Energetics and Equilibrium Properties of Thin Pseudomorphic $Si_{1-x}C_x(100)$ Layers in Si

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We investigate the structure of carbon enriched thin silicon films which involve large strains, using first-principles total energy calculations and Monte Carlo simulations. We identify the energetically most favored configurations of substitutional carbon atoms in the Si(100) surface layers, and obtain the equilibrium depth profile at various temperatures. The interplay between the reconstruction strain field and the solute-atom interactions leads to complicated structural patterns that are different from related weakly strained systems. [S0031-9007(97)03115-3]

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Alloy formation by mixing different elements is typically restricted by the solubility of one species in the lattice of the other as imposed by thermodynamic equilibrium. The presence of the surface and interface regions in a thin film allows for considerably more diverse structures to become stable or metastable. At present, the realization of artificial thin alloy films is being vigorously pursued for a wide range of technological applications. These generally metastable materials, which are often fabricated under nonequilibrium growth conditions, exhibit certain desirable characteristics such as improved mechanical stability and tailored electronic properties. This approach presents new theoretical and experimental challenges to our understanding of structural stability under special conditions. A crucial factor that can affect the stable structure and hence the properties of the material and its relevance to applications is the controlled incorporation of substitutional atoms. Despite its importance, neither the mechanisms nor the consequences of the incorporation process are well understood. Mechanisms for atomic insertion are exceedingly difficult to determine because they involve complicated kinetic processes. Therefore, it is appropriate to first develop models for and insight into the most stable arrangements of substitutional atoms in the host material, a task both more amenable to theoretical study and easier to link to experimental investigations.

The case of carbon incorporation in silicon represents one of the most intriguing situations due to the huge size mismatch between the two elements. This system is promising for applications related to band-gap engineering and manipulation of the lattice constant. The solubility of C in Si is very small (of order 10^{-3} at. %). Current experimental efforts to overcome this obstacle are based on nonequilibrium methods which exploit the less constrained environment and the higher atomic mobility on surfaces [1,2]. The goal is to fabricate thin pseudomorphic $Si_{1-x}C_x$ layers in Si with enhanced carbon concentration, without the formation of SiC precipitates. Theoretical attempts to study this issue [1,3] singled out two possible factors that could play a role in enhancing carbon solubility. Rücker *et al.* [1] proposed that the system relieves strain energy by forming ordered *bulk* structures which optimize the interaction between C substitutionals, while they neglected surface effects. In a significant contribution to the problem, Tersoff [3] pointed out the importance of the elastic interaction of an isolated carbon impurity with the surface, but did not include the interaction between C atoms. Because of the nature of the deposition process, and because high C concentrations are involved, the surface factor and the C-C interactions are strongly interrelated.

Here, we attempt to provide a finite-temperature thermodynamic description of the system, while taking into account in our theoretical model both the surface effects and the solute atom interactions. We concentrate on C incorporation in Si(100). We first performed static calculations to identify the energetically most favorable configurations of C atoms in the near-surface region. Then, the overall surface profile (average site occupancies) was obtained by carrying out Monte Carlo (MC) simulations at a range of temperatures, thus accounting fully for positional, configurational, and vibrational contributions to the free energy. We were able to determine the exact microscopic structure in thin $Si_{1-x}C_x$ layers (up to 22 Å thick), from which it is evident that the surface profile is driven by competition between the tendency of C atoms to occupy favorable sites determined by the reconstruction strain field, and the preferential arrangement of C atoms at certain distances which minimizes the lattice elastic energy.

The static calculations also helped calibrate the empirical interactions employed in the MC simulations by comparing the results to first-principles quantum mechanical calculations. The empirical formalism utilized here is based on the interatomic potentials of Tersoff for multicomponent systems [4], and has been used with success in similar contexts ($Si_{1-x-y}Ge_xC_y$ alloys [5]). In the first-principles calculations, based on density functional theory in the local density approximation, the system is modeled by a slab geometry composed of eight atomic layers in the (100) direction, separated by vacuum regions equal to

12 Å, and with the bottom layer passivated by H atoms. The top layer is reconstructed in the usual manner, forming dimers in a (2 × 1) periodic unit cell [6]. The lattice constant was chosen as that of bulk Si. Norm-conserving atomic pseudopotentials were used to eliminate core states [7]. Reciprocal space integrations were approximated by two sampling points in the irreducible surface Brillouin zone, and a plane wave basis with kinetic energy up to 36 Ry was employed for expanding the electronic wave functions. For each atomic configuration the geometry was relaxed by minimizing the magnitude of the calculated Hellmann-Feynman forces.

We begin with a description of the comparison between the first-principles and the empirical potential calculations for the energetics of C incorporation on and near the Si(100) dimerized surface. We selected a number of representative configurations and compared the relative energy differences obtained from the first-principles calculations to those obtained with the empirical interatomic potentials. The configurations included the same number of C atoms in each unit cell [two C atoms per (2 × 1) unit cell], so that consistent energy comparisons could be made without involving chemical potentials. The first configuration involves C dimers in layer 1, as shown in Fig. 1(a) (in the following the layer index increases from the surface into the bulk). The remaining configurations have the C atoms in subsequent layers below the surface, either at the same layer [layer 2, Fig. 1(b), or layer 3, Fig. 1(c)], or at different layers [layers 3 and 4, Figs. 1(d), 1(e), and 1(f)]. These configurations include structures with C atoms either directly below the surface Si dimers or between them. They also include structures with the C atoms at first, second, and third nearest-neighbor positions. Thus, they encompass a wide range of possibilities that are likely to occur.

The energy of the first configuration is taken to be the zero of the energy scale in each case. The relative energy of the remaining configurations is shown in Fig. 2. The agreement between the first-principles results and the empirical potential results is quite good: in both cases the configurations with the lowest energy are the ones with the C dimers on the surface [Fig. 1(a)]. Apparently, the gain in chemical energy due to the formation of the C dimers overwhelms the energy cost due to the large deformations that accompany this structure. The configuration with the highest energy involves the two C atoms at nearest-neighbor positions [Fig. 1(d)], one in the third and one in the fourth layer, both directly below the surface Si dimers. Next in order of decreasing energy are the two configurations that have the C atoms at second-neighbor distances but in the same layer [Figs. 1(b) and 1(c); the energy of the configuration with both C atoms in layer 4 is slightly higher than when they are both in layer 3]. Finally, the subsurface configurations with lowest energy involve the two C atoms situated in the third and fourth layers (one below and the other between the Si dimers), at third-neighbor positions [Figs. 1(e) and 1(f)]. These comparisons in energetic ordering apply to both sets of calculations *with no exceptions*. Accordingly, we conclude that the accuracy of the empirical potentials is adequate for the investigation of the equilibrium properties of the system.

In Fig. 3 we display selected charge density plots from the various configurations that capture the most interesting features of interatomic bonding. The top two panels correspond to Fig. 1(a), the middle two panels to Fig. 1(d), and the bottom two panels to Fig. 1(e). The panels on the left column are charge density plots on a plane passing through the surface dimers, while those on the right column are on a plane perpendicular to the dimers, which bisects them. We see that the C-C dimer involves the highest charge density, and that the Si-C bonds involve higher charge density than Si-Si bonds, but in a polarized distribution closer to the C atom. In the configuration with the two C atoms at nearest-neighbor distances in layers 3 and 4 (middle panel on the right column) there is no C-C

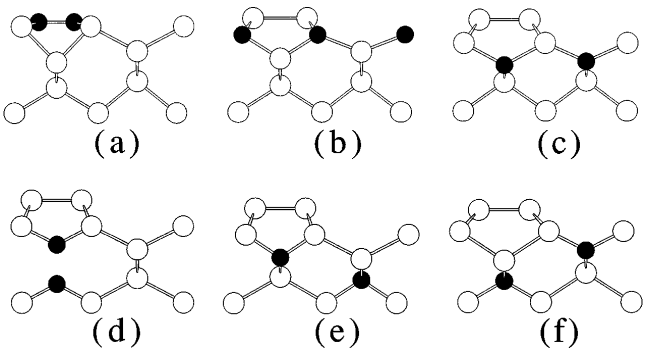

FIG. 1. Various configurations of C atoms on and near the Si(100) dimerized surface (see text for details). Large open spheres denote Si atoms, while dark small spheres are C atoms.

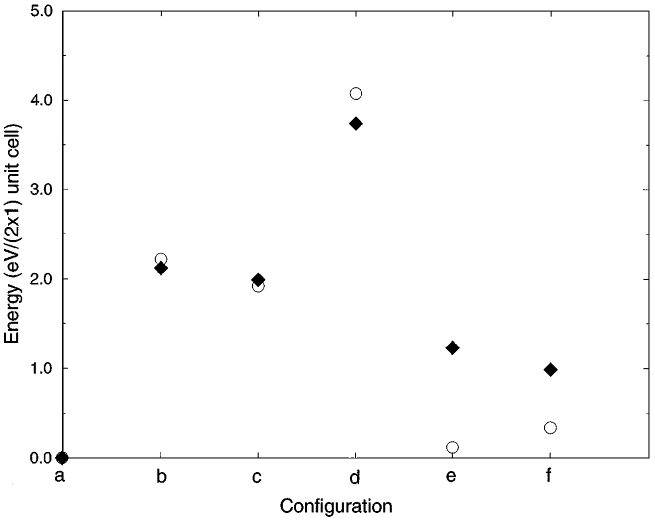

FIG. 2. Energies of the configurations shown in Fig. 1 (relative to the C-C dimerized surface). Filled diamonds denote the *ab initio* values. Open circles show the empirical potential results.

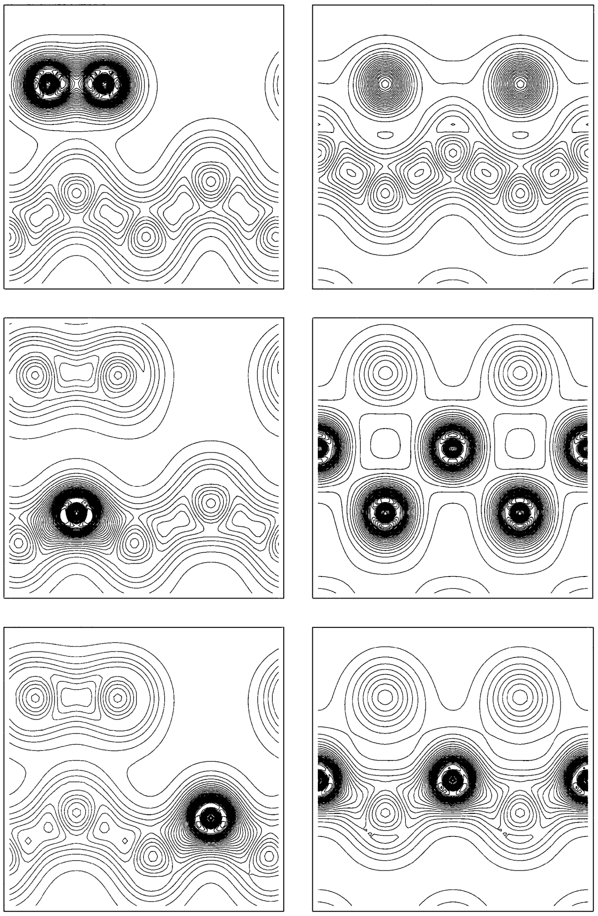

FIG. 3. Charge density plots of various configurations on a plane that passes through the surface dimers (three panels on the left column) and a plane perpendicular to the dimers that passes through their midpoint (three panels on the right column).

bond. These two C atoms repel each other to a distance of 2.66 Å. This is remarkable, because it implies that the two C atoms prefer to form two Si-C bonds to their Si nearest neighbors with relatively small distortion of the lattice, at the expense of not forming two C-C bonds, which would have required a much larger distortion. The absence of C-C bonds in this configuration is evidently the reason for its very high energy.

Next, we calculated the equilibrium composition profile of the surface layers, which is important in understanding and analyzing the experimental results. This study will also determine how feasible it is for C atoms deposited on the surface to migrate into the crystal. The rate of diffusion is expected to depend on the initial C coverage, on whether prior to the migration the C atoms can form surface dimers, and on the temperature. Because of the low energy of the C-C surface dimer structure, we cannot exclude the possibility that under certain conditions the dimerized surface might be realized. Moreover, since the aim is to study the feasibility of producing thin layers with enhanced C concentration, high initial C coverages must be considered.

Average site occupancies are obtained *via* MC simulations using a recently introduced efficient algorithm [5], which effectively lowers the barriers for diffusion in systems composed of atoms with large size mismatch. In this approach, in addition to the usual random atomic displacements and volume changes, we include identity switches (from Si to C and *vice versa*), while keeping the composition constant. In such switches there is an extra "exchange" barrier due to the strain introduced by atoms of one type being placed at sites previously occupied by the opposite type. Accordingly, each identity switch is accompanied by relaxation of nearest-neighbor atoms, which reduces the exchange barrier and leads to equilibration much faster than in molecular dynamics simulations. For the MC studies we use (6×6) supercells consisting of 18 layers. Most of the simulation runs were started with the top layer fully covered with (2×1) C dimers as shown in Fig. 1(a). We equilibrate the structures by allowing diffusion of atoms (by flips) within the first eight layers where atomic motion is rapid enough to establish local equilibrium with the surface, as suggested by experimental observations [1,2]. We then equilibrate the first 16 layers to obtain the limiting behavior.

The resulting profile of C atoms for different temperatures and equilibration depths is shown in Fig. 4. The carbon content is given relative to the value that corresponds to spreading the initial one monolayer of carbon over 8 or 16 layers. Medium and high temperatures refer to typical growth (~800 K) and annealing (1500 K) conditions. The profile shows certain interesting characteristic features. As expected, the coverage of the top layer with C is drastically reduced at high T, reflecting the extra energy needed to break the strong C-C dimer bond. But the most pronounced feature is that all three curves exhibit a well defined oscillatory behavior which is characterized by enhancement of C concentration in layer 3 and reduction in layers 2 and 4. Comparison of the two curves at

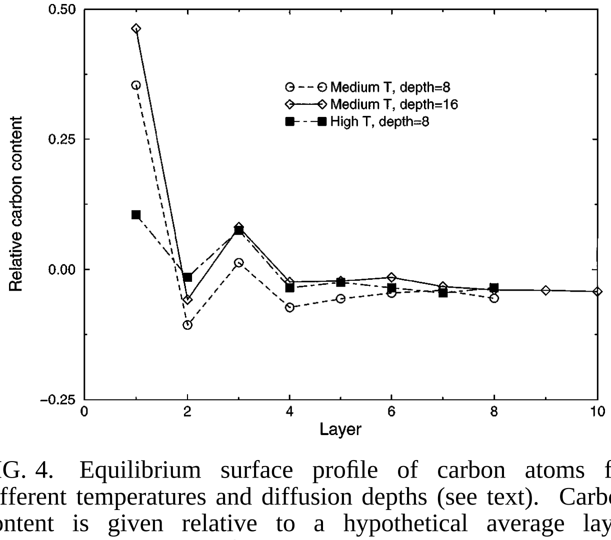

FIG. 4. Equilibrium surface profile of carbon atoms for different temperatures and diffusion depths (see text). Carbon content is given relative to a hypothetical average layer composition. Only the first ten layers are shown.

medium temperature shows that bulklike limiting behavior is already attained by layer 7.

There are two important aspects of these results. The first concerns the diffusion of the adsorbed surface C atoms into substitutional subsurface sites. We find that this is done quite easily despite the highly stable, initial configuration. We have repeated the simulations by artificially preventing the adsorbed C atoms from forming surface C-C dimers, but allowing the formation of Si-Si or Si-C dimers. The result is less C on the surface, enhanced diffusion, and a higher C concentration in the subsurface layers, but with the same oscillatory shape of the profile. This rapid migration of C atoms from the top layer is in agreement with recent experimental work by Osten *et al.* [2] who report that diffusion leads to a narrow layer of a highly concentrated alloy with a thickness of about ten monolayers (the experimental composition profile has not been reported). The role of the reconstructed surface in enhancing C solubility, without the need of raising the C chemical potential, has been demonstrated by Tersoff [3]. In that work, the case where C is in the first layer was not considered, and the solubility enhancement was estimated using energies of an isolated substitutional C atom. The behavior of alloy layers with high C concentration may elude this simple model.

The second aspect concerns the oscillatory behavior of the C concentration. In general, this behavior is driven by the repulsive interaction between nearest-neighbor C atoms [1,5], which prevents them from equally populating adjacent layers. This explains the reduction of C content in layer 2 with respect to layer 1, or in layer 4 with respect to layer 3. The precise profile is a result of a cooperative effect between the energetic preference of C for the various sites, as found by the static calculations (Fig. 2), and the simultaneous coupling of all geometries (see Fig. 1) while averaging over the configuration space during MC sampling. There are, however, further complications in this picture that are introduced by the surface reconstruction and have to do mainly with layers 3 and 4. In these layers there are two inequivalent sites, those below the dimers which are under compressive stress and thus favorable for the smaller atom (in this case C), and those between dimers which are under tensile stress and thus unfavorable for the smaller atom [8]. Now considering both layers, this stress-driven mechanism would work well in the dilute alloy limit, or when the interaction among the solute atoms is attractive or at least neutral (as in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$). But for the strongly repulsive case encountered here, and for a high concentration alloy, this mechanism needs modification. Therefore, besides the overall reduction of C content in layer 4, an additional effect takes place, that is, a smaller population of C at the favorable sites below the dimers compared to the population at respective sites in layer 3. At the same time, the population of C at the unfavorable sites of layer 4 rises and becomes essentially equal to that of the favorable sites. This effect holds at all the temperatures studied. Obviously, the instability which characterizes the configuration in Fig. 1(d), as inferred from the static calculations, is only partially overcome by high-temperature effects.

Finally, we comment on the significance of these findings for the problem of growth of highly concentrated C-alloy layers in Si. It has been suggested [3] that if such layers cease to be accessible to diffusion as further material is deposited on top, they become buried and the relevant geometries are frozen in. In this way, enhanced C content in a thin layer can be realized. From the discussion above, it follows that the most probable geometry to be frozen in during actual deposition conditions consists of a mixture of configurations of the type depicted in Figs. 1(e) and 1(f), with fewer cases of the energetically unfavorable configurations typified by Fig. 1(d). Therefore, assuming that this *freezing-in* mechanism governs the growth of thicker layers, we can conclude that bulk ordering of the type observed in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys [8,9], having as a prerequisite the latter configuration, is rather unlikely. This conclusion is contrary to earlier theoretical predictions [3]. On the other hand, the configurations that have C atoms as third-nearest neighbors, proposed earlier as most probable *bulk* geometries [1], will be contaminated with the unfavorable structures to a certain degree, as our MC simulations predict. Thus, the real picture of C structures in Si is more complicated than either the picture neglecting surface interactions, or the picture neglecting solute-atom interactions. This determination of the near surface structure and composition will hopefully instigate realistic studies of the electronic properties of this material which are as yet not well understood.

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