Substitutional carbon impurities in thin silicon films: Equilibrium structure and properties

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We discuss a set of atomistic calculations of the structure of Si geometries with substitutional carbon atoms, involving the (100) surface or bulk features related to thin films grown in the (100) direction. We use both quantum mechanical density functional theory and empirical potential calculations at finite temperature and constant pressure to study the local structure, bonding characteristics and overall distribution of the carbon atoms in the host silicon lattice. These calculations reveal a strong nearest neighbor repulsion between substitutional carbon atoms, to the point where these atoms prefer to have fewer bonds than normally in order to avoid each other. This effect still holds for high temperatures and high carbon concentrations. As a result, bulk ordering of the type observed in Si–Ge alloys is unlikely to occur. [S0734-211X(98)00103-6]

I. INTRODUCTION

Incorporation of carbon atoms at high concentrations in Si wafers has been considered as a means of altering their structural and electronic properties. The large difference between the covalent radii of carbon and silicon results in very large local strain when a carbon atom replaces one of the atoms in the host Si lattice. This limits the energy that can be gained by forming the typically strong Si–C bonds, and as a consequence the solubility of C in Si is very small (of order 10^{-3} at. %).

One possibility of enhancing the solubility of C is to take advantage of nonequilibrium and surface effects in thin films. Recent theoretical work by Tersoff[1] emphasized the beneficial effect of the surface in mediating the elastic strain that C impurities induce in the Si lattice. Ordered artificial structures have also been considered as a possible way of reducing the strain.[2] Our work on this problem has provided a more comprehensive picture of this effect, including both surface-impurity interactions as well as interactions between impurities, in a realistic way.[3] In the present article we elaborate on these issues and consider the interaction of C impurities in hypothetical structures that should be relevant to thin Si films. The idea here is that for the structures we considered, the proximity of the surface will provide certain advantages to C incorporation, which once buried will remain stable in a bulklike environment.

II. METHODOLOGY

We first discuss our calculations on the distribution of C atoms in the close vicinity of the (001) surface of silicon, the most common substrate orientation for device applications. The calculations reported here employed two different approaches. We use an empirical interatomic potential to determine the structure and the energy of different configurations as well as to perform finite temperature and constant pressure Monte Carlo (MC) simulations to examine the equilibrium distribution of the impurities. In addition, we use first-principles quantum mechanical calculations to fully relax representative structures and obtain a more detailed description of the bonding by analyzing the electronic charge density distributions. The first-principles calculations also serve as a check of the accuracy of the empirical potential calculations. In general, we find that for the systems studied here energy differences computed with the two approaches are in good agreement.[3]

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 (for example, $Si_{1-x-y}Ge_xC_y$ alloys[5]). In the first-principles calculations, based on density functional theory in the local density approximation, the surfaces are modeled by slabs composed of 8 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. The lowest energy structure of Si dimers consists of asymmetric, tilted dimers, but this is stable only at very low temperature. At higher temperature the dimers oscillate between two tilted positions, being on the average symmetric. Since we are interested in relatively elevated temperatures, we assume symmetric C–C and Si–Si in all the dimer configurations.

The lattice constant for the first-principles calculations was chosen as that of bulk Si. Norm-conserving atomic

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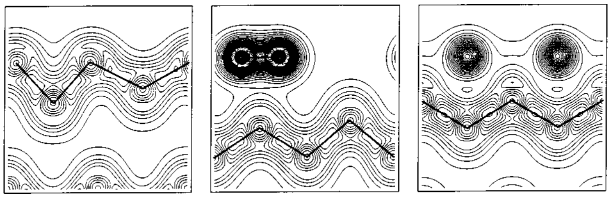

FIG. 1. Electronic charge density distribution for a configuration with the C atoms on the surface forming a dimer. The left panel is on a (110) plane parallel to the dimer, but which does not contain the dimer. The middle panel is on a (110) plane which contains the dimer. The right panel is on a plane perpendicular to the other two, which bisects the dimer. The straight lines correspond to Si–Si covalent bonds. Notice the characteristic high concentration of electronic charge around the more electronegative C atoms (middle panel), and the high density of charge corresponding to the C–C bond (right panel).

pseudopotentials were used to eliminate core states.[6] 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. For the bulk calculations, we used only one sampling point in the Brillouin zone since the unit cell contains more atoms (a total of 64), and a lower cutoff for the plane wave basis (28 Ry), which has been established as adequate for energy comparisons.[7]

III. RESULTS AND DISCUSSION

One of the important findings of our calculations is that the lowest energy configuration involves the C atoms at the very top layer of the Si(001) surface, forming dimers in the (2×1) reconstruction. This is somewhat surprising, because of the size difference. Typically, it is the larger atoms that tend to remain on the surface, where the fewer structural constrains permit them to relax in the direction away from the surface and reduce the amount of strain. This is precisely how other group-IV elements behave on the Si surface, such as Ge.[8] This element lowers the surface energy of the Si substrate when deposited at monolayer coverage. One might expect C to behave in the opposite manner, being smaller than Si, but this is not the case. We suggest that the strong preference of C to remain on the surface is due to the strong bond between the two threefold coordinated C atoms (as the ones on the Si surface that form dimers are). The ability of C to form double bonds makes this a low energy structure.

To demonstrate this effect we show in Fig. 1 the electronic charge density distribution for the system where C dimers form the top layer. This figure is composed of three panels. The left panel is a plane parallel to the dimers, passing through Si ⟨110⟩ chains that are closest to the surface, but not through the surface dimers themselves. This plane contains the Si atoms to which the C atoms are bonded. The middle panel is the plane on which the dimers lie; it also contains a ⟨110⟩ Si chain, which lies below the previous one. The right panel is a plane that intersects the dimers in their middle, and is perpendicular to the two previous planes. From the charge density distributions, the strength of the C–C bond in the dimer is evident, since it has a much higher electron density than the regular Si–Si bonds in the ⟨110⟩ chains. From the middle and right panels, it appears that the C–C dimer is essentially decoupled from the rest of the system (except of course for the back bonds it forms to the Si atoms). What is also remarkable is the height of the C atoms. Close comparison of the middle and right panels where the positions of the two C atoms are evident, to the left panel which includes the positions of the top Si atoms to which the C atoms are bonded, shows that the C atoms and their immediate Si neighbors are essentially at the same height. This is quite interesting, because typically the dimers on the surface are at a position significantly higher than their immediate neighbors. What takes place here is that the requirement that both Si–C and C–C bonds be at their optimal lengths can only be satisfied when the two C atoms approach each other and at the same time come closer to their immediate Si neighbors. A consequence of this structural relaxation is the strong repulsion that the Si atom directly below the C–C dimer feels, and as a result is pushed further down into the substrate. This is evident by inspecting the ⟨110⟩ Si chain in the left panel, in which one of the Si atoms (the one directly below the C–C dimer) is significantly lower than its normal position.

The above analysis makes clear the reasons why the configuration with the C atoms in the top layer is the most stable one. This fact has important ramifications. It implies that if C atoms have a chance to form C–C dimers upon arrival on the Si surface, their subsequent incorporation in the substrate will be limited (see below for finite temperature C profiles). This suggests that in order to optimize C incorporation, it is desirable to have atomic C arriving at the surface and at relatively low flux, so that it can react with the surface before it encounters other C atoms. Sources that maximize the percentage of atomic C in the flux would therefore be preferable.

The next interesting feature of our investigation of the near-surface region concerns the relative position of C atoms in the layers below the surface. We will concentrate on a pair of C atoms occupying sites in the third and fourth atomic layers counting from the surface Si dimers. There are several possible relative positions for these two C atoms. We discuss these along with the corresponding electronic charge density plots, shown in Fig. 2 (on the same three planes as the ones in Fig. 1). The first configuration (top row of Fig. 2) has both C atoms on the plane that bisects the Si dimer: one C atom (in the third layer) is part of a ⟨110⟩ chain which lies on a plane parallel to the dimer (left panel of first row), and the other is part of a chain that lies on the same plane with the dimer and it is situated directly below the center of the dimer (middle panel of first row). The position of both C atoms is evident from the higher concentration of electronic charge around them in the right panel of the first row, which corresponds to a plane that bisects the Si dimer. The second configuration has the two C atoms at third neighbor distances in

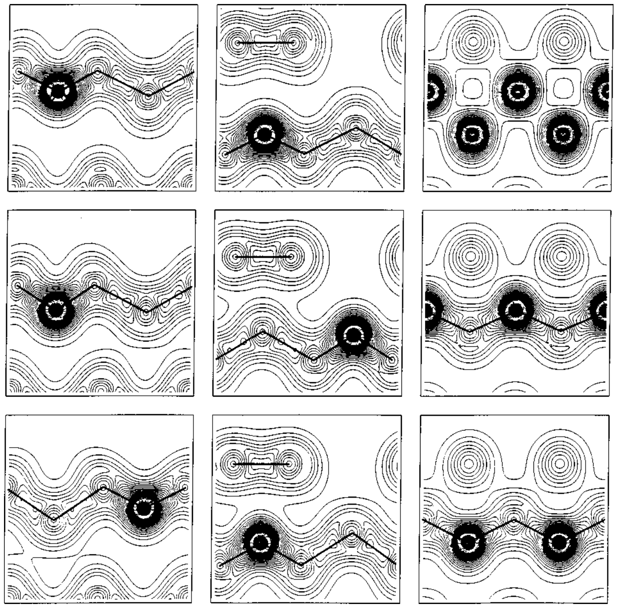

FIG. 2. Electronic charge density distributions for three configurations with the C atoms in the third and fourth layers, counting from the surface dimers. Each row corresponds to one configuration, with the charge density displayed on the same planes as in Fig. 1. The straight lines correspond to Si–Si and C–Si covalent bonds. In the first configuration both C atoms are at sites that have compressive strain due to the surface reconstruction. In the other two configurations only one of the C atoms is at such a site.

the plane which is parallel to the Si dimer (left and middle panels of second row in Fig. 2). Neither of the C atoms is in the position below the Si dimer, as is evident from the right panel of the second row, on the plane that bisects the Si dimer. The third configuration also has the C atoms at third neighbor distances in the plane parallel to the dimer (left and middle panels of the third row), but in this case one of the C atoms is in the position directly below the Si dimer, as is evident from the right panel of the third row.

These comparisons reveal some interesting features of the C–C interaction. First, we note that the positions of the two C atoms in the first configuration are the sites of compressive strain due to the surface reconstruction.[8] Therefore it might be expected that these are the optimal sites to accommodate the smaller C atoms in the Si lattice. In the other two configurations only one of the two C atoms finds itself in one of the sites of compressive strain: in the second configuration it is the atom seen in the left panel, while in the third configuration it is the atom seen in the middle panel directly below the Si dimer. It might be expected that the second and third configurations have higher energy than the first configuration, since in the latter only one C atom is in the potentially favorable compressive-strain site. The energy comparisons reveal that this simple expectation is not borne out: the first configuration has considerable higher energy than the other two [by 3.96 eV and 3.74 eV per (2×1) unit cell, respectively]. The reason is that the size of C atoms is so small compared to atomic distances in the Si lattice, that the simple considerations based on strain arguments are not applicable. In fact there is a rather surprising effect: as can be clearly seen in the right panel of the first row (which should be compared, for example, to the density corresponding to a C–C bond in Fig. 1), the C atoms in the first configuration are not bonded together, despite the fact that they are at nearest neighbor positions in the Si lattice. This is quite remarkable. It indicates that in this configuration the system prefers to minimize the strain energy by forming proper Si–C bonds (see left and middle panels of first row in Fig. 2), at the cost of missing two simple covalent bonds between the C atoms. This translates into an effective strong repulsion between the C atoms when they are at first neighbor positions. The distance between the C atoms in the energetically unfavorable configuration is 2.66 Å. Formation of a C–C bond in this configuration would have required a much larger distortion of the host lattice given that this bond is 35% shorter than the bond length of Si.

The discussion up to this point involved structures that are directly related to the dimerized (001) surface. We next consider three structures that do not have a surface. These structures consist of supercells containing 64 atoms each, with periodic boundary conditions in all three directions. The size of the unit cell is $\sqrt{2}a\times\sqrt{2}a\times4a$, which is a multiple of the unit cell with a base on the (001) plane [with vectors along the (110) and $(1-10)$ directions]. We chose this particular geometry to mimic the structure of the interior of a thin film grown in the (001) direction. Of the 64 atoms in the unit cell, two are C atoms and the rest are Si atoms, which corresponds to a density of $\sim3\%$. The three configurations correspond to having the two C atoms:

(a) at third nearest-neighbor positions, in analogy with the most favorable configurations (besides the C dimer on the surface) encountered in the surface structures (see second and third rows in Fig. 2);
(b) at random positions in the unit cell; and
(c) at the unfavorable nearest-neighbor configuration, in analogy to the structure depicted in the first row of Fig. 2. Perspective views of the three configurations are given in Fig. 3. (Other possible structures that might be frozen-in during growth consist of combinations of the above three configurations and shall be studied in the future).

We find that configuration (a) has the lowest energy, followed by configuration (b) which is higher by only 0.49 eV, while configuration (c) has an energy higher than (a) by 2.85 eV. These results are in good agreement with our earlier findings, namely that C atoms at nearest-neighbor sites in the Si lattice are strongly repelled, while the third neighbor distance appears to be a favorable one energetically. Rücker *et al.* also reached at the same conclusion.[2] The structures shown in Fig. 3 indicate that the nearest-neighbor position of the C atoms is so unfavorable that the two atoms form only three Si–C bonds each and no C–C bond, by analogy to the situation for the surface, where the Si–C bonds are strengthened at the expense of the C–C bonds which are broken.

Finally, in addition to the static calculations of structural features we have performed MC simulations at finite tem-

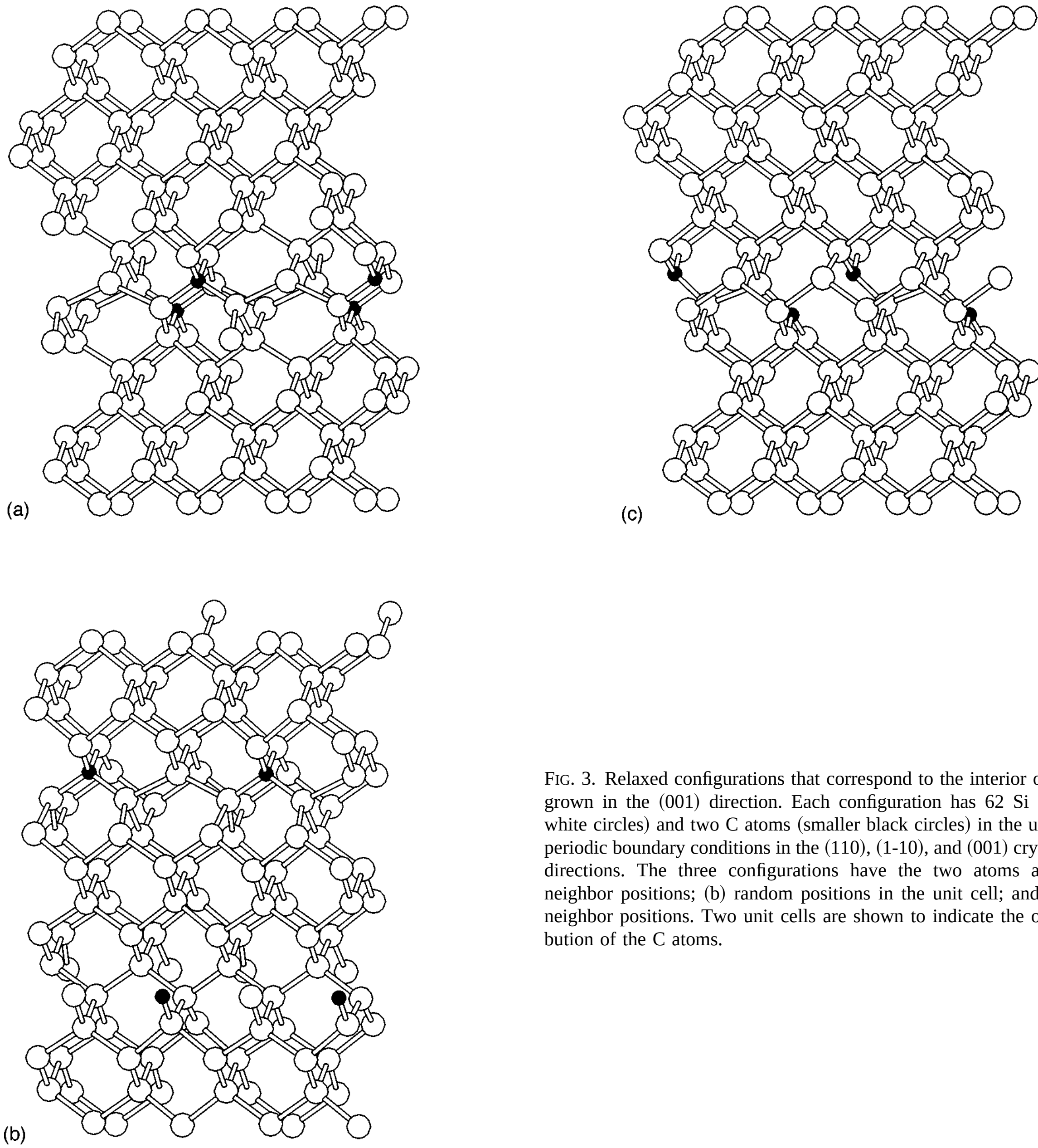

FIG. 3. Relaxed configurations that correspond to the interior of a thin film grown in the (001) direction. Each configuration has 62 Si atoms (large white circles) and two C atoms (smaller black circles) in the unit cell, with periodic boundary conditions in the (110), (1-10), and (001) crystallographic directions. The three configurations have the two atoms at: (a) third-neighbor positions; (b) random positions in the unit cell; and (c) nearest-neighbor positions. Two unit cells are shown to indicate the overall distribution of the C atoms.

perature and constant pressure, to determine the equilibrium distribution of C atoms under realistic conditions. We are mainly interested to check whether high-temperature effects alter the static picture regarding favorable sites for C. The MC simulations are carried out using a recently introduced state-of-the-art algorithm,[5] which lowers the barriers for diffusion in systems composed of atoms with large size mismatch. This is achieved by introducing, besides the usual random atomic displacements and volume changes, identity switches (from Si to C and vice versa) which are accompanied by appropriate relaxations of nearest-neighbor atoms. The composition is kept constant. We use (6×6) supercells consisting of 18 layers. The starting geometries have the top layer fully covered with (2×1) C dimers (the lowest energy configuration).

The surface profile of C atoms for different temperatures

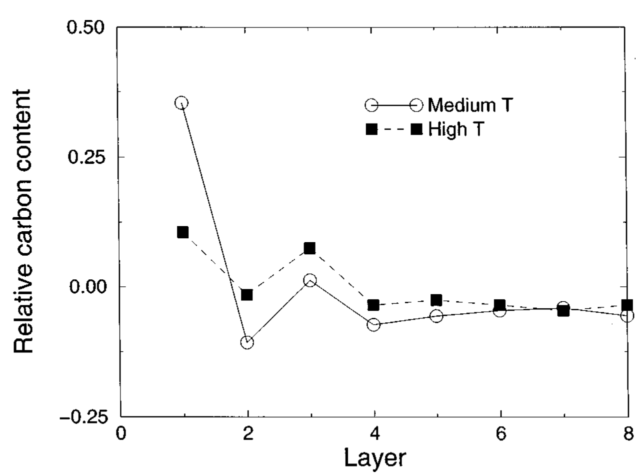

FIG. 4. Equilibrium profile of carbon atoms at different temperatures in the near surface region. Carbon content is given relative to a hypothetical average layer composition.

is shown in Fig. 4. Only the first eight layers are shown since bulklike limiting behavior is attained by layer 7. Medium and high temperatures refer to typical growth ($\sim$800 K) and annealing (1500 K) conditions. The C content is given relative to the initial one monolayer spread over 8 layers. There are two prominent characteristic features in the profile. The first is the migration of C atoms from the top layer, despite the highly stable, initial configuration. It is more pronounced at high T reflecting the extra energy needed to break the C–C dimer bond. This finding is in agreement with experimental work by Osten *et al.*,[9] who find that diffusion from the surface layer into the bulk creates a thin layer of a highly concentrated alloy of about ten monolayers. We have also performed simulations where only Si–Si or Si–C dimers were allowed to form initially on the surface, but not C–C dimers. We found that indeed incorporation of C at growth temperatures is enhanced significantly if C–C dimers are not formed on the surface. This supports our proposition for atomic C fluxes made above based on the static calculations.

The second interesting aspect of the profile is a well defined oscillatory behavior, which is characterized by enhancement of C concentration in layer 3 and reduction in layers 2 and 4. This behavior can be easily understood, in general lines, on the basis of the repulsive interaction between nearest-neighbor C atoms,[2,5] which prevents them from equally populating adjacent layers. Thus, reduction of C content in layer 2 with respect to layer 1, or in layer 4 with respect to layer 3 is explained. The repulsive interaction has further consequences. It has been shown earlier[8] that, due to the surface reconstruction, there are two inequivalent sites in layers 3 and 4. Those below the dimers are under compression and thus favorable for the smaller atom (in this case C), while those between dimers are under tension and thus unfavorable for the smaller atom. If the interaction among the solute atoms is attractive or neutral, then both sites below the dimers in layers 3 and 4 will be *on the average* occupied by the smaller atom while those between dimers by the bigger atom. This is the case in $Si_{1-x}Ge_x$ where *freezing-in* of such configurations during growth leads to thicker layers with the bulk ordering observed experimentally.[10] Here, however, due to the repulsive interaction the occupancy of the favorable sites by C, especially the simultaneous one in layers 3 and 4, is drastically reduced. Thus, besides the overall reduction of C content in layer 4, we observe a rise of C population at the unfavorable sites of this layer at the expense of the population at the favorable sites. This effect holds at the highest temperature studied, so we can conclude that bulk ordering of the type observed in $Si_{1-x}Ge_x$ alloys is unlikely.

IV. CONCLUSION

The overall picture of C structures in Si, as it emerges from these simulations, is quite complex. Consideration of the effect of the surface reconstruction alone leads to predictions for bulk ordering.[1] On the other hand, neglect of the reconstruction effect leads to bulk geometries with C atoms attracting each other as third nearest neighbors.[2] None of these two predictions will take place in an alloy with high C content under real growth conditions. We have shown here that one has to take into account both effects. In actual deposition conditions we predict that the most probable geometries consist mainly of configurations having C atoms as third nearest neighbors, contaminated with the unfavorable structures having C atoms repelled away from each other in a first nearest-neighbor position. Future work aiming at realistic investigations of the electronic properties of this material should take into account this picture.

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