
Structure and Relative Stability of Si_n ($n = 10\text{--}16$) Clusters

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Ab initio molecular dynamics simulated annealing technique coupled with density functional theory in the local density approximation implemented in Spanish initiative for electronic simulations with thousands of atoms method is employed to search the ground state geometries of silicon clusters containing 10–16 atoms. We found a number of new isomers which are not previously reported. The atoms in all these clusters exhibit pronounced preference for residing on the surface. The binding energies increase while the highest occupied–lowest unoccupied molecular orbital gap generally decreases with the increase in clusters size.

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1. Introduction

Clusters are distinctly different from their bulk state and exhibit many specific properties, which distinguishes their studies as completely different branch of science named cluster science. They are a special class of matter with sizes in-between single atoms and semiconductor quantum dots [1]. Small to medium sized semiconductor clusters have received considerable attention since the 1980s, because of their particular properties and their potential applications in the nanoelectronics industry. Silicon is one of the more important semiconductors with widespread applications which have been extensively studied. It is a semiconductor with diamond lattice structure preferring sp^3 hybridization. Due to its unique electrical properties it is the most important technological material in the electronic industry. For this reason silicon clusters were extensively investigated during the last two decades. In the case of small clusters ($n < 10$), structural and electronic properties, especially the lowest energy structures, have been clearly established [2]. For clusters with larger sizes ($n > 10$), a lot of work was carried

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out, both experimentally [1, 3] and theoretically [4], with results not always in agreement between authors. The procedure used in the case of small clusters is not practical for larger ones. Indeed, for systems with many degrees of freedom, the problem of identifying and sorting the lowest energy configurations belongs to the class NP-complete [5], for which the computation time of an algorithm able to find the exact solution increases exponentially with the number N of atoms. Solving the problem becomes rapidly computationally intractable as N increases. Consequently, searching the structure with global energy minimum becomes a difficult task. However, by combining the *ab initio* method with the molecular dynamics [6] simulated annealing technique [7] we can efficiently search the clusters configuration space and determine the ground state geometry [8, 9]. We used this technique in all the calculations reported here. Details of the computational method are given in Sect. 2. In Sect. 3 we present and discuss our results, and in Sect. 4 we summarise our main conclusions.

2. Computational methodology

We have used the Spanish initiative for electronic simulations with thousands of atoms (SIESTA) [10, 11] with simulated annealing optimization technique to find the ground states structures of silicon clusters containing 10 to 16 atoms. The SIESTA method combines the density functional with molecular dynamics simulation. The pseudopotential for silicon is generated by using the program ATOMS [10, 11]. The local density approximation (LDA) of the density functional has been used with the exchange-correlation energy functional parameterized by Perdew and Zunger [12]. During simulation, volume of the system was kept constant. In order to avoid interaction between the clusters a big supercell (including enough of vacuum around the cluster for interaction between the clusters in neighbouring cells to be negligible) was used. The Γ -point approximation was used for the Brillouin zone sampling. To perform simulated annealing, initial velocities were assigned to the system corresponding to 10 K. Random velocities, drawn from the Maxwell-Boltzmann distribution with the corresponding temperature, are assigned to atoms. The constraint of zero centre of mass velocity is imposed. The atoms were moved according to the velocity Verlet algorithm with a time step of 1 a.u. The system of each cluster was taken at high temperature of 1000 K in 1000 steps. Then, they are equilibrated at this temperature in 1000 other steps. Finally, the system was slowly cooled to 0 K in 5000 steps. The binding energies reported below were calculated by subtracting the sum of the energies for the individual atoms, which is calculated with the same method.

3. Results and discussion

In this section we describe the lowest energy of silicon clusters obtained from the SIESTA method in size range of 10 to 16 atoms. In Fig. 1 we have presented the obtained structures of silicon clusters with 10 to 16 atoms. Because of the small

energy differences between different structures of each cluster, the structures may be isomers. We observe that the atom in all these clusters exhibit pronounced preference for residing on the surface. The obtained binding energies per atom (E_c), the point groups and HOMO–LUMO gaps (ΔE) (the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) for each isomer are listed in Table. In the following, our structures are analyzed and discussed.

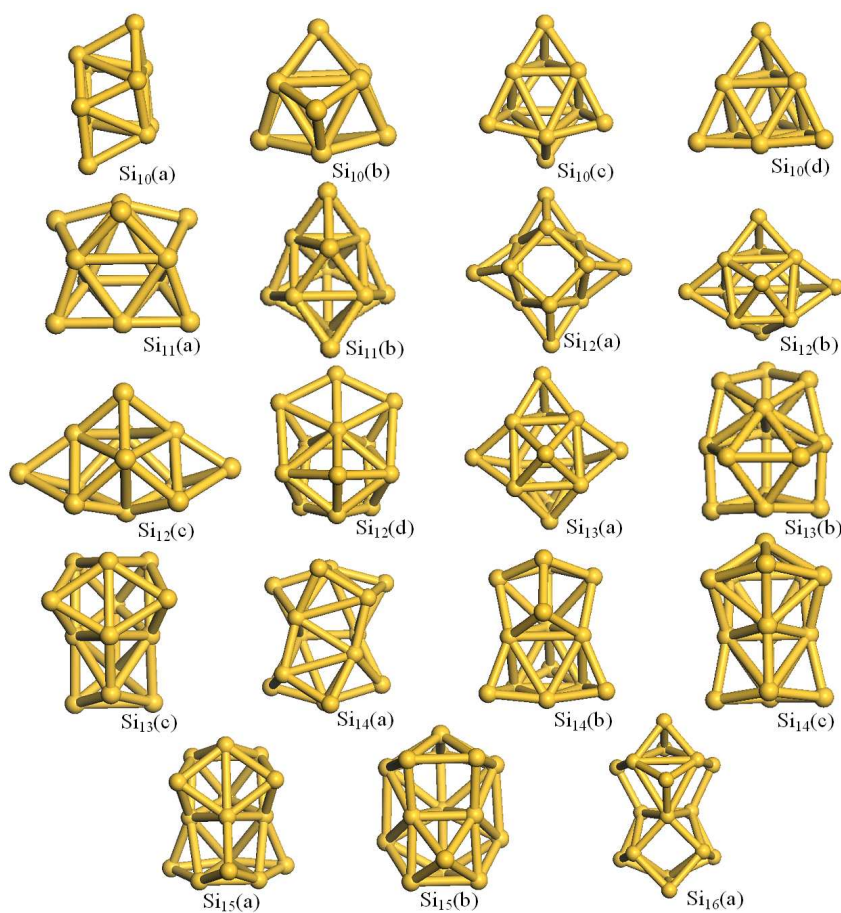


Fig. 1. Geometries of the low-energy structures of Si_{10} – Si_{16} clusters.

Despite many theoretical studies for Si_{10} , the equilibrium structure is not resolved yet. Obtained structures for Si_{10} were shown in Fig. 1; $Si_{10}(a)$, $Si_{10}(b)$, $Si_{10}(c)$ and $Si_{10}(d)$. Our density functional theory–LDA (DFT–LDA) calculations show that the most stable structure is $Si_{10}(b)$ with C_{3v} symmetry, which is more stable by 0.054 eV/atom than $Si_{10}(c)$ with C_s symmetry and by 0.048 eV/atom and 0.045 eV/atom than $Si_{10}(d)$ (T_d) and $Si_{10}(a)$ (C_2), respectively. Our results

TABLE

Binding energy per atom E_c (eV/atom),
HOMO–LUMO gap ΔE (eV) of different
isomers of Si_n ($n = 10\text{--}16$) clusters.

Cluster size (n)	Isomer	E_c [eV/atom]	ΔE [eV]
10	(a) C_2	4.488	1.219
	(b) C_{3v}	4.533	1.856
	(c) C_s	4.479	1.518
	(d) T_d	4.485	2.745
11	(a) C_s	4.500	1.455
	(b) C_s	4.500	1.193
12	(a) C_{4v}	4.480	1.331
	(b) C_s	4.501	0.618
	(c) C_s	4.545	1.798
	(d) C_s	4.470	0.957
13	(a) C_s	4.539	1.225
	(b) C_s	4.520	1.207
	(c) C_s	4.530	0.788
14	(a) C_2	4.605	1.360
	(b) C_s	4.551	1.311
	(c) C_s	4.604	1.496
15	(a) C_s	4.611	1.618
	(b) C_s	4.606	1.516
16	(a) C_s	4.607	1.062

for T_d and C_{3v} symmetries are in good agreement with those reported by Liu et al. [13] by using DFT with generalized gradient approximation (DFT–GGA) calculations. With quantum Monte Carlo calculation, Grossman and Mitas [14] investigated various structures and suggested that a tetracapped trigonal prism structure with C_{3v} symmetry is the most stable. Recently, Pouchan and Bégue [15] have obtained a tetracapped prism structure with C_{3v} symmetry as the lowest energy structure of Si_{10} in good agreement with our C_{3v} structure as $\text{Si}_{10}(\text{b})$ shown in Fig. 1. However, our calculations show two other structures for Si_{10} with C_2 and C_s symmetry and with binding energy of 4.488 eV/atom and 4.479 eV/atom which are not previously described. For Si_{11} several different structures have been reported in the literature. Using tight binding method, Lee et al. [16] show that the distorted tricapped tetragonal antiprism with C_s symmetry is the most stable structure of Si_{11} . However, Liu et al. [13], applying DFT–GGA approach, found a C_{2v} structure and an isoenergetic bicapped tetragonal antiprism with C_s symmetry as the lowest energy isomers. Using an unbiased global search with a

genetic algorithm, Ho et al. [17] found a C_{2v} structure for Si_{11} , which was also found by Rohlfling and Raghavachari [18] using an effective core potential, as the global minimum.

In the present work, we found two lower energy structures for Si_{11} ; $Si_{11}(a)$ and $Si_{11}(b)$ both with C_s symmetry with a binding energy of 4.500 eV/atom and they are not previously reported. For Si_{12} cluster, the structure as $Si_{12}(c)$ with C_s symmetry (see Fig. 1) is the most stable with binding energy of 4.545 eV/atom which is 0.074 eV/atom more stable than $Si_{12}(d)$ and 0.044 eV/atom more stable than $Si_{12}(b)$ both with C_s symmetry. New structure $Si_{12}(a)$ with C_{4v} symmetry was not reported in the literature.

Ramakrishna and Bahel [19] presented results of their extensive search for the ground state structure of Si_{12} obtained with the all-electron full potential self-consistent field DFT–LDA code *NRLMOL*. They reported a structure of Si_{12} consisting of a pentagon–pentagon antiprism sandwich with face caps at the face and bottom with C_s symmetry as the ground state geometry. Liu et al. [13] showed two structures for Si_{12} with C_{2v} and C_s symmetry. However, using genetic algorithm, Ho et al. [17] show a hexacapped trigonal prism structure of Si_{12} with C_{2v} symmetry which is in agreement with Si_{12} geometry reported very recently by Zhu et al. [20], using an *ab initio* molecular orbital calculations.

The Si_{13} clusters are of interest because of the possibility of their having the high symmetry icosahedral (I_h) geometry, which has been found to be a stable geometry for doped Al clusters [21]. However, a lower C_{1h} geometry structure was found by genetic algorithm search [17] to be energetically more favourable for Si. Shvartsburg et al. [22] have found two prolate structures for Si_{13} with C_s and C_{2v} symmetry. On the other hand, using the hybrid density functional–LDA study, Deng et al. [23] have found three structures for Si_{13} with C_{3v} , C_{2v} , and C_s symmetry which is in agreement with the same structure proposed by Liu et al. [13]. In our case, we propose three energy isomers for Si_{13} ; $Si_{13}(a)$, $Si_{13}(b)$ and $Si_{13}(c)$ with C_s symmetry. The most stable is $Si_{13}(b)$ with binding energy of 4.539 eV/atom and largest HOMO–LUMO gap of 1.225 eV. Our structure $Si_{13}(c)$ is in good agreement with those reported by Deng et al. [23] and Liu et al. [13] as a lowest energy structure.

Only a few structures for Si_{14} have been presented in the literature. In our work, two structures were obtained as the best structures, $Si_{14}(a)$ and $Si_{14}(c)$ having C_2 and C_s symmetry and binding energy of 4.605 and 4.604 eV/atom, respectively. These two structures correspond to the largest HOMO–LUMO gap of Si_{14} isomers proposed here; 1.360 eV for $Si_{14}(a)$ and 1.496 eV for $Si_{14}(c)$. In the same way, we show $Si_{14}(b)$ structure with C_s symmetry which is ≈ 0.055 eV/atom less in energy than $Si_{14}(a)$. The structure $Si_{14}(c)$ was obtained by Zhu et al. [20] as the most stable isomer of Si_{14} , using an *ab initio* molecular orbital calculation. All low energy structures with 11 to 14 atoms considered here have various five and even sixfold coordinated atom. The overall bonding scheme is quite different

from the bulk tetrahedral symmetry. The increase in the average number of connection per atom is due to the surface reconstruction in order to minimize total energy of the system. With Si_{15} the number of studies performed to search for global minimum structures decreases further, obviously due to the steeply increasing computational cost, only few studies as Ho et al. [17], Liu et al. [13], and Zhu et al. [20] cover this size of Si_n clusters in the literature. Ho et al. [17] have found the C_{3v} symmetry as the ground state structure for Si_{15} . However, Liu et al. [13] established three structures for Si_{15} ; structure with C_{3v} symmetry which considered as the ground state structure and two others with D_{3h} and C_1 symmetries. Zhu et al. [20] obtained four structures for Si_{15} with C_{3v} , C_s (I and II) and D_{3h} symmetry, all contain the capped trigonal-prism unit. The isomer having the lowest energy is the tricapped trigonal prism fused with a tricapped trigonal antiprism C_{3v} symmetry.

In this work, we show two energy isomers for Si_{15} , which are not previously reported in the literature, shown as $\text{Si}_{15}(\text{a})$ and $\text{Si}_{15}(\text{b})$ with C_s symmetry and binding energies of 4.611 and 4.606 eV/atom, respectively. $\text{Si}_{15}(\text{a})$ is the lowest energy structure and it is 0.005 eV/atom more stable than $\text{Si}_{15}(\text{b})$. For Si_{16} we found the structure $\text{Si}_{16}(\text{a})$, with a prolate shape, as a lowest energy isomer of tested Si_{16} structures with binding energy of 4.607 eV/atom. In the literature data, Zhu et al. [20] proposed three different structures of Si_{16} ; two with C_{2h} and the third with C_{2v} symmetry. Ho et al. [17] have shown two structures with C_{2h} symmetry and with energy difference of 0.004 eV/atom between them. Shvartsburg et al. [22] found different structures with C_{2h} , C_s , C_{2v} and C_{3v} symmetry. Except for C_{2v} , the same symmetry found by Shvartsburg et al. [22] was obtained by Liu et al. [13]. Our result for clusters in size range of 10 to 16 is in good agreement with many previous studies assuming that the prolate and prolate-like structures are very competitive in stability compared to the prolate and prolate-like structure in this size range [13, 17, 20].

In order to check the stability of Si_n clusters, the binding energy of very stable structures of each cluster is plotted in Fig. 2 and listed in Table for the other structures. The values of binding energies are found between 4.470 and 4.611 eV/atom, not far away from, but also not identical to the bulk binding energy value (4.75 eV/atom [24]). As shown in Fig. 3 and Table, the binding energies increase slowly with cluster size n in this range. In cluster physics, the second difference of cluster energies, $\Delta_2 E(n) = E(n+1) + E(n-1) - 2E(n)$, is a sensitive quantity that reflects the stability of clusters [25]. Figure 4 shows the second difference of clusters total energies, $\Delta_2 E(n)$, as a function of the cluster size. Maxima are found for $n = 11, 13$, and 16 implying that these clusters are more stable than neighbouring clusters. However, it should also be noticed that the energy differences between more stable and less stable cluster sizes are not very large. Therefore, there is no magic number in this cluster range.

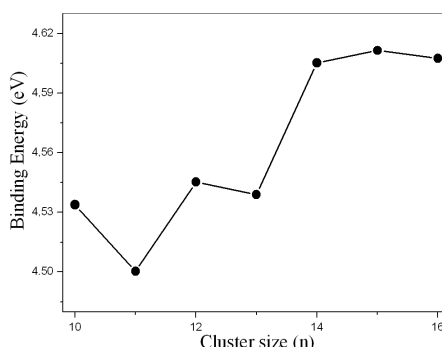


Fig. 2. Binding energy per atom for the most stable structures of Si_n ($n = 10-16$) clusters are plotted as a function of cluster size.

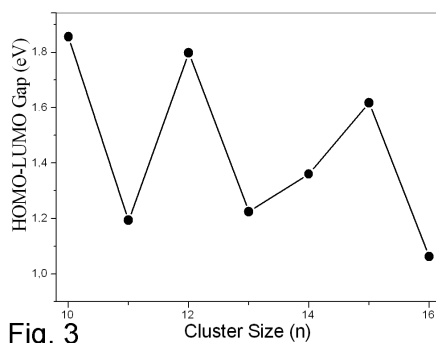


Fig. 3

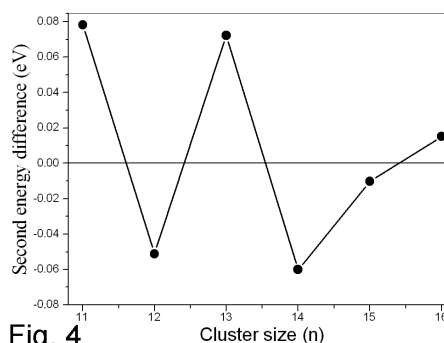


Fig. 4

Fig. 3. HOMO-LUMO gap of Si_n ($n = 10-16$) clusters in their most stable structures are plotted as a function of cluster size.

Fig. 4. Second differences of cluster energies $\Delta_2E(n) = E(n+1) + E(n-1) - 2E(n)$ are plotted as a function of cluster size.

As is known, the HOMO-LUMO gap is smaller in a very large system. In general, interaction between the molecular orbitals results in certain increase in the energy of the HOMO and, at the same time, certain degree of decrease in the energy for the LUMO, and therefore, a reduced HOMO-LUMO gap. For our clusters, we plot in Fig. 3 the variation of the HOMO-LUMO gap as a function of cluster size for the lowest energy isomers of different clusters studied here. The value of HOMO-LUMO gap of the other structures are summarized in Table. As is expected, the energy of HOMO-LUMO gap generally decreases as the cluster size increases. This size-dependent trend is consistent with experimental result [26, 27]. We note that the lowest energy isomers of Si_{10} and Si_{12} have the large HOMO-LUMO gap, while smaller HOMO-LUMO gaps are found for $Si_{12}(b)$ and $Si_{13}(c)$ indicating the highly metallic bonding of these structures. This behaviour is directly reflected in their electronic and optical response. In Fig. 5 we show the total electronic density of states of $Si_{12}(b)$ and $Si_{13}(c)$. The Fermi level is

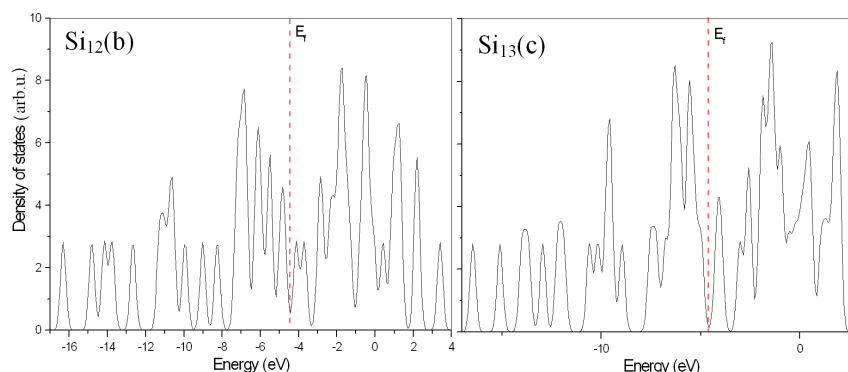


Fig. 5. Total density of states of $\text{Si}_{12}(\text{b})$ and $\text{Si}_{13}(\text{c})$ clusters as a function of energy. The Fermi level is indicated by the vertical dashed line.

indicated by a vertical dashed line. The disappearance of the HOMO–LUMO gap demonstrates the strong metallic character of these clusters.

4. Conclusion

We presented the ground state geometry optimization of silicon clusters containing 10 to 16 atoms using the *ab initio* molecular dynamics simulated annealing calculation with DFT–LDA. Our results show that different new isomers are obtained for each cluster size. The atoms in the majority of these clusters exhibit a strong preference to lie on the surface rather than inside. The second difference of cluster energies shows that the lowest energy isomers of Si_{11} , Si_{13} , and Si_{16} are more stable than neighbouring clusters. The prolate and prolate-like structures are dominant in the size range of $n = 10$ –16. The binding energies increase with cluster size in this range. The HOMO–LUMO gap decreases with the increase in clusters size.

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