Band offsets in $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions measured by admittance spectroscopy

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We have used admittance spectroscopy to measure conduction-band and valence-band offsets in $Si/Si_{1-x}Ge_x$ and $Si/Si_{1-x-y}Ge_xC_y$ heterostructures grown by solid-source molecular-beam epitaxy. Valence-band offsets measured for $Si/Si_{1-x}Ge_x$ heterojunctions were in excellent agreement with previously reported values. Incorporation of C into $Si_{1-x-y}Ge_xC_y$ lowers the valence- and conduction-band-edge energies compared to those in $Si_{1-x}Ge_x$ with the same Ge concentration. 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 indicate 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 Institute of Physics.*
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Extensive research in recent years on $Si/Si_{1-x}Ge_x$ heterostructure materials and devices has led to dramatic improvements in functionality and 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, impressive 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, and leads to the possibility of fabricating Group IV heterostructure devices lattice matched to Si.[1–6] Effective design, fabrication, and characterization of such devices, however, requires the accurate measurement of the energy band offsets in $Si/Si_{1-x-y}Ge_xC_y$ heterojunctions.

In this letter we present admittance spectroscopy measurements of 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 were grown by solid-source molecular-beam epitaxy on Si (100) conducting substrates and consisted 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 $7.4\times10^{16}-1\times10^{17}$ cm^{-3}. Either n-type (Sb doped) or p-type (B doped) structures were used for measurement of, respectively, ΔE_c or ΔE_v. These heterostructures were grown at 450 °C on 2000 Å Si buffer layers. The 1.1% C samples were grown using Sb as a surfactant to improve structural quality.[7] In all cases the thickness of the MQW structure was below the critical thickness for strain relaxation.[8] 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 300 μm in diameter, followed by a mesa etch in a CF_4/O_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.[9–11] 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 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:

$$G_u=\frac{q^2A\nu_{th}(T)N_c(T)}{2kT}\exp\left(-\frac{E_a}{kT}\right), \quad (1)$$

where q is the electron charge, A is the device area, $\nu_{\rm th}$ 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

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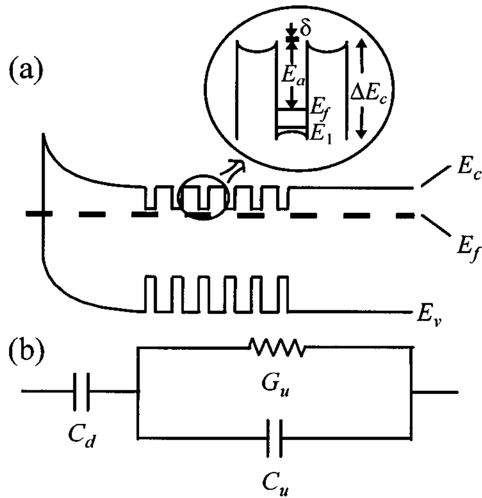

FIG. 1. (a) Energy band diagram for an n-type multiple quantum well (MQW) heterostructure. The Fermi level (E_f), the first confined state (E_1), and the barrier lowering due to tunneling (δ) are added to the activation energy (E_a) to obtain the band offset (ΔE_c). (b) Equivalent circuit model of a Schottky barrier on a MQW 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).

E_a is the activation energy for emission over the QW barriers. The temperature dependence of G_u is expected to be far stronger than any temperature dependencies 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

$$f = \alpha k T_m \exp(-E_a/kT_m) \quad (2)$$

where α is independent of temperature. A 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:[12]

$$\Delta E_c = E_a + E_f + E_1 + \delta \quad (3)$$

where E_f is the Fermi level, E_1 is the energy of the first confined state in the well, 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 for which the peaks occur and is calculated as the ratio of the two-dimensional carrier concentration and density of states.[12] 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),[10,12,13] and is therefore ignored in these calculations.

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.[13,14] Admittance measurements were then performed on various $Si/Si_{1-x-y}Ge_xC_y$ heterostructures. Figure 2 shows the conductance and capacitance

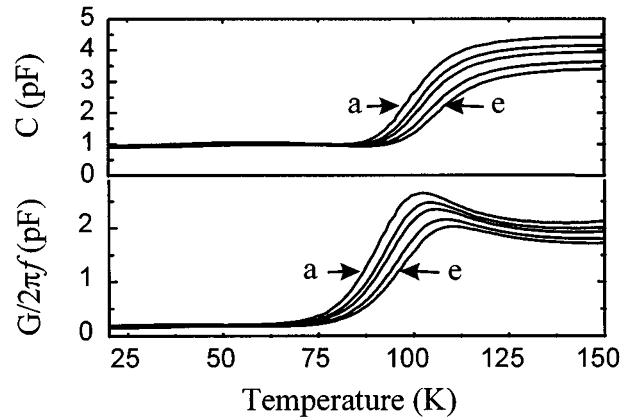

FIG. 2. Capacitance and conductance of a p-type $Si/Si_{0.79}Ge_{0.206}C_{0.004}$ MQW structure as functions of temperature for (a) 1 MHz, (b) 800 kHz, (c) 600 kHz, (d) 500 kHz, (e) 400 kHz.

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. E_1 and E_f were calculated and found to be 11 ± 1 and 9 ± 5 meV, respectively. Combining these values yields a value for ΔE_v of 118 ± 12 meV. The C concentrations determined by x ray and SIMS for this sample were in very close agreement, indicating that the C in this sample was mostly substitutional. Similar measurements on the p-type $Si/Si_{0.595}Ge_{0.394}C_{0.011}$ heterostructure yielded a value for ΔE_v of 223 ± 20 meV.

Admittance measurements were also performed on an n-type $Si/Si_{0.82}Ge_{0.169}C_{0.011}$ MQW sample to determine ΔE_c. The C concentration in this sample determined by x-ray diffraction and by SIMS was 1.1% and 2.7%, respectively, indicating the presence of a significant amount of nonsubstitutional C. Although this nonsubstitutional C could influence the electronic structure of the sample, structural quality determined by XRD and TEM was high, and SIMS and TEM both indicate that the C concentration is uniform throughout the alloy layers in the structure. Admittance mea-

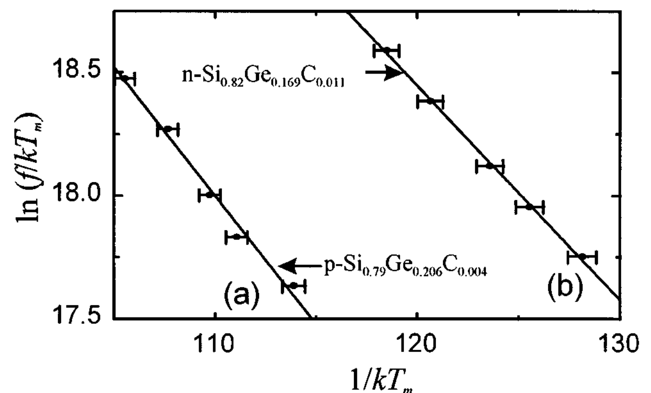

FIG. 3. Arrhenius plots of frequency (f) and the temperatures at which the conductance peaks (T_m) for: (a) p-$Si/Si_{0.79}Ge_{0.206}C_{0.004}$, and (b) n-$Si/Si_{0.82}Ge_{0.169}C_{0.011}$.

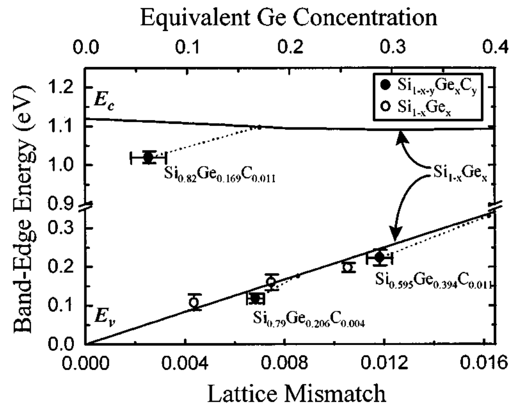

FIG. 4. Summary of measured valence- and conduction-band-edge energies measured as a function of lattice mismatch and equivalent Ge concentration for $Si_{1-x}Ge_x$ (open circles) and $Si_{1-x-y}Ge_xC_y$ (closed circles). The solid lines represent interpolated band-edge energies for $Si_{1-x}Ge_x$, while the dotted lines indicate the effect of C incorporation into $Si_{1-x-y}Ge_xC_y$ with fixed Ge concentration.

surements on this structure yielded an activation energy of 91 ± 8 meV corresponding to a value for ΔE_c of 100 ± 11 meV. DLTS displayed no traps at this activation energy to a sensitivity of $\sim2\times10^{13}$ cm^{-3}, suggesting this resonance arises from thermal activation of carriers over the barriers.

Comparison of our measured $Si/Si_{1-x-y}Ge_xC_y$ band offset values with reported values[15–18] for the change in total band gap, ΔE_g, of 21–26 meV/%C, for $Si_{1-x-y}Ge_xC_y$ compressively strained to Si (001) indicates 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 4 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 the figure, incorporation of C in $Si_{1-x-y}Ge_xC_y$ decreases both the conduction-band and the valence-band edge energies compared to those for pure $Si_{1-x}Ge_x$, while increasing the band gap. The lowering of the band-edge energies is greater in both cases than that expected from strain compensation alone, suggesting that the ''chemical'' 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 compositions using the model-solid approach.[19] Using this approach, we have confirmed that our measured value of ΔE_c is in agreement with estimates of the $Si/Si_{1-y}C_y$ band offset obtained from electrical[20] and photoluminescence[21] measurements. Furthermore, our estimates suggest that values for ΔE_c of ~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 $\sim3\%$. $Si/Si_{1-x-y}Ge_xC_y$ 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 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 in $Si_{1-x-y}Ge_xC_y$ 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 $\sim3\%$.

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