Thermodynamics of C incorporation on Si(100) from \textit{ab initio} calculations

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We study the thermodynamics of C incorporation on Si(100), a system where strain and chemical effects are both important. Our analysis is based on first-principles atomistic calculations to obtain the important lowest energy structures, and a classical effective Hamiltonian which is employed to represent the long-range strain effects and incorporate the thermodynamic aspects. We determine the equilibrium phase diagram in temperature and C chemical potential, which allows us to predict the mesoscopic structure of the system that should be observed under experimentally relevant conditions.

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Carbon-enriched silicon systems are the focus of current interest as candidates for a material with tailored electronic properties, which is compatible with well-established silicon technology. The tetravalent nature and large band gap in the diamond structure make carbon an ideal candidate for incorporation in Si. However, the solubility of C in Si under thermodynamic equilibrium is extremely low ($\approx 10^{-5}$) due to the huge mismatch in bond length (35\%) and bond energy (60\%) between C and Si. Non-equilibrium methods, such as molecular beam epitaxy (MBE), that exploit the higher atomic mobility on surfaces, can be used to overcome this obstacle and enhance solubility [1].

As predicted theoretically by Tersoff [2], C solubility is enhanced by several orders of magnitude near the Si(100) surface, especially in subsurface layers. Osten \textit{et al.} [3] confirmed experimentally this prediction and observed that C atoms diffuse to subsurface layers above a certain temperature. This finding opened new possibilities for growth of C-rich metastable structures.

The enhanced solubility near the surface has important consequences. The large tensile strain associated with C incorporation in Si has proven a very powerful tool in device engineering: a small amount of C can compensate the Ge-induced tension in pseudomorphic SiGe layers [4, 5, 6], and can also suppress dopant outdiffusion. This idea was recently implemented in a novel fusion. This idea was recently implemented in a novel tool in device engineering: a small amount of C can compensate the Ge-induced tension in pseudomorphic SiGe layers [4, 5, 6], and can also suppress dopant outdiffusion. This idea was recently implemented in a novel fusion. This idea was recently implemented in a novel

The microscopic features of C incorporation in Si are rather well understood. Previous work by the authors [7, 8] revealed an oscillatory C profile driven by the competition between two factors: the tendency of C atoms to occupy favorable sites which are determined by the reconstruction strain field, and the preferential arrangement of C atoms at certain distances which minimizes the lattice elastic energy. The profile is characterized by enhancement of C content in the first and third layer, depletion in the second and an exponential reduction from the fourth layer and beyond. The favorable C sites are in the third layer between the surface dimers, being under compressive stress [8, 9] and thus suitable for the smaller-sized C atom. The preferential arrangement of two C atoms in the surface layers is at a third nearest-neighbor position, which is also the lowest-energy configuration in the bulk [10]. The interaction of C atoms in first nearest-neighbor position is highly repulsive [11]. Moreover, a recent experiment [11] showed that C-C dimers are quite rare in the annealed C-Si(100) surface.

On the other hand, a mesoscopic picture of the surface structure that would link the atomistic features to long-range strain effects, and predict structures for different growth conditions more relevant to experiment, is lacking. Here, we present an approach that closes this gap and is able to determine the equilibrium surface phase diagram. It is based on first-principles atomistic studies, incorporating microscopic strain and polarity effects, which are expected to have a dominant role in the understanding of C incorporation in the host Si lattice. The results are linked to a classical effective Hamiltonian in a Monte Carlo scheme that incorporates strain into the thermodynamic aspects of the problem.

We considered first all possible atomistic configurations likely to have low energies. Guided by previous work [7, 8, 9, 10], we can establish a set of rules which should be obeyed by low energy configurations of the C-Si(100) system, namely:

(i) The surface has $c(4 \times 4)$ periodicity.
(ii) C substitutes Si atoms only in the first (surface) or in the third layer.
We discuss its variation below.

For low concentration of C, one atom per unit cell, which corresponds to $\frac{1}{8}$ ML coverage, the structure with subsurface C (1B) has lower energy than the one with a Si-C dimer (1A) on the surface. This result is in agreement with experiment: X-ray spectra indicate that for low C deposition, there is almost no C on the surface. A single C atom at a third-layer site relieves the compression due to the surface reconstruction and makes four Si-C bonds while a single C atom on the surface, as part of a dimer, allows the formation of only three SiC bonds. Passing to configurations with more than one subsurface C atom per unit cell, we find that the energy of configuration 2B is considerably higher than that of 2A, 2C, and 2E. Apparently, the presence of two subsurface C atoms per unit cell produces a large distortion of the surrounding Si-Si bonds. Thus, for two C atoms in the unit cell ($\frac{1}{4}$ ML coverage), the best situation is to have both C atoms on the surface. For three C atoms per unit cell ($\frac{3}{8}$ ML coverage), we observe an equivalence of surface/subsurface sites: configurations 3A and 3B have almost the same energy. For the case of four C atoms ($\frac{1}{2}$ ML coverage), there is just one structure (4A) consistent with the rules we discussed before. For illustration purposes, we include another configuration, 4B, containing C atoms in second neighbor positions, which violates rule (iii); its very high energy can be considered as a justification for these rules. We do not go beyond $\frac{1}{4}$ ML coverage because experiments show that this results in disordered structures.

To compare configurations with different C content, we use Eq. (1). This implies that the surface is in equilibrium with a reservoir of C atoms characterized by $\mu_C$. It is generally accepted that C forms small clusters, whose cohesive energies are in the range between $\pm 5.5$ and $\pm 7$ eV. In Fig. 2(a), we show the energies of configurations 0, 1A, 1B, 2A, 3A and 4A as a function of $\mu_C$. The vertical faint lines denote the transition points at which the preferred structure changes. We observe that the lowest energy structure depends strongly on $\mu_C$ and hence on the conditions of C deposition, making it difficult to predict what the actual structure of the system will be. This implies that the equilibrium surface structure might be composed of different configurations at the atomistic...

### Table I: Relative energies for the 12 configurations of Fig. 1, according to Eq. (1) in eV per c(4 × 4) unit cell. $\mu_C$ is taken as the energy of a C atom in diamond.

| nX | E(nX) (1A) | nX | E(nX) (1B) | nX | E(nX) (2A) | nX | E(nX) (2B) | nX | E(nX) (2C) | nX | E(nX) (2D) | nX | E(nX) (2E) | nX | E(nX) (3A) | nX | E(nX) (3B) | nX | E(nX) (4A) | nX | E(nX) (4B) |
|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|----|-----------|
| 0  | 0.19      | 2A | 0.35      | 2A | 0.35      | 3A | 1.25      | 3A | 1.25      | 4A | 2.81      | 4A | 2.31      | 4A | 2.31      | 4A | 2.31      | 4A | 2.31      | 4A | 2.31      |
The factor of one half takes into account double-counting of the summation on \( i \) where the summation on \( j \) runs over the 8 nearest neighbors of \( i \) (the factor of one half takes into account double-counting of the interaction); \( c_i \) is the configuration in cell \( i \), and \( \Delta E(c_i, c_j) \) is the interaction energy between the neighboring cells \( c_i \) and \( c_j \) (\( \Delta E(c_i, c_j) = 0 \)). In order to obtain these interaction energies, we calculated the total energies of all 144 \( c(12 \times 12) \) cells consisting of a cell \( c_i \) surrounded by 8 \( c_j \) cells. These were obtained using Tersoff’s empirical potential \( V \), with a Monte Carlo relaxation method. The key point here is that we are interested in elastic strain interactions between different cells rather than any specific features of their structure; for this type of interaction between cells the classical potential employed gives very reasonable results as established by previous studies of similar systems \( [1] [2] [3] \). Having determined \( \mathcal{H}_{\text{eff}} \), we performed an equilibrium Monte Carlo study for different values of the temperature and \( \mu_C \). We used a 70 × 70 grid of cells, which was sufficient to get converged averages. For each value of \( \mu_C \) the system was started from a random configuration at high temperature (1200K) and then was cooled down to room temperature.

In Fig. 2(b) we plot the average total C content of the system as a function of \( \mu_C \). The zero for \( \mu_C \) is taken to be the energy of an isolated C atom. For comparison, we plot the same quantity when the elastic strain interactions, \( \Delta E(c_i, c_j) \), are set equal to zero. In both cases the average C content of the system increases with increasing \( \mu_C \). The difference between the two curves shows the importance of elastic interactions, which, being of the order of 0.1-0.2 eV/ \( c(4 \times 4) \) cell, are more important than the total energy differences in the low \( \mu_C \) region. This effect weakens as \( \mu_C \) increases.

Another important consideration, with experimentally observable consequences, is the relative amount of surface versus subsurface C atoms as a function of the total C content \( C_{\text{tot}} \) in the unit cell, shown in the inset of Fig. 2(b). For larger total C coverage the ratio increases monotonically, approaching infinity as \( C_{\text{tot}} \rightarrow 4 \). Again, we give the case with \( \Delta E(c_i, c_j) = 0 \) for comparison. There is a critical coverage of 1.39 C atoms per unit cell, or 0.17 ML, beyond which C prefers mostly surface sites. This critical coverage has a weak temperature dependence: it has a maximum around 850K, and then falls monotonically down to roughly 0.16 ML at 300K and 1100K. The increase of the surface C with increasing total C is not unexpected: although third layer compressed sites seem ideal for the smaller C atom, a large amount of subsurface C is not unexpected: although third layer compressed sites seem ideal for the smaller C atom, a large amount of subsurface C would cause large strain and raise the total energy dramatically, as exemplified by the case of configuration 4B, which we discussed earlier. From Fig. 2(b) we see that the transition from mostly subsurface to mostly surface C content does not coincide with the change from 1 to 2 C atoms per cell, as suggested by our \textit{ab initio} results, indicating that the elastic strain interactions play a dominant role in the structure of the surface.

Representative snapshots of the C distribution from the Monte Carlo run at 850K are shown in Fig. 3. The three cases correspond to the points shown in Fig. 2(a).
An impressive long range order is revealed for the subsurface C (right column of Fig. 3). For low $\mu_C$, Fig. 3(c), this order appears in the form of alternating rows of similar C content. These consist mostly of unit cells corresponding to 0 and 2B structures. Although structure 2B has relatively high energy, as shown in Table I, a structure of alternating 0 and 2B cells seems to be preferable, giving C the chance to take advantage of the desirable third layer compressed sites. The line-pattern is a result of the strong interactions in that range of $\mu_C$, which forces the $c(4 \times 4)$ cells to have the maximum number of different neighbors, 6 for the row pattern and 4 for a chess pattern. The latter pattern is observed for higher $\mu_C$, Fig. 3(b), and is typical for the range of $\mu_C$ and temperature corresponding to 1-2 C atoms per unit cell on average (see also Fig 2(b)). In this case, the self-energies of the different configurations dominate over the elastic strain interactions. In the specific example shown in Fig. 3(b), the structure consists mostly of 3A and 2B cells, at a ratio 2:1. This suggests that for conditions corresponding to this range of $\mu_C$, an alternating pattern of surface/subsurface C is preferable. As $\mu_C$ increases the energies of the cells become large enough so that the elastic interactions are not that important, and thus the system does not have much to gain by self-organizing. This results in the random pattern shown in Fig. 3(a), which consists mainly of 4A cells with a few 3B cells around them. Again, of the two configurations with three C atoms, the one with some subsurface C is preferred when the dominant configuration has all its C atoms on the surface.

Finally, we note that while subsurface C shows this interesting ordering behavior, the surface C seems to be randomly distributed as the patterns of the middle column of Fig. 3 indicate. The ordered structure appearing in the total distribution of C (left column of Fig. 3) is caused by an ordered third-layer C configuration; this is best seen in Fig. 3(c). This idea was implicitly suggested by previous experimental work [10]. From our first-principles calculations, we found that the geometrical features of the Si-Si dimers in all 12 cells are essentially the same. Surface C is invisible, or shows up as a missing Si atom, in STM experiments [1]. This implies that one cannot distinguish, using standard microscopy, between pure Si(100) or Si(100) with vacancies, and a configuration with C in the third layer; the only criterion is the long-range order and the change of the reconstruction.

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FIG. 3: Density plot of the C distribution on the surface at $T$=850K; (a) $\mu_C = -6.1$, (b) $\mu_C = -6.4$eV, (c) $\mu_C = -6.8$ eV for (c). White corresponds to 4 C atoms, black to 0 C atoms. Each panel represents an area of 38×38 nm$^2$ and is $\frac{1}{4}$ of our simulation cell.

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[17] We use a periodic slab of 7 layers terminated by H on one side with 6 layers allowed to relax. We use a plane
wave basis with a cutoff kinetic energy of 36 Ry and the \( \Gamma \) point of the Brillouin zone for reciprocal space sampling. Atomic positions are relaxed until the magnitude of the calculated Hellman-Feynman forces is smaller than 0.001 Ry/a.u. For each configuration, several different starting geometries were considered to ensure that the correct minimum energy structure is found.

[18] To obtain the chemical potentials, we calculate the energies of C and Si in the diamond structure with the same kinetic energy cutoff and the corresponding k-point grid spacing for the bulk. We use the experimental cohesive energy of diamond, namely 7.37 eV/atom.

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