Chapter 13
Quasi-One-Dimensional Silicon Clusters as Elements of Novel Nanowires

F.T. Umarova, P.L. Tereshchuk, and A.B. Normurodov

Abstract The work is devoted to the investigation of structural deformations and stabilities of pristine hollow silicon clusters at quasi-one-dimensional growth using the quantum-chemical tight-binding method. Consideration of the hexagonal clusters family of the layer number n = 2 – 5 allows structural properties to be defined as the function of cluster sizes. The individual hollow clusters with diameter less than 1 nm containing from 12 up to 24 atoms are shown to be stable. Strong structural changes occur at transition from the size of 24 to the size of 30. The cluster of size 24 corresponding to a regular hexagonal prism can be considered as a possible candidate for a structural unit of silicon nanowires. It has also been demonstrated that the elongated filled structures grow, provided that silicon atoms are introduced inside the hollow structures along the main cluster axis.

Keywords Silicon clusters • Quasi-one-dimensional growth • Structure • Nanowire • Tight- binding method

13.1 Introduction

There has been much interest in quasi-one-dimensional nanostructures due to their technological importance for microelectronics. Quasi-one-dimensional silicon clusters, as a new form of silicon materials, can find a wide range of applications in light-emitting devices or high-speed transistors, biological and chemical sensors, etc. Definition of a silicon nanowire structure is one of the most important tasks nowadays. Synthesis of silicon nanowires (see, for examples [1–3]) causes interest

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to atomic structure of prolate or fullerene-type clusters. A number of theoretical models of such separate structures have been reported [4–8].

Investigation of properties of separate clusters cannot throw light upon one-dimensional behaviour of nanowires during their growth. We have simulated the family of hollow hexagon-based silicon clusters of layers n = 2−5 with the purpose to investigate their structural modification and stability with the increase in sizes and the possibility of quasi-one-dimensional growth.

13.2 Computational Methodology

Quantum-chemical simulation has been carried out by the new tight-binding method [9] (NTBM) and the molecular dynamics method. Earlier, this method was tested using small silicon clusters up to seven atoms calculated in Hartree-Fock approximation [10], while our method parameters have been determined for the investigation of larger size clusters. It allows the pentagonal-based growth pattern of quasi-one-dimensional silicon clusters [11] in the range of 8–61 atoms to be revealed.

To investigate hollow clusters, we have chosen two isomers of Si_{12}. Earlier, the stability of such cluster [12] consisting of two hexagons was demonstrated. Contributions to the bonds, which are perpendicular to hexagon's planes, have been made not only by p_z-orbitals but also by p_x- and p_y-orbitals [12].

The first structural type (*a*-type) of clusters under consideration corresponds to a regular hexagonal prism; in the second case (*b*-type) the structure is an antiprism. Si–Si bond lengths equal 2.352 Å. All the investigated clusters have diameters smaller than 1 nm.

13.3 Results and Discussion

In Fig. 13.1, the optimized geometries of the *a*-type clusters are shown. Clusters have retained the hollow structure up to Si_{24}. Atoms are three-coordinated in the edge layer; in the middle layers atoms are four-coordinated. As the sizes increase, the middle layer of clusters $Si_{18}(a)$ and $Si_{24}(a)$ slightly widens, whereas at the top and at the bottom layers bond lengths decrease, and clusters tend to take the fullerene-like form. Further, the spread of bond lengths occurs and as a result of strain accumulation, the cluster $Si_{30}(a)$ distorts.

The optimized structures of *b*-type clusters are given in Fig. 13.2. All atoms are four-coordinated. The lateral faces of cluster $Si_{12}(b)$ consist of isosceles triangles, the base length of which is equal to 2.3695 Å, the lengths of other sides are 2.3985 Å. The cluster $Si_{18}(b)$ acquires a fullerene-like geometry and can be represented as two hexagonal antiprisms, common base of which has a larger radius than the edge layers. The lengths of lateral sides of isosceles triangles are 2.3975 Å.

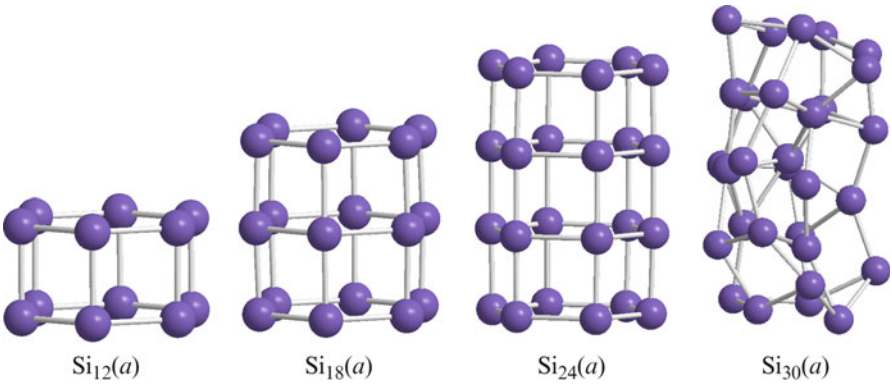

Fig. 13.1 Optimized structures of regular hexagonal clusters (*a*-type)

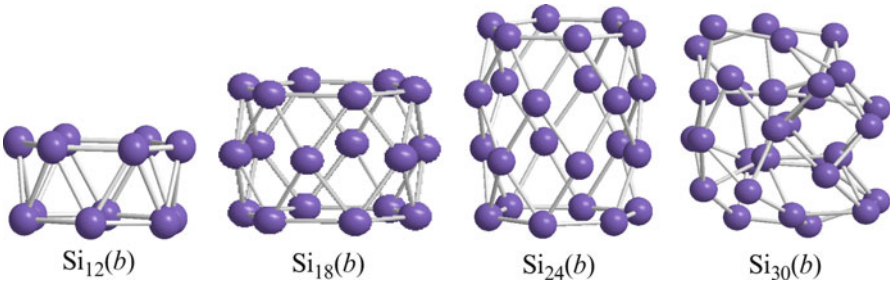

Fig. 13.2 Structure of antiprizmatic (*b*-type) clusters

The structure of the hollow cluster $Si_{24}(b)$ is not ideal. One atom in the middle layer is three-coordinated. The bond lengths change from 2.3255 up to 2.4585 Å. The cluster broadens in the central part. At the same time, the relaxed structure of the cluster $Si_{30}(b)$ entirely loses its hollow structure.

The optimized characteristics of the clusters are given in Table 13.1. The common tendency of increasing the binding energy per atom with the increase in sizes is observed. HOMO-LUMO gap changes irregularly as the sizes increase, because strained bonds appear, which can introduce located levels in the gap.

We have also investigated the stability of the fullerene-like cluster Si_{24} proposed as a building unit of silicon nanowires [3] (Fig. 13.3). This cluster contains 12 pentagons and two hexagons on butt-ends. After optimization, the cluster loses the initial hollow structure and relaxes into amorphous geometry (Fig. 13.3).

In Fig. 13.4, the binding energies per atom for individual clusters are plotted as the function of sizes. For comparison, the data for the cluster [3] are also presented. For all clusters of size 24 the binding energies have close meanings and they are more stable than diamond-like ones for the given size (the meaning for a diamond-like cluster has been obtained to be ~3.61 eV in [3]).

Table 13.1 Characteristics of optimized clusters

Cluster	R_{hor} (Å)	R_{vert} (Å)	CN_{aver}	Binding energy per atom (eV)	Band gap (eV)
Si_{12} (a)	2.2825	2.2655	3	3.588	0.4096
Si_{18} (a)	2.2685 (2.3415[a])	2.2835	3.3	3.813	0.2024
Si_{24} (a)	2.2665 (2.3225[a])	2.2905 (2.3305[a])	3.5	4.013	0.515
Si_{30} (a)	$R_{aver} = 2.3633$		3.5	4.2451	0.1983
Si_{12} (b)	2.3695		4	3.634	0.1549
Si_{18} (b)	2.3455 (2.633[a])		4	3.816	0.4948
Si_{24} (b)	$R_{aver} = 2.3954$		4	3.890	0.0015
Si_{30} (b)	$R_{aver} = 2.4144$		3.5	4.3182	0.227

R the distance between atoms, *CN* coordination number
[a]The bond lengths of the middle layers

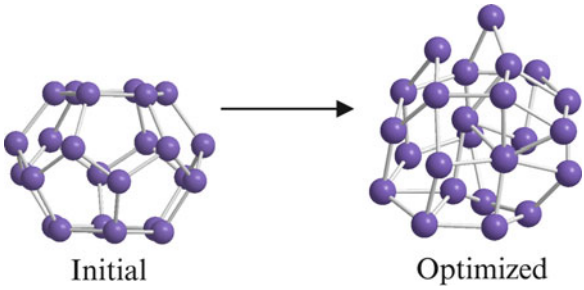

Fig. 13.3 The structure of the fullerene-like cluster [3] Si_{24} before and after optimization

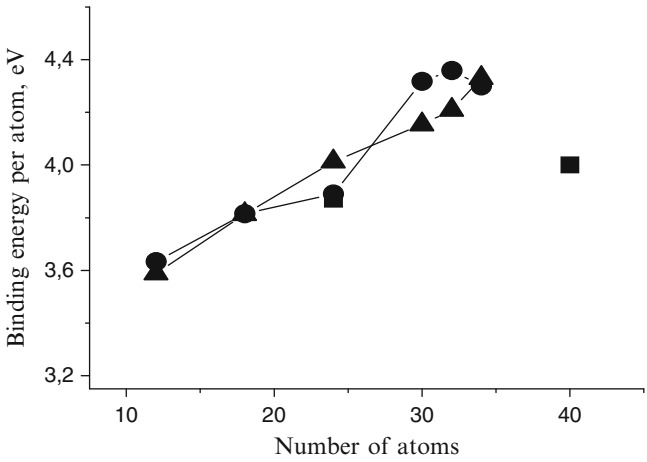

Fig. 13.4 Binding energies per atoms of *a*- (▲) and *b*-type (●) clusters calculated by our method compared with clusters (■) (From Marsen and Sattler [3]. In Fig. 13.5, binding energies per atoms for clusters with additional embedded atoms have been also calculated and are presented below)

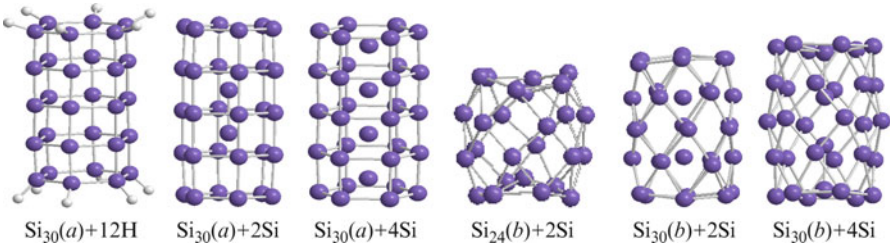

Fig. 13.5 Structures of hydrogen-passivated clusters and with additional embedded atoms

Table 13.2 Structural and energy characteristics of pure optimized clusters Si_{30} with embedded Si atoms

Cluster	R_{hor} (Å)	R_{vert} (Å)	R_e (Å)	Binding energy/atom (eV)	Band gap (eV)
Si_{30}(a) + 2Si	2.2675 (2.3795[a])	2.2795 (2.3025[a])	2.3485	4.2117	0.0667
Si_{30}(a) + 4Si	2.3295 (2.4125[a])	2.3025	2.5323	4.3346	0.2077
Si_{24}(b) + 2Si	2.4022 (2.9070[a])			4.1447	0.119
Si_{30}(b) + 2Si	2.3510 (2.7990[a])		3.8880	4.3612	0.2293
Si_{30}(b) + 4Si	2.4245 (2.8795[a])		2.4045, 2.5760	4.3015	0.1433

R the distance between atoms, R_e the distance between embedded atoms
[a]The bond lengths of the middle layers

To check the possibility of further quasi-one-dimensional growth of hollow clusters, we apply ways of stabilization of hollow structures that are hydrogen passivation of surface atoms and introducing additional silicon atoms inside the structures. As can see in Fig. 13.5, further quasi-one-dimensional growth is continued under such conditions. The optimized hydrogen-passivated structure $Si_{30}(a) + H_{12}$ (Fig. 13.5) has a hollow topology. Bond lengths between silicon atoms in hexagonal base change nonmonotonic from 2.4595 to 2.3305 Å, while bond lengths between hexagons are in the range of 2.2385–2.3705 Å. For Si–H bond lengths do not change and equal 1.4895 Å. The cluster $Si_{36}(a) + H_{12}$ has also been optimized and possesses the same hollow structure.

Optimized clusters with inserted silicon atoms are also shown in Fig. 13.5, their characteristics are presented in Table 13.2. Additional atoms are disposed along the central axis of clusters. All *b*-type clusters have fullerene-like structures. For clusters of size 30 capped by one atom at the bottom and at the top, we have not received the expected results. In this case, the cluster of *a*-type falls apart, the *b*-type keeps the amorphous form. $Si_{30}(a)$ and $Si_{30}(b)$ clusters with two and four inner atoms have a small expansion in the central part. Cluster $Si_{30}(b)$ + 4Si is symmetric relative to the central layer and has 2 two-atomic inner chains. The distance between these chains is 2.5760 Å, and the distance between atoms of one chain is 2.4045 Å. In Fig. 13.4, the binding energies per atom of these clusters are also plotted.

The critical size at which the cluster structure changes from hollow to amorphous form is between 24 and 30 atoms. Earlier [13], it was experimentally shown that the transition from elongate to oblate forms proceeds at sizes between 24 and 27.

The cluster $Si_{24}(a)$ is of major interest as a possible candidate to the structural unit of nanowires. It has only one direction of growth along central axis due to the presence of dangling bonds on the top and bottom layers. This fact creates conditions for the further growth in bundles of nanowires by forming additional bonds with three-coordinated atoms of neighboring wires.

The elongated filled structure $Si_{30}(b)$ + 4Si consists of two Si_{18} + 2Si clusters with a common central layer and can grow forming a nanowire, provided that additional silicon atoms are introduced inside the hollow structures.

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