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Energy band gaps of silicon-carbon alloys

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The energy band gaps of silicon-carbon alloys are calculated using a *GW* approach with local density approximation (LDA) eigenfunctions. These band gaps are compared with those calculated with nonlocal corrections for the exchange-correlation energy functional. For small concentrations of carbon, it is found that carbon-silicon alloys are semiconducting with a very small band gap. These results are consistent with former LDA calculations, which predicted that the band gap of carbon-silicon alloy at low carbon concentrations is smaller than the band gap of pure silicon.

It is desirable, from the standpoint of band-gap engineering, to make alloys of carbon and silicon similar in concept to alloys of germanium and silicon. Unfortunately, C in Si has a very low solubility. This problem has recently been overcome apparently first by Posthill *et al.*,[1] and then by Iyer *et al.*[2] Posthill *et al.* used a plasma-enhanced chemical vapor deposition technique and fabricated 7 μm thick layers, with a carbon concentration of 3.5%. Iyer *et al.*[2] used solid source molecular beam epitaxy to grow 0.2–0.3 % carbon alloys with Ge to compensate strain. More recent work[3–5] has produced a variety of different samples including much higher concentrations, and samples which show no signs of silicon carbide formation.

Recently, Demkov and Sankey[6] have studied silicon-carbon alloys in the framework of the local density approximation (LDA) formalism. They found that both random and ordered silicon-carbon alloys have smaller band gaps than pure silicon for low carbon concentrations. This was found to be true even in the completely relaxed geometry in which the net force acting on every atom is zero. In fact, at approximately 10% carbon, silicon-carbon alloys were predicted to become metallic. This is a quite unexpected result since both silicon carbide and diamond have larger band gaps than pure silicon. Thus, using a simple interpolation, one could expect that the energy gap of the silicon-carbon alloys would increase with the carbon concentration, as shown by Soref.[7]

The above results were based solely on LDA calculations which are known to considerably underestimate energy band gaps. If the LDA predictions are correct, the potential technological applications of Si-C alloys may be quite different than expected. Therefore in this paper we have checked the LDA predictions for silicon-carbon alloys using a *GW* approach. It is well known that the *GW* method gives energy band gaps in excellent agreement with experiment, as shown by several authors[8–11] for such semiconductors as Si, Ge, GaAs, AlAs, and diamond. An important observation from these calculations is that the quasiparticle energies in a semiconductor can be obtained from LDA wave functions. In the first order approximation, the quasiparticle energies $\epsilon_{\vec{k}n}$ are given by

$$\epsilon_{\vec{k}n} = \epsilon_{\vec{k}n}^{\mathrm{LDA}} + \langle \psi_{\vec{k}n} | \Sigma(\epsilon_{\vec{k}n}) - V_{\mathrm{xc}} | \psi_{\vec{k}n} \rangle \, ,$$

where Σ is the self-energy operator, V_{xc} is the exchange-correlation potential, and $\epsilon_{\vec{k}n}$ and $\psi_{\vec{k}n}$ are LDA eigenvalues and eigenfunctions for the nth electron band. As pointed out by Godby *et al.*[9] the above expression correctly describes contributions to the quasiparticle energies resulting from nonlocality and energy dependence of the self-energy operator.

In our calculations we have followed recent papers by Rohlfing *et al.*[11] and by Hott[12] in evaluating the matrix elements of the self-energy operator. We have used the plasmon-pole approximation, together with the dielectric function due to Falter *et al.*[13] and experimental values of dielectric constants ϵ_∞ of diamond and silicon. The LDA energies $\epsilon_{\vec{k}n}^{\mathrm{LDA}}$ and wave functions $\psi_{\vec{k}n}$ have been calculated using the pseudopotential method and a plane wave basis set with an energy cutoff of 500 eV. The spin-orbit interaction is ignored. For several compositions, we have also carried out LDA calculations using a mixed basis set consisting of *spd* localized orbitals and a small number of plane waves. Both methods give essentially identical results. As in Ref. 6, we used soft pseudopotentials due to Troullier and Martins.[14] To evaluate matrix elements of the self-energy operator, the LDA energies and wave functions must be known for a large number of points in the irreducible wedge of the Brillouin zone. We calculated these quantities in two steps. First we solved the Kohn-Sham equations for a coarse grid of $\vec{k}$ points. Next we used the $\vec{k} \cdot \vec{p}$ method to determine energies and wave functions for a very fine mesh of $\vec{k}$ points.

For comparison with the *GW* results, we also carried out band structure calculations using nonlocal (gradient) corrections to the exchange and correlation energy (NLDA). We used Becke[15] corrections for the exchange energy and the Perdew[16] nonlocal expression for the correlation energy. Figure 1 shows the electron band structure of silicon near the top of the valence band calculated in the LDA, NLDA, and *GW* approximations. We see that the valence bands in all three methods are nearly identical, whereas the NLDA and the *GW* conduction bands are shifted upward with respect to the LDA bands.

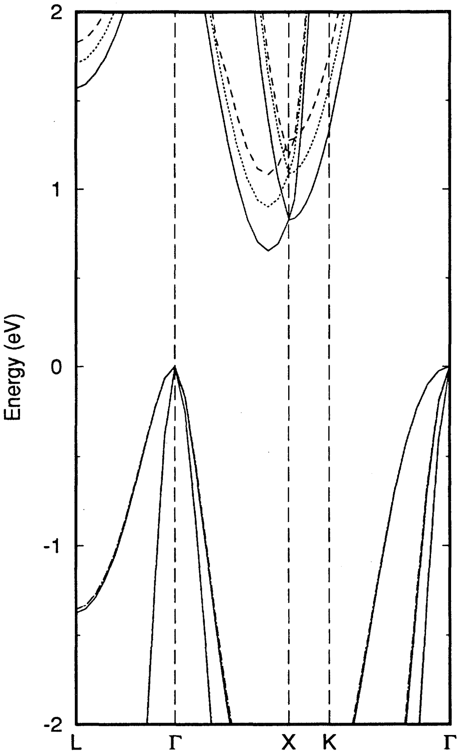

FIG. 1. Electronic band structure of silicon near the top of the valence band. Solid line, LDA; dotted line, nonlocal exchange correlation (NLDA); and dashed line, *GW* approximation. The top of the valence band is at 0.0 eV.

As a result of this shift, the energy band gap increases from 0.65 eV (LDA) to 0.90 eV (NLDA), and 1.08 eV in the *GW* approximation. The experimental value of the band gap for silicon is 1.17 eV. The difference between NLDA and LDA band gaps for silicon is 0.25 eV. This value is consistent with results reported by Ortiz,[17] who found that the X_{1c} energy for silicon increases by 0.20 eV when nonlocal corrections are taken into account.

We have found that the difference between NLDA and LDA band gaps has a similar trend for diamond and for silicon carbide. This is illustrated in Fig. 2, which shows the energy of the lowest conduction bands for a cubic carbon-silicon supercell of general formula C_nSi_{8-n} as a function of the number of carbon atoms for several points in the cubic Brillouin zone. The carbon atoms were placed in the unit cell so that they were as far apart as possible. For one or two carbon atoms in the eight-atom unit cell, the band gap is negative (i.e., metallic). We see that the NLDA bands are shifted upward relative to the LDA bands by 0.20–0.35 eV. The shift is approximately the same for all compositions. Therefore, although the NLDA band gap for pure silicon is in better agreement with experimental data than the LDA value, the NLDA band gap of diamond (4.5 eV) or SiC (1.3 eV) is still approximately 1.0 eV smaller than the experimental value.

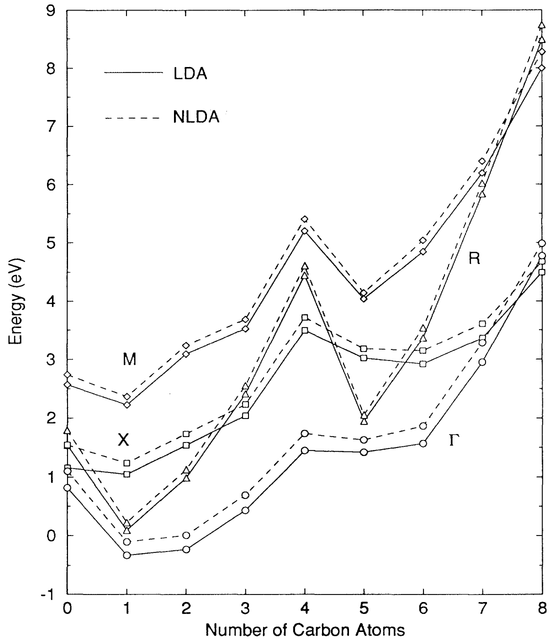

FIG. 2. The energy of the lowest conduction band at Γ (0,0,0), $X\ \frac{\pi}{a}(1,0,0)$, $M\ \frac{\pi}{a}(1,1,0)$, and $R\ \frac{\pi}{a}(1,1,1)$ points for cubic C_nSi_{8-n} supercell alloys computed within the LDA and NLDA. The top of the triply degenerate valence band at Γ is defined to be 0.0 eV. The cubic lattice constants were determined from Vegard's rule, with atoms placed at diamond lattice positions.

Figure 3 shows the LDA electronic band structure of cubic CSi_7 supercell alloys for two configurations: (a) carbon and silicon atoms were located on an ideal diamond lattice; and (b) the atomic positions were relaxed, so the net force acting on each atom is zero. During the relaxation process, silicon atoms located inside the unit cube move toward carbon atoms, which are located at every cube vertex. Therefore the silicon-carbon bond length decreases from 2.25 Å to approximately 2.04 Å, and the total energy decreases by 1.46 eV. We note that the silicon-carbon bond in the relaxed CSi_7 alloy is only 0.15 Å longer than Si-C bond in silicon carbide. This reduction in the bond length strengthens the C-Si bonding state, causing a "hyperdeep" level at −13.5 eV to become split off [Fig. 3(b)].

The energy levels above −10 eV for the unrelaxed CSi_7 alloy at the Γ point calculated in LDA, NLDA, and *GW* approximations are compared in Fig. 4. The top valence band (at $E = 0$) is triply degenerate in all three approximations (no spin-orbit coupling). The electronic structure is very similar to that of pure silicon, except that there is an "additional" band, located −0.33 eV (LDA) and −0.11 eV (NLDA) below the top valence band. This level, denoted by a dashed line in Fig. 4, is singly degenerate. Therefore only two of the three top valence bands in the LDA or the NLDA spectrum are occupied by electrons, and the unrelaxed CSi_7 alloy is in principle metallic. In the *GW* approximation, the additional level moves above the valence band and therefore CSi_7 becomes a semiconductor with a small energy band gap of 0.17 eV.

After relaxation of atomic positions, the LDA bands at Γ have a very similar structure to *GW* bands of the unrelaxed CSi_7 alloy, with a band gap of 0.18 eV, as shown in Fig. 3(b). However, at the R point the lowest conduction band is 0.35 eV below the top of the valence band. Therefore the relaxed CSi_7 alloy in the LDA is also metallic, with an indirect band gap of -0.35 eV. In the GW approximation, the band gap increases to 0.29 eV, and the energy of the lowest conduction band at the R point is 0.42 eV above the top of the valence band. Therefore the GW approximation predicts that the relaxed CSi_7 alloy is a semiconductor with a small direct band gap of 0.29 eV at the Γ point.

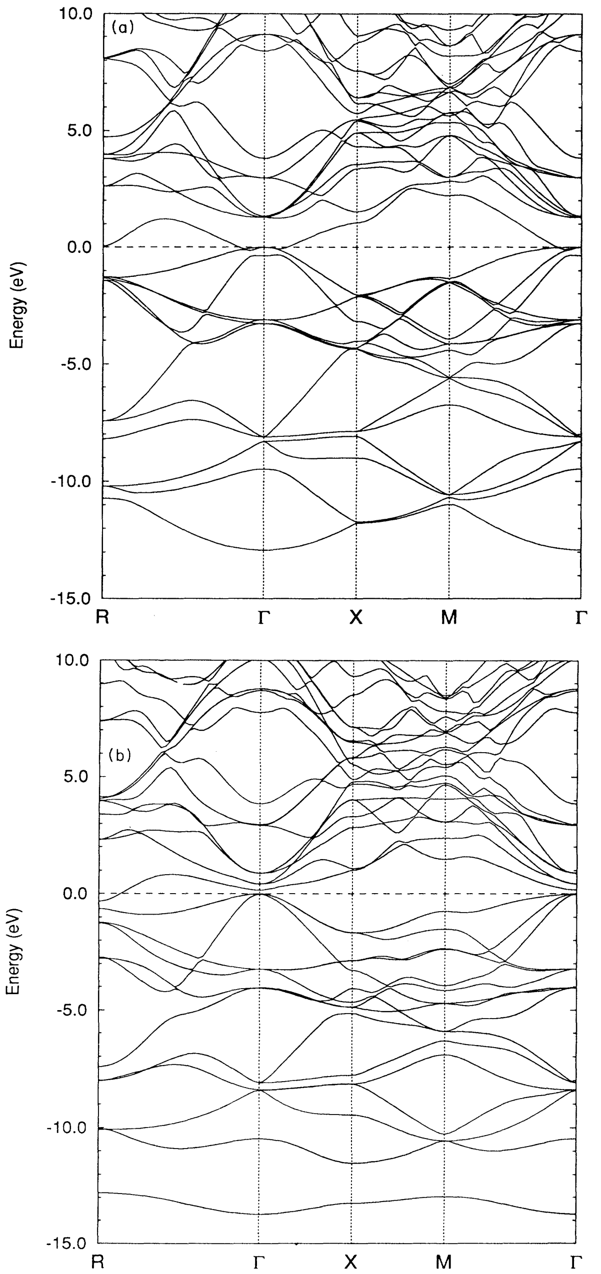

FIG. 3. Electronic band structure for unrelaxed and relaxed CSi_7 alloy calculated in the LDA approximation. The mixed basis set consisted of *spd* orbitals and a small number of plane waves. For both configurations, the lattice constants were determined from Vegard's rule.

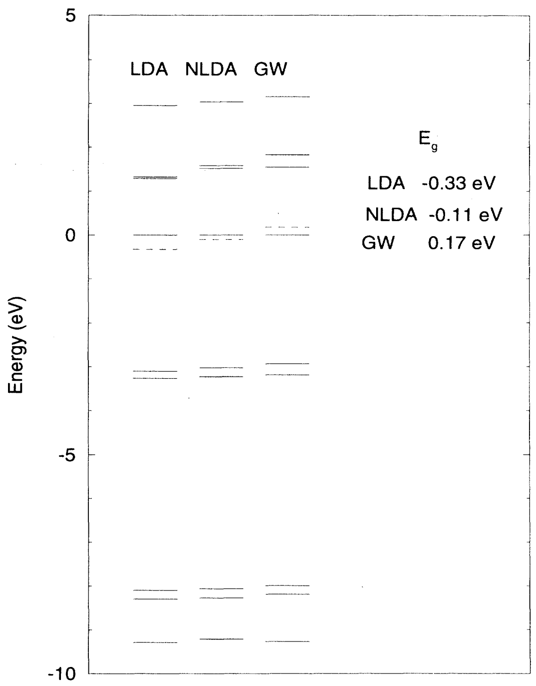

FIG. 4. The energy levels of unrelaxed CSi_7 in LDA, NLDA, and GW approximations at the Γ point.

One of the interesting features of the LDA electron band gaps found by Demkov and Sankey[6] was an unusual "double-well" shape for the value of the minimum band gap versus composition (see Fig. 12 of Ref. 6). We

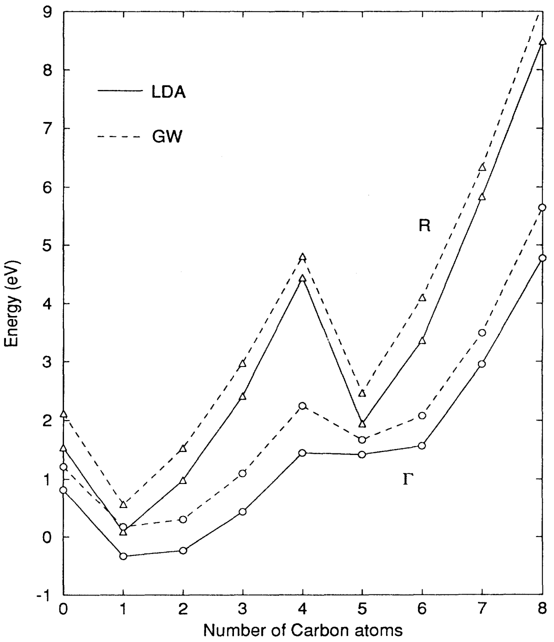

FIG. 5. The energy of the lowest conduction band of cubic carbon-silicon alloys in the GW and the LDA approximations for Γ (0,0,0) and $R\ \frac{\pi}{a}(1,1,1)$ points.

have found that this feature is also preserved in the *GW* approximation. Figure 5 shows the energy of the lowest conduction band calculated in the *GW* and the LDA approximations as a function of carbon composition. Both *GW* and LDA curves have the characteristic double-well shape with minima for CSi_7 and C_5Si_3 alloys, and a local maximum for silicon carbide. The *GW* curve is shifted upward with respect to the LDA curve. The trend is similar to that discussed above for NLDA energies, except that the shift is larger for diamond than for silicon.

The results reported here provide strong evidence that the band gap of silicon-carbon alloys is a quite complex function of alloy composition. The band gap reaches its absolute minimum for approximately 10% of carbon. At this composition the band gap is smaller than the band gap of pure silicon. This is valid for both relaxed and unrelaxed alloys. This phenomenon is related to the large chemical difference of silicon and carbon, and not to the detailed geometric distribution of atoms within the unit cell.

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