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

V.S. Baturin[1,2], S.V. Lepeshkin[1,2], N.L. Matsko[1,2,3] and Yu.A. Uspenskii[1]

[1] *P.N. Lebedev Physical Institute, Russian Academy of Sciences - 119991 Leninskii prosp. 53, Moscow, Russia*

[2] *Moscow Institute of Physics and Technology - Dolgoprudny, Moscow Region 141700, Russia*

[3] *Tomsk State University - 634050* Lenin Prospekt 36, Tomsk, Russia

Nanoclusters and nanoparticles belong to the most intensively studied objects of solid state physics. This keen interest is stimulated by their potential applications in many fields, such as nanoelectronics, nano-optics, solar energetics and biomedicine. It is known that the properties of nanoobjects are greatly different from the properties of bulk solids with the same chemical composition. This difference even being experimentally observed is not easy for understanding. Fist-principles calculations, which are so informative in crystal research, meet here considerable difficulties caused by an unknown atomic structure of clusters. From the mathematical point of view, the problem of structure prediction is reduced to searching the spatial arrangement of atoms giving the global minimum of the total cluster energy. Because of a huge number of possible atomic configurations, focusing the search on areas, where the total energy is fairly low, is highly important, as it makes practicable the first-principles calculation of cluster structure.

Solving this problem, the evolutionary algorithm implemented in the USPEX code has shown its superiority over other methods of structure optimization. In this presentation we apply this method in combination with density functional calculations to study the structure and electronic spectra of silicon nanoclusters passivated by hydrogen ($Si_{10}H_{2m}$, m = 0,…,11) and oxygen ($Si_{10}O_{2m}$, m = 0,…,14). A significant number of investigated objects and their wide diversity give rich information about the advantages and sensitive points of such computational method. In particular, we note that the fast convergence of evolutionary search is not universal, but strongly depends on the energy distribution of metastable isomer structures and their energy separation from the ground state structure. It was found that hydrogen and oxygen atoms have distinct positions in silicon nanoclusters and dissimilarly affect their structure. Hydrogen atoms are situated on the cluster surface, where they passivate the dangling bonds of Si atoms. With hydrogen addition the cluster structure becomes sparser and approaches the structure of polymers. The positions of oxygen atoms follow more complicated trends. At low concentration they 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 that makes a cluster more reactive. Using our first-principles results, we also considered the thermodynamics of $Si_{10}H_{2m}$ and $Si_{10}O_{2m}$ cluster ensembles and selected the most stable cluster compositions (so called “magic” clusters). To understand these structure trends, we use electron bond analysis and considered the electronic spectrum of clusters, involving their quasiparticle spectrum calculated by the precise GW method. Despite such first-principles simulation requires large computation, it provides valuable information about the processes of cluster formation.