Direct optical measurement of the valence band offset of $p^+ Si_{1-x-y}Ge_xC_y/p^- Si(100)$ by heterojunction internal photoemission

C. L. Chang,[a)] L. P. Rokhinson, and J. C. Sturm

Department of Electrical Engineering, Center for Photonics and Optoelectronic Materials, Princeton University, Princeton, New Jersey 08544

Optical absorption measurements have been performed to study the effect of substitutional carbon on the valence band offset of compressively strained $p^+ Si_{1-x-y}Ge_xC_y/(100) p^- Si$. The compressively strained $p^+ Si_{1-x-y}Ge_xC_y/(100) p^- Si$ heterojunction internal photoemission structures were grown by rapid thermal chemical vapor deposition with substitutional carbon levels up to 2.5%. Carbon decreased the valence band offset by 26 ± 1 meV/% substitutional carbon. Based on previous reports of the effect of carbon on the band gap of $Si_{1-x-y}Ge_xC_y$, our work suggests that the effect of carbon incorporation on the band alignment of compressively strained $Si_{1-x-y}Ge_xC_y/Si$ is to reduce the valence band offset, with a negligible effect on the conduction band alignment. © *1998 American Institute of Physics.* [S0003-6951(98)04150-3]

Strained $Si_{1-x}Ge_x/Si$ heterostructures have been extensively studied and have led to many device applications. The advantage of using strained $Si_{1-x}Ge_x/Si$ heterostructures results from the flexibility in band gap engineering by controlling the amount of incorporated Ge into Si matrix. However, due to the 4% larger lattice constant of Ge than that of Si, the strain involved in $Si_{1-x}Ge_x$ prevents one from growing a thick $Si_{1-x}Ge_x$ layer on a Si substrate without introducing misfit dislocations. Recently $Si_{1-x-y}Ge_xC_y$ has attracted strong interest due to the ability of substitutional carbon to compensate the strain caused by Ge atoms, with 1% substitutional carbon compensating the strain caused by 8%–10% Ge.[1−6] Up to 2.5% substitutional carbon in Si and $Si_{1-x}Ge_x$ have been reported, even though the equilibrium solubility of carbon in Si is only 0.01%.[7,8]

Photoluminescence (PL) studies and electrical measurements on pseudomorphic compressively strained $Si_{1-x-y}Ge_xC_y$ on Si (100) show that 1% C increases the band gap of $Si_{1-x-y}Ge_xC_y$ alloys by 21–26 meV.[9−12] Given only a slight increase of band gap by C incorporation, a strained $Si_{1-x-y}Ge_xC_y$ layer would have a smaller band gap than that of an equally strained $Si_{1-x}Ge_x$ layer.[9] Alternatively, for the same band gap reduction from Si, pseudomorphic $Si_{1-x-y}Ge_xC_y$ would have less strain and a higher critical thickness than $Si_{1-x}Ge_x$.

Although it is generally agreed that 1% carbon increases band gap by 21–26 meV, it is still under debate regarding how this band gap increase is allocated in the conduction and valence band alignments of $Si_{1-x-y}Ge_xC_y$ to the Si substrate. Generally, the valence band offset of $Si_{1-x-y}Ge_xC_y/Si$ has been studied. A temperature-dependent leakage current study on $p^+ Si_{1-x-y}Ge_xC_y/p^- Si$ unipolar diodes indicated that carbon decreased the valence band offset (ΔE_v) of the resulting $Si_{1-x-y}Ge_xC_y/Si$ heterostructure.[13] However, no accurate quantitative number was extracted due to scatter in data among devices caused by

strong dependence of leakage current on local defects. Capacitance–voltage ($C-V$) measurement, on the other hand, has demonstrated a clear downward trend of ΔE_v of $Si_{1-x-y}Ge_xC_y/Si$ by carbon incorporation with minimal scatter of data among devices, and is insensitive to nonideal leakage current. These measurements indicated that the increase in band gap by carbon is fully accommodated in the valence band, with ΔE_v to Si decreasing by 20–26 meV/% substitutional carbon for small carbon concentrations.[7,14] Similar results were also obtained from $C-V$ analysis of $Si_{1-x-y}Ge_xC_y$ based metal-oxide-semiconductor (MOS) structures.[15] Moreover, x-ray photoelectron spectroscopy (XPS) measurement on $Si_{1-x-y}Ge_xC_y/Si$ indicated no significant change in ΔE_v with C incorporation (accuracy limit ± 30 meV).[16] Conflicting results have also been reported. The XPS study on the $Si_{1-x-y}Ge_xC_y/Si$ with high Ge content determined that carbon increased the ΔE_v by ~50 meV/%C.[17] Admittance spectroscopy on $Si_{1-x-y}Ge_xC_y/Si$ multiquantum wells suggested a large effect by carbon (~80 meV/%C) on both the conduction and valence band offset of $Si_{1-x-y}Ge_xC_y/Si$.[18]

Given conflicting reports, it is therefore necessary to have a direct optical measurement on the band offset in $Si_{1-x-y}Ge_xC_y/Si(100)$ heterostructures. In this letter, we report such a measurement by heterojunction internal photoemission (HIP) on the valence band offset of $p^+ Si_{1-x-y}Ge_xC_y/p^- Si$ structures to determine ΔE_v of $Si_{1-x-y}Ge_xC_y/Si$. The samples in this study contain 39% Ge and up to 2.5% substitutional carbon and were grown by rapid thermal chemical vapor deposition (RTCVD) as in Ref. 7. They contain a $p^+ Si$ buffer for substrate contact, followed by 0.2 μm $p^- Si$, 2 nm undoped $Si_{1-x-y}Ge_xC_y$ spacer and 18 nm $p^+ Si_{1-x-y}Ge_xC_y$ (~$10^{19}/cm^3$). Finally, a 20 nm heavily doped (~$10^{20}/cm^3$) Si layer was grown for a top contact. It is noted that the doping concentration in $p^+ Si_{1-x-y}Ge_xC_y$ is not expected to induce band gap narrowing since we reported in capacitance–voltage measurement that no effect on ΔE_v is observed with varying doping concentrations.[7] Ge content was determined by x-ray diffrac-

---

[a)]Present address: Semiconductor Product Sector, Motorola, Austin, TX 78721. Electronic mail: clchang@ee.princeton.edu
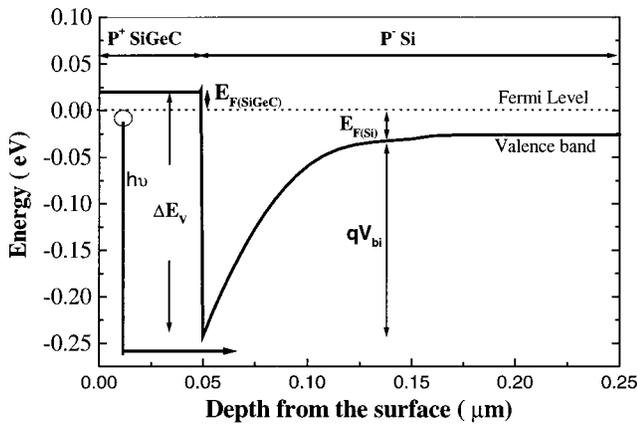
Appl. Phys. Lett., Vol. 73, No. 24, 14 December 1998

Chang *et al.*   3569

FIG. 1. Zero-bias valence band diagram of p^+Si$_{1-x-y}$Ge$_x$C$_y$/p^-Si.

FIG. 2. Photoresponse curves of p^+Si$_{1-x-y}$Ge$_x$C$_y$/p^-Si as well as p^+Si$_{1-x}$Ge$_x$/p^-Si. Samples were measured at 4 K.

tion and the number is consistent with results by secondary ion mass spectroscopy (SIMS) and photoluminescence studies. Substitutional C fractions were measured by x-ray diffraction, assuming 8.3 Ge/C strain compensation ratio. For the rest of this letter, all carbon levels refer to the substitutional levels measured by this method.

Devices were fabricated by a simple mesa etching in CF$_4$/O$_2$ plasma and Al metallization by lift-off. Good rectifying characteristics were observed at low temperatures (~77 K), indicating a significant valence band offset between p^+Si$_{1-x-y}$Ge$_x$C$_y$/p^-Si. Samples were further cooled down to ~4 K to minimize thermionic leakage current for infrared photocurrent measurements and a good ohmic contact was still observed. Optical absorption measurements were performed at 4 K using a calibrated glowbar infrared (IR) source, a spectrometer, and a phase sensitive detection.

Figure 1 shows the band diagram of the p^+Si$_{1-x-y}$Ge$_x$C$_y$/p^-Si HIP structure. Under a reverse bias, hole current is mostly blocked by the valence band offset and the ideal leakage current comes from thermionically emitted holes from p^+Si$_{1-x-y}$Ge$_x$C$_y$ layer. When an infrared light is incident on the p^+Si$_{1-x-y}$Ge$_x$C$_y$ layer, holes will be excited to higher energy states, and if the photon energy is large enough for the hole to overcome the barrier posed by the valence band offset, a photocurrent will result. From the band diagram, ΔE_v can be expressed as

$$\Delta E_v = E_{F(\text{SiGeC})} + qV_{\text{bi}} + E_{F(\text{Si})}, \tag{1}$$

where $E_{F(\text{SiGeC})}$ is the distance between Fermi level and the valence band of Si$_{1-x-y}$Ge$_x$C$_y$, qV_{bi} is the built-in voltage of the junction, and $E_{F(\text{Si})}$ is the distance of the valence band of Si and the Fermi level. Since the Si$_{1-x-y}$Ge$_x$C$_y$ is heavily doped, the threshold energy for the onset of photocurrent is $E_v - E_{F(\text{SiGeC})}$. To extract ΔE_v, one also needs to know the doping concentrations in Si$_{1-x-y}$Ge$_x$C$_y$ to calculate $E_{F(\text{SiGeC})}$. Doping concentrations were obtained by SIMS measurement on similarly grown samples and SIMS data show no dependence of dopant (boron) incorporation on the carbon level. We assume the onset current will track accurately with ΔE_v.

Figure 2 shows plots of the square root of photoresponse curves as a function of photon energy (Fowler plot) of Si$_{1-x-y}$Ge$_x$C$_y$/Si with different carbon concentrations. The
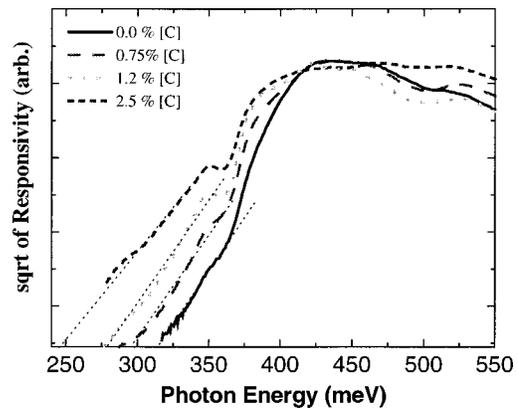
onset of photocurrent decreases as carbon level increases, indicating a decreasing ΔE_v with carbon concentrations. Carbon decreases the ΔE_V of Si$_{1-x-y}$Ge$_x$C$_y$/Si by 26 $\pm$1 meV/%C, as shown in Fig. 3. This is consistent with previously reported values measured by $C-V$ in HIP[7] and MOS[15] structures, and similar to the increase in band gap with carbon. We conclude that the increase in band gap is reflected in the valence band of Si$_{1-x-y}$Ge$_x$C$_y$, with very little or no change in the conduction band. Thus small ΔE_c in Si$_{1-x-y}$Ge$_x$C$_y$/Si is expected as in Si$_{1-x}$Ge$_x$/Si.

Figure 4 shows the valence band offset of Si$_{1-x}$Ge$_x$/Si[14] and Si$_{1-x-y}$Ge$_x$C$_y$/Si as a function of lattice mismatch and equivalent Ge levels for Si$_{1-x}$Ge$_x$ of the given strain. Adding carbon lowers ΔE_v of Si$_{1-x-y}$Ge$_x$C$_y$/Si; carbon reduces the lattice mismatch at a faster rate than reducing ΔE_v, compared to that achieved by reducing Ge alone in Si$_{1-x}$Ge$_x$. For example, the valence band offset of Si$_{0.585}$Ge$_{0.39}$C$_{0.025}$/Si is ~100 meV larger than that of an equally strained Si$_{0.82}$Ge$_{0.18}$/Si heterostructure. Figure 4 also predicts that, by extrapolating the dashed line to the vertical axis, a strain-free Si$_{0.563}$Ge$_{0.39}$C$_{0.047}$/Si heterostructure will have ~200 meV valence band offset. Since the Ge content determined by x ray, SIMS, and PL agrees within 5%, the effect of uncertainty in Ge concentration on this extrapolation is not significant. Even though the effect of uncertainty in determining C level could be as high as 30%, depending on the Ge/C strain compensation ratio used, the strain effect due to C incorpo-
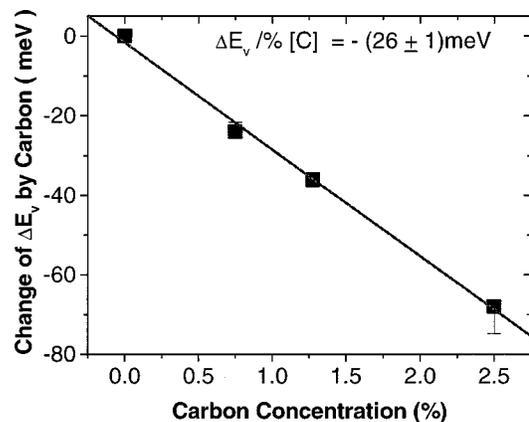

FIG. 3. Change of ΔE_v of Si$_{1-x-y}$Ge$_x$C$_y$/Si as a function of C concentrations.
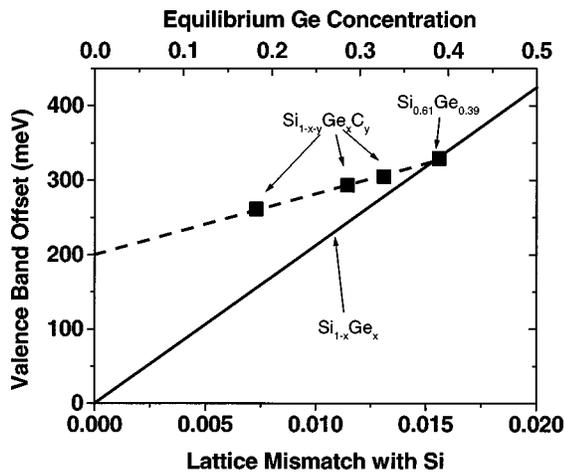
FIG. 4. Summary of valence band offsets obtained from optical absorption measurement as a function of lattice mismatch with Si and equivalent Ge concentration. The solid line represents the valence band offsets of $Si_{1-x}Ge_x/Si$.

ration on ΔE_v is not affected. Note that Fig. 4 was plotted based on lattice mismatch with Si.

Recently reported measurements on the ΔE_v of $Si_{1-x-y}Ge_xC_y/Si$ by admittance spectroscopy[18] suggested that C raised the valence band by $\sim$80 meV/% carbon and decreased the conduction band by 80 meV/%C, in direct conflict with our work. A $Si_{1-x}Ge_x/Si$ heterostructure with 24% Ge has ΔE_v about 180 meV. This reported C effect would imply that, a $Si_{1-x-y}Ge_xC_y/Si$ heterostructure with 24% Ge and 1% C has $\Delta E_v \sim$90 meV, a magnitude not enough to allow a complete hole transfer in the modulation-doped $Si_{0.75}Ge_{0.24}C_{0.01}$ two-dimensional gas. However, this prediction is inconsistent with the observed complete carrier transfer from a doped Si supply layer to a modulation doped $Si_{1-x-y}Ge_xC_y$ two-dimensional hole gas.[19] Band offset studies by admittance spectroscopy measure the temperature-dependent conductance of $Si_{1-x-y}Ge_xC_y$ quantum wells and assumes that the conductance scales ideally as $\exp(-\Delta E_v/kT)$, as for thermionic emission. However, small signal conductance, like leakage current, can be easily dominated by nonideal defects.[14]

In summary, we have studied the valence band offset of compressively strained pseudomorphic $Si_{1-x-y}Ge_xC_y/$

Si(100) by heterojunction internal photoemission. Carbon decreased the valence band offset of $Si_{1-x-y}Ge_xC_y/Si$ by 26 ± 1 meV/%C. Combining this number with a previously reported similar increase in the band gap caused by carbon, we conclude that the band structure of $Si_{1-x-y}Ge_xC_y/Si$ exhibits a large valence band offset and a negligible conduction band offset, similar to that of $Si_{1-x}Ge_x/Si$ heterostructures.

[1] K. Eberl, S. S. Iyer, S. Zollner, J. C. Tsang, and F. K. LeGous, Appl. Phys. Lett. **60**, 3033 (1992).

[2] J. L. Regolini, F. Gisbert, G. Dolino, and P. Boucaud, Mater. Lett. **18**, 57 (1993).

[3] H. J. Osten, H. Rücker, M. Methfessel, E. Bugiel, S. Ruminov, and G. Lippert, J. Cryst. Growth **157**, 405 (1995).

[4] P. Boucaud, C. Guedj, F. H. Julien, E. Finkman, S. Bodnar, and J. L. Regolini, Thin Solid Films **278**, 114 (1996).

[5] J. Kolodzey, P. R. Berger, B. A. Orner, D. Hits, F. Chen, A. Khan, X. Shao, M. M. Waite, S. Ismat Shah, C. P. Swann, and K. M. Unruh, J. Cryst. Growth **157**, 386 (1995).

[6] C. W. Liu, A. St. Amour, J. C. Sturm, Y. R. J. Lacroix, M. L. W. Thewalt, C. W. Magee, and D. Eaglesham, J. Appl. Phys. **80**, 3043 (1996).

[7] C. L. Chang, A. St. Amour, and J. C. Sturm, Appl. Phys. Lett. **70**, 1557 (1997).

[8] K. Brunner, K. Eberl, and W. Winter, Phys. Rev. Lett. **76**, 303 (1996).

[9] A. St. Amour, C. W. Liu, J. C. Sturm, Y. Lacroix, and M. L. W. Thewalt, Appl. Phys. Lett. **67**, 3915 (1995).

[10] L. D. Lanzerotti, A. St. Amour, C. W. Liu, and J. C. Sturm, Elec. Dev. Lett. **17**, 334 (1996).

[11] P. Boucaud, C. Francis, F. Julien, J. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert, and J. Regolini, Appl. Phys. Lett. **64**, 875 (1994).

[12] K. Brunner, W. Winter, and K. Eberl, Appl. Phys. Lett. **69**, 1279 (1996).

[13] C. L. Chang, A. St. Amour, L. Lanzerotti, and J. C. Sturm, Mater. Res. Soc. Sym. Proc. **402**, 437 (1995).

[14] C. L. Chang, A. St. Amour, and J. C. Sturm, Tech. Dig. Int. Electron Devices Meet., 257 (1996).

[15] K. Rim, S. Takagi, J. J. Welser, J. L. Hoyt, and J. F. Gibbons, Mater. Res. Soc. Symp. Proc. **379**, 327 (1995).

[16] M. Kim and H. J. Osten, Appl. Phys. Lett. **70**, 2702 (1997).

[17] J. Kolodzey, F. Chen, B. A. Orner, D. Guerin, and S. Ismat Shah, European Material Research Society Spring Meeting Strasbourg, France, 1996.

[18] B. L. Stein, E. T. Yu, E. T. Croke, A. T. Hunter, T. Laursen, A. E. Bair, J. W. Mayer, and C. C. Ahn, Appl. Phys. Lett. **70**, 3413 (1997).

[19] C. L. Chang, S. P. Shukla, W. Pan, V. Venkataraman, J. C. Sturm, and M. Shayegan, 7th International MBE Symposium, Banff, Canada, 1997, Thin Solid Films (to be published).