We have used admittance spectroscopy to measure conduction-band and valence-band offsets in Si/Si$_{1-x-y}$Ge$_x$C$_y$ heterostructures grown by solid-source molecular-beam epitaxy. Valence-band offsets measured for Si/Si$_{1-y}$Ge$_y$ heterojunctions were in excellent agreement with previously reported values. Incorporation of C into Si$_{1-x-y}$Ge$_x$C$_y$ lowers the valence- and conduction-band-edge energies compared to those in Si$_{1-y}$Ge$_y$ 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$_x$C$_y$ 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.

Extensive research in recent years on Si/Si$_{1-y}$Ge$_y$ 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$_{1-y}$Ge$_y$ heterostructures. Recently, impressive progress has been made in the growth and characterization of Si$_{1-x-y}$Ge$_x$C$_y$ alloys. 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$_x$C$_y$ heterojunctions.

In this letter we present admittance spectroscopy measurements of both conduction-band and valence-band offsets, $\Delta E_c$ and $\Delta E_v$, respectively, in Si/Si$_{1-x-y}$Ge$_y$ and Si/Si$_{1-x-y}$Ge$_x$C$_y$ 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$_{1-x-y}$Ge$_y$ or Si$_{1-x-y}$Ge$_x$C$_y$ alternating with 350 Å Si for ten periods with dopant concentrations of $7.4 \times 10^{16} - 1 \times 10^{17}$ cm$^{-3}$. Either n-type (Sb doped) or p-type (B doped) structures were used for measurement of, respectively, $\Delta E_c$ or $\Delta E_v$. 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. In all cases the thickness of the MQW structure was below the critical thickness for strain relaxation. 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. 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:

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

where $q$ is the electron charge, $A$ is the device area, $\nu_{th}$ 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
were then performed on various Si/Si$_{1-x}$Ge$_x$ structures to verify the validity of the measurement technique. Valence-band offsets measured for these structures to verify the validity of the measurement technique with accepted values. Admittance measurements were also performed on an n-type Si/Si$_{1-x}$Ge$_x$ heterostructure 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 $98 \pm 10$ meV is obtained. $E_1$ and $E_f$ were calculated and found to be $11 \pm 1$ and $9 \pm 5$ meV, respectively. Combining these values yields a value for $\Delta E_v$ of $118 \pm 12$ meV. The C concentration 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 $\Delta E_v$ of $223 \pm 20$ meV.

Admittance measurements were also performed on an n-type Si/Si$_{0.62}$Ge$_{0.169}$C$_{0.011}$ MQW sample to determine $\Delta E_c$. 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. 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 ($\delta$) are added to the activation energy ($E_a$) to obtain the band offset ($\Delta E_c$). (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

$$f = \alpha kT_m \exp\left(-\frac{E_a}{kT_m}\right)$$  

(2)

where $\alpha$ 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), $\Delta E_c$ is related to the activation energy for an n-type structure by the expression:

$$\Delta E_c = E_a + E_f + E_1 + \delta$$  

(3)

where $E_f$ is the Fermi level, $E_1$ is the energy of the first confined state in the well, and $\delta$ 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. $E_1$ is calculated by solving Schrödinger’s equation and Poisson’s equation self-consistently. $\delta$ has generally been found to be extremely small (< 3 meV), 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. Admittance measurements were then performed on various Si/Si$_{1-x}$Ge$_x$C$_y$ 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 $98 \pm 10$ meV is obtained. $E_1$ and $E_f$ were calculated and found to be $11 \pm 1$ and $9 \pm 5$ meV, respectively. Combining these values yields a value for $\Delta E_v$ of $118 \pm 12$ meV. The C concentration 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 $\Delta E_v$ of $223 \pm 20$ meV.

Admittance measurements were also performed on an n-type Si/Si$_{0.62}$Ge$_{0.169}$C$_{0.011}$ MQW sample to determine $\Delta E_c$. 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. 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.

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$_{0.62}$Ge$_{0.169}$C$_{0.011}$.
measurements on this structure yielded an activation energy of $91 \pm 8$ meV corresponding to a value for $\Delta E_c$ of $100 \pm 11$ meV. DLTS displayed no traps at this activation energy to a sensitivity of $\sim 2 \times 10^{13}$ cm$^{-3}$, suggesting this resonance arises from thermal activation of carriers over the barriers.

Comparison of our measured $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ band offset values with reported values$^{15-20}$ for the change in total band gap, $\Delta E_g$, of $21-26$ meV/%C, for $\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ 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 $\Delta E_g$ over the range of compositions for which we have measured the band offsets. Combining our measurement of $\Delta E_c$ with a value for $\Delta E_g$ of $23.5 \pm 2.5$ meV/%C, we would expect the values of $\Delta E_g$ for the $\text{Si}/\text{Si}_{0.79} \text{Ge}_{0.20} \text{C}_{0.004}$ and the $\text{Si}/\text{Si}_{0.39} \text{Ge}_{0.39} \text{C}_{0.011}$ samples to be $132 \pm 11$ and $219 \pm 12$ meV, respectively. In comparison to our measured values of $118 \pm 12$ and $223 \pm 20$ meV, respectively, these numbers are, to within the error, in very close agreement. Figure 4 shows conduction- and valence-band-edge energies for $\text{Si}_{1-x-y} \text{Ge}_x$ and $\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ as determined from our band offset measurements. As shown in the figure, incorporation of C in $\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ decreases both the conduction-band and the valence-band edge energies compared to those for pure $\text{Si}_{1-x-y} \text{Ge}_x$, 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 $\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ is significant.

We may extrapolate our measured band offsets to a wider range of Ge and C compositions using the model-solid approach.$^{21}$ Using this approach, we have confirmed that our measured value of $\Delta E_c$ is in agreement with estimates of the $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ band offset obtained from electrical$^{20}$ and photoluminescence$^{21}$ measurements. Furthermore, our estimates suggest that values for $\Delta E_c$ of $\sim 200$ meV or higher appear to be attainable in $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ heterostructures coherently strained to Si (001) for C concentrations of $\sim 3\%$. $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ heterojunctions may therefore provide an attractive alternative to $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x$ grown on strain-relaxed $\text{Si}_{1-x-y} \text{Ge}_x$ buffer layers for fabrication of n-type heterostructure devices.

In conclusion, we have used admittance spectroscopy to measure both $\Delta E_c$ and $\Delta E_g$ for $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x$ and $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ heterojunctions. These measurements have shown that incorporation of C in $\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ lowers both the conduction- and valence-band-edge energies, while increasing the total band gap, as compared to $\text{Si}_{1-x-y} \text{Ge}_x$. This increase in the band gap is consistent with previously reported values for $\Delta E_g$ in $\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ for the range of compositions we have measured. Moreover, our measured value for $\Delta E_c$ is in excellent agreement with previously reported $\Delta E_c$ values for $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x$, and in addition suggests that significant conduction-band offsets may be achievable for $\text{Si}/\text{Si}_{1-x-y} \text{Ge}_x \text{C}_y$ heterostructures with C concentrations of $\sim 3\%$.

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