COMPUTER SIMULATION OF NANOSIZED SILICON CLUSTERS WITH RECONSTRUCTED SURFACES

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Nanosized silicon clusters have been attracting much attention, due to their luminescent properties. The core of luminescent Si nanoparticles is commonly presumed to be diamond-like as in bulk silicon, and has a form of the perfect tetrahedron. But a large value of surface curvature and presence of dangling bonds on surface may strongly distort tetrahedral coordination of inner atoms and change length of covalent bonds, that, in turns, influence on their electronic properties. Unlike bulk materials, in the case of clusters the problem is absence of appropriate models describing energetically favorable surface structures. In this work influence of surface reconstructions on inner structure of clusters Si29, Si38, and Si59 are investigated by non-conventional tight-binding molecular dynamics method.

Some possible variants of surface reconstructions of bare silicon clusters are simulated. For clusters with a diamond-like core, energetically unfavorable dangling bonds on their surface were partially eliminated by dimerization (trimerization) of Si atoms with two dangling bonds and/or overcoordination of surface atoms. Optimized geometries of clusters with a diamond-like core were sensitive to the initial surface reconstruction model. Clusters with dimerized and trimerized surface atoms Si29D, Si38D, Si59T preserve its tetrahedral coordination after optimization. One can see significant shrinking of the surface formed by dimerized atoms in the cluster Si29D. The dimerized cluster Si38D showed strong surface reconstruction that led to the formation of capped pentagon motifs on the surface. In other cases (embedding additional atoms in surface positions (Si29E6, Si38E6, Si59E12) correspond to a tetrahedral interstitial positions in bulk silicon, or smoothing surface by removing three-coordinated vertex atoms in possible strain configurations Si32S, Si38S, Si65S) optimized cluster geometries give structures, those do not contain a diamond-like core. Simulation of clusters with various surface reconstructions shows, that the surface regions of large diamond-like clusters are expected to be reconstructed such that they consist of pentagon-based fragments attached to the diamond-like core.

The highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO-LUMO) gap of the clusters calculated here considerable changes with growth of its size and is in qualitative agreement with the experiment (B. Marsen, M. Lonfat, P. Scheier, K. Sattler, Phys. Rev. B 62, 6892 (2000)), reflecting non-regularity of gap with cluster size and a similar maximum gap of 0.523 eV for cluster Si29 with embedding six additional atoms in surface positions. The surface reconstruction models, based on dimerization, can explain metallic or semi-metallic behavior of the clusters as well. The mixing of the closed HOMO-LUMO states, the number of those increases with cluster size, can cause disordering and even amorphization of clusters.

The HOMO-LUMO gap of clusters with H-terminated surface increases with increasing the number of hydrogen atoms on surface. For example, the gap width for cluster Si29D achieves value of 2.7-3.0 eV at full saturation of dangling bonds by 24 atoms of hydrogen.