
**AMORPHOUS, VITREOUS, POROUS, ORGANIC,
AND MICROCRYSTALLINE SEMICONDUCTORS;
SEMICONDUCTOR COMPOSITES**

Thermal Instability of Silicon Fullerenes Stabilized with Hydrogen: Computer Simulation

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Abstract—The structure and kinetic properties of a hollow single-layer fullerene-structured Si₆₀ cluster are treated theoretically by molecular dynamic simulation in the temperature range 10 K ≤ T ≤ 1760 K. Five series of calculations are conducted, with simulation of several media inside and outside the Si₆₀ cluster, specifically, vacuum and interior spaces filled with 30 and 60 hydrogen atoms with and without the exterior hydrogen environment of 60 atoms. The average radius of the silicon cluster, \bar{R}_{cl} , increases with increasing temperature, reaching a maximal value in the absence of hydrogen near the cluster and taking smaller values if the unpaired bonds of silicon atoms are fully compensated with hydrogen atoms located inside the cluster and there is no exterior hydrogen “coat.” An increase in temperature yields a decrease in the average number of Si–Si bonds per atom in the silicon cluster, \bar{n}_b , and in the average length \bar{L}_b of the Si–Si bonds. The higher stability of the quantities \bar{n}_b and \bar{L}_b in the entire temperature region under consideration is characteristic of the Si₆₀ fullerene surrounded by a hydrogen “coat” and containing 60 hydrogen atoms in the interior space. Such clusters have smaller self-diffusion coefficients at high temperatures. The fullerene stabilized with hydrogen is stable to the formation of linear atomic chains up to the temperatures 270–280 K.

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1. INTRODUCTION

Clusters of semiconductor materials play an important role in the development of microelectronics. The present-day production of micro-scaled circuits requires materials in the form of particles very small in size. Semiconductor clusters feature covalent bonding and are formed under low vapor pressures. For microelectronics, of importance is the change in the physical and chemical properties when we deal with a nanoparticle instead of a cluster. In the methods of study of the processes of growth of clusters, one must take into account the changes in chemical composition, energy dissipation, evaporation, and the dynamics of molecular levels over a time of a few picoseconds. In this context, it is reasonable to conduct computer simulations based on molecular dynamics (MD) and Monte-Carlo calculations. In particular, the MD simulation was applied to study the stability of noncrystalline nano-sized silicon structures, whose size corresponded to 300–500 atoms [1].

In the last few years, a large number of studies were performed for silicon clusters subjected to the effect of hydrogen. The most extensive theoretical studies were performed for small- and medium-sized clusters, in

which the number of atoms was $N < 25$ and $25 \leq N \leq 60$, respectively [2]. Experimentally, the electrically charged silicon–hydrogen clusters were studied to a larger extent. The electric charge of the clusters virtually does not influence their stability [3]. With the use of an ion trap, Si₅H_x⁺ and Si₁₀H_x⁺ cations were detected [4, 5]. Using a discharge source providing radio-frequency heating of silane (SiH₄), Si_NH_x[−] ions ($N = 1–44$) were produced [6]. From the mass spectra, it was established that clusters with $N > 10$ have a broad distribution of the ratio N_H/N_{Si} , with a maximum at $\sim 4/3$. Such a relation between the numbers of hydrogen atoms N_H and silicon atoms N_{Si} in the clusters cannot be interpreted as a result of only external coating of the silicon particle with hydrogen. Small-sized silicon clusters with low hydrogen content were produced also by expanding the argon–hydrogen–silane plasma [7].

The methods of quantum mechanics were used to study the structure, stability, and physical and chemical properties of the Si_NH_x⁺ and Si_NH_x[−] clusters [8–10]. Monte-Carlo calculations have shown that the most stable structure of the Si_NH_x⁺ clusters is not always formed

of the diamond lattice fragments [11]. However, when saturated with hydrogen compensating the dangling bonds, such fragments become stable for virtually any size. Because of the formation of Si_NH_x particles, porous silicon exhibits photoluminescence [12, 13]. The hydrogen content in the Si_NH_x clusters decreases with increasing temperature. Specifically, the limit of the possible hydrogen content in the $\text{Si}_{14}\text{H}_x^+$ clusters decreases from $x = 28$ at $T = 301$ K to $x = 8$ at $T = 943$ K [3]. With variations in temperature, the highest stability is shown by clusters stoichiometric in composition, i.e., Si_NH_N clusters.

The structure of the C_{60} cluster, i.e., fullerene, is represented by a truncated icosahedron consisting of 20 hexagons and 12 pentagons that form a nearly spherical surface. Silicon is a neighbor of carbon in Group IV of the periodic table. Until now, however, it has been impossible to produce a stable Si_{60} fullerene, although some publications on the Si_{60} structure are available [14]. Theoretical models provide confirmation that the Si_{60} fullerene structure is more preferable than a network (naphthalene-like) structure or a cylinder structure. The fullerene structure of icosahedral symmetry has a local minimum at the potential energy surface. However, for silicon, this structure is unstable and experiences relaxation to the structure of “a ball with folds.” In general, a transformation of the atomic structure also occurs in this case, with the trend towards reconstruction of the tetrahedral atomic arrangement. Disregarding the instability of the Si_{60} fullerene structure, the authors of [15] calculated the electronic structure of Si_{60} and the changes in the electronic structure as a result of oligomerization. It was concluded that, from an energetic standpoint, a large number of open and closed structures based on Si_{60} fullerene were possible. However, no methods for synthesizing this new family of compounds have been found yet.

The purpose of this study is to gain insight into temperature variations in the structure of hollow silicon clusters placed in vacuum or hydrogen environment. The silicon particles are fullerenes consisting of 60 atoms. Hydrogen atoms can be both inside and outside the clusters.

2. POTENTIAL FUNCTIONS FOR COVALENT BONDS

In [16, 17] a new form of bonding between two atoms was suggested in the model taking into account multiatomic correlations. The basic idea is that, in real systems, the strength of each bond depends on the local surroundings, so that the bonds formed by a particular atom with many neighboring atoms are weaker than the

bonds with only few nearest neighbors. Tersoff's potential [16, 17] can be represented as

$$U = \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (1)$$

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})].$$

Here, r_{ij} is the distance between atoms i and j , f_A and f_R are the attractive and repulsive pair potentials, and f_C is the smooth cut-off function. The explicit form of the functions f_A and f_R is given as the Morse potential, so that

$$f_R(r) = Ae^{-\lambda_1 r}, \quad f_A(r) = -Be^{-\lambda_2 r}. \quad (2)$$

$$f_C(r) = \begin{cases} 1, & r < R - D, \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi r - R}{2D}\right), & R - D < r < R + D, \\ 0, & r > R + D. \end{cases} \quad (3)$$

The parameters A and λ_1 define the attractive force, and the parameters B and λ_2 define the repulsive force. The potential parameters R and D are chosen in such a manner that only the layer of nearest neighbors are taken into account for the bulk structures of silicon, graphite, and diamond. The function f_C decreases from unity to zero in the range $R - D < r < R + D$. The main feature of this potential is the presence of the term b_{ij} . The strength of bonding depends on the local surroundings, and is smaller if the number of neighbors is rather large. This behavior of bonding is represented by the term b_{ij} , which increases or decreases the ratio between the attractive and repulsive forces according to the functional form

$$b_{ij} = \frac{1}{(1 + \beta^n \zeta_{ij}^n)^{1/2n}}, \quad (4)$$

where

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ij})g(\theta_{ijk})\exp[\lambda_3^3(r_{ij} - r_{ik})^3], \quad (5)$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (h - \cos\theta)^2]}.$$

The term ζ_{ij} is representative of the coordination number, i.e., the number of nearest neighbors of atom i . The coordination number is determined by taking into account the relative distance between two neighbors, $r_{ij} - r_{ik}$ and the bond angle θ . The function $g(\theta)$ characterizes the dependence of the coordination number on the bond angle. The parameter d defines how steep the function $g(\theta)$ is, and the parameter c specifies the character of variation in the strength of bonding with the angle θ . The parameters of the potential V_{ij} were chosen

Table 1. Parameters of Tersoff's potential for silicon

A , eV	B , eV	λ_1 , nm ⁻¹	λ_2 , nm ⁻¹	λ_3 , nm ⁻¹	n	c	d	R , nm	D , nm	β	h
1830.8	471.18	2.4799	1.7322	0	0.78734	1.0039×10^5	16.217	0.285	0.015	1.1×10^{-6}	-0.59825

Table 2. Parameters of the potential of the Si-H and Si-Si pair interactions

A_1 , eV	A_2 , eV	λ_1 , nm ⁻¹	λ_2 , nm ⁻¹	B_H , eV	α , nm ⁻²	α_{H_2} , nm ⁻²	r_{c_1} , nm	r_{c_2} , nm	μ_1 , nm	μ_2 , nm	ϵ , eV	α_{HH}	r_m , nm
1113.967	-700	27.801	23.616	22.6526	30.34373	60.334	0.39527357	0.18	0.0312058	0.02	0.147	15.20	0.19

by fitting the theoretical results to the experimental data obtained for real and hypothetical atomic configurations. Among the data can be the bonding energy, lattice constant, and bulk elastic modulus. The parameters of Tersoff's potential used in the calculations for silicon are listed in Table 1. In the initial configuration representing the Si₆₀ fullerene, each Si atom is bound to its neighbors by three bonds, each 0.24 nm long.

3. REPRESENTATION OF Si-H AND H-H INTERACTIONS

In simulating Si-H interactions, the problem of providing the univalence of hydrogen arises. To simulate an amorphous Si-H system, Mousseau and Lewis [18] developed an approach in which different potentials were used to describe coupled and uncoupled Si-H interactions. Such an approach makes the MD calculations very slow at practically any finite temperature. Kwon et al. [19] suggested a potential that describes the Si-H interaction in an arbitrary configuration with no need to take into account coupled and uncoupled Si-H pairs. This potential consists of two parts, one of which describes pair interactions and the second of which determines ternary interactions. The two-particle Si-H potential is given as

$$V_{\text{Si-H}}^{(2)} = [A_1 \exp(-\lambda_1 r) + A_2 \exp(-\lambda_2 r)] f_c^H(r), \quad (6)$$

where f_c^H is the cut-off function:

$$f_c^H(r) = \begin{cases} 1, & r \leq 0.17 \text{ nm}, \\ 0.5 + 0.5 \cos \left[\frac{\pi}{0.2} (r - 0.17) \right], & 0.17 \text{ nm} < r < 0.19 \text{ nm}, \\ 0, & r \geq 0.19 \text{ nm}. \end{cases} \quad (7)$$

The parameters A_1 , A_2 , λ_1 , and λ_2 obtained by fitting the corresponding energy to the ab initio calculated energy of hydrogen on a silicon cluster [19] are listed in Table 2. The two-particle potential (6), (7) yields the minimal energy -3.05 eV at $r = 0.15$ nm, in good agreement with

the Si-H bonding energy and the average bond length in the amorphous Si-H system. In addition, this potential gives the frequency 2023 cm⁻¹ for the Si-H stretching vibration mode, also in good agreement with the experimentally determined frequency of this mode in α -Si:H. The short-range character of the interaction is represented by the cut-off function f_c^H expressed as a simple smooth function.

The three-particle potential, important for simulating the covalent Si-H interaction and stabilizing the tetrahedral structure of silicon, is specified as [19]

$$V^{(3)}(r_{12}, r_{13}, \theta) = B_H \phi_{1,2}(r_{12}) \phi_2(r_{13}) (\cos \theta + 1/3)^2 g_{c_{1,2}}(r_{12}) g_{c_2}(r_{13}). \quad (8)$$

The subscripts 1 and 2 refer to the Si-Si and Si-H interactions, respectively. The radial functions $\phi_1(r)$ and $\phi_2(r)$ are defined as

$$\phi_1(r) = \exp(-\alpha r^2) \quad \text{and} \quad \phi_2(r) = \exp(-\alpha_H r^2),$$

and the cut-off functions g_{c_1} and g_{c_2} are defined as

$$g_{c_{1,2}}(r) = \{1 + \exp[(r - r_{c_{1,2}})/\mu_{1,2}]\}^{-1}.$$

The parameters B_H , α , α_H , r_{c_1} , and μ_i are listed in Table 2. The parameters B_H and α_H are obtained by fitting the corresponding vibration modes to the Si-H swinging (630 cm⁻¹) and bending modes (897 cm⁻¹) in α -Si:H. This three-particle potential describes the Si-Si-H, H-Si-H, and Si-H-Si interactions, and the lowest energy corresponds to the arrangement in which an H atom is bound to one Si atom.

The H-H repulsive potential used in the simulation prevents the nonphysical proximity of the H atoms to each other [20]:

$$V_{\text{HH}}^{(2)}(r) = \frac{\epsilon}{1 - \frac{6}{\alpha_{\text{HH}}}} \left\{ \frac{6}{\alpha_{\text{HH}}} \exp \left[\alpha_{\text{HH}} \left(1 - \frac{r}{r_m} \right) \right] - \left(\frac{r}{r_m} \right)^6 \right\}. \quad (9)$$

In this model, the formation of H_2 molecules is impossible. The model involves the consideration of atomic hydrogen only. The parameters ϵ , α_{HH} , and r_m are given in Table 2.

4. MOLECULAR-DYNAMIC MODEL OF $Si_{60}H_x$ CLUSTERS

The MD calculation was based on the integration of the equations of motion by means of the fourth-order Runge-Kutta procedure, with the time step $\Delta t = 10^{-16}$ s. Five series of calculations were carried out for silicon clusters. In each series of calculations, the initial state was specified by the temperature 10 K. For each temperature, the duration of the calculations corresponded to 10^6 time steps, or 100 ps. The final atomic configuration obtained at a lower temperature was further used as the initial configuration for the next calculation for higher temperature. In each subsequent calculation, the temperature was about 100 K higher than the temperature in the preceding calculation. The last calculation was conducted for the temperature 1711 K. In the first series of calculations, fullerene consisting of 60 atoms served as the initial configuration. In this configuration, the minimal distance between the atoms (0.24 nm) was close to the corresponding parameter in the macroscopic Si crystal (0.235 nm). In the second series of calculations, the initial configuration corresponded to fullerene with 30 hydrogen atoms placed inside. These H atoms were located in the straight lines connecting the center of mass of the fullerene with the centers of each second Si atom forming the fullerene. In every case, the distance between Si and H atoms was 0.18 nm. The third series of calculations for the fullerene began with the placing of 60 H atoms inside the fullerene in the manner described above. Before the beginning of the fourth and fifth series, the Si_{60} fullerene filled with 30 or 60 H atoms was placed in virtual spheres with the same diameter. The radius of the sphere was chosen in such a way that 60 H atoms spaced from each other and from Si atoms by a distance no shorter than 0.22 nm could be randomly placed into the space between the particle and the sphere. Thus, the initial density of the hydrogen "coat" was 42–43 kg/m³. The experimental density of liquid hydrogen at 20 K is ~ 70 kg/m³. The calculations for silicon particles in the presence of hydrogen and without hydrogen were carried out for a canonical ensemble.

5. STRUCTURE OF THE CLUSTERS

The effect of hydrogen on the shape and structure of the Si_{60} cluster is illustrated in Fig. 1, where the configuration of the Si_{60} cluster without hydrogen and with hydrogen inside and outside the cluster at the temperature 1500 K at the time instant 100 ps is shown. The H atoms initially placed inside the fullerene are marked by crosses within circles, and the H atoms arranged outside the Si cluster at the time $t = 0$ at $T = 10$ K are shown

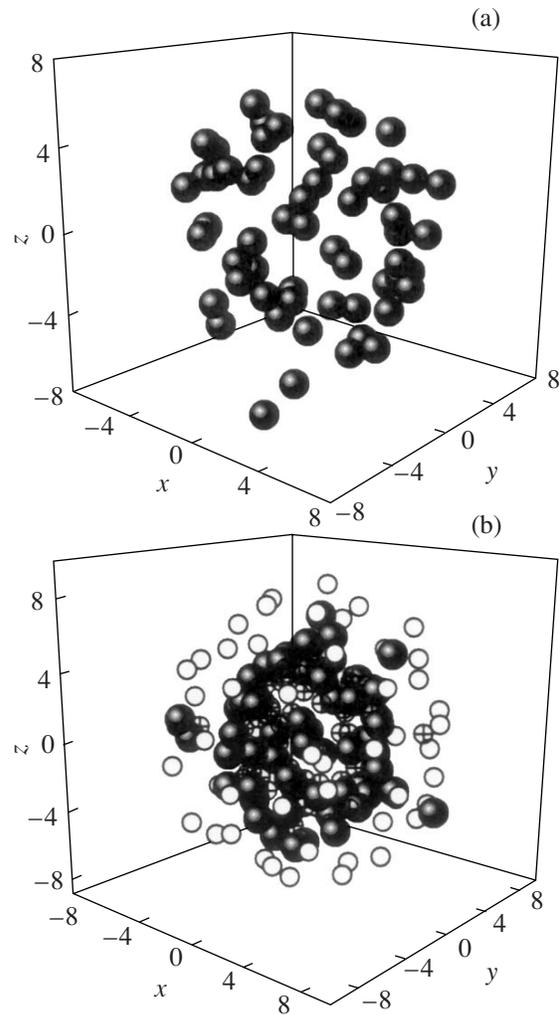


Fig. 1. Atomic configuration of the silicon fullerene at the temperature 1500 K (a) in vacuum and (b) in a hydrogen "coat" in addition to 60 hydrogen atoms filling the interior space. The atomic coordinates are expressed in nanometers.

by open circles. It is evident that the volume of the cluster in vacuum (Fig. 1a) is much larger than the volume of the Si_{60} fullerene filled with 60 H atoms and surrounded with the same number of H atoms on the outside (Fig. 1b). Evaporated Si atoms are present in both cases; however, in vacuum, these Si atoms are separated from the cluster by larger distances. In addition, the Si cluster placed in the hydrogen medium better retains spherical shape and a more homogeneous distribution of the constituent atoms over the spherical surface. Thus, the positive role of hydrogen in stabilizing the shape and structure of the Si_{60} cluster is obvious. Nevertheless, it is found that, even in the hydrogen environment, the silicon fullerene is not quite stable and loses its atoms with increasing temperature. It is also worth noting that some H atoms initially located inside the cluster (at $T = 10$ K) escape from the cluster to the outside.

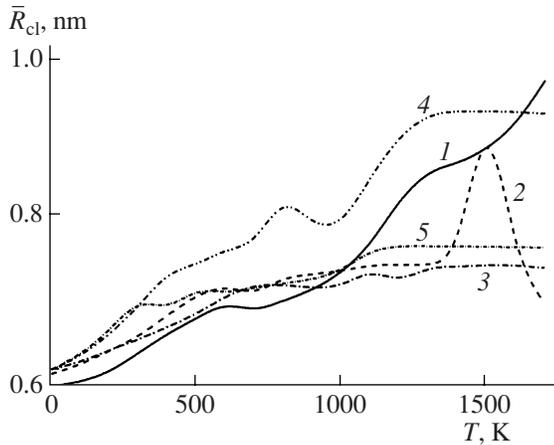


Fig. 2. The average radius of the silicon fullerene \bar{R}_{cl} in the conditions of (1) vacuum, (2, 3) compensation of unpaired Si bonds by (2) 30 and (3) 60 H atoms inside the fullerene, and (4, 5) coating with H atoms and filling of the interior space of the fullerene with (4) 30 and (5) 60 H atoms.

In the calculations, we traced the cluster size by determining the effective radius of the cluster. A Si atom was considered to belong to the cluster if the atom was linked to the cluster by at least one Si–Si bond. To identify the Si–Si bond at every time step, we checked whether each of the Si atoms was separated from the other Si atoms by a distance $r > r_{max} = 0.3$ nm. The linkage between the Si atom and the cluster was considered to be lost if this atom was separated from the other Si atoms by a distance larger than r_{max} at more than five of ten consecutive time steps. Evaporated atoms had a rather high relative kinetic energy and did not return to the clusters. For the whole series of calculations, the number of atoms that evaporated from the Si_{60} cluster during the observation time of 100 ps was no larger than three. For the effective radius of the cluster, R_{cl} , we took the distance from the center of mass of the cluster to the center of the most distant Si atom bound to the cluster by at least one Si–Si bond. The temperature dependences of the time-average effective radius \bar{R}_{cl} in five series of the calculations for the Si cluster (in the presence and absence of hydrogen) are shown in Fig. 2. In general, the quantity \bar{R}_{cl} increases with increasing temperature in all cases. When \bar{R}_{cl} is determined taking into account an evaporated atom, the dependence $\bar{R}_{cl}(T)$, as a rule, exhibits peaks. Such peaks are clearly pronounced in dependences 2 (1510 K) and 4 (820 K), i.e., in the case of 30 H atoms inside the cluster surrounded and not surrounded with external hydrogen. In the temperature range $10 \text{ K} \leq T \leq 1711 \text{ K}$, the parameter \bar{R}_{cl} shows a most profound increase if the cluster is in vacuum (dependence 1); the smallest values of \bar{R}_{cl} are obtained in the case of 60 H atoms inside the cluster

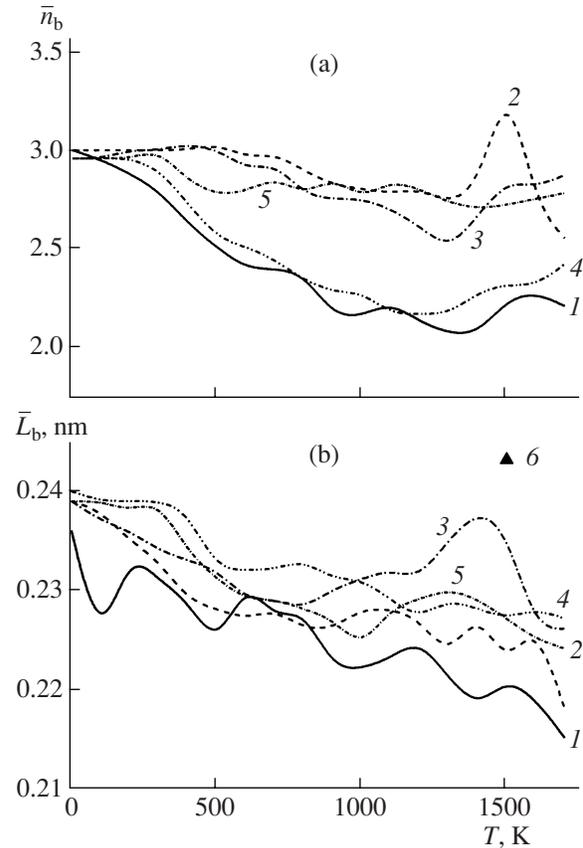


Fig. 3. Temperature dependences of (a) the average number of bonds per atom \bar{n}_b and (b) the average Si–Si bond length \bar{L}_b for the Si_{60} fullerene. The numbers of curves 1–5 correspond to the same conditions as in Fig. 2. Symbol 6 refers to the result of molecular dynamic simulation for the Si_{200} cluster [21].

(dependence 3). A slight increase in \bar{R}_{cl} at high temperatures can also be seen for the cluster with 60 H atoms inside and outside the cluster (dependence 5). The cluster size is found to be unstable if there are 30 H atoms inside the cluster (dependences 2, 4). In this case, if such a cluster is surrounded by 60 H atoms on the outside (dependence 4), the average radius \bar{R}_{cl} has the largest values compared to \bar{R}_{cl} obtained in the other series of calculations for the temperature range $310 \text{ K} \leq T \leq 1630 \text{ K}$.

6. PARAMETERS OF THE Si–Si BOND

The temperature variations in the number of bonds per atom, \bar{n}_b , determined by the above-described procedure and in the average bond length, \bar{L}_b , are shown in Fig. 3. At low temperatures (below ~ 500 K), the parameter \bar{n}_b remains unchanged or slightly increases for the Si_{60} cluster filled with H atoms and not surrounded with a hydrogen “coat”; for the other

fullerenes, \bar{n}_b decreases. However, as the temperature is increased further, the quantity \bar{n}_b decreases for all clusters. The quantity \bar{n}_b reduces most dramatically if the cluster is in vacuum (dependence 1) and if there are 30 H atoms inside the cluster and 60 H atoms outside (dependence 4). The quantity \bar{n}_b is most stable for the Si cluster filled and surrounded with 60 H atoms (dependence 5). In this case, in the entire temperature region, the quantity \bar{n}_b does not go below 2.7. Both with and without hydrogen in the vicinity of Si cluster, the values of \bar{n}_b are no larger than 3.2.

In the Si cluster, the average bond length \bar{L}_b decreases with increasing temperature (Fig. 3b). The parameter \bar{L}_b exhibits the most substantial decrease (~9%) in the cluster placed in vacuum (dependence 1). At high temperatures, the largest values of \bar{L}_b are exhibited by the cluster, within which there are 60 H atoms (dependence 3). The most stable quantity \bar{L}_b is typical of the Si clusters surrounded with hydrogen, with the interior space filled with H atoms (dependences 4, 5). In this case, if there are 30 H atoms inside the cluster, the parameter \bar{L}_b exhibits a 5% decrease in the temperature range $10 \text{ K} \leq T \leq 1711 \text{ K}$; if there are 60 H atoms inside the cluster, the reduction of \bar{L}_b is 6%.

In Fig. 3b, symbol 6 refers to the Si–Si bond length in the Si_{200} cluster, whose surface was covered by a hydrogen monolayer of 74 atoms [21]. To simulate the Si–Si interactions, the authors of [21] used modified Stillinger–Weber’s potential [22]. The Si–H and H–H interactions were described by Kohen–Tully–Stillinger’s potential [23]. The Si_{200} cluster presented a small part of a continuous, i.e., voids-free material. In the Si_{200} cluster at 1500 K, the average Si–Si bond length (0.243 nm) is larger than \bar{L}_b of the Si crystal (0.235 nm).

If the fullerene is placed in vacuum or if there are 30 H atoms inside the fullerene and it is surrounded with a hydrogen “coat,” the quantity \bar{n}_b shows a sharp decrease in the temperature range from 10 to 1350 K. If there is no hydrogen, the decrease in \bar{n}_b is accompanied by a sharp decrease in the average bond length \bar{L}_b . Under temperature variations, the function $\bar{L}_b(T)$ oscillates. The well-pronounced maxima in the dependence $\bar{L}_b(T)$ for series 1 correspond to the temperatures 241, 630, 1195, and 1528 K.

It should be noted that, for the cluster without hydrogen, there is a temperature range, $710 \text{ K} \leq T \leq 800 \text{ K}$, in which the quantity \bar{L}_b stops decreasing. At the temperature 773 K, Khokhlov et al. [24] annealed α -Si films with thicknesses from 100 to 500 nm; as a

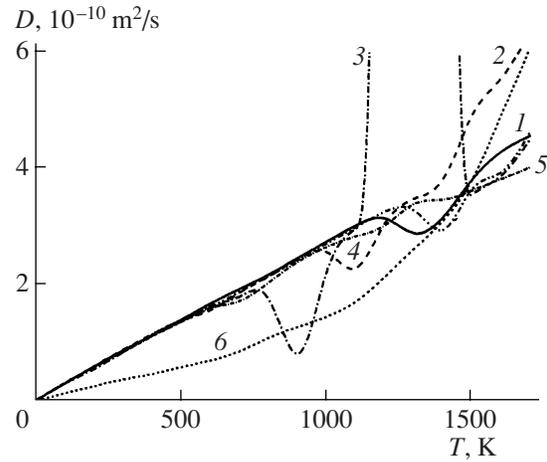


Fig. 4. The temperature dependence of the self-diffusion coefficient in the Si_{60} fullerene. The numbers of curves 1–5 correspond to the same conditions as in Fig. 2. Curve 6 refers to the result of molecular dynamic simulation for the Si_{200} cluster [21].

result, a new modification of silicon, silicyne, was produced. Silicyne consists of linear atomic chains that show sharp bends at every 5–10 atoms. In the chains, the constituent atoms have two Si–Si bonds, while at the bends, the atoms have three Si–Si bonds. The average number of Si–Si bonds per atom in silicyne is close to the number \bar{n}_b obtained here for the Si fullerene at $T > 789 \text{ K}$ in series 1 and 4 (Fig. 3a). In Fig. 1a, the chains of 2–5 Si atoms can be seen, and along with the chains there are three-dimensional clouds of atoms. Thus, when the fullerene is broken down at high temperatures, linear chains of atoms are formed. Similar chains are involved in the silicyne structure.

7. COEFFICIENTS OF DIFFUSION AND LINEAR EXPANSION

The mobility of atoms in the clusters studied here is illustrated in Fig. 4. At low temperatures (up to 550 K), hydrogen does not produce any noticeable effect on the self-diffusion coefficient D of Si atoms. All five series of calculations give virtually the same dependence $D(t)$. The noticeable influence of hydrogen on the kinetics of Si atoms is observed at $T > 770 \text{ K}$. Particularly profound changes in D occur for the Si cluster containing 60 H atoms in the interior space. At first, the pressure created by hydrogen reduces the mobility of atoms in silicon, and then the quantity D sharply increases due to evaporation of Si atoms. For this cluster at $T \approx 1500 \text{ K}$, the quantity D follows again the dependence $D(t)$ for the clusters treated in series 1, 4, and 5. When the number of H atoms inside the Si cluster is half of that in series 3, i.e., equal to 30 (dependence 2 in Fig. 4), a sharp increase in the dependence $D(t)$ can be seen at higher temperatures, starting from $\sim 1370 \text{ K}$; this

increase is also due to evaporation of Si atoms. If there is hydrogen inside and outside the cluster (series 4, 5), we can see oscillations of the function $D(t)$ at $T > 1180$ K. In this case, equalization of the numbers of H atoms inside and outside the Si cluster suppresses the oscillations of $D(t)$ at high temperatures. For the Si cluster in vacuum (dependence 1) at $T > 1180$ K, the function $D(t)$ oscillates with an amplitude even larger than that for dependences 4 and 5 in Fig. 4.

Curve 6 in Fig. 4 is the result of MD calculations [21] of the self-diffusion coefficient of the Si cluster consisting of 6400 atoms. At the surface of that cluster, there was a monolayer of 785 H atoms. In contrast to the Si_{60} cluster studied here, the Si_{6400} cluster was free of voids. It can be seen that, in the temperature range $10 \text{ K} \leq T \leq 1350 \text{ K}$, the self-diffusion coefficient of the Si_{6400} cluster, as a rule, is noticeably smaller than the corresponding coefficient D of the clusters considered in this study. However, at $T > 1500 \text{ K}$, the increase in the coefficient D of the Si_{6400} cluster becomes steeper than the increase in D of the clusters considered here. This is most likely due to the Stillinger–Weber potential used to describe the Si–Si interactions in the clusters. This potential provides a coefficient D larger than those obtained with the potential used here because of the substantially higher mobility of surface atoms at a high temperature.

The estimation of the linear expansion coefficient β for the Si_{60} cluster in the temperature range 511–611 K shows that the Si fullerene filled with 60 H atoms exhibits the largest value of β ($6.09 \times 10^{-5} \text{ K}^{-1}$), while the Si_{60} cluster covered with hydrogen shells of 60 atoms features the smallest value ($-1.51 \times 10^{-5} \text{ K}^{-1}$). The negative value of β shows that, in the latter case, we have interplay of various factors associated with the pressure produced by hydrogen both inside and outside the cluster and with the surface tension of the fullerene in vacuum. In vacuum, the Si fullerene that has kinetic energy corresponding to the temperature 561 K is characterized by a coefficient β at least an order of magnitude larger than the average value of β ($3.5 \times 10^{-6} \text{ K}^{-1}$) for crystalline silicon [25] at the same temperature.

8. CONCLUSIONS

In this study, MD simulation is used to study the effect of stabilization of the structure and shape of the hollow single-layer Si_{60} cluster, an analogue of the C_{60} fullerene, by creating a hydrogen layer inside or outside the cluster. In the temperature range $10 \text{ K} \leq T \leq 1711 \text{ K}$, the behavior of five systems formed by the silicon fullerene and internal and/or external shells of hydrogen atoms is studied. The calculations show that the Si_{60} fullerene is not a stable cluster, as can happen with its C_{60} analogue. At low temperatures, the Si_{60} fullerene placed in vacuum collapses, which is promoted by the formation of short chains and small bulk fragments and by the decrease in the average bond length. At high

temperatures, the broken Si_{60} fullerene increases its initial volume, and a fraction of the constituent atoms evaporate, whereas the remaining atoms are grouped into chains and ultrasmall clusters consisting of several (2–8) atoms. In this case, the number of Si–Si bonds per atom, \bar{n}_b , is reduced, and the average bond length, \bar{L}_b , decreases. Filling of the Si_{60} fullerene with hydrogen, especially in the amount completely compensating unpaired Si bonds, noticeably limits the decrease in the quantities \bar{n}_b and \bar{L}_b (the number of bonds per atom and the average bond length), but does not prevent evaporation of atoms at temperatures higher than 1100 K. At lower temperatures ($100 \text{ K} \leq T \leq 800 \text{ K}$), the complete compensation of unpaired Si–Si bonds with hydrogen inside the fullerene produces the effect of diffusion “resistance”; in this case, the self-diffusion coefficient is nearly halved. In addition to the filling of the fullerene interior space with hydrogen, the creation of a hydrogen “coat” outside the fullerene tends to decrease the probability of evaporation of Si atoms, but does not protect the system from a sharp decrease in the number of bonds per atom at high temperatures. The number \bar{n}_b sharply decreases with temperature for incomplete compensation of the number of unpaired bonds of Si atoms with hydrogen inside the fullerene. In the most successful series of simulations (60 hydrogen atoms both inside and outside the fullerene), the effect of hydrogen-induced stabilization can be evaluated in the temperature range 270–280 K, by which the onset of irreversible decreases in \bar{n}_b and \bar{L}_b can be elongated due to hydrogen. In other words, at a temperature close to 270–280 K, the Si_{60} fullerene filled with 60 hydrogen atoms and covered with a hydrogen “coat” is close to the boundary of thermal stability.

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