

The effect of carbon on the valence band offset of compressively strained $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/(100)$ Si heterojunctions

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Capacitance–voltage measurements have been used to study the effect of carbon on the valence band offset of compressively strained $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/(100)$ Si heterojunctions grown by rapid thermal chemical vapor deposition with substitutional C levels from 0% to 2.5%. The valence band offset between $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ and unstrained (100) Si decreases at a rate of 20–26 meV per % C. Our work indicates that the change in the bandgap of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ as carbon is added is entirely accommodated in the valence band. © 1997 American Institute of Physics. [S0003-6951(97)00512-3]

The strain in pseudomorphic $\text{Si}_{1-x}\text{Ge}_x$ layers on (100) Si substrates and resulting critical thickness imposes a severe limit on the engineering of Si-based heterostructures. It has been shown that the addition of carbon to form pseudomorphic $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys reduces the strain, with each C atom compensating the strain of 8–10 Ge atoms.^{1,2} Photoluminescence (PL) measurements on $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ as well as transport studies of heterojunction bipolar transistors (HBTs) with $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ as the base showed that the addition of 1% C increases the band gap of $\text{Si}_{1-x}\text{Ge}_x$ by 21–26 meV.^{3–5} However, reducing the strain in $\text{Si}_{1-x}\text{Ge}_x$ by adding C increases the band gap less than does reducing the strain by merely removing Ge. These results imply that, for a given band gap, $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ has less misfit strain and therefore allows a greater critical thickness than does $\text{Si}_{1-x}\text{Ge}_x$. To date, however, the relative effect of the C on the valence band and/or conduction band has not been extensively studied. In this letter, we report the complete measurement of the valence band offset of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/(100)$ Si as a function of C concentration by capacitance–voltage technique and admittance spectroscopy. We also report a substitutional C level of 2.5% in single $\text{Si}_{1-x}\text{Ge}_x$ films grown by rapid thermal chemical vapor deposition (RTCVD).

The capacitance–voltage measurements were performed on p^+ $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/p^-$ Si unipolar diodes grown by RTCVD at a chamber pressure of 6 Torr. Dichlorosilane ($\text{Si}_2\text{H}_2\text{Cl}_2$), germane (GeH_4), and methylsilane (SiCH_3) were used as the precursors of Si, Ge, and C, respectively. The flow rates were 26 sccm for dichlorosilane, 1–4.5 sccm for germane, and 0–0.35 sccm for methylsilane, in a H_2 carrier, resulting in $[\text{Ge}] = 20\%–39.5\%$, and $[\text{C}] = 0\%–2.5\%$. All $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers were *in situ* doped with diborane. In each sample, a p^+ Si layer with doping in the range of 3×10^{19} to $6 \times 10^{19}/\text{cm}^3$ was first grown at 1000 °C on a p^- Si substrate for use as a bottom contact, followed by the deposition of p^- Si layers with thickness around 250 ± 50 nm. The p^- Si layer was not intentionally doped by a diborane flow, but was doped by the boron outdiffusion from bottom contact layer during high temperature growth as well as background doping caused by residual boron inside the chamber after the growth bottom contact layers.

$\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers were then deposited with a growth temperature between 575 and 625 °C. A 1-nm-thick undoped $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layer was first deposited as a precaution of preventing heavily doped boron from diffusing to p^- Si layers followed by p^+ $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ (~ 20 nm) with dopings ranging from 6×10^{18} to $4 \times 10^{19}/\text{cm}^3$. The diodes were created by the plasma etching of mesas ($320 \times 180 \mu\text{m}^2$) followed by Ti/Al metallization.

Figure 1 shows the (400) x-ray diffraction (XRD) performed on the strained $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers with 39.5% Ge and various C concentrations. The concentration of Ge was obtained by measuring the no-carbon XRD peak relative to that of Si substrate. This value is consistent with the Ge concentration obtained by PL measurements. As C is added, the peak starts shifting toward the Si peak, indicating decreased lattice constant, i.e., reduced strain. Broad peaks of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ are an indication of Scherer broadening in the thin films which becomes more prominent as more C is added, qualitatively consistent with an assumed reduction in growth rate as C is added. High resolution transmission electron microscopy (HRTEM) performed on the $\text{Si}_{0.593}\text{Ge}_{0.395}\text{C}_{0.012}$ sample shows good interface quality and no evidence of dislocations or SiC precipitates. The measured thickness of the $\text{Si}_{0.593}\text{Ge}_{0.395}\text{C}_{0.012}$ layer is 21 nm. As-

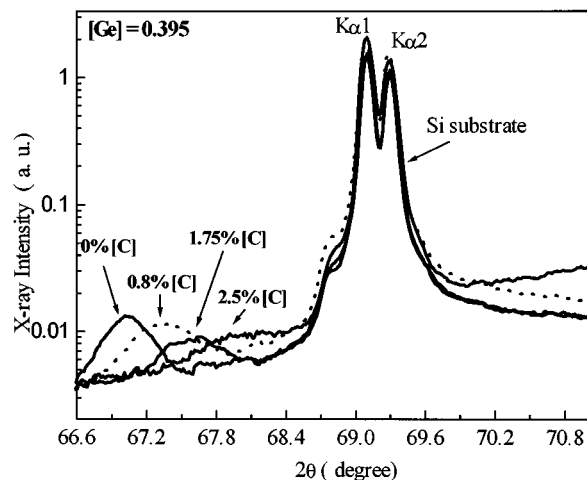


FIG. 1. (004) x-ray diffraction spectra for $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ thin films on Si(001). Two Si substrate peaks are due to Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ x-ray lines. Broad $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ peaks are due to Scherer broadening in thin films.

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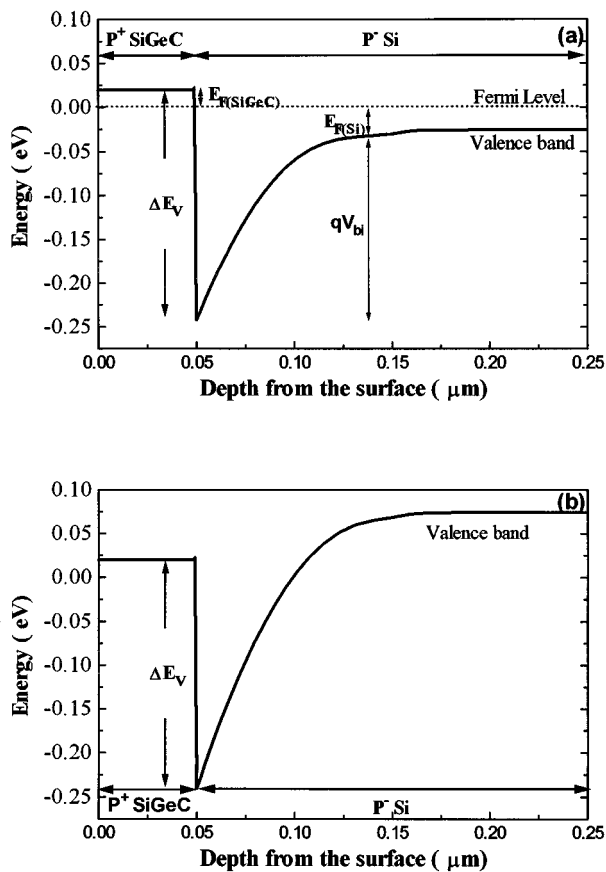


FIG. 2. (a) Zero-bias valence band diagram of $p^+ \text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/p^- \text{Si}$ diode. (b) Reverse-biased (-0.1 V) valence band diagram of $p^+ \text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/p^- \text{Si}$ diode.

suming that the Ge content was unchanged by the addition of methylsilane at constant germane flow, the substitutional C content was quantified by measuring the relative shift of the XRD peak of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers with respect to that of $\text{Si}_{1-x}\text{Ge}_x$, assuming a Ge:C strain compensation ratio of 8.3.² A substitutional C level of up to 2.5% was measured. To the best knowledge of the authors, this is the highest single crystal value reported to date by chemical vapor deposition (CVD).

Under reverse bias ($V_{\text{SiGeC}} > V_{\text{Si}}$), the valence band offset (ΔE_V) between $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ and Si blocks hole current from $p^+ \text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$, so that the device rectifies at low temperature. Shown in Fig. 2 are the zero biased and reverse biased valence band diagrams. $E_{F(\text{SiGeC})}$ is the position of Fermi level relative to the valence band of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$, V_{bi} is the built-in voltage of the junction, $E_{F(\text{Si})}$ is the position of the valence band of Si relative to the Fermi level. In theory, ΔE_V may be measured by temperature dependence of the leakage current which is ideally from thermionic emission of holes from $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ into Si. However, the leakage current for the entire device can be easily dominated by nonideal sources at a few local defects, edge effects, depletion region generation, etc. Therefore, to measure the band offset, we used a capacitance-voltage technique, which is less affected by local defects and leakage currents. We found that capacitance-voltage measurements were more repeatable from sample to sample and had far less scatter among

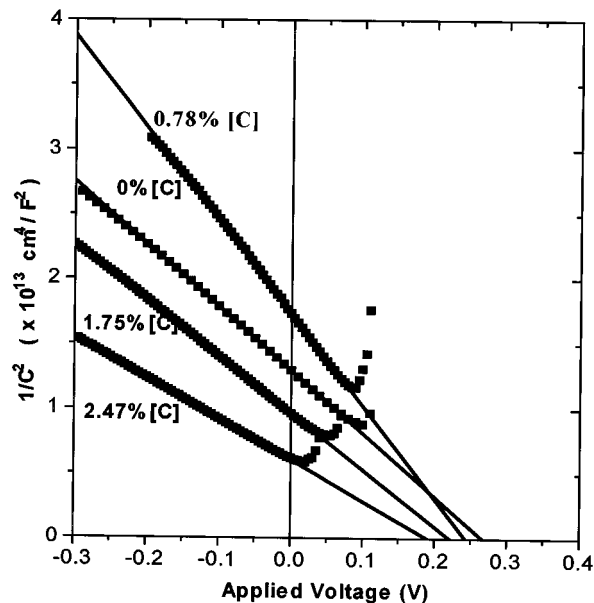


FIG. 3. $1/C^2$ is plotted against voltage for $p^+ \text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/p^- \text{Si}$ with $x=0.395$ and different C concentrations.

devices on the same wafer than leakage current measurements.⁶ The capacitances were measured as a function of reverse bias at 100 K with an ac frequency from 10 kHz to 4 MHz, and an ac amplitude at 25–50 mV. Much like a Schottky barrier or a one-sided p - n junction, the capacitance per unit area C is given by⁷

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{q\epsilon N_A},$$

where V is the dc bias and N_A is the doping concentration on the Si side of the heterojunction. By plotting $1/C^2$ versus applied dc voltage, the doping level on the $p^- \text{Si}$ side as well as built-in potential of the junction can be obtained. Figure 3 shows the capacitance-voltage characteristics of the samples containing 39.5% Ge and various C contents. The $1/C^2$ - V data points are linear over the range of applied voltages, and the extracted Si doping concentrations are in the range of $10^{17}/\text{cm}^3$. The variation of the doping level among samples was due to the variation in the doping level of bottom contact layers and background doping. Spreading resistance measurement was performed on one of the samples and the measured doping concentration is consistent with that obtained by $1/C^2$ - V data. It is also noted that the slope and intercept were not affected by ac amplitude used in this study (25–50 mV), and the data shown in Fig. 3 were measured with ac amplitude equal to 30 mV. Based on the doping level, we calculated $E_{F(\text{Si})}$ at 100 K in each sample. The extrapolated built-in voltages decrease as more C is added. $E_{F(\text{SiGeC})}$ was obtained by a straightforward calculation from the doping concentrations in the $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$, which were measured by secondary ion mass spectroscopy (SIMS) on similarly grown layers, and by assuming an effective mass independent of C level. SIMS measurements show that the boron incorporation in $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ does not depend on the C level for a given diborane flow.

ΔE_V was calculated by combining qV_{bi} , $E_{F(\text{SiGeO})}$, and $E_{F(\text{Si})}$, as illustrated in Fig. 2(a). There is a consistent de-

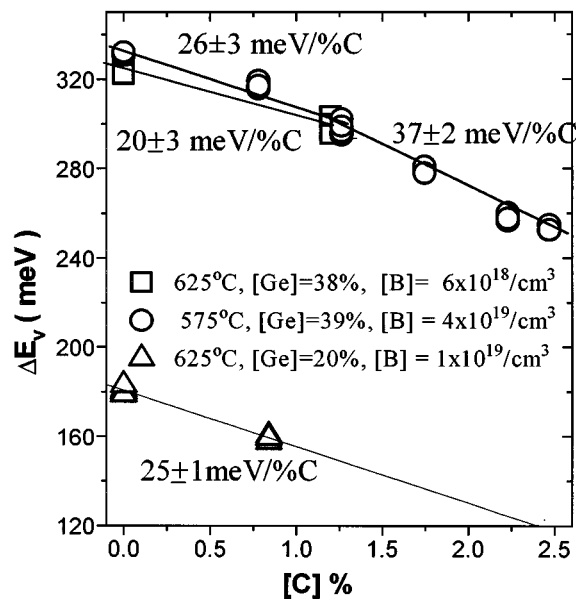


FIG. 4. $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ valence band offset to Si as a function of substitutional C content for different dopings, Ge concentration, and growth temperature. The lines are the best linear fits over the range of 0–1.3% C, and 1.3%–2.5% C.

crease in the valence band offset of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ as C is added, as shown in Fig. 4. Growth temperature, dopings, and Ge level have no significant effect on the effect of C on ΔE_v . The observed dependence for the three samples plotted are 25 ± 1 meV/%C, 20 ± 1 meV/%C, and 26 ± 3 meV/%C for lines fitted to data points up to 1.3%. For the one series with 2.5% C, the slope is somewhat larger from 1.3% to 2.5% C (37 ± 2 meV/%C). It is not known if this change in slope is significant (e.g. bowing in curve of bandgap versus lattice constant) or not. We also found that the *absolute* ΔE_v measured by the capacitance–voltage technique varied slightly with different ac frequencies (within 15 meV from 10 kHz to 1 MHz). However, the *change* of ΔE_v with C at a given frequency was negligibly influenced by the measurement frequency (< 4 meV/%C). Comparison to the total band gap change of 21–26 meV (measured up to 1% C) indicates that all of the change in band gap as C is added to strained $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ is accommodated in the valence band within experimental results.

Previously reported measurements of $W/\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ Schottky diodes⁸ indicated that the Schottky barrier to *p*-type $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ (Φ_{B_p}) increased ~ 240 meV/%C for $y \leq 0.007$, and the barrier to *n*-type $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ (Φ_{B_n}) was independent of x and y , implying a ΔE_g of 240 meV/%C, inconsistent with our results. It is possible that interface states at the metal/semiconductor interface cause Schottky barrier results to be substantially different than the offsets measured in our samples. Eberl *et al.*⁹ also reported PL spectra from multiple $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ quantum wells with 16% Ge and various C concentrations. Their results are consistent with ours for $y \leq 0.008$, but for $0.008 < y < 0.015$ they imply an increase of the valence band offset of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/(100)$ Si as the C level is raised, inconsistent with our work. The difference may be due to the higher Ge concentrations in our work, or due to the fact that the near

strain-free condition in their $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ films alters the band alignment.

The valence band offset was also measured in a few cases by complex admittance spectroscopy measurements from 100 kHz to 4 MHz as a function of temperature. From the temperature dependence of the conductance, the band offset may be obtained. This technique has previously been applied on $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ structures.¹⁰ Our structures were similar, except that Al/Ti Schottky diodes were used instead of *p*-*n* junction to provide the surface depletion. Measurements showed a 39 meV reduction in valence band offset for 1.6% C in the case of 33% Ge, corresponding to 25 meV/%C,¹¹ in good agreement with results obtained by capacitance–voltage technique. We point out, however, that, this method fundamentally assumes that the zero-bias small signal conductance of $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ (or $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$) heterojunction scales ideally as $\exp(-E_v/kT)$. The small signal conductance, like leakage current, can also be dominated by local defects and layer quality. Therefore, we feel the capacitance–voltage technique is inherently more reliable for band offset measurements.

In summary, we have shown that the valence band offset of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{unstrained (100) Si}$ decreases by 20–26 meV for the first percent of C, for films which are still substantially compressively strained, with slightly stronger result up to 2.5% C. The resulting band structure with large ΔE_v and negligible ΔE_c is similar to that of pseudomorphic $\text{Si}_{1-x}\text{Ge}_x$ on (100) Si. Admittance spectroscopy measurement gives good agreement. We have also demonstrated that, by RTCVD, as much as 2.5% substitutional C can be incorporated into the single crystal $\text{Si}_{1-x}\text{Ge}_x$ layers.

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