

## Direct gap in ordered silicon carbon alloys

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We show that alloying silicon with a few percent of carbon can render the band gap direct with strong optical absorption, provided the carbon atoms are ordered. The addition of carbon introduces a significant *s* character into the conduction band minimum, resulting in a large dipole matrix element. First-principles calculations of the optical absorption in ordered in  $C_xSi_{1-x}$  alloys for  $x = 1/54$  and  $1/32$  show a near band edge absorption coefficient about half that of GaAs. © 1999 American Institute of Physics. [S0003-6951(99)03845-0]

With silicon as the workhorse of the semiconductor industry, the possibility of obtaining direct gap in silicon has enormous technological importance for applications such as silicon-based lasers and optical computing. In the past, several studies predicted a possibility of direct gap in a superlattice made of indirect gap materials, Si and Ge.<sup>1-4</sup> A direct gap was observed in strained, short-period SiGe superlattices and was explained in terms of zone folding in the superlattice direction.<sup>5-8</sup> However, the optical coupling of the valence band maximum (VBM) to the conduction band minimum (CBM) was found to be weak. These observations were explained as follows in terms of zone folding, strain, and chemical disorder.

In an appropriate (100)-oriented, one-dimensional superlattice (SL) with Si and Ge, the bands in  $\Gamma$ -*X* direction fold into new “mini” Brillouin zone (BZ) and the two equivalent conduction band minimum (CBM) are brought to the zone center. The in-plane strain lifts the other four equivalent minima to a slightly higher energy, resulting in direct gap material. Although the new gap is formed at  $\Gamma$  from zone-folded Si *X* states, the optical matrix element connecting the CBM states to valence band state is larger than that in Si, because of alloy induced mixing of *s*-type states to the CBM. However, due to relatively smaller alloy potential (about 1 eV), the mixing is limited and only a small increase in the absorption coefficient is observed.<sup>8</sup> In addition, because of near degeneracy of the direct CBM with indirect minima in the transverse directions, the indirect character dominates the absorption curves.<sup>8</sup>

Hence, it is realized that for the direct gap to be useful, we need that (a) the other indirect states have to be sufficiently separated in energy and (b) the lowest state at  $\Gamma$  should have a more *s* content for increased absorption coefficient.

In this letter, we show that an ordered C in Si host satisfies both requirements above. The three-dimensional ordering provides a well defined direct gap and the very large

difference in term values between Si and C adds considerable *s* content to the lowest conduction band state, leading to a large dipole coupling of the VBM to the CBM. We show that a true direct gap in  $C_xSi_{1-x}$  alloys is possible for two concentrations  $x = 1/32$  and  $1/54$  with the carbon atoms forming an ordered structure in the silicon host. Explicit calculations of the optical matrix elements between valence and conduction band states show that the fundamental absorption coefficient near the band edge is comparable to that in GaAs.

The electronic structure calculations were carried out using the local density approximation (LDA) as implemented within the full-potential linearized muffin-tin orbitals (FP-LMTO) basis.<sup>9-11</sup> The lattice was relaxed until the calculated forces were small. Only relaxations retaining the cubic symmetry were considered; the relaxations were found to be large with the Si-C bond length at 2.05 Å. We identified several  $C_xSi_{1-x}$  alloys that produce a direct gap when carbon atoms form a specific superlattice. Figure 1 shows calculated energy bands for a supercell in a body-centered-cubic arrangement with primitive lattice vectors of length  $\sqrt{3}a$ ,

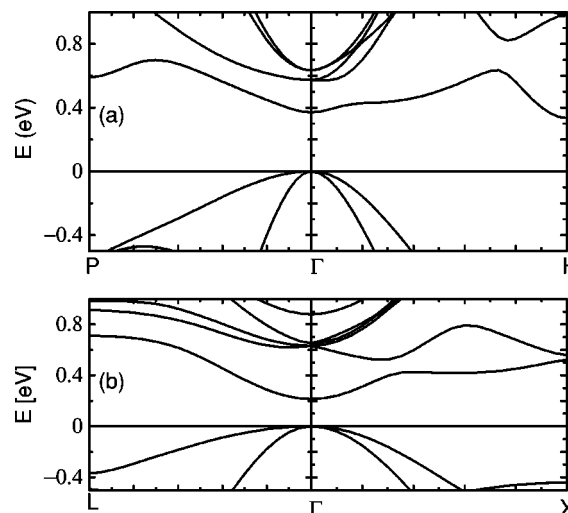


FIG. 1. Band structure of ordered alloys (a)  $CSi_{31}$  in the body-centered-cubic arrangement and (b)  $CSi_{53}$  in the face-centered-cubic arrangement.

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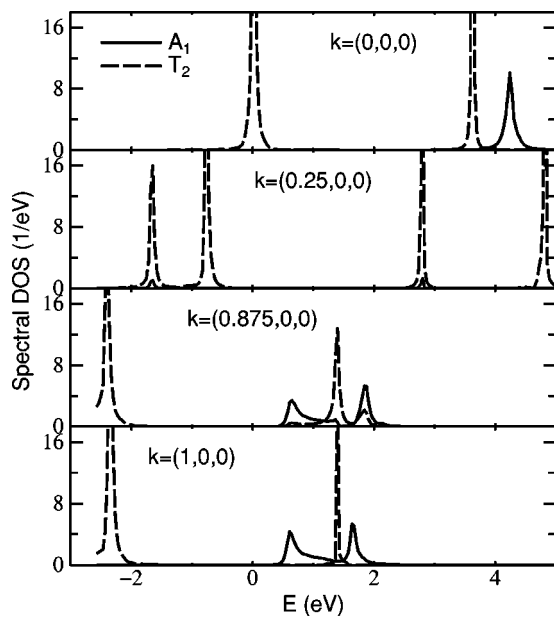


FIG. 2. Calculated symmetry-decomposed spectral density of states for  $C_{0.025}Si_{0.975}$  random alloy at various points along the  $\Delta$  direction in the Brillouin Zone.

where  $a$  is the lattice constant of the silicon host. This supercell contains 31 silicon atoms and one carbon atom. We see that the conduction band has a minimum at  $\Gamma$  with an LDA gap of 350 meV, with several satellite minima within a few meV of the CBM. For comparison, the LDA band gap of silicon is 410 meV.

Figure 1 also shows the bands for  $C_xSi_{1-x}$  with  $x = 1/54$ . In this case, the carbon atoms were ordered in a face-centered-cubic lattice, with primitive lattice vectors three times those of the usual zinc blende. The band gap is now direct with all satellite minima raised considerably higher in energy. The LDA gap is 250 meV.<sup>12</sup> Note that the band gap decreases when C concentration is decreased. This is consistent with another theory<sup>13</sup> and experiments<sup>14,15</sup> where the band gap reduction is observed at very low C concentrations and explained<sup>15</sup> in terms of the competition between these two mechanisms—a tendency to widen the gap because of the wider C gap and to narrow the gap from the strain. While this is one effect, there is additionally a “superlattice effect” for the ordered structures. Band gaps are quite sensitive to the particular way atoms in an alloy are configured in the lattice.<sup>16,17</sup>

The analysis of the site-decomposed total density of states (DOS) showed that prominent features in the DOS near the CB edge are due to carbon. The DOS from the shells farther than the third shell are mostly Si like. A further decomposition of the total DOS into  $s$ ,  $p$ , and  $d$  contribution clearly showed that the CBM is substantially  $s$  and VBM is predominantly  $p$  in character.

To identify the origin of C- $s$  dominated chemical bond epitaxy (CBE), we consider the random  $C_{0.025}Si_{0.975}$  alloy within the molecular coherent potential approximation (MCPA), using a hybrid pseudopotential tight-binding Hamiltonian.<sup>18,19</sup> The  $s$  term value of carbon is lower than that of silicon by 6.5 eV and the corresponding  $p$  difference is 1 eV. Figure 2 shows the calculated spectral density of states at several wavevectors along the  $\Delta$  direction. These

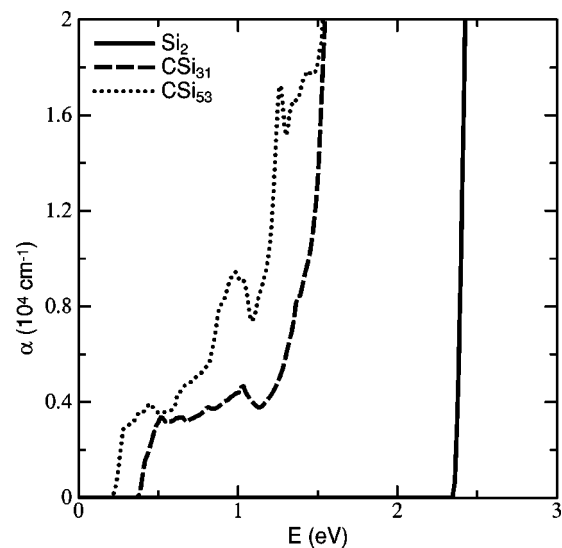


FIG. 3. Calculated absorption coefficient in silicon supercells and in  $CSi_{31}$  and  $CSi_{53}$  ordered alloys.

spectra have been decomposed into  $A_1$  ( $s$  like) and  $T_2$  ( $p$  like) symmetries. At  $\Gamma$ , the highest valence band states and the lowest conduction band states have  $T_2$  symmetry. This trend continues as  $k_x$ , the  $x$  component of the wavevector, is increased in the  $\Delta$  direction. As  $k_x$  approaches the  $X$  point of the Brillouin zone (BZ), the  $A_1$  contribution to the lowest conduction band becomes significant. This figure clearly shows that the lowest conduction band edge of this disordered alloy is at  $X$  and is fully  $A_1$  in character. This is in strong contrast to the case for pure Si, for which the  $s$  contribution to CBM is absent. Thus, both the MCPA and the ordered supercell calculations show that the lowest conduction band is of  $A_1$  or  $s$  character as a result of interaction of the silicon conduction band states with the C-derived  $s$  states. Because of extremely strong disorder scattering arising from the large differences in atomic  $s$  levels of C and Si, a small amount of C is sufficient to split-off the higher-lying conduction band. The split-off  $s$ -rich CB becomes the lowest CB near  $X$  and the appropriate zone folding moves the minimum to the  $\Gamma$  point of the BZ. The finite curvature of the lowest CB seen in Fig. 1(b), clearly indicates that the calculated  $s$  character in that band is *not* fortuitous coincidence of C deep states with the CB.

The above analysis suggests that, for the ordered structures, the optical absorption should be large, because with a sizeable  $s$  component to the conduction band wave functions there is a sizeable dipole matrix element. The optical absorption coefficient,  $\alpha$  as a function of photon energy  $E$  was calculated, within the LMTO method and the atomic spheres approximation, for the relaxed 32- and 54-atom structures indicated above. (The energy band structure was found to be very similar to those of the FP-LMTO calculations.) Phonon and local field effects were not included in the calculations. The imaginary part of the dielectric function  $\epsilon_2$  is obtained in perturbation theory from the interband momentum matrix elements, and a simple relationship leads to the absorption coefficient.

The calculated  $\alpha$  are shown in Fig. 3. The solid line corresponds to the calculated direct absorption in pure silicon with two atoms per unit cell. When the cell size is in-

creased to 54 atoms, 512  $k$  points are used in the BZ sum of optical matrix elements to minimize the band-tailing effect on the absorption curve. The calculated  $\alpha$  in the ordered  $\text{CSi}_{31}$  and  $\text{CSi}_{53}$  alloys are shown in Fig. 3 as dashed and dotted, respectively. A strong direct absorption at the band edge of these ordered alloys is clearly seen:  $\alpha$  increases sharply with photon energy, to  $>3000\text{ cm}^{-1}$  within 0.1 eV of the band edge. In particular, the  $\text{CSi}_{53}$  alloy exhibits the steepest increase, reaching a peak value of about  $3500\text{ cm}^{-1}$  within 70 meV of the CBM. This peak value is about 40% of the corresponding experimental value in  $\text{GaAs}$ <sup>20,21</sup> and a couple of orders of magnitude higher than what is observed in bulk Si.<sup>22</sup> If we assume the correction to the LDA gap in the  $\text{CSi}_{53}$  alloy is the same as that in Si,<sup>23</sup> we predict a strong direct gap at 0.95 eV. Owing to the uncertainty in the LDA gaps, the predicted value of the gap may be somewhat in error, but of the *qualitative* picture of C-derived states in the vicinity of the bulk silicon gap we can be fairly confident.

We have shown that a true direct-gap absorption can be obtained in silicon by adding 2% to 3% carbon in an ordered arrangement. The large bond-length mismatch between silicon (2.35 Å) and carbon (1.55 Å) limits the solubility of carbon in silicon to approximately  $<0.001\%$  at the melting point of silicon. Only with nonequilibrium techniques, much higher concentrations of carbon ( $<3\%$  at best<sup>24-27</sup>) have been substitutionally incorporated into silicon hosts. These practical limitations on carbon concentrations in silicon restricted our search for direct gap  $\text{C}_x\text{Si}_{1-x}$  alloys to low concentrations of C. It may be possible to grow ordered structures by exploiting superstructures introduced by either surface reconstruction or ledges on the Si growth surfaces combined with surfactants<sup>26</sup> and monolayer control of the growth.

In conclusion, we have shown that ordering of low concentrations of carbon in silicon can produce a slightly lower and *direct* gap with orders of magnitude *increase* in optical absorption when compared with that in Si. The direct gap originates from the zone folding of an ordered superlattice of carbon atoms, and the increase in  $\alpha$  results from a large infusion of  $s$  character into states near the CBM. This latter derives from the strong interaction of the deep carbon  $s$  orbital with Si conduction band, giving rise to considerable  $s$ -like content in the vicinity of the CBM. Owing to the very large difference in term values between Si and C, a small amount of C is sufficient to cause the material to have a direct gap with large optical absorption coefficient. Clever experimental techniques such as surfactants and surface relaxation-driven ordering may be needed to incorporate car-

bon in silicon with the specific long-range ordering identified here.

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