

LETTER TO THE EDITOR

Structural Properties and Chemical Ordering in Hydrogenated Silicon–Carbon Alloys

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Hydrogenated silicon–carbon alloys ($\text{Si}_{1-x}\text{C}_x\text{:H}$) are studied in a cluster approach using the modified neglect of differential overlap method (MNDO-PM3). Full geometry optimizations have been performed on clusters consisting of 66 Si atoms partially replaced by C atoms in the presence of interstitial hydrogen. The resulting geometries are analyzed with respect to structural properties. The results obtained are in good agreement with the experimental data and support the idea of chemical ordering in these systems. © 1995

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I. INTRODUCTION

Hydrogenated silicon–carbon alloys ($\text{Si}_{1-x}\text{C}_x\text{:H}$) with different relative contents of carbon and silicon have attracted much attention as promising amorphous materials (1–3). It has been suggested that these heterogeneous materials are composed of three different phases, a SiC alloy component, graphitic carbon, and polymeric carbon, as well as voids (4). A variety of Si–Si, Si–C, and C–C bonding types have been identified, and it was clearly demonstrated that these are only slightly affected by the content of carbon in the samples (1, 4). From a theoretical point of view the structural study of these alloys is just beginning (5, 6). Particular attention has been given to analyzing metastable geometries of interstitial carbon and of carbon–carbon pair defects in silicon (7), and to theoretical reproduction of the valence–band density of states (8).

The purpose of this work is to analyze structural properties utilizing semiempirical quantum-mechanical methods applied to large clusters. We are particularly interested in extracting the bond length and bond angle distributions from theoretical output and comparing these results with the experimental data, which indicate a tendency toward chemical ordering in these materials (1, 4). Thus we are also looking for an effective

way to model the structures of these complex systems.

II. METHOD AND MODEL

In this work we used the Modified Neglect of Differential Overlap method (MNDO) in its PM3 version as available in the MOPAC program package (9). The MNDO method has been previously applied to silicon clusters (10) and its reliability in reproducing Si structures is well established (8).

In order to model a solid of Si atoms, we have chosen a cluster consisting of 66 silicon atoms with 64 dangling bonds saturated by H atoms; see Fig. 1. This cluster is obtained by expanding the zinc-blende-type Si structure around the T_d intersite up to the fifth shell of Si atoms. The cluster thus obtained allows for the insertion of several interstitial hydrogen atoms in the model structures so as to approach closely the experimental Si : C : H ratios (1–4). Another advantageous feature of the chosen cluster is the existence of a kernel consisting of 21 Si atoms, most of which are completely surrounded by Si atoms. This allows for an effective modeling of the C substitution in the cluster, avoiding surface effects which might dramatically change the energetics of the cluster calculations. Additionally, the number of interatomic Si–Si distances in the $\text{Si}_{21-x}\text{C}_x\text{Si}_{45}\text{H}_{64}$ cluster is sufficiently large (2145) to provide a basis for the bond distance analysis.

We have replaced up to 16 silicon atoms with C atoms in the Si_{21} kernel and have inserted up to 6 hydrogen atoms in the intersites. An even number of H atoms have been introduced to avoid computational difficulties due to the presence of unpaired electrons. The H atoms have been inserted as either separate atoms or H_2 molecules. We have noted, however, that the presence of interstitial hydrogen in the $\text{Si}_{21-x}\text{C}_x$ -

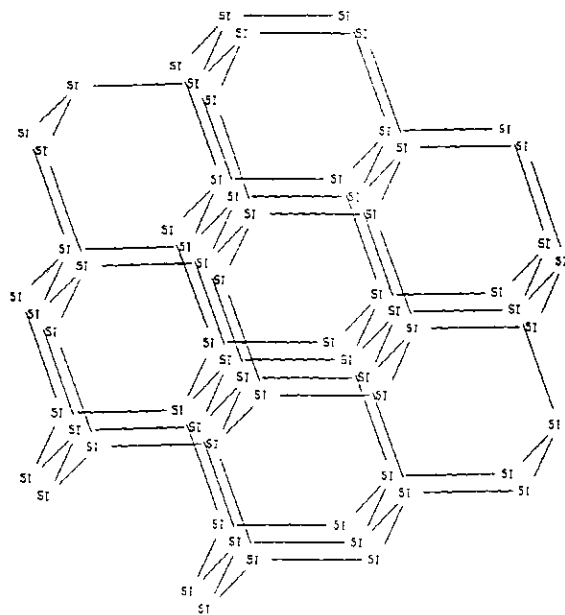


FIG. 1. The $\text{Si}_{66}\text{H}_{64}$ cluster as obtained from expansion around the c-Si tetrahedral interstitial site. The H atoms saturating the dangling bonds on the cluster surface are omitted for clarity.

$\text{Si}_{45}\text{H}_{64}$ cluster does not markedly affect the structural properties examined, as also observed experimentally (1, 4). Therefore, we present here results only for two separate hydrogen atoms or one H_2 molecule inside clusters of different composition.

Full geometric optimization was performed for each cluster in order to achieve maximum relaxation of the model structures. No restrictions were imposed on the degrees of freedom of the atoms, except for the Si-H bond length between peripheral Si atoms and the saturating H atoms; this was kept constant (1.48 Å) in the calculations. The gradient energy cutoff for all the optimizations was set at 0.001 eV.

III. RESULTS AND DISCUSSION

In this section we summarize the main bonding features and structural properties deduced from various calculations performed on different clusters.

In all optimized structures, the C atoms remain 4-coordinated and bonded to surrounding atoms. Note that, here and in the following, the sum of the atomic covalent radii is used as the criterion to determine whether two atoms are bonded or not.

Substitution of C for Si causes significant geometrical distortions; for example, the average second neighbor Si-Si distance changes from 3.82 Å in silicon to 3.30 Å after the incorporation of C atoms on Si sites. Similar changes are also observed for the bond angles, *vide infra*.

Additionally, when Si atoms are brought closer by the presence of C atoms, Si coordination numbers higher than 4 can be observed and 5- to 7-coordinated Si atoms appear in the clusters.

The interstitial H atoms, or H_2 molecules, bind preferentially to Si atoms. No C-H bonds have been detected in the examined clusters even at the highest C content in the samples. A possible explanation of this result is that a Si atom can have a coordination number larger than 4, due to the availability of empty 3d orbitals, and may, therefore, bind one H simply by a weakening of the other four bonds. This could not be achieved in the case of tetrahedrally coordinated C atoms, and in this case, the coordination of hydrogen atoms might result in breaking apart Si-C or C-C bonds that already exist.

The bond distance in H_2 molecules inserted into clusters with up to seven carbon atoms retains molecular values (0.74–0.76 Å). At higher C concentrations, this bond length increases noticeably to 0.8–0.9 Å. In some cases, corresponding to higher carbon concentrations, e.g., $\text{H}_2 : \text{Si}_{21-x}\text{C}_x\text{Si}_{45}\text{H}_{64}$ with $x = 12$, we observe an even larger stretching of the H-H bond, closer to the dissociation limit of the H_2 molecule. However, this result should be viewed cautiously with respect to the methodology used. The self-consistent field (SCF) restricted Hartree-Fock method is typically unreliable for the description of significantly stretched bonds. In such cases, extensive configuration interaction calculations, or other post-SCF techniques, need to be applied to restore the electron correlation. Unfortunately, such calculations are computationally prohibitive for large systems of the size we study in this work.

At still higher C concentrations, $x = 13$ through 16, it may happen that the H_2 molecule could not attach to Si atoms, and, therefore, retains its equilibrium geometry. Note that similar bonding patterns were predicted for interstitial hydrogen (8), and stretched H_2^* molecules were suggested to be present in hydrogenated amorphous silicon (11).

Although all the C atoms remain in the kernel part of the clusters after the geometry optimization, the distortions caused by the Si-C relaxations are so large that they destroy the initially crystalline alignment of the atoms and bring the structures obtained closer to the amorphous form rather than to the c-SiC. Nevertheless, we can still rationalize our results by introducing an "average lattice constant" for each cluster, obtained by averaging over its interatomic distances. This parameter gives an estimate of the cluster size as a function of the carbon content and helps make evident the structural effects due to the inclusion of atomic or molecular hydrogen. Figure 2 shows how the calculated lattice constant changes with the substitution of Si atoms by C atoms for samples with and without hydrogen. The following results can be outlined:

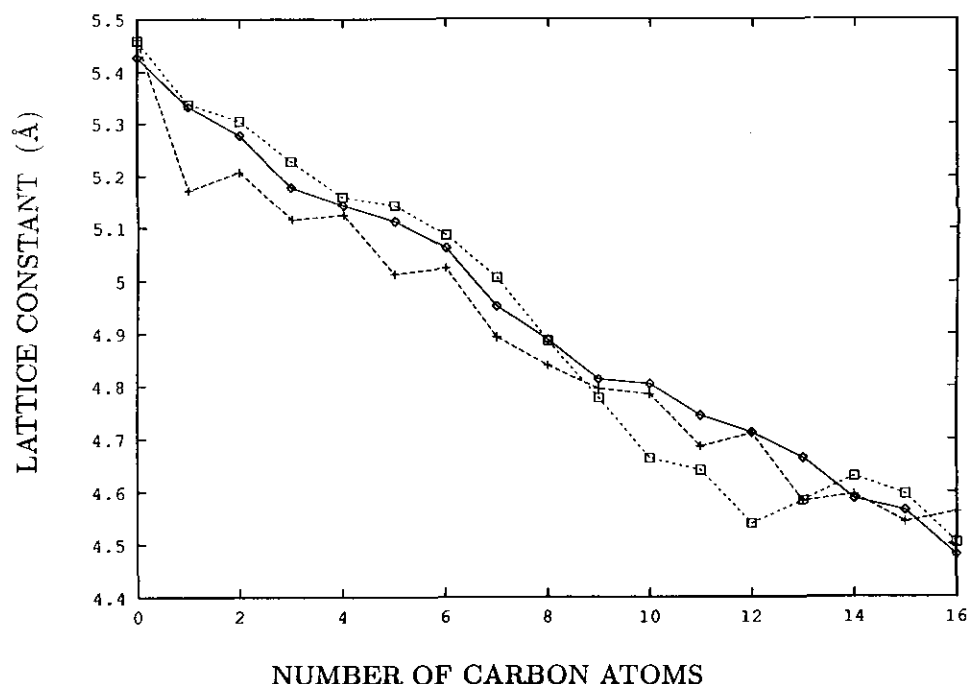


FIG. 2. Dependence of the averaged lattice constant on the carbon content. The solid line refers to the $\text{Si}_{66-x}\text{C}_x$ cluster; the broken and dotted lines stand for the same cluster with two isolated H atoms and one interstitial H_2 molecule, respectively.

First, we observe a clear difference in the lattice constants depending on the character of the interstitial hydrogen. Atomic hydrogen interacts more strongly with the Si-C surroundings and this leads to lattice constant values lower than those for clusters without hydrogen (the lattice shrinks).

Second, for clusters with $x = 1$ through 8, the insertion of molecular hydrogen gives rise to structures with lattice constants larger than those for clusters without hydrogen (the lattice expands). For higher carbon concentrations, instead, the lattice shrinks again. This might well be due

to the stretching of the H_2 molecule, as previously discussed, an effect which produces a lattice contraction even stronger than that due to isolated H atoms. At still higher C concentrations it may happen, as explained before, that the H_2 molecule may be sterically impeded to coordinate to Si atoms, and this results in lattice constants only a little larger than those obtained for clusters without hydrogen.

The results obtained from the analysis of the Si-Si, Si-C, and C-C bond length distributions in the optimized $\text{H}_2 : \text{Si}_{21-x}\text{C}_x\text{Si}_{45}\text{H}_{64}$ structures are summarized in Table 1. The values of this table are averaged over the clusters with relatively high C content ($x = 7$ through 16) to provide a sufficiently large Si/C distance database. The results obtained are in good agreement with both type and sequence of bonds that have been detected experimentally (1, 4). Also the quantitative comparison between theoretical and experimental bond length distributions is quite

TABLE 1

Averaged Interatomic Distances of Different Nearest- and Next-Nearest Neighbors in the $(\text{H}_2 : \text{Si}_{66-x}\text{C}_x)$ Series; Comparison with Experimental Data (4).

Type of distance	This work (Å)	Experiment (Å)
Si-C	1.84	1.86
Si-Si	2.35	2.35
C-C(C)	2.59	2.53
C-C(Si)	3.28	3.12
Si-Si(C)	3.32	3.12
C-Si(Si)	3.72	3.55
Si-Si(Si)	3.81	3.84

Note. Atoms in parentheses are intermediates between the corresponding next-nearest neighbors.

TABLE 2
Averaged Bond Angles in the $(\text{H}_2 : \text{Si}_{66-x}\text{C}_x)$ Series

Type of angle	Bond angle
Si-Si-Si	108.3°
C-C-C	115.1°
C-Si-C	126.0°
Si-C-Si	128.7°

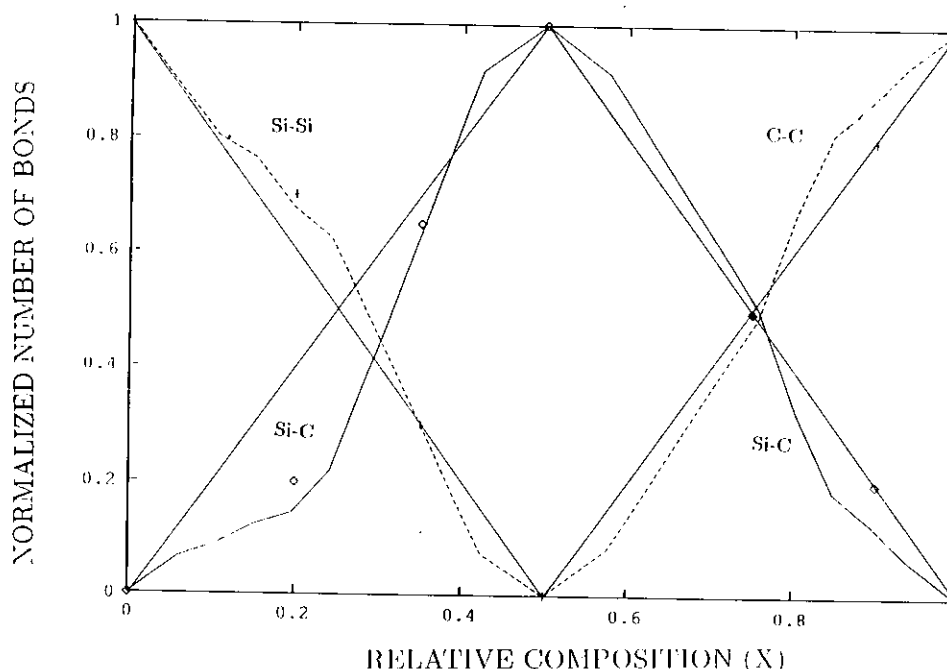


FIG. 3. Chemical ordering inferred from the analysis of the normalized bonds vs the carbon content in the optimized $\text{Si}_{66-x}\text{C}_x\text{H}_{64}$ clusters. Three types of bond distances, Si-Si, Si-C, and C-C, are plotted for different Si/C compositions specified by X , the relative C content. Points indicate the experimental data taken from Ref. (4). The symmetric straight lines correspond to the expected trend assuming a complete chemical order.

satisfactory; the largest discrepancies (on the order of 0.2 \AA) are those relative to distances between identical second neighbors with a different atom at the bond center. In these cases, however, the experimental indetermination is larger and the theoretical results depend more sensitively on the carbon concentration. At any rate, we observe a relevant stability of the bond lengths around their averaged values when the carbon content is changed. The fluctuations are on the order of a few 10^{-2} \AA and this result is in good agreement with experimental observations (1, 4).

The same stability of the average bond lengths was also observed with varying hydrogen content in the model structures. Our results indicate that the interatomic distances are only slightly affected (less than 1%) by the presence of interstitial hydrogen, a finding which is again consistent with the experiment (1, 4).

A similar analysis was also performed for the bond angles that can be defined inside our clusters. The data summarized in Table 2 provide information on the degree of distortion of the tetrahedral environments of the Si and C atoms and, therefore, on the degree of hybridization of the bonding orbitals. Thus, the averaged C-C-C angle is approximately 115° , while the Si-Si-Si angle is closer to the tetrahedral value of 109.47° , in accordance with empirical estimates (4). These findings suggest that the preferred hybridization state for the C atoms in the alloys

is between the planar sp^2 and the tetrahedral sp^3 bonding types, while the Si atoms tend to preserve the T_d arrangement. We reiterate here that there are no 3-coordinated carbon atoms in our optimized structures, so that the hybridization type can be inferred only from the bond angle deviations from the ideal (T_d) symmetry. This can be done even more precisely by considering also the mixed Si-C-Si and C-Si-C angles reported in Table 2, and their departure from the c-SiC values.

Finally, the results of the structural analysis for the simulated $\text{Si}_{1-x}\text{C}_x\text{:H}$ alloys are summarized in Fig. 3, where the behavior of the normalized first shell coordination number is given as a function of the carbon content. In order to make evident the various cluster compositions at which the geometry has been optimized and the coordination numbers calculated, we have connected these points with straight lines. In the same figure, we have also shown the normalized numbers of bonds derived from X-ray scattering spectra (4) and the expected behavior assuming complete chemical order, i.e., a distribution characterized by the maximum number of heterobonds (4). As can be seen in Fig. 3, the calculated coordination numbers are very close to the experimental points and the general behavior indicates a considerable tendency toward chemical order in these alloys, especially those with high C concentrations.

We conclude from this study that the structural features

of the hydrogenated silicon-carbon alloys can be successfully understood on the basis of an unsophisticated theoretical analysis which predicts bond distance and angle distributions that follow the experimentally observed chemical ordering.

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