Theoretical predictions of a bucky-diamond SiC cluster

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2012 Nanotechnology 23 235705
(http://iopscience.iop.org/0957-4484/23/23/235705)
View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 136.165.190.24
This content was downloaded on 13/06/2017 at 00:17
Please note that terms and conditions apply.

You may also be interested in:

Low-dimensional boron structures based on icosahedron B12
C B Kah, M Yu, P Tandy et al.

A hybrid density functional study of zigzag SiC nanotubes
Kazi M Alam and Asok K Ray

Carbon-based nanotechnology on a supercomputer
David Tománek

First-principles studies on pure and doped C32clusters
Q Sun, Q Wang, J Z Yu et al.

Initial stage of growth of single-walled carbon nanotubes: modeling and simulations
I Chaudhuri, Ming Yu, C S Jayanthi et al.

An environment-dependent interatomic potential for silicon carbide: calculation of bulkproperties, high-pressure phases, point and extended defects, and amorphousstructures
G Lucas, M Bertolus and L Pizzagalli

First-principle calculations on the structural stability and electronic properties of superhard BxCy compounds
M M Li, Xiaofeng Fan and W T Zheng

Structural growth sequences and electronic properties of manganese-doped germaniumclusters: MnGen(2–15)
Jianguang Wang, Li Ma, Jijun Zhao et al.
Theoretical predictions of a bucky-diamond SiC cluster

Ming Yu, C S Jayanthi and S Y Wu

Department of Physics and Astronomy, University of Louisville, Louisville, KY 40292, USA

E-mail: m0yu0001@louisville.edu

Received 27 February 2012, in final form 28 February 2012
Published 17 May 2012
Online at stacks.iop.org/Nano/23/235705

Abstract
A study of structural relaxations of Si$_n$C$_m$ clusters corresponding to different compositions, different relative arrangements of Si/C atoms, and different types of initial structure, reveals that the Si$_{68}$C$_{79}$ bucky-diamond structure can be obtained for an initial network structure constructed from a truncated bulk 3C-SiC for a magic composition corresponding to $n = 68$ and $m = 79$. This study was performed using a semi-empirical Hamiltonian (SCED–LCAO) since it allowed an extensive search of different types of initial structures. However, the bucky-diamond structure predicted by this method was also confirmed by a more accurate density functional theory (DFT) based method. The bucky-diamond structure exhibited by a SiC-based system represents an interesting paradigm where a Si atom can form three-coordinated as well as four-coordinated networks with carbon atoms and vice versa and with both types of network co-existing in the same structure. Specifically, the bucky-diamond structure of the Si$_{68}$C$_{79}$ cluster consists of a 35-atom diamond-like inner core (four-atom coordinations) suspended inside a 112-atom fullerene-like shell (three-atom coordinations).

1. Introduction
Silicon carbide based nanostructures have recently been explored extensively because of their promising technological applications [1–4]. These materials are promising electronic materials for devices and have potential as photovoltaic materials for solar cells, electrode materials for Li-ion batteries, etc. Bulk SiC possesses extraordinary mechanical and physical properties [5–12]. It is a material with low density, high strength, high thermal conductivity, high index of refraction, low thermal expansion, and wide band gap. It is stable at high temperature and chemically inert [13–15]. These exceptional intrinsic properties make SiC-based nanostructures outstanding candidates as environmentally friendly light weight materials for energy, electronics, and drug-delivery applications.

It is well known that C and Si atoms bond through four-coordinated sp$^3$ type bonding in bulk SiC. But, in a recent theoretical study, we have shown that graphitic-like 2D SiC sheets are stable, indicating the feasibility of a three-coordinated sp$^2$ type bonding between the C and the Si atoms [16]. The above facts imply that the bonding between a C atom and a Si atom must be similar to that between two C atoms. It forms a four-coordinated sp$^3$ bonding when in the (3D) bulk and forms a three-coordinated sp$^2$ bonding when in a (2D) sheet, opening up the possibility of finding the same sorts or types of nanostructures as those found in carbon (e.g., compact clusters, caged clusters, fullerenes, nano-wires (NWs), nanotubes (NTs), etc).

The most stringent test for validating the similarity of the bonding nature between a pair of C atoms and that between a C atom and a Si atom is to determine whether there could be a stable bucky-diamond structure for SiC clusters. In the bucky-diamond C$_{147}$, there is a diamond core of 35 C atoms bonded by four-coordinated sp$^3$ bonds in a tetrahedral network, with a shell of 112 C atoms bonded by three-coordinated sp$^2$ bonds in a fullerene structure [17–19]. There is only weak interaction between the inner core and the outer shell as evidenced by the fact that the nearest-neighbor distances between the surface atoms in the inner core and the atoms in the outer shell range from 1.60 to 3.34 Å [17, 18], far longer than either the sp$^2$ bond length in graphene sheet
(1.42 Å) or the sp$^3$ bond length in diamond (1.52 Å). Hence the bucky-diamond structure must be a structure where sp$^2$ and sp$^3$ bonds co-exist in the same structure, leading to an sp$^3$ bonded diamond inner core weakly coupled to a sp$^2$ bonded fullerene shell.

Since a C atom forms the three-coordinated sp$^2$ bond with a Si atom in a 2D graphitic-like sheet and a four-coordinated sp$^3$ bond in the bulk, there is then the likelihood that a SiC bucky-diamond structure may exist. If so, the existence of this unusual structure of the Si/C-based system should convincingly demonstrate the equivalence of the bonding nature between a C atom and a Si atom in Si/C-based systems and that between a pair of C atoms in C-based systems. It also implies that, similarly to the case of carbon nanostructures, SiC-based nanostructures could exist in multiple forms (i.e. polymorphic structures). Furthermore, in the case of SiC-based systems, there is one more factor, the composition, that could be manipulated. The manipulation of this extra factor could provide additional routes to explore the geometrical and functional possibilities for stable SiC-based nanostructures. Thus, the study of the likelihood of the existence of SiC bucky-diamond structure is not only academically interesting, but also could have implications for innovative device-related applications.

In this work, we studied the possible existence of the bucky-diamond structure of Si$_n$C$_m$ clusters for $n + m = 147$ using the SCED–LCAO-based molecular dynamics (MD) method [20], where SCED refers to the self-consistent and environment-dependent Hamiltonian and LCAO to linear combination of atomic orbitals (a brief discussion of the SCED–LCAO method, which has been extensively reported in the literature [16–18, 20, 21], is given in the appendix). Specifically, we investigated the role played by the composition in possibly achieving a stable bucky-diamond structure for Si$_n$C$_m$ clusters in terms of the interplay among the bonding nature, the bond length, and the bond strength between Si–Si, C–C, and Si–C atoms. We were able to determine that a stable bucky-diamond structure indeed exists for the Si$_n$C$_m$ cluster with a specific magic composition ($n = 68$ and $m = 79$). We will demonstrate that the interplay among the above mentioned three factors, coupled with the suppression of the dangling bonds for the surface atoms, facilitates the formation of the stable bucky-diamond structure of the Si$_n$C$_m$ cluster for the specific composition corresponding to $n = 68$ and $m = 79$.

In this work, an extensive search for a plausible Si$_n$C$_m$ bucky-diamond structure (with $n + m = 147$) was conducted by constructing various possible initial structures that included (i) Si$_{35}$C$_{112}$ with all the atoms arranged in a diamond-like network, (ii) Si$_{35}$C$_{112}$ with the 35 Si atoms in the core arranged in a diamond-like network and the remaining 112 C atoms in a fullerene-like shell, (iii) spherical truncation of the 3C-SiC bulk network such that the resulting Si$_n$C$_m$ network contained 147 atoms with $n = 112$, 79, 73, 68, 35 and $m = 35, 68, 74, 79, 112$, respectively with n Si atoms in the interior core and m C atoms on the exterior shells (Si core/C shell), a vice versa arrangement, namely m C atoms in the interior and n Si atoms on the exterior (C core/Si shell), a segregated arrangement of n Si and m C atoms in the network, and finally an alternating arrangement of Si and C atoms as found in the 3C-SiC bulk, corresponding to $n = 79$ and $m = 69$ as well as $n = 68$ and $m = 79$ (i.e. with Si as the central atom or C as the central atom). Section 2 will describe how our chosen intuitive initial structures given in (i) and (ii) failed to yield bucky-diamond Si$_n$C$_m$ structures for $n + m = 147$. Therefore, we considered the initial structures outlined in (iii), where both the compositions and the distribution of Si and C atoms in the 3C-SiC network were manipulated. This later study led to the identification of the bucky-diamond Si$_68$C$_{79}$ structure for the magic composition $n = 68$ and $m = 79$. The formation route of the bucky-diamond Si$_{68}$C$_{79}$ from its initial diamond-like 3C-SiC network structure is explained in section 4. The conversion of bucky-diamond Si$_{68}$C$_{79}$ to a cage structure of the same composition upon annealing and quenching is discussed in section 5. The concluding remarks and the prospects for future extensions are given in section 6.

2. Towards a search for the bucky-diamond Si$_{35}$C$_{112}$ structure: initial structures based on a diamond-like tetrahedral network and a carbon bucky-diamond structure

It is known that carbon exhibits bucky-diamond structure [17, 19]. Specifically, for C$_{147}$ it is known that 35 interior atoms exhibiting sp$^3$ bonding form the core in the diamond network while 112 exterior carbon atoms with sp$^2$ bonding form a fullerene-like shell. Since ordinarily Si atoms prefer sp$^3$ bonding while carbon atoms in a shell prefer sp$^2$ bonding, it then seems prudent to ‘guess’ that a plausible bucky-diamond Si$_n$C$_m$ could be formed with a Si$_{35}$ core in the diamond network and a C$_{112}$ fullerene-like shell. While this initial guess is intuitively very appealing, we decided to first test a more stringent scenario, namely, all atoms are arranged in a diamond-like tetrahedral network with 35 Si atoms filling up the first five inner shells and 112 carbon atoms occupying the six exterior shells. The bond length between any pair of atoms was chosen to be the same as the equilibrium bond length of bulk SiC (1.97 Å).

This initial configuration of smaller core (compared to the bulk Si bond length) and larger shell (compared to the bulk C bond length) was designed to promote and expedite the relaxation to a stable equilibrium configuration. This initial structure was relaxed using the SCED–LCAO-MD method [18, 20]. The resulting process of approach to equilibrium, shown through the total energy/atom versus time curve, is given in figure 1(a). It can be seen that the Si–Si bonds on the surface of the inner Si core start to break off right away as the ‘surface’ Si atoms are pulled by the adjacent C atoms with stronger C–Si bonds towards the exterior. This process continues without interruption until there is no longer any inner core and all the Si atoms have migrated to the surface. The energy has also stabilized to within 0.002 eV/atom. The resulting equilibrated configuration is a complex cage-like structure with an open mouth. From the pair distribution of the equilibrated configuration shown in the inset of figure 1(a), it can be seen that there are only
is composed of 35 Si atoms filling up the first five shells of the tetrahedral network with a nearest-neighbor Si–Si bond length of 2.14 Å surrounded by a fullerene-like shell of 112 C atoms with nearest-neighbor C–C distances in the range of 1.88–1.91 Å to accommodate the large core. The result is shown in figure 1(b). It can be seen that the approach to equilibrium follows a very similar pattern to the case shown in figure 1(a), leading to an almost equivalent final equilibrium configuration, i.e., an open-mouthed cage structure.

The message conveyed by this study can be summarized as follows: (1) the $Si_{35}C_{112}$ cluster with its composition deduced from intuition will not lead to the stable $Si_mC_m$ bucky-diamond structure; (2) a Si atom on the surface of a Si/C-based system may not have dangling bonds as long as it forms Si–C bonds with its carbon nearest-neighbors, another example of the SiC bond being of three-coordinated $sp^2$ type on the surface rather than of four-coordinated $sp^3$ characteristics as in the bulk; (3) the likelihood of the existence of a stable $Si_mC_m$ bucky-diamond structure must depend on a delicate balance of factors including the strength and the bonding nature of the Si–C bond, the C–C bond, and the Si–Si bond, the bond length of these three bonds, and the composition of the $Si_mC_m$ ($m+n=147$) cluster. Therefore, the determination of whether the bucky-diamond structure for a $Si_mC_m$ ($m+n=147$) cluster exists must rely on an extensive search of all plausible structural configurations of $Si_mC_m$ clusters.

3. Towards a search for the bucky-diamond $Si_mC_m$ structure: tuning the composition and Si/C arrangements in the network created from 3C-SiC

With no a priori knowledge of the composition for a plausible bucky-diamond $Si_mC_m$ structure, an extensive search of different possible combinations of compositions is necessary. Such a search using the DFT-based method would be computationally expensive for this particular problem even though the structural optimization of a single SiC cluster of 147 atoms can, in fact, be studied through DFT calculations. On the other hand, the molecular dynamics (MD) scheme based on the SCED–LCAO Hamiltonian [18, 20] (a semi-empirical Hamiltonian) has been shown to be efficient and appears to be perfectly suited to conduct the search for the SiC bucky-diamond structure. We have tested this scenario by considering the relaxation of a 147-atom SiC cluster spherically cut from 3C-SiC bulk, using both the VASP [22] package and the SCED–LCAO method [18, 20]. The test was run on an AMD Opteron (2.0 GHz) based Linux cluster using 16 CPUs. It was found that, on average, it takes about 104 h for the DFT-based VASP to relax a SiC-147 cluster while it only takes about 10 h using the SCED–LCAO method. Therefore it is computationally much more efficient to use the SCED–LCAO-based MD method to conduct an extensive search for the possible SiC bucky-diamond structure. The semi-empirical SCED–LCAO Hamiltonian, which includes environment-dependent electron–ion interactions and evaluates charge redistributions self-consistently, has predicted correctly the surface structures of silicon

Figure 1. Total energy/atom versus MD step (1 MD step = 1.5 fs), depicting the relaxations of $Si_{35}C_{112}$ clusters for two different initial configurations: (a) diamond-like, tetrahedral arrangements for all Si (in the five inner shells) and C atoms (in the six outer shells), (b) 35 Si atoms (corresponding to the first five inner shells) in a tetrahedral network and the remaining 112 C atoms arranged in a fullerene-like shell (see the inset, where the yellow, gray, and yellow–gray lines represent the Si–Si, C–C, and Si–C bonds, respectively). The optimized structures corresponding to both initial configurations do not lead to bucky-diamond structures (see MD step ~ 1900) but to distorted cage-like structures. The inset in (a) shows the total and partial pair-distribution functions (i.e., $g(r)$ (black), $g_{C-C}(r)$ (red), $g_{C-Si}(r)$ (green), and $g_{Si-Si}(r)$ (blue)) corresponding to the relaxed structure shown in (a). It can be seen that there are no Si–Si bonds but the peaks corresponding to nearest-neighbor C–C and C–Si bonds are prominent.

nearest-neighbor C–C bonds and C–Si bonds, but hardly any nearest-neighbor Si–Si bonds in the final ‘equilibrium’ configuration. While the guessed initial configuration has not led to the bucky-diamond structure for the $Si_{35}C_{112}$ cluster with this core/shell structure, it still demonstrates that a C–Si bond does favor the three-coordinated $sp^2$-bonding nature on the surface of a SiC-based structure. However, the result does not exhibit a structure where three-coordinated $sp^2$ SiC bonds co-exist with four-coordinated $sp^3$ Si bonds.

Since the $Si_{35}C_{112}$ arranged in a diamond network did not lead to a bucky-diamond structure, we decided to consider another initial structure favorably disposed to the formation of SiC bucky-diamond structure. This new trial configuration
including Si(111)-7 × 7, low-dimensional structures of carbon (fullerenes, bucky-diamonds, carbon nanotubes, etc), SiC graphene-like and graphitic structures, and bulk structures of Si, C, and SiC [17, 18, 20, 21]. The predictions from the SCED–LCAO method have been extensively tested against the results from DFT-based methods (using VASP [22]). Such validations will also be conducted for the final relaxed structures of SiₙCₘ.

The search for the SiₙCₘ (m + n = 147) bucky-diamond structure was conducted using initial configurations of the clusters of various compositions based on the following scenarios. (1) The initial configurations of the SiₙCₘ clusters were constructed from a spherically truncated 3C-SiC diamond-like network for m + n = 147 (containing 11 completed shells) with atoms arranged as either Si core/C shell, or Si shell/C core, or segregated Si/C configurations of various plausible m/n combinations, using the bulk Si–C equilibrium bond length (1.97 Å) for their nearest-neighbor distances, or (2) the initial configurations were constructed by truncating the bulk 3C-SiC according to the bulk 3C arrangement of Si/C atoms, namely one shell of Si atoms followed by another shell of C atoms and so on until m + n = 147 with either a Si or a C atom at the center (first shell), using the nearest-neighbor C–Si equilibrium bond length. The results showing the relaxed configurations from some of the more relevant initial configurations are given in figure 2.

From figure 2, it is seen that the bucky-diamond structure Si₆₈C₇₉ emerges for the magic composition corresponding to n = 68 and m = 79 with the lowest cohesive energy compared to other Si₆₈C₇₉ clusters shown in the sixth row in figure 2. It is rewarding that the search resulted in the identification of a stable Si₆₈C₇₉ bucky-diamond structure, with a 35-atom Si₁₆C₁₉ diamond-like core (with the central atom being a C atom) inside a 112-atom Si₅₂C₆₀ fullerene shell, confirming our anticipated scenario that Si and C can form either three-coordinated sp² or four-coordinated sp³ bonds and these two bonds can co-exist in the same structure. Specifically, for the Si₆₈C₇₉ cluster, a four-coordinated sp³-bonded diamond core can co-exist with a three-coordinated sp²-bonded fullerene to form the bucky-diamond structure. A detailed analysis of the relaxed bucky-diamond structure shows that the relaxed 35-atom diamond-like inner core is barely distorted from its unrelaxed counterpart, with only each of its outermost six atoms linked to the outer fullerene shell. The 112-atom Si₅₂C₆₀ outer shell is composed of 12 pentagons and 46 hexagons, satisfying the rule of the fullerene.

The analysis of our search also points to another interesting observation. It should be noted that the specific composition of the SiₙCₘ cluster, namely n = 68 and m = 79, that yields the bucky-diamond structure, arises from the bulk 3C-SiC network truncated at m + n = 147 containing alternating C shells and Si shells. This observation suggests a likely natural route for synthesizing the SiC bucky-diamond structure.

We have also validated our result for Si₆₈C₇₉ bucky-diamond structure by relaxing the 147-atom SiC network.
created from bulk 3C-SiC through DFT-based \textit{ab initio} simulations (VASP) [22]. The calculations were performed within DFT/GGA using plane-wave basis sets, ultra-soft pseudo-potentials (US-PP) [23], and Perdew and Wang (PW ’91) exchange–correlations [24]. We employed the three-dimensional periodic boundary condition with a vacuum region (15 Å) to ensure that there were no interactions between the Si tempt C\textsubscript{m} clusters. The cut-off energy for the plane-wave basis set was 358 eV. The energy convergence for the self-consistent calculation was set to $10^{-4}$ eV, and the structure was relaxed using the conjugate-gradient (CG) algorithm until the atomic forces were less than $10^{-3}$ eV Å\(^{-1}\). The comparison between the two calculations is shown in figure 3. It can be seen that the two calculations yielded almost identical bucky-diamond structure when started from an identical initial configuration (i.e., the truncated bulk 3C-Si\textsubscript{68}C\textsubscript{79} network). We have also examined the stability of the relaxed Si\textsubscript{68}C\textsubscript{79} structure using Gaussian 03 HF with the STO-3G orbitals [25]. We found that the squared angular frequencies of all the vibrational modes were positive, confirming that the SiC bucky-diamond structure is a stable structure.

4. The mechanism underpinning the formation of the bucky-diamond structure

The initial configuration of the Si\textsubscript{68}C\textsubscript{79} cluster corresponding to the atomic arrangement of the bulk 3C-SiC network truncated at 147 atoms with a C atom at the center has a composition Si\textsubscript{68}C\textsubscript{79}. It is composed of 11 completed shells with alternating C-occupied and Si-occupied shell. The numbers of atoms in the shells from shell 1 to shell 11 are 1, 4, 12, 6, 12, 24, 16, 12, 24, and 24 respectively. Thus the outer shell of the interior core (i.e. 35 atoms occupying the first five shells) has only six carbon atoms while the outermost shell of the remaining six-shell 112-atom configuration has 24 carbon atoms.

The initial configuration is depicted in figure 4(a). It can be seen that there are groups of two adjacent pairs of un-bonded outermost surface (C) atoms (see the surface C atoms (pink balls) with the attached arrows, where the arrowheads indicate the direction of forming C–C bonds). When the configuration is relaxed, both pairs of C atoms will form strong C–C bonds to eliminate the dangling bonds. The forming of one pair of strong C–C bond pulls against the respective Si atoms in the second outer shell (green balls), each being a nearest-neighbor (nn) to the C atom (pink balls) on the surface, owing to the strong C–Si bond. This in turn will pull up the C atom in the fifth outer shell (red balls), which is the nn of both Si atoms in the second outer shell (green balls), by the combination of the two Si–C bonds. This series of actions results in the formation of a pentagon on the surface. Likewise, each C atom (pink balls) of the other pair of induced C–C bonds formed on the surface pulls against its own respective nn Si atom on the second outer shell (green balls), which in turn leads to the formation of an identical pentagon through the nn interaction between the Si atoms and their common neighboring C atom from the fifth outer shell (red balls). This pentagon actually faces the previous pentagon associated with the previously discussed (induced) C–C bond. This action also pulls the two Si atoms from the fourth outer shell (gray balls) towards their respective neighboring C atom in the bonded pairs, through the Si–C bonds, leading to the formation of a hexagon on the surface adjacent to both pentagons located on opposite sides, with the hexagon having two pairs of C–C bonds facing one another that connect two identical pentagons (figure 4(b)). Finally, a hexagon neighboring the hexagon with two C–C bonds can be seen (figure 4(b)) as formed in the following manner. These two hexagons have a common bond formed between the C atom from the first outer (surface) shell and a Si atom from the fourth outer shell (gray balls). As the relaxation process continues, the C atom in the common C–Si bond that is originally from the first shell pulls its nn Si atom on the second outer shell (green balls) towards the surface, which

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The relaxed bucky-diamond Si\textsubscript{68}C\textsubscript{79} cluster as obtained from the SCED–LCAO-MD method [18, 20] (a) and that using the DFT/VASP [22] (b). The yellow and green balls represent C and Si atoms, respectively.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(a) The initial configuration of the Si\textsubscript{68}C\textsubscript{79} cluster cut from bulk 3C-SiC, (b) the relaxed configuration showing a fullerene shell and a diamond-like core as obtained by SCED–LCAO-MD [18, 20], and (c) a fragment of the shell showing the structure anchored by three adjacent pentagons. Pairs of C atoms on the first outer shell (pink balls), indicated by the arrows in (a), form C–C bonds upon relaxation and they become part of the pentagon–hexagon–pentagon ensembles on the surface of the bucky-diamond cluster. The pink, green, brown, gray, red, blue, and yellow balls represent the atoms on the first, second, third, fourth, fifth, and sixth outer shells, as well as the inner core, respectively.}
\end{figure}
Figure 5. (a) The bucky-diamond Si$_{68}$C$_{79}$ cluster (left) transforms to a cage-like structure (right) after annealing it to 2600 K and then slowly quenching to 0 K. The corresponding cohesive energies (eV/atom) are also given. The pair-distribution functions corresponding to the bucky-diamond (b) and cage structures (c) are also shown.
Si–C bonds as the formation of the network is driven by nn Si–C interactions. This is indeed the case exhibited by the resulting fullerene.

The next shell after the sixth outer shell of the initial configuration of the Si$_{68}$C$_{79}$ cluster with a C atom at the center obtained by truncating the bulk 3C network at $n + m = 147$ (i.e., $n = 68$ and $m = 79$) is only occupied by six C atoms. When the equilibrium configuration of the Si$_{68}$C$_{79}$ bucky-diamond cluster is established, our analysis shows that the direct distances between the six surface atoms of the 35-atom inner core and atoms on the 112-atom fullerene shell range from 1.97 to 4.28 Å. This then indicates that the inner core is only weakly bonded to the outer fullerene shell, suggesting that the 35-atom inner core will maintain more or less the unperturbed diamond-like 3C-SiC configuration. Hence the resulting equilibrated Si$_{68}$C$_{79}$ bucky-diamond structure is composed of a 35-atom diamond-like core weakly suspended in the cage of a 112-atom fullerene shell, a concrete example of the co-existence of three-coordinated sp$^3$ and four-coordinated sp$^3$ bonding in the same structure.

5. The relative stability of the bucky-diamond Si$_{68}$C$_{79}$ structure with respect to the cage structure

In our study on all families of C clusters, we have shown that although the bucky-diamond structure is more stable compared to its corresponding compact cluster of the same size, it is less stable compared to a cage structure of the same size [17]. We would like to ascertain whether this scenario is still valid in the case of SiC-based clusters. Since the SiC bucky-diamond structure results from the relaxation of the truncated 3C-Si$_{68}$C$_{79}$ network, it apparently is the more stable structure among compact clusters of the same composition (e.g., Si$_{68}$C$_{79}$ clusters in the fourth row of figure 2). Therefore, we focus our investigation on the relative stability of the SiC bucky-diamond structure with respect to the cage structure of the same composition.

Previously, we have studied the possible conversion of a C bucky-diamond structure to its corresponding cage structure by a finite temperature MD simulation scheme based on the SCED–LCAO Hamiltonian [17, 18]. It resulted in first the disintegration of the interior diamond core as the carbon bucky-diamond was heated and then the migration of the interior atoms to the surface. Hence we believe that, in the case of SiC bucky-diamond, the inner diamond core will also disintegrate first when the SiC bucky-diamond is heated.

In this study, we heated the SiC bucky-diamond from 0 K. At $T = 1800$ K, the inner 35-atom diamond core started to disintegrate. The atoms that broke from the inner core started to migrate towards the fullerene shell at $T = 2000$ K. This process continued until most of the interior atoms reached the surface. At $T = 2600$ K, there were hardly any interior atoms left. When the resulting structure was slowly quenched to 0 K, a reasonably smooth cage structure at a lower binding energy ($\sim 7.881$ eV/atom) compared to that of the bucky-diamond structure ($\sim 7.610$ eV/atom) finally emerged, as can be seen in figure 5(a). We found that this cage structure is composed of mostly hexagons and pentagons, but also some heptagons and octagons. It is somewhat surprising that the cage structure of the same composition is still more stable compared to the bucky-diamond structure as the cage structure is dominated by the three-coordinated sp$^3$ C–Si bond while the strength of the three-coordinated sp$^3$ C–Si bond is somewhat weaker than that of the four-coordinated sp$^3$ C–Si bond (7.96 eV/atom for the three-coordinated sp$^3$ C–Si bond versus 8.02 eV/atom for the four-coordinated sp$^3$ C–Si bond). In figure 5, the pair-distribution functions of the two structures are also shown (figures 5(b) and (c)). It can be seen that there is almost quadrupling of the much stronger C–C three-coordinated sp$^3$ bonds (8.79 eV/atom for the three-coordinated sp$^3$ C–C bond) in the case of the cage structure compared to the bucky-diamond structure, leading to the more stable cage structure. The appearance of other polygons in addition to hexagons and pentagons is indicative that they provide the relief for the strain due to the formation of the cage structure.

6. Conclusion

Our search has led to the successful and, to some extent, surprising finding of the SiC bucky-diamond structure at the specific composition of Si$_{68}$C$_{79}$. It confirms our assertion that a pair of Si and C can form an sp$^3$ bond in the bulk and an sp$^2$ bond on the surface of a SiC-based structure. It also provides the evidence that these two types of bonding can co-exist in the same structure. What is tantalizing is that the SiC bucky-diamond structure actually results from the relaxation of the Si$_{68}$C$_{79}$ cluster obtained by truncating the bulk 3C-SiC network at $m + n = 147$, suggesting a possible route to synthesize the SiC bucky-diamond.

We have also unraveled the mechanism responsible for the formation of the SiC bucky-diamond structure as due to the induced strong C–C bonds between pairs of un-bonded C atoms on the surface of the cluster and the ensuing incorporation of all the atoms in the first six outer shells through the nearest-neighbor Si–C interactions. We believe that a similar mechanism must be responsible for the formation of the carbon bucky-diamond structure.

The finding of the stable SiC bucky-diamond structure confirms similar bonding nature between Si and C atoms and a pair of C atoms, suggesting that SiC-based nanostructures may manifest themselves in forms similar to C-based nanostructures. Our study has highlighted the importance of the composition in the formation of the SiC bucky-diamond. We are actively investigating the role played by the composition in determining the structures of other families of SiC-based clusters.

Acknowledgments

The funding received from US DOE (DE-FG02-00ER4582), NSF (DMR-0112824), and KSEF and the computing cycles obtained from the Cardinal Research Cluster at the University of Louisville are acknowledged.

Appendix

An overview of the SCED–LCAO method is provided here. The matrix elements of the SCED–LCAO Hamiltonian are
where $\varepsilon_{ia}$ may be construed as the orbital energy of the $\alpha$-orbital of the atom at site $i$, $N_i$ is the number of electrons associated with the atom at site $i$, $Z_i$ is the number of valence electrons at site $i$, $U_i$ is the Hubbard-like energy representing the on-site correlation energy, $V_N(R_{ik})$ is the electron–electron energy per number of electrons at site $k$ between the electron distribution at site $i$ and the electron distribution at site $k$, $V_Z(R_{ik})$ is the electron–ion interaction energy between electrons associated with the atom at site $i$ and the ion at site $k$ per number of ionic charge, $\epsilon_{ia}$ is an energy related to $\varepsilon_{ia}$ that reflects the presence of its neighbor $j$, $K(R_{ij})$ is a scaling function, and $s_{ia,jb}(R_{ij})$ is the overlapping matrix. Specifically, we express $V_N(R_{ik})$ in terms of $V_Z(R_{ik})$ using a short-range function $V_N(R_{ik}) = V_Z(R_{ik}) + \Delta V_{ik}(R_{ik})$. This is because both $V_N(R_{ik})$ and $V_Z(R_{ik})$ approach $\epsilon^2/4\pi\varepsilon_0 R_{ik} = E_i \text{ in } R_{ik} \to \infty$. We model $V_Z(R_{ik})$ by the following parameterized function: $V_z(R_{ik}) = (E_0/R_{ik})(1 - (1 + B/R_{ik})e^{-\alpha R_{ik}})$. The overlap matrix elements $s_{ia,jb}(R_{ij})$ are expressed in terms of $S_{\tau}\beta$ with $\tau$ denoting, for example, molecular orbitals sso, sp 2, pp 2, and pp 3 in an sp 3 configuration. We found that it is flexible to model these short-range functions ($S$ functions and $\Delta V$) by a parametric function of the type $(A_N + B_N + C_N)(1 + e^{-\alpha R_{ik}})/\left(1 + e^{-\alpha R_{ik}}(d_{\alpha} - R_{ik})\right)$, thus the SCED–LCAO Hamiltonian is defined in terms of a set of parameters according to equations (A.1) and (A.2). The set of parameters has to be determined through an optimization process fitting against a database composed of a series of judiciously chosen properties of the particular material under consideration [20]. $N_i$, the number of electrons associated with the atom at site $i$, is to be determined through iterated solutions to the general eigenvalue equation based on the SCED–LCAO Hamiltonian of the system ($H$ = $E_i S_i^2$, with $E_i$ being the eigenvalue for the eigenvector $c_i^2$) until $N_i = \sum_{a,b} f_a c_i^2 + \sum_{a,b,d,j} f_a c_i^2 d_j c_d^2$ reflects self-consistency (SC) [18, 20].

From equations (A.1) and (A.2), it can be seen that the framework of the Hamiltonian also includes environment-dependent (ED) multi-center interactions. Thus it provides the Hamiltonian with the flexibility of treating the screening effect associated with electrons, while at the same time, handling the effect of charge redistribution for systems with reduced symmetry on equal footing. Furthermore, the Hamiltonian is set up in such a way that the physics underlying each term in the Hamiltonian is transparent. Therefore, it will be convenient to trace the underlying physics for the properties of the system under consideration when such a Hamiltonian is used to investigate a many-atom aggregate and predict its properties.

It should be noted that the accuracy of the SCED–LCAO Hamiltonian depends critically on how the database for the optimization of the parameter set is selected. An accurate parameter set can be fitted by optimization if it is possible to construct the database from a series of carefully chosen properties determined experimentally for a particular material. Since this was not possible, we chose to use the properties calculated by DFT-based methods to construct the database. We have optimized the parameter sets of SCED–LCAO Hamiltonians for column IV elements, including Si, Ge and C [18, 20, 21], using this approach. The SCED–LCAO Hamiltonians for Si and C based on the respective optimized parameter sets have been applied to a wide range of Si- and C-based structures [18, 20, 21]. It has been demonstrated that these SCED–LCAO Hamiltonians are reliable and transferable, thus possessing predictive power.

In [16], we developed the Hamiltonian for binary SiC systems. Since the electronic structures of Si and C are expected to be similar, we chose to construct the overlapping matrices $S$ and the scaling function $K$ for the binary SiC SCED–LCAO Hamiltonian by averaging the corresponding parameters defining the respective $S$ and $K$ for Si and C. Because of the definitions of the potential functions $V_N$ (electron–electron interaction) and $V_Z$ (electron–ion interaction), we constructed $V_N$ and $V_Z$ for the SiC binary system by averaging the corresponding potentials of Si and C. The SCED–LCAO Hamiltonian thus constructed for binary SiC was shown in [16] to yield results consistent with DFT calculations. For example, to validate the SCED–LCAO Hamiltonian constructed for SiC, we carried out a structural optimization for bulk SiC. The optimized lattice constants were found to be 4.55 Å for the zinc-blende structure and 3.20 Å for the wurtzite structure. The results are in good agreement with our DFT calculations (4.38 Å for the zinc-blende structure and 3.09 Å for the wurtzite structure). We also obtained a flattened graphitic-like structure of the SiC sheet with an optimized lattice constant of 3.14 Å from an initially buckled graphite-like sheet, similar to the results obtained by the DFT calculation mentioned in [16]. Having validated the parameters used in the SCED–LCAO Hamiltonian for SiC, we used the same Hamiltonian to study SiC bucky-diamond structures as reported in this work.

The MD scheme based on the SCED–LCAO Hamiltonian requires the calculation of the forces acting on the atoms in the atomic aggregate at each MD step. The force acting on atom $i$ can be calculated by $F_i = -\nabla E_{\text{tot}}$ where

$$E_{\text{tot}} = E_{\text{BS}} + \frac{1}{2} \sum_i (Z_i^2 - N_i^2) U - \frac{1}{2} \sum_{i,k(i\neq k)} N_i N_k V_N(R_{ik})$$

$$+ \frac{1}{2} \sum_{i,k(i\neq k)} Z_i Z_k V_C$$

(A.3)
with

$$E_{BS} = \sum_{\alpha, \beta, \nu} \alpha \beta, \nu \varepsilon_{\alpha} \varepsilon_{\beta} H_{\alpha, \beta, \nu}$$  \hspace{1cm} (A.4)$$

and

$$V_C = \frac{e^2}{4\pi \varepsilon_0 R_{ik}} = \frac{E_0}{R_{ik}}.$$  \hspace{1cm} (A.5)$$

The calculation of the band structure contribution to the atomic forces can be carried out using the Hellmann–Feynman approach [26]. With the presence of terms involving $N_i$ and $N_k$ in the SCED–LCAO Hamiltonian (see equations (A.1), and (A.2)), terms such as $\nabla_k N_i$, where $\nabla_k$ refers to the gradient with respect to $\vec{R}_k$, will appear in the electronic (band structure) contribution to the atomic forces. However, these terms are canceled exactly by terms arising from the gradients of the second and third terms in the total energy expression (A.3). Thus terms involving $\nabla_k N_i$ will not contribute to the calculation of atomic forces. This fact greatly simplifies the calculation of atomic forces needed in the MD simulations. In other words, if one disregards the extra time due to the self-consistency requirement, the calculation of atomic forces based on the SCED–LCAO Hamiltonian is no longer difficult compared with conventional TB approaches [20].

References

[18] Yu M, Wu S Y and Jayanthi C S 2009 Physica E 42 1–16
[30] GAUSSIAN03, HF/STO-3g