Band offsets in Si/Si$_{1-x-y}$Ge$_x$C$_y$ heterojunctions measured by admittance spectroscopy

B. L. Stein and E. T. Yu
Department of Electrical and Computer Engineering, University of California San Diego, La Jolla, California 92093-0407

E. T. Croke and A. T. Hunter
Hughes Research Laboratories, Malibu, California 90265

T. Laursen, A. E. Bair, and J. W. Mayer
Center for Solid State Science, Arizona State University, Tempe, Arizona 85287-1704

C. C. Ahn
California Institute of Technology, Pasadena, California 91125

(Received 19 December 1996; accepted for publication 18 April 1997)

We have used admittance spectroscopy to measure conduction-band and valence-band offsets in Si/Si$_{1-x-y}$Ge$_x$ and 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$_x$ 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$_x$ 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$_x$C$_y$ and Si$_{1-x-y}$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 previous reports.

© 1997 American Institute of Physics.

Extensive research in recent years on Si/Si$_{1-y}$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$_{1-y}$Ge$_x$ heterostructures. Recently, impressive progress has been made in the growth and characterization of Si$_{1-x-y}$Ge$_x$C$_y$ alloys. Si$_{1-x-y}$Ge$_x$C$_y$ offers considerably greater flexibility, compared to that available in the Si/Si$_{1-y}$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. 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$_{1-y}$Ge$_x$ 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$_{1-y}$Ge$_x$ 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 Si:C 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:

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

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...
$E_a$ 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

$$f = \alpha kT \exp(-E_a/kT)$$

(2)

where $\alpha$ is independent of temperature. A plot of $\ln\left(f/kT\right)$ vs $1/kT$ 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 ($\lesssim 3$ 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$_{0.011}$ 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 $\Delta E_c$ of $118 \pm 12$ 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 $\Delta E_c$ of $223 \pm 20$ meV.

Admittance measurements were also performed on an $n$-type Si/Si$_{0.82}$Ge$_{0.169}$C$_{0.011}$ MQW sample to determine $\Delta E_c$. 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.
measurements on this structure yielded an activation energy of 91±8 meV corresponding to a value for $\Delta E_c$ of 100±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 Si/Si$_{1-x-y}$Ge$_{x}$C$_y$ band offset values with reported values$^{15-18}$ for the change in total band gap, $\Delta E_g$, of 21–26 meV/%C, for Si$_{1-x-y}$Ge$_x$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 ± 2.5 meV/%C, we would expect the values of $\Delta E_v$ 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$_{1-x-y}$Ge$_x$ and Si$_{1-x-y}$Ge$_x$C$_y$ as determined from our band offset measurements. As shown in the figure, incorporation of C in Si$_{1-x-y}$Ge$_x$C$_y$ decreases both the conduction-band and the valence-band edge energies compared to those for pure Si$_{1-x-y}$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$_x$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.$^{19}$ Using this approach, we have confirmed that our measured value of $\Delta E_c$ is in agreement with estimates of the Si/Si$_{1-x-y}$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 Si/Si$_{1-x-y}$Ge$_x$C$_y$ heterostructures coherently strained to Si (001) for C concentrations of $\sim 3\%$. Si/Si$_{1-x-y}$Ge$_x$C$_y$ 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 $\Delta E_c$ and $\Delta E_v$ for Si/Si$_{1-x}$Ge$_x$ and Si/Si$_{1-x-y}$Ge$_x$C$_y$ heterojunctions. These measurements have shown that incorporation of C in Si$_{1-x-y}$Ge$_x$C$_y$ 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 $\Delta E_g$ in Si$_{1-x-y}$Ge$_x$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 Si/Si$_{1-x}$Ge$_x$, and in addition suggests that significant conduction-band offsets may be achievable for Si/Si$_{1-x-y}$Ge$_x$C$_y$ heterostructures with C concentrations of $\sim 3\%$.

The authors would like to acknowledge support from DARPA MDA972-95-3-0047 for work at UCSD, HRL, and ASU, and from ONR Grant No. N00014-95-1-0996 for work at UCSD. B.L.S. and E.T.Y. would also like to thank S. S. Lau for part of the equipment used in this work.