (SIMS) 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

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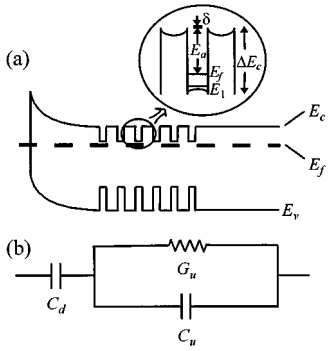

FIG. 1. (a) Energy band diagram for a Schottky barrier on an n-type multiple quantum well (MQW) heterostructure. The first confined state (E_1), the Fermi level relative to E_1(E_f), and the barrier lowering due to tunneling (δ) are added to the activation energy (E_a) to obtain the band offset (ΔE_c). (b) Equivalent circuit model for this structure, including the depletion layer capacitance (C_d), and the capacitance and conductance of the undepleted portion of the sample (C_u and G_u, respectively).

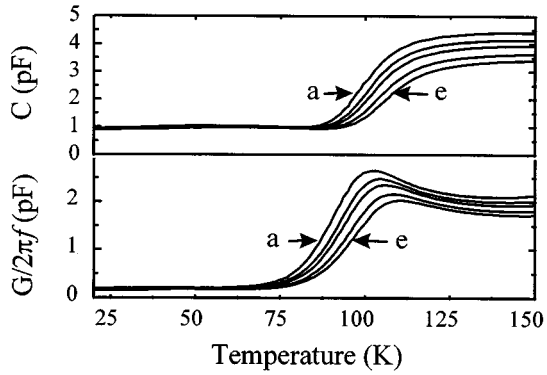

FIG. 2. Capacitance and conductance of a p-type $Si/Si_{0.79}Ge_{0.206}C_{0.004}$ MQW structure as functions of temperature for (a) 1 MHz, (b) 800 kHz, (c) 600 kHz, (d) 500 kHz, and (e) 400 kHz.

diameter, followed by a mesa etch in a CF_4O_2 plasma. Al Ohmic contacts were then deposited on the backsides of the samples.

Admittance spectroscopy has been used to measure band offsets in a variety of material systems.[13–15] Figure 1(a) shows a band diagram of a Schottky barrier on an n-type MQW structure. This structure can be modeled using an equivalent circuit consisting of the depletion layer capacitance, C_d, in series with the parallel capacitance and conductance of the undepleted portion of the sample, C_u and G_u, respectively, as shown in Fig. 1(b). In admittance spectroscopy, the total capacitance and conductance are measured as functions of temperature at various frequencies. It is generally assumed that the only circuit element that is temperature dependent is the conductance of the undepleted region, which can be modeled by thermionic emission over the Si barriers and can, therefore, be expressed as[16]

$$G_u=\frac{q^2Av_{\text{th}}(T)N_c(T)}{2kT}\exp\left(-\frac{E_a}{kT}\right), \tag{1}$$

where q is the electron charge, A is the device area, v_{th} is the thermal velocity of the carriers, N_c is the effective density of states, k is Boltzmann's constant, T is the temperature, and E_a is the activation energy for emission over the QW barriers. The exponential temperature dependence of G_u is expected to be far stronger than any temperature dependences of the other circuit parameters. A resonance in the circuit shown in Fig. 1(b) occurs when $G_u=2\pi f(C_u+C_d)$. For an admittance measurement at a fixed frequency f, this resonance will occur at a temperature $T=T_m$, at which a peak in the conductance and step in the capacitance as functions of temperature will be observed. The measurement frequency is related to the temperature at which resonance occurs by the expression

$$f=\alpha kT_m\exp(-E_a/kT_m), \tag{2}$$

where α is independent of temperature. An Arrhenius plot of $\ln(f/kT_m)$ vs $1/kT_m$ will, therefore, yield the activation energy, E_a.

As shown in the inset in Fig. 1(a), ΔE_c is related to the activation energy for an n-type structure by the expression[16]

$$\Delta E_c=E_a+E_f+E_1+\delta, \tag{3}$$

where E_1 is the energy of the first confined state in the well, E_f is the Fermi level relative to E_1, and δ is the barrier lowering due to tunneling. An analogous expression may be derived for the valence band. E_f is assumed to be temperature independent over the range of temperatures within which the conductance peaks occur and is calculated as the ratio of the two-dimensional carrier concentration and density of states.[16] It was estimated that the error introduced by this assumption did not exceed 5 meV. E_1 is calculated by solving Schrödinger's equation and Poisson's equation self-consistently. δ has generally been found to be extremely small (<3 meV),[14,16,17] and is, therefore, ignored in these calculations.

III. RESULTS

We first examined several p-type $Si/Si_{1-x}Ge_x$ heterostructures to verify the validity of the measurement technique. Valence-band offsets measured for these $Si/Si_{1-x}Ge_x$ structures were found to be in excellent agreement with accepted values.[17,18] 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 a p-type $Si/Si_{0.79}Ge_{0.206}C_{0.004}$ MQW structure; the conductance peaks and capacitance steps arising from temperature-dependent thermionic emission from the quantum wells are clearly observed on top of a background arising from leakage currents. Figure 3 [curve (a)] shows an Arrhenius plot of f and T_m, from which an activation energy of 98 ± 10 meV is obtained. The confinement energy of the lowest hole level, E_1, was calculated to be 11 ± 1 meV, and the Fermi energy, E_f, calculated in the manner described above, was found to be 9 ± 5 meV above the first confined state. Combining these values yields a value for ΔE_v of 118 ± 12 meV. Similar measurements on the p-type

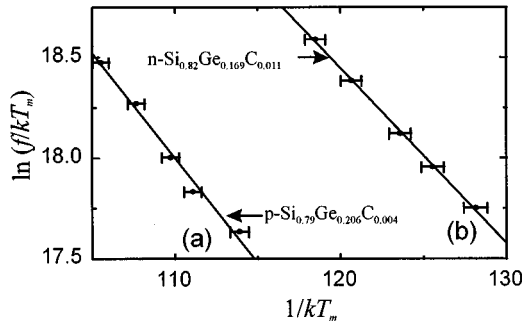

FIG. 3. Arrhenius plots of frequency (f) and the temperatures at which the conductance peaks occur (T_m) for (a) p-$Si/Si_{0.79}Ge_{0.206}C_{0.004}$, and (b) n-$Si/Si_{0.82}Ge_{0.169}C_{0.011}$.

$Si/Si_{0.595}Ge_{0.394}C_{0.011}$ MQW structure yielded a value for ΔE_v of 223 ± 20 meV. The C concentrations determined by x-ray diffraction and SIMS for these samples were in very close agreement, indicating that the C in this sample was mostly substitutional. Information is not currently available on the presence of traps in these structures, but comparison of the admittance spectra of the $Si/Si_{1-x}Ge_x$ samples to the $Si/Si_{1-x-y}Ge_xC_y$ samples provides evidence that the peak observed is due to thermal activation of carriers over the barriers.

Admittance measurements were then performed on an n-type $Si/Si_{0.82}Ge_{0.169}C_{0.011}$ MQW sample to determine ΔE_c. The C concentrations in this sample determined by x-ray diffraction and by SIMS were 1.1% and 2.7%, respectively, indicating that a significant fraction of the C was incorporated nonsubstitutionally. Although this nonsubstitutional C could influence the electronic properties of the sample, overall structural quality determined by x-ray diffraction and TEM was good, and SIMS and TEM both indicate that the C concentration is uniform throughout the alloy layers in the structure. Figure 4 shows the conductance and capacitance for this sample measured as a function of temperature at various frequencies, displaying the peaks arising from thermal activation of carriers over the barriers, with an activation energy of 91 ± 9 meV. Preliminary deep-level transient spectroscopy measurements on this structure suggest

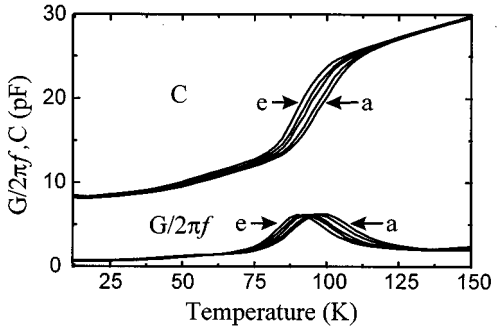

FIG. 4. Capacitance and conductance of an n-type $Si/Si_{0.82}Ge_{0.169}C_{0.011}$ MQW structure as a function of temperature for (a) 1 MHz, (b) 800 kHz, (c) 600 kHz, (d) 500 kHz, and (e) 400 kHz.

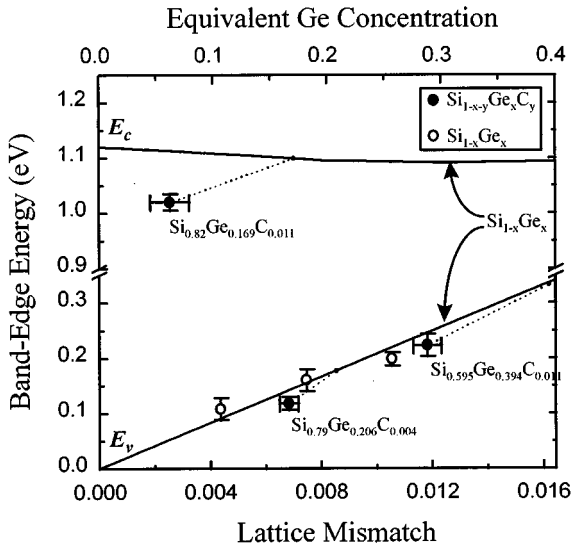

FIG. 5. Valence- and conduction-band-edge energies as a function of lattice mismatch and equivalent Ge concentration for $Si_{1-x}Ge_x$ (open circles) and $Si_{1-x-y}Ge_xC_y$ (closed circles) determined using our measured band offset values. The solid lines represent interpolated band-edge energies for $Si_{1-x}Ge_x$, and the dotted lines indicate the effect of C incorporation into a $Si_{1-x-y}Ge_xC_y$ alloy with fixed Ge concentration.

the presence of several deep levels at least 230 meV below E_c, but in concentrations not exceeding $\sim3\times10^{15}$ cm^{-3}. At measurement parameters corresponding to the resonance in the admittance spectra, no traps were observed to a sensitivity of $\sim2\times10^{13}$ cm^{-3}, implying this resonance is due to thermal activation over the barriers. Using the activation energy derived from the conductance peaks, a value for ΔE_c of 100 ± 11 meV is obtained.

IV. DISCUSSION

Comparisons of our measured $Si/Si_{1-x-y}Ge_xC_y$ band offset values with reported results for the change in the total energy band gap, ΔE_g, of 21–26 meV/%C for $Si_{1-x-y}Ge_xC_y$, compressively strained to Si(001),[7–10] indicate that the band alignment for our samples is type I, and furthermore, 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 measurement of ΔE_c with a value for ΔE_g of 23.5 ± 2.5 meV/%C, we would expect the values of ΔE_v for the $Si/Si_{0.79}Ge_{0.206}C_{0.004}$ and the $Si/Si_{0.595}Ge_{0.394}C_{0.011}$ samples to be 132 ± 11 and 219 ± 12 meV, respectively. In comparison to our measured values of 118 ± 12 and 223 ± 20 meV, respectively, these numbers are, to within the error, in very close agreement. Figure 5 shows conduction- and valence-band-edge energies for $Si_{1-x}Ge_x$ and $Si_{1-x-y}Ge_xC_y$ as determined from our band offset measurements. As shown in Fig. 5, incorporation of C in $Si_{1-x-y}Ge_xC_y$ decreases both the conduction-band-edge and the valence-band-edge energies compared to those for pure $Si_{1-x}Ge_x$, while increasing the total energy band gap as compared to $Si_{1-x}Ge_x$ with the same Ge concentration. The

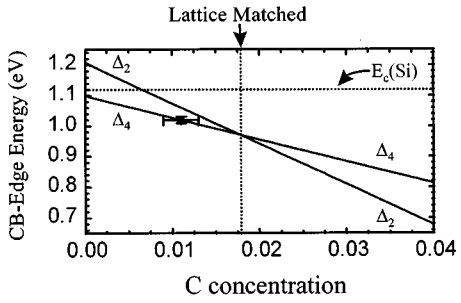

FIG. 6. Extrapolation of Δ_2 and Δ_4 conduction-band-edge energies to larger C concentrations for 16.9% Ge. Substantial conduction-band offsets may be achievable for heterostructures that are lattice matched or under tensile strain.

lowering of the band-edge energies is greater in both cases than that expected from strain compensation alone, suggesting that the compositional influence of C on the electronic structure of $Si_{1-x-y}Ge_xC_y$ is significant.

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.[19] Using this approach, which systematically separates the compositional or ''alloy'' contribution from 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[20] and photoluminescence[21] measurements. Figure 6 shows our extrapolated conduction-band-edge energies for $Si_{1-x-y}Ge_xC_y$. As shown in Fig. 6, our estimates suggest that values for ΔE_c of $\sim$200 meV or higher appear to be attainable in $Si/Si_{1-x-y}Ge_xC_y$ heterostructures coherently strained to Si(001) for C concentrations of $\sim$3%. $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions may, therefore, 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. In the valence band, extrapolations to higher C concentrations are somewhat problematic because the low C concentration for which we have measured ΔE_v tends to result in large uncertainties at higher concentrations.

V. CONCLUSION

In conclusion, we have used admittance spectroscopy to measure both ΔE_c and ΔE_v for $Si/Si_{1-x}Ge_x$ and $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions. These measurements have shown that incorporation of C into $Si_{1-x-y}Ge_xC_y$ lowers both the conduction- and valence-band-edge energies, while increasing the total band gap, as compared to $Si_{1-x}Ge_x$. This increase in the band gap is consistent with previously reported values for ΔE_g in $Si_{1-x-y}Ge_xC_y$ for the range of compositions we have measured. Moreover, our measured value for ΔE_c is in excellent agreement with previously reported ΔE_c values for $Si/Si_{1-y}C_y$, and in addition, suggests that significant conduction-band offsets may be achievable for $Si/Si_{1-x-y}Ge_xC_y$ heterostructures with C concentrations of $\sim$3%, providing a possible alternative to $Si/Si_{1-x}Ge_x$ heterostructures grown on strain-relaxed $Si_{1-x}Ge_x$ buffer layers for fabricating *n*-type heterostructures.

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