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Abstract. We present the results of tight-binding molecular dynamics calculations for studying the equilibrium structures and the bonding properties of Si_n clusters for n up to 18. To prevent unphysically large charge transfer between different atoms in clusters, we employ the atomic charge neutrality constraint that each atom has approximately four valence electrons. With a limited number of parameters in the tight-binding scheme, the structures of minimum energy are well reproduced, as compared with results from previous *ab initio* quantum mechanical calculations. We find the abundant cluster sizes $n = 4$, 7 and 10, which are in good agreement with other theoretical and experimental results. For $n \geqslant 7$, surface-like compact structures with a pentagon or a hexagon base are found to be energetically favourable, resulting in the metallic nature of the cluster bonding, while a core-based structure appears first for Si_{15}.

1. Introduction

The properties of small atomic clusters have attracted considerable attention because of their important role in catalytic and photographic processes [1]. In microclusters of covalent materials, the dependence of the stability and reactivity on the specific size is significant because the environment of each atom in clusters is different from that in bulk solids [2]. Recent experimental studies showed that, for Si cluster ions Si_n^+ undergoing a reaction with NH_3, dramatic oscillations in reactivity occur with n; such studies have expanded our understanding of Si clusters [3, 4]. In many previous calculations it was found that the stable structures of small Si clusters are of metallic character, although the bulk crystal of Si is clearly covalent [5–14]. Since the metallic structures are characterized by high coordination numbers their bond angles are close to 60°, while in the covalent limit the bond angles are concentrated near 110° [12].

First-principles quantum mechanical calculations based on the local-density approximation are quite accurate, and have successfully predicted the structures of Si_n clusters through molecular dynamics simulations [8]. However, the calculations were only performed for $n \leqslant 10$ because the computational demand grows quickly as the size of the cluster increases. To overcome such numerical difficulties, the tight-binding or the valence force field model has been employed and it has proved to be numerically efficient for large clusters [5, 9–13]. Based on the force field model, Chelikowsky and his co-workers predicted the equilibrium structures and the chemical reactivities of Si_n clusters for n up to 30, and also estimated the critical size of cluster for the cross-over from the character of a metallic bond to that of a covalent bond [10–13]. Using a tight-binding model [5], Tománek and Schlüter parametrized a Hamiltonian by fitting to the *ab initio* configuration interaction calculations for the cohesive

energy of Si_2 and examined the structural properties for n up to 14. However, since these semi-empirical methods were applied to a limited number of configurations, it is sometimes difficult to avoid the local energy minimum. Recently, Goodwin and co-workers proposed new tight-binding parameters, and their molecular dynamics calculations successfully determined the equilibrium geometries of Si_n clusters [15]. However, tests were only made for Si_2–Si_6 clusters.

The purpose of this paper is to analyse the stable structure and the bonding character of large Si_n clusters up to $n = 18$ using the tight-binding molecular dynamics technique. The transferable tight-binding parameters generated by Goodwin and co-workers [15] are used with the charge neutrality condition under which an unphysically large flow of charge between different atoms in clusters is prevented. The total energy of each cluster is fully minimized to search for the absolute minimum with a dynamical simulated annealing strategy. For the size of the Si clusters considered, the surface-like compact symmetric structures with a metallic nature of bonding are found to be energetically favourable. Rather than octahedron-based structures, pentagon- or hexagon-based structures are found to be the equilibrium structures of Si_n ($n \geqslant 7$). For Si_{10}, we find a distorted bicapped tetragonal antiprism to be lowest in energy. A core-based structure is found to appear first for Si_{15}. In section 2, the calculational method is briefly described. Section 3 contains the results of calculations and a discussion of those results. In section 4, conclusions are drawn.

2. Computational methods

Our calculations are based on tight-binding molecular dynamics to determine the equilibrium structures of Si microclusters. We use transferable tight-binding parameters, which were extracted by rescaling the energy functional and fitting to *ab initio* calculations for various Si bulk phases [15]. Although the successful applications of the parameters were only made for small Si_n clusters ($n \leqslant 6$), the transferability for larger clusters has not been tested. For large clusters ($n \geqslant 10$), since the potential surfaces are complicated and numerous isomers exist, the computational demands are extensive and thus accurate *ab initio* simulations are prohibited even with modern computer resources. In view of this, the parametrized tight-binding molecular dynamics calculations appear to be more appropriate in searching for the equilibrium structures of large clusters.

In the tight-binding method, the minimal orbital sp basis set employed may not fully describe the electronic behaviour of a disordered system. The charge transfer between atoms is often overestimated, and may result in errors when determining the structures and the binding energies of clusters. To eliminate such problems, we employ the atomic-charge neutrality constraint, which was implemented in previous work [15]. Although the neutrality constraint forbids an excessive flow of charge, slight charge transfer may occur by adjusting the site energies. This scheme provides an approximation to self-consistency within a tight-binding framework. We estimate a maximum deviation from the charge neutrality condition to be about ±0.1 electrons per atomic site.

The equilibrium structures of Si clusters are determined by the molecular dynamics simulations. The equations of motion for each atom are integrated by a predictor–corrector algorithm [16], with a timestep of $\Delta t = 1.09 \times 10^{-3}$ ps. The annealing process usually depends on the following parameters: timestep, annealing time and cooling ratio. Of these parameters the most important is the cooling rate, which controls the temperature of a system. We carry out the dynamical annealing with a constant ratio of 0.99 between the target and current kinetic energies [17]; the kinetic energy (E_k) relation

$$E_k^{\text{target}} = 0.99 E_k^{\text{current}} \tag{1}$$

is maintained between successive timesteps. At each timestep, since the wavefunctions are exact within a tight-binding framework, the Hellmann–Feynman theorem is valid [18]. Thus, the calculated Hellmann–Feynman forces are used to search for the equilibrium geometries. The atomic relaxations are executed by the molecular dynamics annealing scheme, in which the kinetic energy is slowly removed by (1). Since the number of isomers dramatically increases as the cluster size increases, the determination of the globally minimized structure is very difficult for large clusters. All the clusters considered here are equilibrated at high temperatures around 2000 K and cooled gradually through up to 6000 timesteps until the atomic forces are less than 10^{-3} eV Å^{-1}. Thus, each cluster reaches the equilibrium structure. We point out here that such an annealing scheme is not always guaranteed to lead to the energy minimum structure. In our calculations, we try several constant ratios in (1) and use different *seed* configurations to ensure the global minimum configuration. We also mention here that rapid quenching from relatively low temperatures may lead to a metastable state for large clusters with $n > 10$.

3. Results and discussion

The equilibrium structures of Si$_n$ clusters up to $n = 18$ are shown in figure 1. We reproduce exactly the same geometries for Si$_2$–Si$_6$ clusters as those previously obtained from the same tight-binding parameters [15]. The structures of minimum energy are also consistent with other *ab initio* calculations [6, 7]. In table 1, we compare our calculated bond lengths and bond angles for smaller Si clusters with other theoretical results, and find good agreement between the calculations. The bond length of Si$_2$ is calculated to be 2.23 Å. For Si$_3$, the ground-state configuration is found to be an isosceles triangle, with the equal sides of length 2.25 Å and an opening angle of 78.1°. Si$_4$ is a flat rhombus with a side of length 2.36 Å and a minor diagonal of length 2.56 Å; Si$_5$ is a trigonal bipyramid capped both on the top and bottom. The base is an equilateral triangle with a side of length 3.38 Å, and the distances between the corners of the triangle and the capped atoms are calculated to be 2.39 Å. The lowest-energy structure for Si$_6$ is found to be a slightly distorted bipyramid with a square base of length 2.47 Å and a capping bond length of 2.75 Å, and this structure is in good agreement with other *ab initio* quantum molecular-orbital and pseudopotential local-density functional calculations [6, 14]. Considering the small number of basis functions used in our tight-binding calculations, the agreement between this calculation and other *ab initio* calculations is satisfactory.

For Si$_7$–Si$_{10}$ clusters, our calculations show that the octahedron-based structures are not energetically stable. The ground-state structure of Si$_7$ is a bicapped pentagon, which is consistent with the stable structure found in *ab initio* calculations [7, 8, 14]. This structure corresponds to an initial stage of the pentagonal growth pattern which is composed of 1–5–1 layers. The pentagon base has a side of length 2.52 Å and is capped on top and bottom, in a similarly fashion to Si$_5$ and Si$_6$ clusters. The bond distance from the corner of the pentagon to the capped atom is found to be 2.58 Å. The equilibrium geometry of Si$_8$, as shown in figure 1, is a singly capped pentagonal bipyramid and follows the pentagonal growth pattern with the addition of a capping atom. *Ab initio* quantum mechanical calculations showed a bicapped octahedron as the equilibrium structure [8]; however, this structure is found to be 0.23 eV per atom higher in energy than our calculated equilibrium geometry. In Si$_9$, the stable structure maintains the pentagonal growth pattern with tricapped atoms on a side, keeping the pentagon base of Si$_8$.
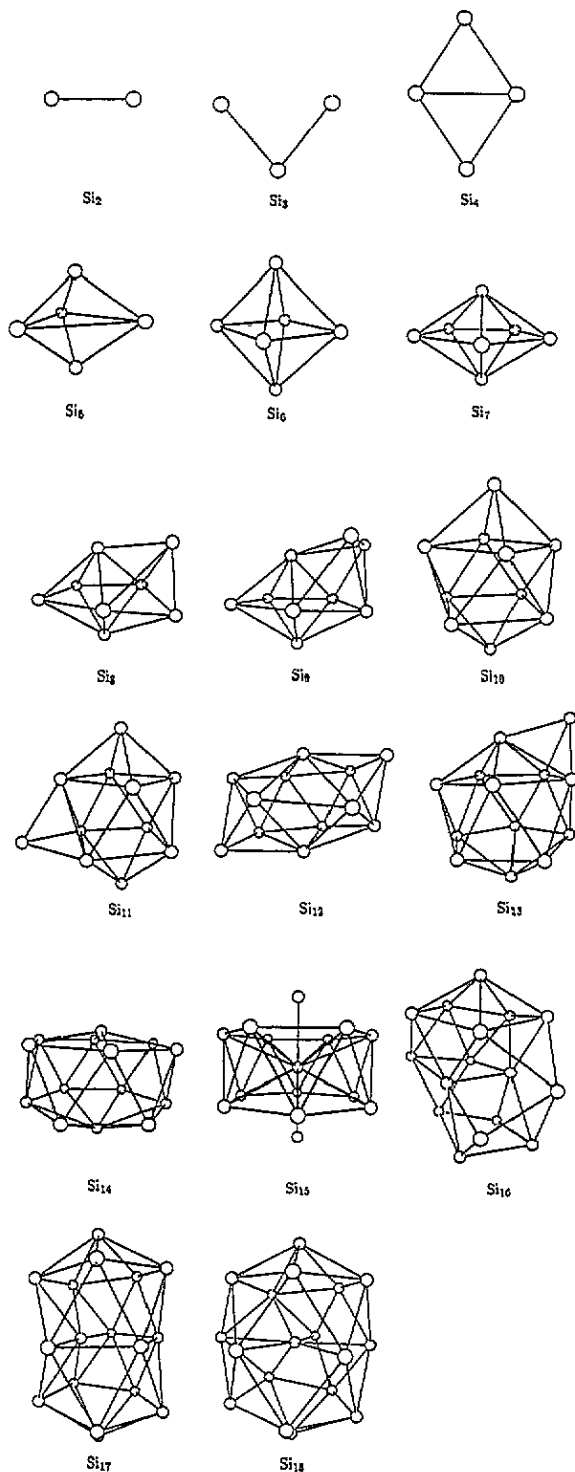
Figure 1. Ball-and-stick models for the calculated equilibrium geometries of Si_n clusters for n up to 18. The lines are drawn for pairs with distance less than 2.82 Å.

Table 1. The calculated bond lengths and bond angles are compared with other calculations for small Si$_n$ clusters. The bond lengths are given in Å.

n	Structure	Parameters	Present calc.	Other calc.
2	Dimer	Bond length	2.23	2.23[a], 2.27[b]
3	Isosceles triangle	Side length	2.25	2.17[a], 2.189[b]
		Opening angle	78.1°	77.8°[a], 78.8°[b], 80°[c]
4	Rhombus	Side length	2.36	2.30[a], 2.32[b], 2.4[c]
		Minor diagonal	2.56	2.40[a], 2.39[b], 2.5[c]
5	Trigonal bipyramid	Base length	3.38	3.26[a], 3.02[b], 3.3[c]
		Capping length	2.39	2.34[a], 2.30[b], 2.5[c]
6	Square bipyramid	Base length	2.47	2.36[a], 2.36[b], 2.8[c]
		Capping length	2.75	2.44[a], 2.71[b], 2.5[c]
7	Bicapped pentagon	Base length	2.52	2.46[b]
		Capping length	2.58	2.45[b]

[a] *Ab initio* molecular-orbital calculations [6].
[b] Pseudopotential local-density functional calculations [14].
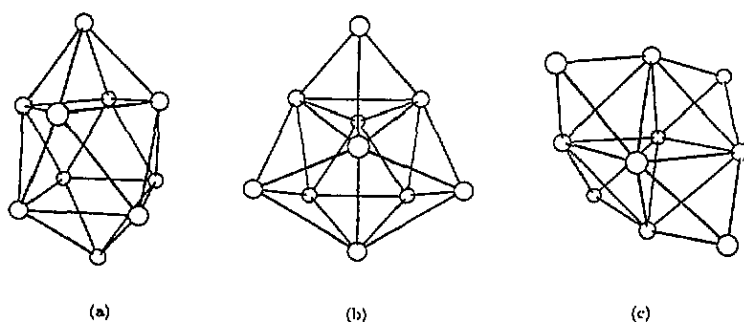[c] Tight-binding model calculations [5].

(a)   (b)   (c)

Figure 2. Three different structures are shown for Si$_{10}$: (*a*) distorted bicapped tetragonal antiprism, (*b*) distorted tetracapped trigonal prism, and (*c*) tetracapped octahedron. Lines are drawn for pairs with distance less than 2.82 Å.

Despite many theoretical studies for Si$_{10}$, there has been no general agreement on its stable structure [5,7,8,11,19]. Figure 2 shows the three different atomic structures that are most often considered as the equilibrium geometry. *Ab initio* molecular dynamics calculations based on the local density approximation [8] reported a distorted tetracapped trigonal prism structure (TTP) as being the most stable, while the valence force model of Chelikowsky and co-workers [21] suggested a bicapped tetragonal antiprism (BTA) as the equilibrium structure. With an *ab initio* quantum molecular-orbital method, Raghavachari and Rohlfing [7] investigated various structures and suggested that a tetracapped octahedron structure (TO) is slightly more stable than a tetracapped trigonal prism structure. However, they found that stability between the TO and TTP structures depends on the perturbative treatment of the electron correlation. More recently, Rantala and co-workers [19] found from their tight-binding calculations that the most stable structure is the distorted BTA induced by Jahn–Teller effects. In our calculations, we find that the structure of minimum energy is a distorted BTA, which is consistent with the tight-binding result [19]. This geometry is more stable by 0.03 eV per atom in energy than the distorted TTP, and by 0.38 eV per

atom than the TO structure found by Tománek and Schlüter [5]. The ordering of stability of the three structures is consistent with previous theoretical calculations [19]. Since the BTA structure has high D_{4d} symmetry, its energy gap, defined as the difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, is found to be zero. The Jahn–Teller distortion twisting the BTA breaks off the degeneracy at the Fermi level and reduces the symmetry to C_2. In the distorted BTA geometry, the energy gap is found to increase to 1.0 eV, compared to the BTA, in good agreement with other tight-binding estimates [19] and photoelectron spectra measurements for Si_{10}^- [20]. However, the distorted TTP structure gives a gap of 2.0 eV, twice as large, which agrees with the results of *ab initio* and tight-binding calculations [8, 19]. Our calculated TO structure is slightly distorted, compared with the ideally tetracapped octahedron of Tománek and Schlüter [5].

For large clusters with $n > 10$, a relatively rapid quenching in molecular dynamics may produce a metastable geometry. In fact, we frequently find structures with a bicapped pentagon as a subunit in the metastable geometry. A capping of an atom on the stable structure of Si_{10} induces the stable form of Si_{11}, as shown in figure 1. For Si_{12}, we find a strongly distorted icosahedral structure, which is more stable in energy by 0.04 eV per atom than the ideal icosahedral structure. The distortion from ideal icosahedral structure is found to induce an increase of the energy gap from 0.02 eV to 0.4 eV. Despite such a strong distortion, this cluster has many trigonal faces in its ground state. Si_{13} shows a singly capped icosahedral structure with a gap of 1.27 eV. This structure has a more surface-like bonding character, compared to a core-based bond structure which Chelikowsky and Phillips found as the equilibrium geometry [12]. The core-based icosahedral structure is a sequence of the pentagonal growth, which leads to the 1–5–1–5–1 layers. However, our calculations show that this structure is found to be higher in energy by 0.15 eV per atom than the capped icosahedron, and it has a larger energy gap of 2.24 eV, while an energy gap of 1.27 eV is found for the capped icosahedron. Because of the small energy difference between the core-based and capped icosahedral structures, the two structures may be isomers. The surface-like bonding character is also found for Si_{14}, with the bond angles closely related to a metallic phase rather than a covalent one. This structure consists of two hexagons on top each other, with a capping atom on each hexagon. We find that one of the capping atoms is more closely bonded to its neighbouring hexagon atoms with a bond length of 2.65 Å, whereas the other has a capping bond length of 2.73 Å, thus the corresponding hexagon has slightly larger edges by about 3%. Two hexagons having sixfold symmetry are interconnected by isosceles triangles with equal sides of length 2.56 Å. Furthermore, this structure can be viewed as a distorted icosahedron with the pentagon bases strongly distorted by the additional capping atoms. For Si_{15}, although two hexagons still exist, a different growth pattern with a core atom and larger relaxations for capped atoms is found, resulting in the core-based bicapped hexagonal antiprismatic structure. This phase is found to have a large gap of 2.19 eV. As in the case of Si_{14}, this core-based structure can also be viewed as a distorted cored icosahedron with additional capping atoms, similar to the stable structure found by Chelikowsky and Phillips [12]. Because of the core atom in Si_{15}, the volume of the structure is slightly increased, resulting in an enlarged bond length of 2.66 Å between the two hexagons, as compared to the structure of Si_{14}. The core atom is found to be more strongly bonded to the capping atoms with equal bond lengths of 2.44 Å, while the bond lengths to the neighbouring hexagon atoms are 2.82 Å. For both capping atoms, the bond distances to their neighbouring hexagon atoms are estimated to be 2.87 Å, which is larger than those for Si_{14}. The structure of Si_{16} is very complicated and shows characteristics intermediate between Si_{15} and Si_{17}, because the hexagon bases of Si_{15} are strongly distorted and developed into the pentagon shape, which is the building block of Si_{17}. In Si_{17} we find

a sequence of pentagonal growth with 1–5–5–5–1 layers. The equilibrium structure of Si_{18} is similar to that of Si_{17}, except for the core atom. The second pentagon base is enlarged with the formation of new bonds between the cored atom and the atoms on the base plane.

For the silicon microclusters studied here, the face capped structures are energetically favourable with the additional capping atoms, which induces high coordination metallic bonding. When atoms begin to be cored in a cluster, covalency in bonding is likely to develop. Since the single-atom core-based structure is shown to be stabilized for Si_{15} and Si_{18}, the onset of the phase transition from metallic-to-covalent bonding may occur at an intermediate size of clusters above $n = 20$. Based on first-principles calculations for Si_{33} and Si_{45}, Kaxiras suggested that a core-based stable structure exists for Si_{33}, and estimated the critical size of $n = 33$ from high-coordination metallic-to-low coordination covalent bonding [21]. Chelikowsky also suggested a similar critical size of $n \simeq 50$ from his valence force field calculations [10].
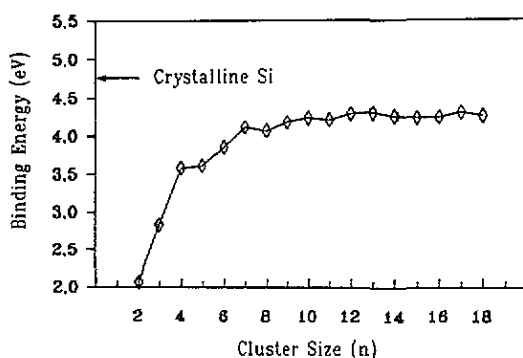

Figure 3. Binding energies per atom for the most stable structures of Si_n clusters are plotted as a function of n and compared with that of bulk Si.
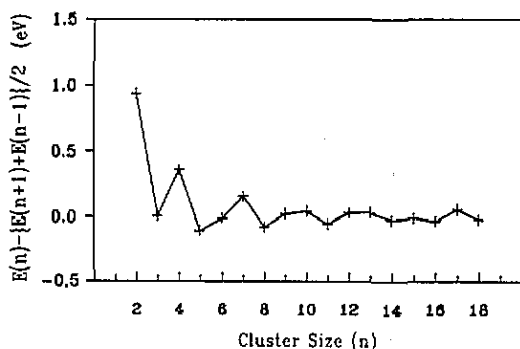

Figure 4. Binding energy difference defined in the text reveals the local stability of Si_n clusters.

In figure 3, we present the results of the calculated binding energies for Si_n clusters in their equilibrium structure. The binding energy is found to slowly converge to that of crystalline Si ($\approx 4.8\,eV$ per atom in the tight-binding calculations) for n above 10. For Si_n,

the binding energies for n up to 8 are generally overestimated by about 0.4 eV, as compared to other tight-binding and valence force field calculations [5, 9, 10]. However, the overall behaviour of the cohesion is in good agreement with other calculations, except for $n = 7$, the binding energy of which is higher than that of Si_6. By evaluating the quantity defined as

$$E(n) - [E(n+1) + E(n-1)]/2 \qquad (2)$$

where $E(n)$ is the binding energy of Si_n, the local relative stability of different clusters can be examined, as is commonly done elsewhere [9, 22]. It is evident from figure 4 that the most stable clusters are $n = 4, 7$ and 10. These results are consistent with the prominent presence of $n = 4, 6, 7$ and 10 in the mass spectral distributions of Si clusters, and the observations of the low photofragmentation cross sections [2, 7]. However, the local stability of Si_6 is not seen in our calculations.
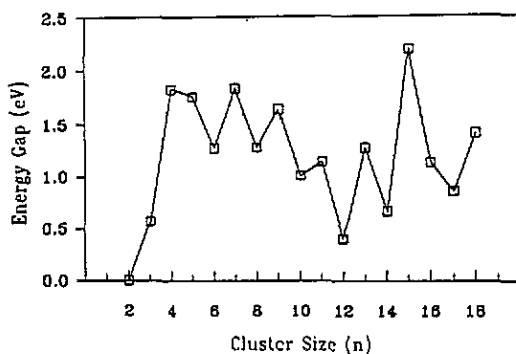

Figure 5. Energy gaps of Si_n clusters in their most stable structures are plotted as a function of cluster size.

We also plot, in figure 5, the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital as a function of cluster size. For Si_4–Si_{10} clusters, the gap energies are found to be of the order of 1–1.7 eV, as compared to the bulk band gap of 1.14 eV. As is expected, the energy gap generally decreases as the cluster size increases. We note that the stable structures for Si_4 and Si_7 have large gap energies. However, the energy gap of about 1 eV for the stable twisted BTA structure of Si_{10} is relatively lower than those calculated for other structures [8, 19], as discussed earlier. The smallest energy gap is found at the cluster size of $n = 12$, indicating highly metallic bonding in the distorted icosahedron. For n above 10, the core-based structures for Si_{15} and Si_{18} exhibit large energy gaps, while smaller gaps are found for Si_{12}, Si_{14} and Si_{17} with the surface-like structures. To see the varying stability of the clusters, we plot the densities of states (DOS) for Si_{10} and Si_{18} in figure 6 and compare with that of bulk Si. We note clearly that the DOS of the cluster is developed into the bulk Si DOS as the cluster size increases. The s-derived states in both the clusters are far below the bulk s band probably because of less screening of the s electrons. However, the sp-hybridized and p-derived energy levels in Si_{18} much resemble the bulk DOS. Since the structure of Si_{18} is core based, the core atoms seem to be important to provide covalent bonding character.
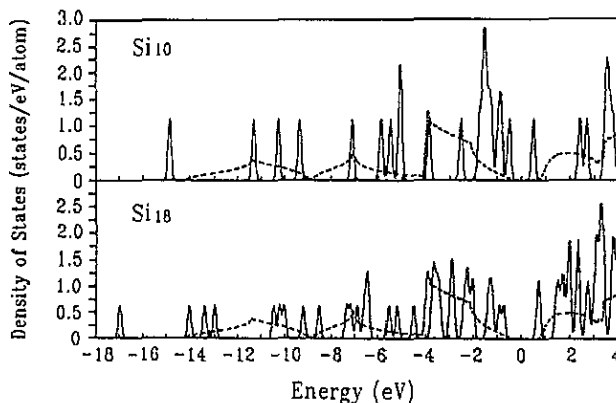
Figure 6. Densities of states for Si_{10} and Si_{18} are compared with that of bulk Si. The Fermi energy is chosen as the zero level. For clusters, the Gaussian broadening with a width of 0.167 eV is used for each energy level. The DOS of bulk Si (broken curve) is calculated by the tight-binding method introduced in the text.

4. Conclusion

We have determined the equilibrium structures of Si_n clusters for $n \leqslant 18$ through tight-binding molecular dynamics calculations. Considering the limited number of parameters used in the method, the agreement of the structural properties of clusters with previous *ab initio* and semi-empirical calculations is quite satisfactory. We have found the abundant cluster sizes of $n = 4, 7$ and 10, which are in good agreement with the other theoretical and experimental results. Our calculations show that for $n \geqslant 7$, the close-packed and surface-like structures with a pentagon or a hexagon base are energetically favourable, resulting in the metallic nature of cluster bonding. A core-based structure with a large gap is found to be developed for a relatively small size of cluster such as $n = 15$ and 18.

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