

# Defect-free band-edge photoluminescence and band gap measurement of pseudomorphic $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloy layers on Si (100)

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Pseudomorphic  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloy layers on Si (100) with band-edge photoluminescence and without defect-related luminescence have been achieved. The photoluminescence was measured from 2 to 77 K and was used to make a direct measurement of the band gap shift as a function of strain reduction as C was added. Compared to the effect of just reducing Ge content, results show that as C is added, strain is reduced more efficiently than the band gap is increased. Furthermore, results imply that a fully strain-compensated  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  layer on Si (100) would have a band gap much less than that of Si, and suggest that initial C incorporation reduces the band gap of relaxed, unstrained  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. © 1995 American Institute of Physics.

The strain in pseudomorphic  $\text{Si}_{1-x}\text{Ge}_x$  alloys on Si (100) substrates imposes a severe design constraint in heterojunction devices employing these layers. In concept, because C atoms are smaller than both Si and Ge atoms, C may be used to compensate the strain by adding it substitutionally to form  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. However, the solid solubility of C in Si is only about 1 ppm even at the melting point of Si;<sup>1</sup> at higher concentrations, the stable phase is the ordered compound SiC rather than a random alloy. In spite of this, previous work has demonstrated that low-temperature, nonequilibrium epitaxy can produce  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  films with substitutional C concentrations greater than 2%. The bulk of this previous work has been of a structural nature, with reports of strain as a function of C concentration, for example.<sup>2,3</sup> To the best knowledge of the authors, however there has been only one previous experimental report of a direct measurement of the band gap of  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ . Boucaud *et al.* reported 77 K photoluminescence (PL) spectra from  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys with  $x=0.155$ ;<sup>4</sup> but these spectra showed luminescence peaks assigned to dislocations, casting doubt on the strain condition of the films.

In this letter, we report photoluminescence spectra from pseudomorphic  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys on Si (100) showing only band-edge,  $\text{Si}_{1-x}\text{Ge}_x$ -like PL with no dislocation lines or luminescent defects. The PL was measured between 2 and 77 K and showed band-edge,  $\text{Si}_{1-x}\text{Ge}_x$ -like luminescence at all temperatures. We show that for a given band gap, a larger critical thickness can be attained for films with C compared to those without C. Furthermore, from our experimental measurements of the band gap of pseudomorphic  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  on Si (100), we calculated the band gap of relaxed  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ . It was found that the initial addition of C will tend to decrease the band gap of unstrained  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys.

The samples used in this work were grown by rapid thermal chemical vapor deposition (RTCVD) on Si (100)

substrates at reduced pressure (6 Torr).<sup>5</sup> All samples consisted of nominally undoped single, buried  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  layers. The  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  layers were deposited at 575 °C from dichlorosilane, germane, and methylsilane in a hydrogen carrier, while the Si caps were deposited at 675 °C from dichlorosilane. The samples received no thermal treatment after growth. There were two sets of samples: one with  $x=0.24$ , the other with  $x=0.38$ . SIMS confirmed layer thicknesses, flat C profiles, and that the Ge concentration was unchanged as methylsilane was added. For the rest of this letter, quoted substitutional C concentrations were quantitatively determined from shifts in the (400) x-ray diffraction (XRD) peaks using a Ge:C strain compensation ratio of 8.3,<sup>3</sup> which corresponds to a strain reduction of  $-0.0035\%/C$ . The C concentrations measured by SIMS were consistently proportional to those measured by XRD but were significantly lower, opposite to what would be expected if some C was not substitutional. We associate the inconsistency between SIMS and XRD with poor SIMS calibration.

For the photoluminescence measurements, the excitation source was an argon laser with a pump power density of  $\sim 50$  W/cm<sup>2</sup>, and the detector was a liquid nitrogen-cooled Ge diode. Figure 1(a) shows PL spectra measured at 25 K from samples with  $x=0.38$  and various C concentrations. These spectra are indeed  $\text{Si}_{1-x}\text{Ge}_x$ -like and exhibit no features other than the usual no-phonon (NP) and TO phonon replica peaks.<sup>6</sup> There was a clear blueshift in these band-edge PL features as the C content was increased, indicating that adding C tends to increase the band gap of strained  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ . As C was added the NP intensity increased relative to the TO intensity, suggesting enhanced alloy scattering due to the C atoms in the lattice. Also, note that the features in the 25 K spectra became narrower and weaker as C was added. This may have been due to reduced band filling<sup>7</sup> caused by a lower carrier lifetime in the samples with C. The spectra measured at 77 K were similar to those at 25 K, but were thermally broadened. Several samples were measured at 2 K as well, although the luminescence was weaker and the linewidth broader for unknown reasons [Fig. 1(b)].

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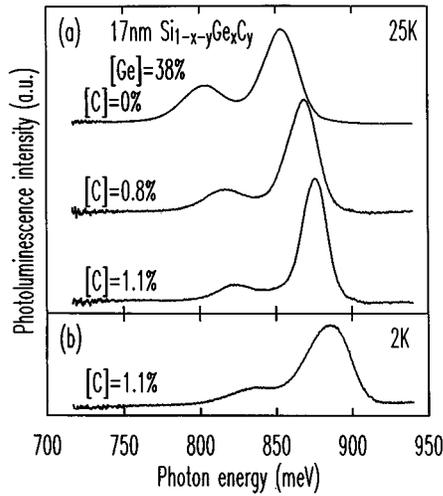


FIG. 1. Photoluminescence spectra for  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  samples with  $x=0.38$  and various C. The pump power density was  $\sim 50 \text{ W/cm}^2$ . The spectra were normalized and corrected to account for the spectral response of the experimental optical path.

To demonstrate the tradeoff between band gap reduction and strain in  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  heterojunction devices, we have plotted in Fig. 2 band gap (as measured by PL) as a function of strain (as measured by XRD). The absolute band gap of the control sample with  $x=0.24$  and  $y=0$  was determined from its 2 K PL spectrum. The band gaps of the other samples were then determined by comparing the low-energy edge of the NP peak of their 77 K PL spectra to that of the control sample. We estimate error bars of  $\pm 6 \text{ meV}$  for the absolute band gap measurements but only  $\pm 2 \text{ meV}$  for the relative band gaps.

The position of the  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  (400) XRD peaks relative to the Si substrate peak were measured to give the vertical lattice constant of the epilayers. Assuming no relaxation (there was no evidence of significant dislocations in the PL spectra) and a Poisson ratio of 0.28, the relaxed lattice constants and, therefore, the strain were computed. The relatively thin  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  layers ( $\sim 30 \text{ nm}$ ) yielded broad XRD peaks, resulting in an estimated uncertainty in the strain of  $\pm 0.0004$ . Because of the constraints of critical thickness, a fully strained film with  $x=0.38$  and no C and with sufficient thickness for XRD could not be produced. Therefore, we determined the strain in this film by measuring the Ge content by Auger electron spectroscopy depth profiling and employing Vegard's law. We conservatively estimated the error in Ge content to be  $\pm 0.02$ , yielding an error of  $\pm 0.0008$  for the strain in this film.

Figure 2 shows band gap versus biaxial compressive strain for both pseudomorphic  $\text{Si}_{1-x}\text{Ge}_x$  on Si (100) (adapted from the work of Van de Walle and Martin<sup>8</sup>) and our experimental  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  data points. As C is added to  $\text{Si}_{1-x}\text{Ge}_x$  and the Ge content is held fixed, the strain decreases and the band gap increases, but the band gap increase is much less than it would be if the strain was reduced simply by reducing the Ge concentration without adding C. That is, for a given band gap,  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  has less strain (and presumably a greater critical thickness) than does  $\text{Si}_{1-x}\text{Ge}_x$ . The average slope of the  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  points,

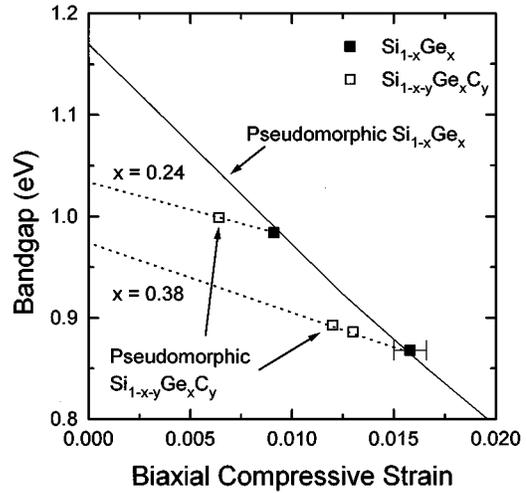


FIG. 2. Band gap as a function of strain for pseudomorphic  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  on Si (100). The errors bars for relative band gaps and strain are  $\pm 2 \text{ meV}$  and  $\pm 0.0004$ , respectively. The  $\text{Si}_{1-x}\text{Ge}_x$  line is from Ref. 10.

$\Delta E_G/\Delta \epsilon = -6.1 \text{ eV/unit strain}$ , corresponding to  $\Delta E_G/\Delta y = +21 \text{ meV}/\% \text{C}$ . Furthermore, if one assumes a linear extrapolation of our  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  data to zero strain, one predicts a significant band gap offset to Si for strain-free  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  films. For  $x=0.38$ , the offset would be  $\sim 190 \text{ meV}$ .

To demonstrate that adding C to  $\text{Si}_{1-x}\text{Ge}_x$  can indeed increase its critical thickness, we prepared two samples under identical conditions ( $x=0.38$ , thickness=34 nm, and capped with 10 nm of Si), except that in one case we added C to the  $\text{Si}_{1-x}\text{Ge}_x$  layer. The sample without C showed luminescence originating from dislocations<sup>9</sup> (Fig. 3), indicating that the sample was relaxed. The sample with C, however, showed only band-edge,  $\text{Si}_{1-x}\text{Ge}_x$ -like PL with no dislocation lines. By adding C to  $\text{Si}_{1-x}\text{Ge}_x$ , we achieved a strained film thicker than 30 nm with a band-offset to Si of almost 300 meV. In comparison, the Matthews-Blakeslee equilibrium critical thickness for a comparable  $\text{Si}_{1-x}\text{Ge}_x$  film is  $\sim 7 \text{ nm}$ .<sup>10</sup>

The substitutional incorporation of C into pseudomorphic  $\text{Si}_{1-x}\text{Ge}_x$  should have two effects on the band gap of the alloy. First, the smaller C atoms will reduce the strain in the film, thus increasing the band gap. Additionally, the presence of C in the matrix should have a separate effect on the band gap of the relaxed alloy. However, there are no published experimental results on the effect of small amounts of C on the band gap of relaxed  $\text{Si}_{1-y}\text{C}_y$  or  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ , and theoretical predictions vary widely from  $+18 \text{ meV}/\% \text{C}$ <sup>11</sup> to  $\sim -100 \text{ meV}/\% \text{C}$ .<sup>12</sup> To subtract the expected effect of strain reduction from our experimentally measured band gaps of strained layers, we assumed that the deformation potentials in our pseudomorphic  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  are similar to those in  $\text{Si}_{1-x}\text{Ge}_x$  ( $\Delta E_G = -11.7 \text{ eV/unit biaxial compressive strain}$ ).<sup>8</sup> In Fig. 4 we have plotted the expected band gap of relaxed  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  as a function of lattice constant. Note that the relaxed  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  points lie below the relaxed  $\text{Si}_{1-x}\text{Ge}_x$  line<sup>13</sup> and, more importantly, that their slope is positive ( $\sim 10 \text{ eV/nm}$ ). That is, as C is added and the lattice

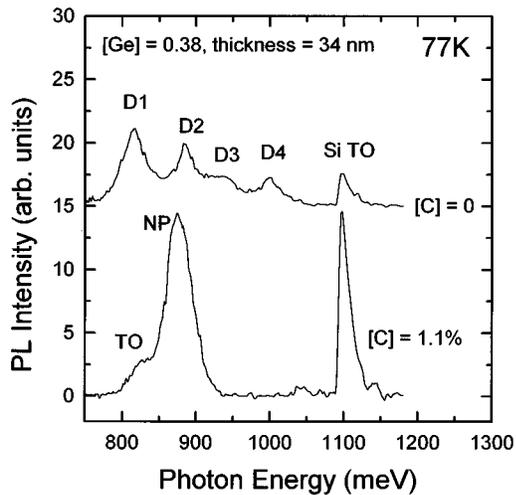


FIG. 3. Uncorrected photoluminescence spectra for two  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  samples with  $x=0.38$ . For the top spectrum,  $y=0$ ; whereas for the bottom spectrum,  $y=0.011$ .

constant decreases, the relaxed band gap does as well ( $-20$  meV/%C). This is slightly surprising in light of the fact that SiC and diamond have band gaps much larger than both Si and  $\text{Si}_{1-x}\text{Ge}_x$ . However, it is not unprecedented; similar “bowing” is observed or predicted in the band gap versus lattice constant data of other alloy systems which have a large lattice mismatch (e.g., GaAs/GaSb and GaAs/GaN).<sup>14</sup>

Extrapolating our  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  data back to zero strain (Fig. 2), gives the band gap of relaxed. This can then be compared to the known band gap of the relaxed  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ . This alloy<sup>13</sup> with the same Ge content to determine the effect of C on the band gap of relaxed films. Doing so, we found that for relaxed  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$   $\Delta E_G/\Delta y = -19$  meV/%C. That this agrees with the above result (which assumed  $\text{Si}_{1-x}\text{Ge}_x$  deformation potentials) confirms that the deformation potentials of  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  are indeed similar to those of  $\text{Si}_{1-x}\text{Ge}_x$ .

Note that our indirect fundamental band gap results are consistent with those of ellipsometry and electroreflectance measurements of the direct optical transitions (3–5 eV) in pseudomorphically strained  $\text{Si}_{1-y}\text{C}_y$  alloys.<sup>15,16</sup> Zollner *et al.* showed that the use of linearly interpolated transition energies and Si deformation potentials overestimated the  $E'_0$  transition energy as C was added, suggesting a downward trend in the band gaps of relaxed  $\text{Si}_{1-y}\text{C}_y$  and  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys.

In summary, we have grown pseudomorphic  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  thin films on Si (100) and measured their photoluminescence from 2 to 77 K. The PL spectra exhibited only band-edge,  $\text{Si}_{1-x}\text{Ge}_x$ -like features, with no defect-related lines. Adding C substitutionally to  $\text{Si}_{1-x}\text{Ge}_x$  reduced the strain in the films and increased the band gap, but the increase in band gap was only about half of that which would be obtained by reducing the Ge content to achieve similar

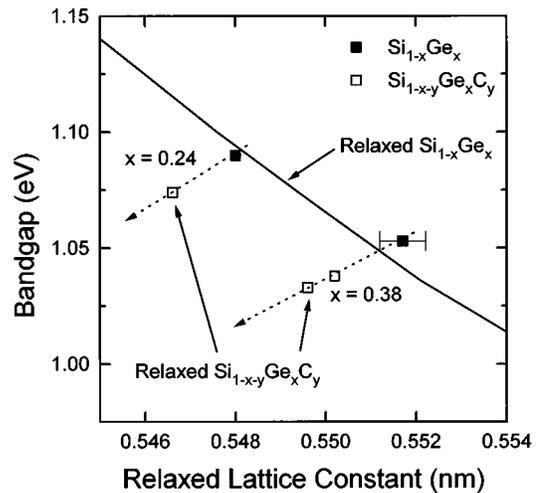


FIG. 4. Band gap as a function of lattice constant for unstrained material. The  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  points are adapted from measurements on pseudomorphic films. The  $\text{Si}_{1-x}\text{Ge}_x$  line is from Ref. 16.

strain reduction. Therefore, it appears possible to create defect-free films without strain on Si (100) with a band gap substantially less than that of Si. Finally, our results suggest that initial C incorporation in relaxed  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  will decrease the band gap.

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# Erratum: "Defect-free band-edge photoluminescence and band gap measurement of pseudomorphic $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloy layers on Si (100)" [Appl. Phys. Lett. 67, 3915 (1995)]

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On page 3917, the second paragraph contains errors that were introduced during the production of the article. The correct paragraph is reproduced here.

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