On the structure and stability of germanium nanoparticles

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In order to control and tailor the properties of nanodots, it is essential to separate the effects of quantum confinement from those due to the surface, and to gain insight into the influence of preparation conditions on the dot physical properties. We address these issues for the case of small Ge clusters (1-3 nm), using a combination of empirical and first-principles molecular dynamics techniques. Our results show that over a wide temperature range the diamond structure is more stable than tetragonal, ST12-like structures for clusters containing more than 50 atoms; however, the magnitude of the energy difference between the two geometries is strongly dependent on the surface properties. Based on our structural data, we propose a mechanism which may be responsible for the formation of metastable ST12 clusters in vapor deposition experiments, by cold quenching of amorphous nanoparticles with unsaturated, reconstructed surfaces.

In semiconductor nanoparticles quantum confinement leads to an increase of the optical gap compared to the bulk value and thus opens new possibilities for controlling photoluminescence effects, with narrow emission spectra tunable over a wide range of wavelengths [1,2]. These properties make semiconductor dots attractive for many applications including photovoltaics, lasers and infrared dyes. Furthermore, their brightness, low toxicity and the ability to use a single excitation wavelength make them good alternatives to organic dyes for biological labelling, but their low water solubility has limited biological applications. However, recent experiments have shown that using specific coatings, the surface of selected semiconductor nanodots can be tailored to enhance the chemical interaction with a biological sample and the water solubility [3,4].

Understanding the influence of surface reconstruction and passivation on the ground state properties of semiconductor nanodots is a key prerequisite not only in designing biological applications, but also for controlling deposition of nanoparticles on surfaces and aggregation of multiple dots into new structures. In order to tailor the properties of nanodots, it is important to separate the effects of quantum confinement from those due to the surface, and to gain insight into the mechanism by which preparation conditions can influence the dot atomic structure and thus its optical properties.

Here we address these issues for the case of small Ge dots (1-3 nm), whose atomic structure is the most controversial amongst those of group IV and II-VI semiconductors. While some preparation techniques, including chemical methods [5–9], yield diamond-like Ge dots irrespective of size, several experiments [10–12] suggest a structural transition, as the dot diameter becomes smaller than 4-5 nm. In particular, some experiments [13,14] using vapor deposition techniques indicate a change from a cubic diamond (DIA) to a tetragonal structure, possibly ST12, in contrast to the behavior found for Si [15–17] and other II-VI dots [18,19]. In the bulk, the ST12 phase is only obtained from high-pressure experiments [20]. The ST12 gap is direct and about 1.5 eV, as opposed to an indirect gap of 0.7 eV in the cubic phase. The relationship between a possible structural transition as a function of nanoparticle size and cluster preparation conditions, as well as the influence of a structural transition on the dot optical properties are as yet unknown.

Using first principles calculations we have studied the structure and stability of Ge clusters with diameters smaller than approximately 2.5 nm. We have considered both cubic diamond and tetragonal ST12 structures with H-terminated and bare reconstructed surfaces. Summarizing our results, we found that over a wide temperature range, the DIA structure is more stable than ST12-like structures for all clusters with more than 40 atoms (about 1 nm in diameter). The energy difference between the two geometries monotonically increases as a function of size, for both H-terminated and bare reconstructed surfaces. However the magnitude of this energy difference is strongly dependent on the reconstruction and on H-passivation. Our calculations also suggest that surface effects may be responsible for the formation of metastable ST12 clusters from amorphous nanoparticles in vapor deposition experiments: when the dot diameter becomes smaller than \( \simeq 2-3 \) nm, a structural transition from amorphous to ST12-like nanodots may be driven by the pressure on the inner core of the dot arising from the reconstructed surface.

In our calculations, Ge nanocrystallites were represented by free-standing clusters [21] in a large supercell [22]. The total energy of the dots was computed using Density Functional Theory (DFT) in the Local Density Approximation (LDA), using iterative optimization techniques [23]. The electronic wave functions were expanded in plane waves,
with an energy cutoff of 11 Ry, and non-local pseudopotentials were used to represent the interaction between the 
electrons and ionic cores \[^{24}\]. We considered nanoclusters with spherical shapes, with a number of Ge atoms ranging 
from 28 to 300 \[^{28}\]. In all cases we considered sizes which allowed us to use the same number of Ge and H atoms for 
both DIA and ST12 structures, in order to have direct total energy comparisons \[^{29}\].

The energy difference between DIA and ST12 Ge clusters with H-saturated surfaces is plotted as a function of cluster 
size in Fig. 1 (dotted line). Our results show that H-passivated dots with a DIA-like structure are more stable than 
those with a ST12-like structure for all sizes, with the energy difference increasing as a function of the nanoparticle 
diameter. The average volume per atom (V) of the cluster, shown in Fig. 2, is reduced in comparison to the volume 
per atom (V_0) corresponding to the bulk first neighbor distances for both DIA and ST12 geometries; for example, the 
ratio V/V_0 for DIA (ST12) dots varies from 0.97 (0.96) to 0.99 (0.98) when going from a 45 to a 145 atom cluster. 
Over the same range of sizes, the effective pressure acting on the cluster core, as evaluated using bulk moduli data, 
decreases from about 2 to 1 GPa. The magnitude of the DIA-ST12 energy difference, as well as the contraction of 
the average cluster atomic volume are significantly modified in the presence of unsaturated, reconstructed surfaces, 
as described below.

In order to find reconstructed geometries for the cluster surfaces we used a combination of empirical and DFT-

LDA techniques. Formation of facets is expected for clusters larger than 5 nm, but facets are unlikely in spherical 
nanoclusters with 1-5 nm diameters \[^{2}\]. In addition clusters prepared by deposition on surfaces usually exhibit 
disordered, defected interfaces \[^{2}\]. We therefore chose to determine surface reconstructed geometries using an annealing 
procedure. First, using molecular dynamics with a Tersoff potential \[^{27}\], we melted the cluster surface by heating it 
up to 2000 K for 0.08 ns; the temperature was then slowly decreased to zero over 0.2-0.5 ns. During this phase of the 
calculation, the crystalline core of the nanoclusters was kept frozen, and the shape conserved by confining the system 
in a spherical cavity. The annealing/quenching series was repeated 2-4 times. The final structure was fully relaxed 
within DFT-LDA \[^{22}\], all of the atoms being allowed to move. During these relaxations, energy gains varied from 310 
(275) meV/atom for 95 atom clusters to 88 (81) meV/atom for 300 atom clusters, for dots with a DIA (ST12)-like 
core structure. Fig. 3 shows the surface structure and the crystalline core for a selected cluster (Ge\(_{190}\)).

As shown in Fig. 1 (dotted versus dashed lines), we observed a strong reduction of the energy difference \(\Delta E(N)\) 
between DIA and ST12 clusters when the H-passivated surface is replaced by one which is unsaturated and recon-
structured. In the absence of H atoms, and given the spherical shape of the clusters, the computed values of \(\Delta E\) 
can be fitted by separating surface and bulk contributions: \(\Delta E(N) = N \Delta \epsilon + (36 \pi \frac{\pi}{\pi})^\frac{\pi}{\pi} \Delta \gamma\). Here \(\Delta \epsilon = -87\) meV/atom 
and \(\Delta \gamma = +59\) meV/atom are the volume and surface contributions to the energy difference \(\Delta E(N)\), respectively. 
The value of \(\Delta \epsilon\) is smaller than the calculated energy difference between solid DIA and ST12 (for the bulk energy differ-
ence we find 130 meV/atom, in good agreement with previous calculations \[^{28,29}\]). As indicated by the value of 
\(\Delta \gamma = +59\) meV/atom, surface energy is smaller for ST12 clusters and its sign is opposite to that of the volume 
contribution to \(\Delta E(N)\). This is largely responsible for the reduction of \(\Delta E\) in dots with reconstructed surfaces, compared 
to H-saturated clusters. Our results indicate that the ST12 structure should be more stable than DIA for \(N \leq 40\); 
however for such small sizes, Ge clusters are not expected to exhibit bulk-like geometries, but rather to form complex, 
non spherical shapes.

As mentioned above, the average atomic volume of a dot with a bare reconstructed surface is reduced in comparison 
to that of a cluster with a hydrogenated surface \[^{20}\]. As plotted in Fig. 2, the ratio V/V_0 is 0.93 (0.947) for ST12 
(DIA) Ge\(_{190}\) clusters. The volume reduction remains strong for our biggest Ge\(_{300}\) clusters, with 0.95 (0.967) for 
ST12 (DIA). These last values are to be compared, e.g., with the value of 0.982 (0.988) for ST12 (DIA) in the case 
of the smaller Ge\(_{145}\)H\(_{108}\) dot, which has roughly the same number of atoms belonging to the crystalline dot core as 
Ge\(_{300}\). The average volume reduction of the cluster amounts to an effective pressure on the crystalline core of about 
4 and 2.3 GPa, for Ge\(_{190}\) and Ge\(_{300}\), respectively. The effective pressure is slightly higher for ST12 than for DIA 
geometries (see Fig. 2).

An analysis of the reconstructed surfaces reveals disordered structures in all cases, as expected from a fast quench 
from a liquid state. For the larger clusters, the bond angles range approximately from 63 ° to 144 °, and the average 
bond length is close to the calculated first neighbor-distances in amorphous Ge (2.46 Å), i.e. 2 % larger than in the 
crystalline DIA structure. In general, we observed a strong reduction of the undercoordinated surface atoms after 
reconstruction, due to atomic dimerization. This effect is stronger for ST12 than for diamond, with ST12 reconstructed 
nanoclusters exhibiting approximately 20% fewer dangling bonds. This circumstance is due to the smaller size of the 
ST12 crystalline core and to the broader distribution of bond angles in the bulk ST12 structure, both of which provide 
greater freedom in the rearrangement of surface atoms. For one cluster size, we studied the effect on the dot stability 
of H-passivating the dangling bonds of its reconstructed surface. We observed an increase of \(\Delta E\), the DIA structure 
being favored over ST12 (the full relaxation of selected hydrogenated reconstructed surfaces were carried out within
As a final step in our study of the stability of Ge nanodots, we estimated the effect of temperature on $\Delta E(N)$, for clusters with reconstructed surfaces, by computing free energy differences in the harmonic approximation. The vibrational free energy $F_{vib} = \sum_{i=1}^{3N-6} \left( \frac{\hbar \omega_i}{2} + k_B T \ln \left( 1 - \exp\left( -\frac{\hbar \omega_i}{k_B T} \right) \right) \right)$ was determined by computing the vibrational frequencies $\omega_i$ using the Tersoff potential. Although not as accurate as total energy differences obtained within DFT-LDA, $F_{vib}$ can be used to estimate finite temperature effects as a function of size \[^{[11]}\]. Our results, shown in Fig. 1 by open dots, indicate that energy differences between DIA and ST12 are slightly reduced. However temperature effects do not invert the relative stability of the two structures. For examples, at $N = 145$ a temperature greater than 1180 K, i.e. close to the melting point of Ge, would be required for the reconstructed ST12 cluster to be more stable than DIA.

Our total energy calculations have shown that cubic diamond is the most stable structure of both H-terminated and bare reconstructed Ge clusters in the 1-3 nm size range, despite the importance of surface reconstruction effects. Ge dots with the ST12 structure are metastable and it is interesting to investigate whether there exist experimental conditions which might give rise to metastable ST12 clusters. For example, in vapor deposition or sputtering experiments \[^{[32]}\], amorphous Ge nanoparticles are initially present and annealing treatments are usually required for crystallization to occur. It is therefore relevant to understand whether metastable ST12 nanoparticles can be quenched from amorphous dots.

Based on our calculations, the cores of ST12 and DIA dots with both H-terminated and reconstructed surfaces are compressed. The effective pressure on the dot cores is much larger in the presence of reconstructed surfaces. These results suggest that pressure effects may play a role in quenching metastable ST12 clusters from amorphous nanoparticles. In order to address this issue, we have first investigated the amorphous (a-Ge) to ST12 transition in bulk Ge. Fig. 4 shows the total energy of diamond, ST12 and a-Ge as a function of volume, at $T=0$, as obtained from our calculations. Both a-Ge and ST12 are metastable, with the amorphous phase being slightly lower in energy than the ST12 crystal. A pressure $P_t$ of 1.5 GPa is required to induce an a-Ge to ST12 transition. Whether such a transition actually occurs depends on the height of the barrier between the two structures and on the temperature. We have not attempted to compute the a-Ge to ST12 energy barrier; however, phenomenological arguments suggest that it should be lower than that between a-Ge and cubic diamond, at temperatures typical of, e.g. dot deposition experiments. Indeed, ST12 is a weakly ordered crystal, which has been used to model a-Ge: it has 12 atoms per unit cell and a space group with few symmetry operations \[^{[33]}\]. Most importantly, unlike diamond, the ST12 crystalline network exhibits 7- and 5-fold atom rings, similar to a-Ge. It is therefore conceivable that a transition between a-Ge and ST12 be possible at relatively low $T$, when a-Ge is under a pressure of 1.5 GPa or higher. Similar considerations for the case of nanodots suggest that the pressure exerted by reconstructed surfaces on amorphous nanoparticle cores initially present in vapor deposition experiments may be large enough to induce a transition from amorphous to ST12 metastable nanoparticles. An extrapolation of the calculated effective pressures on dot cores (see Fig. 2) suggest that for dots with bare reconstructed surfaces and a diameter smaller than 2.5-3 nm, the pressure on the crystalline core is larger than the pressure required in the bulk to induce an a-Ge to ST12 transition (2.5-3 GPa, as compared to 1.5 GPa). Therefore for dots with diameters smaller than 2.5-3.0 nm prepared in vapor deposition experiments \[^{[13,14]}\], an a-Ge to ST12 transition induced by an effective surface pressure may be possible. On the contrary, the pressure exerted on the core of H-passivate clusters is equal to or smaller than the bulk transition pressure even for clusters with 70-100 atoms (i.e. with a diameter less than 1.5 nm).

The LDA used in our work does not permit quantitative evaluations of optical gaps for Ge dots. However, it is interesting to note that the difference between the energy of the highest occupied orbital (HOMO) and lowest unoccupied orbital (LUMO) as obtained for H-passivated clusters is larger for DIA-like geometries than for ST12-like geometries \[^{[24]}\]. While the HOMO position in energy is similar in DIA and ST12 clusters, the LUMO position is higher for DIA than for ST12 clusters. If the same trend was to be confirmed for quasi-particle energies, then a measure of the optical gap of small Ge dots could be a way to discriminate between DIA and ST12 geometries. Work is in progress to go beyond the LDA and estimate optical gaps.

In conclusion, we have shown that Ge clusters with the diamond structure are more stable than tetragonal ST12 dots over a wide temperature range, irrespective of the cluster size, for dot diameters larger than $\simeq 1.5$ nm. We have proposed a mechanism which may be responsible for the formation of metastable ST12 clusters in vapor deposition experiments \[^{[13,14]}\], by cold quenching of amorphous nanoparticles with unsaturated, reconstructed surfaces. The pressure exerted on the nanoparticle core by the surface can induce an amorphous to ST12 transition, for clusters with diameters smaller than 2.5-3.0 nm. This may explain why different types of structures are seen in experiments using chemical preparation methods \[^{[4,5]}\] versus physical vapor deposition methods \[^{[13,14]}\]. According to our calculations, chemical methods should always yield diamond structures, consistent with the results of H. W. Lee et al. \[^{[53]}\]. Our
study indicates that quantum confinement as well as surface effects are both key features in understanding the physical properties of small semiconductor dots. By tuning the surface properties with, for example, a particular choice of surfactant or by otherwise controlling the surface reconstruction, the pressure exerted on the dot core can be modified and used to tailor the atomic structure of the dot and indirectly the electronic properties.

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FIG. 1. Energy differences between Ge dots with diamond and ST12 structures as a function of the number of atoms and the approximate dot diameter (top horizontal axis). We show results for clusters with H-passivated, non-reconstructed surfaces at 0 K, and for clusters with bare reconstructed surfaces at 0 K (black circles) and 300 K (grey circles). The approximate boundary between clusters with complex, non-spherical shapes and dots with crystalline like geometries has been drawn to guide the eye, based on the data of Hunter et al [36].
FIG. 2. Ratio between the average atomic volume in Ge clusters ($V$) and the bulk equilibrium atomic volume ($V_0$), as calculated within the LDA (upper panel), and the corresponding internal pressure (lower panel) as a function of the cluster size. Filled (empty) circles represent H-passivated diamond (ST12) nanoclusters; filled (empty) squares represent diamond (ST12) dots with bare reconstructed surfaces. In the lower panel the horizontal axis indicates the transition pressure between amorphous and ST12 crystalline germanium in the bulk.

FIG. 3. Cross-section view of $\text{Ge}_{190}$ with a crystalline diamond like core, indicated by the white area. The grey area indicates the cluster disordered site area. The grey area

FIG. 4. Total energy per atom as a function of the atomic volume for bulk Ge in the diamond, ST12 and amorphous (a-Ge) structures. The Murnaghan equation of state fits are shown as solid lines. The transition pressure ($P_t$) between a-Ge and ST12 is equal to the slope of the common tangent to the ST12 and a-Ge total equation of state curves. The diamond curve has been calculated by varying the lattice parameter of a cubic cell containing 216 Ge atoms. This corresponds to a sampling of 5 k-points in the Irreducible Brillouin Zone (IBZ). The structural parameters of the ST12 structure have been optimized by relaxing simultaneously the ionic positions and lattice parameters of a 96 atom supercell. Then the total energy at the minimum has been recomputed using a 324 atom cell, thus allowing for a better k-point sampling (13 k-points in the IBZ). Amorphous samples with 144 atom have been prepared first by using a Tersoff potential, with thermalization to 2000 K and subsequent slow quenches. The final relaxations have been carried out within DFT-LDA and the atomic positions have been optimized at different densities, with constant pressure ab-initio MD runs. Finally, the energy difference between diamond and a-Ge was adjusted to the experimental enthalpy difference between the two phases \cite{38}.

[1] U. Woggon, \textit{Optical Properties of Semiconductor Quantum Dots} (Springer-Verlag, Berlin Heidelberg, 1997).
We carried out total energy optimizations within DFT-LDA for Ge$_{28}$H$_{36}$, Ge$_{45}$H$_{48}$, Ge$_{51}$H$_{76}$, Ge$_{111}$H$_{88}$, and Ge$_{145}$H$_{108}$, Ge$_{65}$, Ge$_{145}$, Ge$_{190}$ and Ge$_{300}$.

We used a cubic supercell with a lateral dimension $a = 60$ a.u. For the largest clusters we have verified that the charge density is negligible at the supercell boundary.

All of our DFT-LDA calculations were carried out using an optimized first principles molecular dynamics code, JEEP 1.4.6 (F. Gygi, LLNL 1999-200), and state-of-the-art parallel supercomputers.

The atomic volume inside the clusters is calculated by comparing the relaxed configuration with a ideal reference system (built by using the bulk lattice parameter calculated by DFT-LDA). The effective pressure corresponding to the atomic volume reduction is then obtained from the results of the constant-pressure calculations detailed in the caption of the Figure 4.

The vibrational properties of Ge as given by the Tersoff potential are in a qualitative agreement with experiments and DFT calculations. For instance, we calculated a Ge$_2$ stretching mode frequency of 251 cm$^{-1}$ with the Tersoff potential, close to 245 cm$^{-1}$ as determined in DFT-LDA.

We estimate that the LDA HOMO-LUMO gap of H-passivated Ge nanodots becomes larger for ST12-like than DIA-like structures when the dot diameter is greater than 3 nm.

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