Structure and stability of silicon nanoclusters passivated by hydrogen and oxygen: evolutionary algorithm and first-principles study

V S Baturin\textsuperscript{1,2}, S V Lepeshkin\textsuperscript{1,2}, N L Matsko\textsuperscript{1,2} and Yu A Uspenskii\textsuperscript{1}

\textsuperscript{1} P.N. Lebedev Physical Institute, Russian Academy of Sciences - 119991 Leninskii prosp. 53, Moscow, Russia
\textsuperscript{2} Moscow Institute of Physics and Technology - Dolgoprudny, Moscow Region 141700, Russia

E-mail: lepeshkin@lpi.ru

Abstract. We investigate the structural and thermodynamical properties of small silicon clusters. Using the graph theory applied to previously obtained structures of Si\textsubscript{10}H\textsubscript{2m} clusters we trace the connection between geometry and passivation degree. The existing data on these clusters and structures of Si\textsubscript{10}O\textsubscript{4n} clusters obtained here using evolutionary calculations allowed to analyze the features of Si\textsubscript{10}H\textsubscript{2m} clusters in hydrogen atmosphere and Si\textsubscript{10}O\textsubscript{4n} clusters in oxygen atmosphere. We have shown the basic differences between structures and thermodynamical properties of silicon clusters, passivated by hydrogen and silicon oxide clusters.

1. Introduction
Silicon nanoclusters are in the center of intensive theoretical and experimental studies for over two decades. The reason of such a great attention comes from several different fields. These systems are the promising objects to perform the further minimization of silicon-based microelectronic devices via the use of single electron transistors on quantum dots [1]. Clusters of silicon with different doping atoms exhibit photoluminescence which differs them from bulk silicon in a fundamental way (see e.g. [2]). This phenomena, having numbers of possible applications, has no clear explanation yet. Though it is obvious that the surface atoms and, generally, size-induced rearrangements of atoms play crucial role here. Thus, knowing of the atomic structure is of great importance. Another problem relevant for applications is the determination of conditions that allow mass production of identical particles. The most of widely used cluster synthesis methods, such as laser ablation produce ensembles of atoms, which are non-uniform in general case [3]. However, experimental and theoretical data on the atomic structure of nanoclusters is limited. Here we present the study on structural and thermodynamical properties of small silicon clusters, passivated by hydrogen and oxygen, with formulas Si\textsubscript{10}H\textsubscript{2m} (\textit{m}=0–11) [4] and Si\textsubscript{10}O\textsubscript{4n} (\textit{n}=0–6).

2. Computational techniques
The scheme we used to find the most stable structures of clusters is based on the evolutionary algorithm and code USPEX [5,6] coupled with ab-initio total energy calculations and local structure
optimization. The principle of genetic algorithm lies within the analogy with natural selection. First, the code generates the initial set of structures called the first generation. Each of these structures is made satisfying several conditions. First, they have one of the randomly chosen symmetries. The number of symmetries is infinite, but here we use all 32 crystallographic point groups plus pentagonal, decagonal and icosahedral groups. Second, the distances between the neighboring atoms should be larger than some predefined threshold value. The third condition is connectivity, i.e. all the strong bonds in the clusters form only one, non-separated network. Besides these conditions, in all other respects, atoms are placed in random positions. As the first generation is created, all the structures are locally optimized and ranked by energy. Then the most energetically unfavourable ones are discarded and the rest (about 60%) are used in creation of the next generation. A few best clusters are left unchanged, while the rest undergo the action of evolutionary operators. The latter can be divided in two groups. The first one — mutations — produce an offspring structure from a single parent, by performing mutations along soft vibrational mode, permutations of atoms, random distortions, etc. The second group, heredity, makes the essence of the evolutionary algorithm and distinguishes it from other heuristic optimization schemes. It consists of operators which use a few (usually two) parent structures to make an offspring. The most common example is the cut-and-splice operation [7]. It is important to note, that despite the use of symmetry at the stage of initialization, the algorithm slightly breaks it right before the local minimization. This is done because the optimal structure can be asymmetrical and also because highly symmetrical structures are often correspond to a very shallow local minima or even maxima of total energy. As the next generation created and relaxed the procedure repeats and terminates when the lowest energy structure remains unchanged for sufficiently large number of generations. In our studies the number of generations per each cluster was 30-60 with 20-50 structures in each generation. The local minimization and energy calculation is performed within PAW-PBE approach in density functional theory [8, 9] as implemented in VASP code [10]. We used supercell with 10 Å vacuum distance between clusters and the cutoff energy of 350 eV.

3. Structural analysis of Si$_{10}$H$_{2m}$ clusters

Here we present the results of structure analysis and thermodynamical consideration performed on silicon clusters Si$_{10}$H$_{2m}$, (m=0–11). The ground-state structures of clusters, obtained from ab-initio USPEX calculations in our previous study [4] are presented on figure 1.

![Figure 1. Ground-state structures of Si$_{10}$H$_{2m}$ clusters (m=0–11)](image)

Looking at low-passivated structures, Si$_{10}$ – Si$_{10}$H$_{10}$, we see that unlike in the usual silicon compounds, silicon atoms have coordination numbers (numbers of closest neighbors) different from the standard valence of silicon, i.e. four. This can be explained by means of the graph theory and the angles between adjacent bonds. On the one hand, atoms of silicon tend to have four neighbors, by the number of valent electrons. On the other hand, bonds of fourfold-coordinated silicon atoms, e.g. in bulk silicon, are oriented with tetrahedral angles, equal to 109°28’. We build the graph, corresponding to
the cluster, in the following way. Hydrogen atoms are neglected, and the edges of graph represent the non-branching chains of Si-Si bonds, so the Si atoms participating in three or more Si-Si bonds are represented as graph’s vertices (figure 2).

Figure 2. Cluster and corresponding graph. Atoms in circles do not form the graphs vertices.

It is clear from figure 2, that silicon atom forms the vertex if it is bound to one or zero hydrogen atoms. Assuming that graphs constructed in such way are planar, which is true for all Si_{10}H_{2m} clusters under consideration, we can say that it satisfies cycle double cover problem [11], meaning that it can be drawn on a sphere as a superposition of minimal cycles, with each graph edge participating only in two cycles (all other further assumptions concerning graphs do not affect the generality of results). Such cycles are called faces (by analogy with convex polyhedra). If a graph has \( v \) vertices, \( e \) edges and \( f \) faces, it satisfies Euler formula

\[
f = e - v + 2
\]

If we demand fourfold coordination of Si atoms in Si_{10}H_{2m} cluster, then its graph has \( v = 2(n-m) \) vertices, \( e = (3/2)v = 2(n-m) \) edges and \( f = n-m+2 \) faces. The average number of atoms per one face is \( n_{av} = (4n-2m)/f = (4n-2m)/(n-m+2) \). The numerator here comes from the fact, that each vertex atom is related to three cycles, and each on-edge atom - to two cycles. In case of Si_{10}H_{2m} we have \( n_{av} = 2+16/(12-m) \). The important consequence is that the average angle between adjacent atoms is \( \alpha_{av} = 180°-360°/n_{av} \). If a cycle has 5 or more atoms \((m>5)\), the mean angle can be greater than 103° which is close to tetrahedral angle. If a cycle is big enough (i.e. \( m>7 \)), it has degrees of freedom to bend, so the angles will be equal to energetically favourable tetrahedral angles. On the other hand, if \( m<5 \) (Si_{10} - Si_{10}H_{10}) average angle \( \alpha_{av} < 96° \), so the structure would experience so called ‘ring strain’. The structure ‘avoids’ it by deviating the coordination number of silicon atoms from their valency or by following the delocalized bonding scheme instead of covalent one as in case of Si_{10}. This simple consideration is one of many examples when graph theory gives useful insights in understanding of motifs in structure formation, e.g. in automatic distinguishing of structural isomers or classification of crystal structures.

Figure 3. Phase diagram of Si_{10}H_{2m} (\( m=0–11 \)) clusters in hydrogen atmosphere.
The thermodynamical approach allows to find the most abundant clusters in hydrogen atmosphere with given temperature and pressure. The results, obtained from minimization the corresponding Gibbs free energy of formation is presented on Figure 3. We can see that at normal pressure only Si$_{10}$, Si$_{10}$H$_{14}$, Si$_{10}$H$_{16}$, Si$_{10}$H$_{20}$ and Si$_{10}$H$_{22}$ clusters can exist at reasonable temperatures ($T$<1000 K).

4. Si$_{10}$O$_{4n}$ clusters

In this part we present the ground-state atomic structures of silicon nanoclusters Si$_{10}$O$_{4n}$ ($n=0$–6) which are calculated using the evolutionary algorithm within density functional theory (see figure 4).

![Figure 4. Ground state of Si$_{10}$O$_{4n}$ ($n=0$–6) clusters.](image)

The atomic structures of Si$_{10}$O$_{4n}$ changes drastically with increasing of number of oxygen atoms. At low concentrations oxygen atoms go presumably to the cluster core forming there small regions of quartz-like structure. When oxygen concentration exceeds the SiO$_2$ composition, new added O atoms occupy the cluster surface and make a cluster more reactive.

![Figure 5. Phase diagram of Si$_{10}$O$_{4n}$ ($n=0$–6) clusters in oxygen atmosphere.](image)

Figure 5 shows phase diagram of Si$_{10}$O$_{4n}$ clusters in oxygen atmosphere. In a wide range of pressures and temperatures the most stable clusters are Si$_{10}$O$_{20}$ and Si$_{10}$O$_{24}$. Clusters with low number of oxygen atoms appears only at very small pressures and high temperatures.

5. Conclusions

The structural analysis based on graph theory has shown that the unusual coordination numbers of silicon atoms in Si$_{10}$H$_{2m}$ clusters can be explained by the tendency of the system to form tetrahedral angles between adjacent bonds. We obtained a formula showing that tetrahedral angles can be achieved only in cases of $m>5$, which is in agreement with results of global optimization. Using evolutionary algorithm results we performed the thermodynamical consideration of silicon
nanoclusters $\text{Si}_{10}H_{2m}$ ($m=0–11$) and $\text{Si}_{10}O_{4n}$ ($n=0–6$). We found that of all possible clusters with formula $\text{Si}_{10}H_{2m}$ only $\text{Si}_{10}$, $\text{Si}_{10}H_{14}$, $\text{Si}_{10}H_{16}$, $\text{Si}_{10}H_{20}$ and $\text{Si}_{10}H_{22}$ clusters can exist in thermodynamical equilibrium with hydrogen atmosphere in a wide range of pressures and temperatures. In oxygen atmosphere the most stable clusters are $\text{Si}_{10}$, $\text{Si}_{10}O_{16}$, $\text{Si}_{10}O_{20}$ and $\text{Si}_{10}O_{24}$ of all possible clusters with formula $\text{Si}_{10}O_{4n}$, but $\text{Si}_{10}$ and $\text{Si}_{10}O_{16}$ clusters can exist only at very small pressures and high temperatures.

Acknowledgments
This work is supported by the Russian Foundation for Basic Research (grants 13-02-00655, 14-02-00583, 13-02-00913) and the Government of the Russian Federation (No. 14.A12.31.0003). Calculations were performed at the Joint Supercomputer Center (Russian Academy of Sciences, Moscow, Russia).

References
[1] Wilson W. L. Szajkowski P. F. Brus L. E. Science 262 1241 (1993)
[2] Belomoin G. et. al. Appl. Phys. Lett. 80 841 (2002)
[3] Akiko Okano, Kunio Takayanagi, Applied Surface Science 127–129 362-367 (1998)
[4] V S Baturin, S V Lepeshkin, N L Matsko, Artem R Oganov and Yu A Uspenskii EPL 106 37002 (2014)
[5] Oganov A. R. and Glass C. W. J. Chem. Phys. 124 24474 (2006)
[6] Oganov A. R., Lyakhov A. O. and Valle M. Acc. Chem. Res. 44 227 (2011)
[7] Deaven, D.M. and Ho, K.M. Phys. Rev. Lett 75 288 (1996)
[8] Blöchl, P.E. Physical Review B 50 (24) 17953–17978
[9] Perdew J. P., Burke K. and Ernzerhof M. Phys. Rev. Lett 77 3865 (1996)
[10] G. Kresse and J. Hafner Phys. Rev. B 47 558 (1993).
[11] Huck A. Discrete Appl. Math. 99 71-90 (2000)