

Structural and electronic properties of quantum dot surfaces

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ABSTRACT

We report on recent progress in studying the structural, electronic and optical properties of Si and Ge quantum dots, using first principles calculations. We used both *ab initio* molecular dynamics techniques and quantum monte carlo calculations to unravel the effects of different surface structures and passivations on the properties of Si and Ge dots. Here we discuss the results on the effects of surface structure on the core properties of Ge dots up to 300 atoms and the effects of oxygen and other passivants on the optical properties of Si dots.

Keywords: Silicon quantum dots, Germanium quantum dots, Surface properties, First-principles molecular dynamics, Quantum Monte Carlo.

1 INTRODUCTION

Reducing the size of a semiconductor to the nanometer scale changes its physical properties in a fundamental way. For example, semiconductor nanorods are extraordinarily compliant [1], dots exhibit an increased optical gap and narrower emission spectra compared to the bulk values [2], and the transport properties of semiconductor nanostructures are dramatically influenced by quantum coherence [3]. In addition, reducing a particle size to the nanometer scale causes a dramatic increase of the surface area to volume ratio; therefore the physical and chemical properties of semiconductor nanoparticles, as well as their aggregation and assembly into superstructures, are greatly influenced by surface reconstruction and composition.

These novel properties of matter at the nanoscale have opened an entirely new field of materials science, holding great promise for new applications, e.g., photovoltaics, lasers, biological labels and sensors and nanomechanical devices. However, semiconductor nanotechnology is still in its infancy and semiconductor nanoscience is a field full of open questions regarding fundamental physical and chemical issues. For example, while the crystalline structure of Si and Ge have been known extremely accurately for decades and most Si and Ge surfaces have been characterized with a variety of techniques, controversies remain about the structure of the crystalline core of Ge nanocrystals as a function of size and very little

data are available on the physical and chemical properties of nanocrystal surfaces and interfaces. Many conventional experimental techniques used to study bulk materials and bulk surfaces cannot be applied straightforwardly to nanocrystals. In addition, theoretical and computational modeling is particularly challenging since nanostructures are metastable states of matter which, because of their size, show an inherently quantum mechanical behavior.

Given the large surface area of a nanoparticle, in order to tailor nanostructures with given properties for specific applications, it is essential to understand and control how the surface properties influence their optical gap and in general their physical properties. Understanding the influence of surface reconstruction and passivation on the ground state properties of semiconductor nanodots is a key prerequisite, not only in designing technological applications of single dots, but also for controlling deposition of nanoparticles on surfaces and aggregation of multiple dots into new structures.

In this paper we report on the surface physical and chemical properties of small Ge and Si dots (up to 2 nm), which we have investigated with *ab-initio* molecular dynamics (MD) and Quantum Monte Carlo (QMC) calculations. These are highly accurate computational techniques, which do not require fitting any experimental data, and can provide results to complement and interpret experiments. The use of predictive computational capabilities is essential in an area where key data are difficult to extract from experiment. We used *ab-initio* MD techniques to investigate the structural and electronic properties of semiconductor dots and QMC techniques to compute optical gaps.

Over the past decade, several different approaches have been applied to the calculation of the structural, electronic and optical properties of semiconductor quantum dots. These include methods based on the effective mass approach (EMA) [4] and its more sophisticated K.P implementations [5] and the use of Empirical Pseudopotential techniques (EPM) [6] and Tight-Binding (TB) Hamiltonians [7]. Within the EMA, the quantum dot is described by an effective medium with experimentally determined parameters and the surface is treated as either an infinite or finite barrier for the wavefunctions. Within the EPM methodology, the atomistic character of the quantum dot is included by introducing an empirically

determined pseudopotential for each atom. The EPM approach represents a significant advance over the effective medium based EMA techniques. For large, self-assembled quantum dots such as those grown from InAs/GaAs and Si/Ge, EPM techniques have proved extremely successful [6] in predicting the dependence of optical properties on the size, shape and composition of the dots. However, these methods are unable to accurately treat the effects introduced by surfaces and interfaces. Similarly, Tight-Binding Hamiltonians have been successfully used [7] to describe pristine dots or dots with hydrogenated surfaces, but they usually cannot account for complex charge transfers such as those occurring on dots interfaced with organic molecules or other complex surfactants.

In the following two sections we describe our first principles results on the surface properties of Ge (section 2.) and Si (section 3.) dots, followed by conclusions (section 4.) and references (section 5.).

2 SURFACE PROPERTIES OF GE DOTS

In our calculations for Ge nanoparticles [8], both non-reconstructed H-passivated, and reconstructed Ge nanocrystallites were considered, and they were represented by free-standing clusters in a large periodically repeated supercell (60~a.u.). We considered nanoclusters with spherical shapes, the number of Ge atoms ranging from 28 to 300. Ab-initio calculations were carried out using Density Functional Theory (DFT) in the local density (LDA) and gradient corrected (GGA) approximations.

For cluster with more than a few atoms, the number of metastable configurations with different surface structures is extremely large, and the exploration of such a configuration space is still out of reach of ab initio MD. Therefore, in order to determine relaxed surface structures of Ge dots, we first performed classical molecular dynamics calculations with the Tersoff potential. Then the minimal energy configuration obtained at the end of several classical annealing runs (of the order of several ns) was selected as the starting structure for minimizations using ab initio MD.

First, we focus on H-passivated nanoparticles with non-reconstructed surfaces. The average first neighbor distances for several sizes were computed and we observed a monotonic decrease of the atomic separation as the Ge dot becomes smaller. This reduction of the atomic separation with respect to the bulk values can be viewed as a contraction of the nanoparticles volume. We used the calculated relation between atomic volume and pressure in bulk germanium to estimate the effective pressure exerted on the cluster because of this volume reduction and we found values ranging from 2~GPa for small nanoparticles to 1~GPa for 2.5nm dots. For nanoparticles with reconstructed

surfaces we observed a much stronger volume reduction with respect to bulk values, than in the case of hydrogenated dots. In particular we found up to 5\% reduction in volume for a 2~nm nanoparticle. The corresponding effective pressure is substantial, i.e. 4~GPa.

Our calculations showed that the volume reduction and the surface effects are quantitatively different in dots with a diamond core and in those with a tetragonal structure (see Fig.1). We found that while diamond-like dots are always more stable than tetragonal dots in the size range examined here, the energy difference between the two core structures is greatly decreased in the presence of reconstructed surfaces. Based on these results, we have recently proposed [8] that metastable Ge dots with a tetragonal core may be formed under specific conditions obtained in Physical Vapor Deposition experiments.

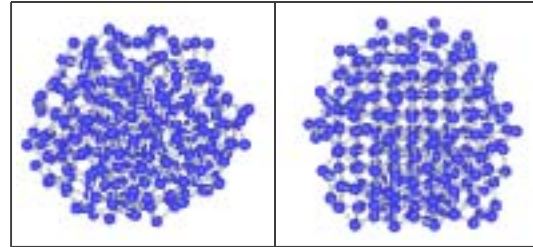


Fig. 1.: Ge nanoparticles with a tetragonal-like (left) and diamond-like (right) core structures, exhibiting reconstructed surfaces. Our results [17] show that surface reconstruction can influence the relative stability of dots with different structures, as well as the pressure exerted on the dot core by the surface. From L.Pizzagalli, G.Galli, F.Gygi and J.Klepeis, Phys. Rev. B **63**, 165324 (2001).

We now turn to the discussion of the surface properties of Si dots.

3 SURFACE PROPERTIES OF SI DOTS

We studied the electronic and optical properties of Si clusters using both DFT and QMC calculations. [9]. After performing DFT geometry optimizations and calculating the gap between the Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals(LUMO), we carried out QMC calculations to verify that the DFT trends for the HOMO-LUMO gap as a function of size and surface chemistry are predictive. In particular, we performed QMC Calculations for the optical gap $[E^*(N) - E(N)]$, where $E(N)$ and $E^*(N)$ are the total energies of the cluster in its ground and excited state, respectively. We carried out calculations for hydrogenated clusters, as well as for clusters with oxygen and other passivants on the surface. We note that the present QMC calculations represent the largest calculations to date on hydrogenated silicon clusters and were made possible by a recent development in the QMC approach [10] (see Fig.2).

Our results showed that quantum confinement represents just one mechanism responsible for the change in optical gap in silicon nanoclusters as a function of size, and that the specific surface chemistry must be taken into account in order to quantitatively explain the observed optical properties of these systems. Indeed, we have found that a range of absorption gaps could be seen using different passivants and that one contaminant can have a large impact on the measured value of the optical gap. We carried out an analysis of densities associated with the HOMO and LUMO states for silicon nanoclusters passivated with hydrogen up to 1.8 nm in diameter as well as Si₃₅H₃₅X and Si₃₅H₃₄Y species where X = H, F, Cl, or OH and Y = O, S, or CH₂. Our calculations show that surface effects due to single bonded passivants make a small contribution to optical transitions, even in the case of highly electronegative atoms. On the other hand, for double bonded passivants, e.g. atomic oxygen, we found that the gap is reduced by at least 1 eV for clusters 1 nm in diameter (see Fig.3 for the HOMO-LUMO analysis). This reduction is accompanied by a sizeable local distortion of the sp³ network at the surface.

Our results indicate that the wide discrepancy between previous theoretical data [11] and experimental results [12] may be due to multiple oxygen contamination. One possible proposed verification of our results is to expose a silicon cluster (<2 nm) to sulfur, while care is taken not to expose it to oxygen. We predict that such a cluster will

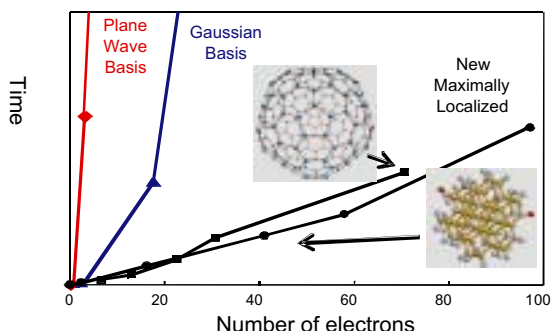


Fig. 2: Scaling of the CPU time required to calculate the total energy of hydrogen terminated silicon clusters and carbon fullerenes as a function of the cluster size, using Quantum Monte Carlo (QMC) techniques. Scalings are shown for QMC calculations based on Plane Wave (PW), Gaussian (G) and Maximally Localized Wannier (MLW) function basis sets. While PW- and G-based QMC calculations scale as the third power of the number of electrons in the system, MLW-based QMC calculations scale linearly. From A. Williamson, R.Q. Hood and J.C. Grossman, *Phys. Rev. Lett.* **87**, 246406 (2001).

exhibit a similar red shift as those clusters exposed to oxygen, thus demonstrating the importance of double bonded passivants

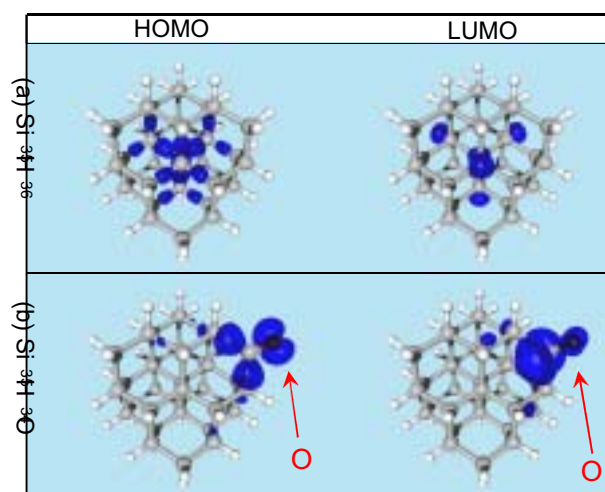


Fig.3: The highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals of the 1 nm diameter silicon clusters (a) terminated with hydrogen, and (b) terminated with hydrogen and one oxygen atom. The blue isosurfaces shows that in case (b) the HOMO and LUMO are localized on the silicon-oxygen double bond. From A. Puzder, A. Williams, J.C. Grossman and G. Galli, *Phys. Rev. Lett.* 2002.

4 CONCLUSIONS

Our recent results for the surface properties of Ge clusters and the surface chemistry of silicon clusters indicate that ab-initio techniques are very useful tools to study the properties of small nanostructures and to give predictive information which can be used to interpret and complement experiments. In particular, we have shown that recent algorithmic advances [10] allow one to calculate excitonic excitation energies in semiconductor clusters up to about two hundred atoms. This represents an order of magnitude increase in size over current state of the art QMC calculations and provides quantities directly comparable with spectroscopic measurements.

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