PHYSICAL REVIEW B, VOLUME 63, 165324

Structure and stability of germanium nanoparticles

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(Received 10 January 2001; published 5 April 2001)

In order to tailor the properties of nanodots, it is essential to separate the effects of quantum confinement from those due to the surface, and to determine the mechanisms by which preparation conditions can influence the properties of the dot. We address these issues for the case of small Ge clusters (1–2.5 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-like structures for clusters containing more than 40 atoms; however, the magnitude of the energy difference is strongly dependent on the structure and termination of the surface. On the basis of our calculations, we propose a possible mechanism for the formation of metastable tetragonal clusters observed in vapor deposition experiments, by cold quenching of amorphous nanoparticles exhibiting unsaturated, reconstructed surfaces.

DOI: 10.1103/PhysRevB.63.165324 PACS number(s): 61.46.+w

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.[1–3] This property makes semiconductor dots attractive for many applications including photovoltaics, lasers, and infrared dyes. Furthermore, their brightness, and the ability to use a single excitation wavelength, make them good alternatives to organic dyes for biological labeling, although their low water solubility has limited the number of biological applications to date. However, recent experiments have shown that using specific coatings, the surface of selected semiconductor nanodots can be tailored to enhance both the chemical interaction with a biological sample and the water solubility of the dot.[4,5]

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[6,7] and to gain insight into the mechanisms by which preparation conditions can influence the dot atomic structure and thus its optical properties.

In this work, we have focused on the effects of quantum confinement and surface termination on the atomic structure of small Ge dots (1–2.5 nm), whose structural properties are very controversial among those of group IV and II-VI semiconductors. The effects of surface reconstructions on the cluster stability are difficult to determine experimentally and have often been ignored in many of the theoretical investigations that have appeared in the literature thus far. Using an *ab initio* approach, we have investigated the effect of the surface termination on the relative stability of Ge nanodots having different internal structures and containing up to 300 Ge atoms. At the same time, we have studied the fundamental differences between bulk and dot geometries, for given underlying crystal structures. Furthermore, we have used our total energy and structural data to interpret existing experiments and gain insight into the influence of experimental preparation conditions on the final dot structure. Our calculations suggest ways of tailoring the properties of Ge dots, by controlling their surface termination.

While some preparation techniques, including chemical methods,[8–12] yield diamondlike Ge dots irrespective of size, several experiments[13–15] using vapor deposition techniques suggest a structural transition, as the dot diameter becomes smaller than 4–5 nm. In particular, some experiments[16,17] indicate a change from a cubic diamond (DIA) to a tetragonal structure, possibly ST12,[22] in contrast to the behavior found for Si (Refs. 18–20) and other II-VI dots.[6,21] 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. In our calculations, we have considered both cubic diamond and tetragonal ST12 structures with either H-terminated or bare reconstructed surfaces. In particular, using a combination of first-principles and empirical simulation techniques, we have computed energy and free-energy differences between DIA and ST12-like structures as a function of size, and we have investigated the effect of the surface termination on the relative stability of the two geometries.

In our calculations, Ge nanocrystallites were represented by free-standing clusters[23] in a large supercell.[24] The total energy of the dots was computed within density-functional theory (DFT) in the local-density approximation (LDA), using iterative optimization techniques.[25] The electronic wave functions were expanded in plane waves, with an energy cutoff of 11 Ry, and nonlocal pseudopotentials were used to represent the interaction between the electrons and ionic cores.[26] We considered nanoclusters with spherical shapes, with the number of Ge atoms ranging from 28 to 300.[27] In all cases we considered sizes that 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.[28]

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,

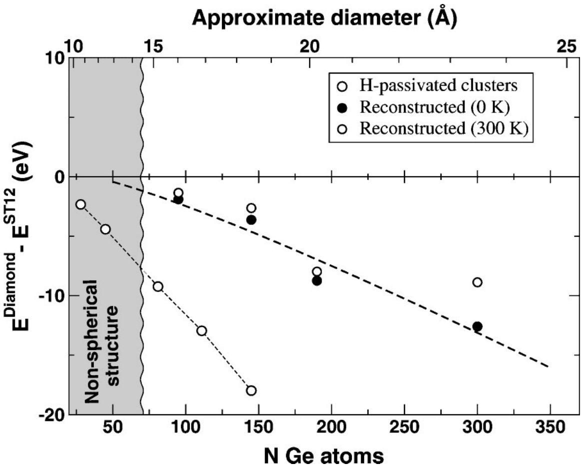

FIG. 1. Energy differences between Ge dots with diamond and ST12 structures as a function of the number of atoms (bottom horizontal axis) and the approximate dot diameter (top horizontal axis). We show results for clusters with H-passivated, nonreconstructed surfaces at 0 K (empty circles), and for clusters with bare reconstructed surfaces at 0 K (black circles) and 300 K (gray circles). The 300-K results refer to vibrational free energies (see text). The dotted and dashed lines were obtained from fits to the calculated energy differences (see text). The approximate boundary between clusters with complex, nonspherical shapes and dots with crystallinelike geometries has been drawn to guide the eye, based on the data of Hunter *et al.* (Ref. 38).

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 H-passivated DIA (ST12) dots varies from 0.97 (0.96) to 0.99 (0.98) when going from a cluster containing 45 Ge atoms to one with 145 atoms. Over this same range of sizes, the effective pressure acting on the cluster core, as evaluated using bulk moduli data,[29] decreases from about 2 to 1 GPa. The magnitude of the DIA-ST12 energy difference, as well as the reduction of the average cluster atomic volume, are both significantly modified in the presence of unsaturated, reconstructed surfaces, as described below.

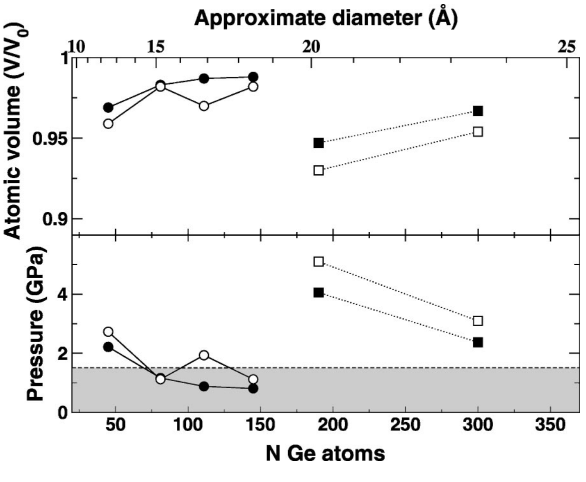

FIG. 2. Ratio between the average atomic volume in Ge clusters (V) and the bulk equilibrium atomic volume (V_0), as calculated within the LDA (upper panel), and the corresponding internal pressure (lower panel) as a function of the cluster size. Filled (empty) circles represent H-passivated diamond (ST12) 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.

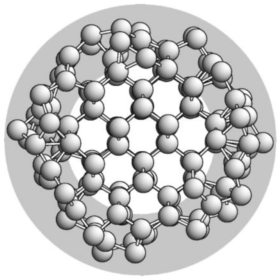

FIG. 3. Cross-sectional view of Ge_{190} with a crystalline diamondlike core, indicated by the white area. The gray area indicates the disordered cluster surface.

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 diameter.[3] In addition, clusters prepared by deposition on surfaces usually exhibit disordered, defected surfaces.[3] We therefore chose to determine surface reconstructed geometries using an annealing procedure. First, using molecular dynamics with a Tersoff potential,[30] 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 alternation between annealing and quenching was repeated two to four times. The final structure was fully relaxed[25] within DFT-LDA, 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. Figure 3 shows the surface structure and the region of 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 that is unsaturated and reconstructed. Our results indicate that the ST12 structure should be more stable than DIA for $N \leqslant 40$; however, for such small sizes, Ge clusters are not expected to exhibit bulklike geometries, but rather to form complex, nonspherical shapes. In the absence of H atoms, and given the spherical shape of the clusters, our DFT-LDA computed values of $\Delta E(N)$ can be fitted by separating surface and bulk contributions: $\Delta E(N) = N\Delta\epsilon + (36\pi)^{1/3}N^{2/3}\Delta\gamma$. The fit parameters $\Delta\epsilon = -87$ meV/atom and $\Delta\gamma = +59$ meV/atom are the volume and surface contributions to the energy difference $\Delta E(N)$, respectively, and together they yield the dashed line in Fig. 1. The value of $\Delta\epsilon$ is smaller than the calculated energy difference between crystalline DIA and ST12 (for the bulk energy difference, we find -130 meV/atom, in good agreement with previous calculations[31,32]), and roughly corresponds to the energy difference between DIA and ST12 at a volume that is 95% of their respective equilibrium volumes. This is consistent with the compression found for the core of the dots, as discussed below. As indicated by the value of $\Delta\gamma=+59$ meV/atom, the surface energy is smaller for ST12 clusters and the sign of the surface contribution is opposite to that of the volume contribution. This circumstance is largely responsible for the reduction of ΔE in dots with reconstructed surfaces, compared to H-saturated clusters. Indeed, in hydrogenated clusters without any Ge dangling bond, we expect each Ge atom to be predominantly in a bulklike environment. Therefore in this case the volume contribution to $\Delta E(N)$ dominates (as indicated by the nearly straight line connecting the energy differences for H-saturated clusters in Fig. 1) and no significant surface contribution is present.

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.[33] As plotted in Fig. 2, the ratio V/V_0 is 0.93 (0.95) for ST12 (DIA) clusters with 190 atoms. The volume reduction is sizeable also for Ge_{300}: 0.95 (0.97) for ST12 (DIA) clusters. These values are to be compared, e.g., with the value of 0.98 (0.99) for $\mathrm{Ge}_{145}\mathrm{H}_{108}$ ST12 (DIA) like dots, 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[29] 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). These results show conclusively that for given crystalline topologies, the structures of Ge nanoparticles differ significantly from corresponding bulk structures, the differences being quantitatively more important in the case of dots with reconstructed surfaces.

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 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.

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 $F_{\mathrm{vib}}=\Sigma_{i=1}^{3N-6}\{(\hbar\omega_i/2)+k_BT\ln[1-\exp(-\hbar\omega_i/k_BT)]\}$ was determined by computing the vibrational frequencies ω_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.[34] Our results, shown in Fig. 1 by the gray circles, 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 example, 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 in spite of differences between nanoparticle and bulk structures, cubic diamond Ge clusters are more stable than ST12 in the 1–3 nm size range, similar to bulk Ge. The relative stability is the same for both H-terminated and bare reconstructed Ge clusters, 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 that might give rise to metastable ST12 clusters. For example, in vapor deposition or sputtering experiments,[35] 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. Figure 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. Most importantly, unlike diamond, the ST12 crystalline network exhibits sevenfold and fivefold atom rings, similar to a-Ge. It is therefore conceivable that a transition between a-Ge and ST12 may 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 suggests 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) suggests 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

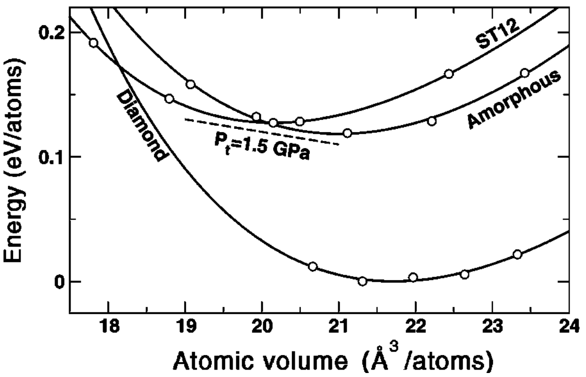

FIG. 4. Total energy per atom as a function of the atomic volume for bulk Ge in the diamond, ST12, and amorphous (a-Ge) structures. The Murnaghan equation-of-state fits are shown as solid lines. The transition pressure (P_t) between a-Ge and ST12 is equal to the slope of the common tangent to the ST12 and a-Ge 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 atoms 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 only was adjusted to the experimental enthalpy difference between the two phases (Ref. 40).

the pressure required in the bulk to induce an a-Ge to ST12 transition (i.e., 2.5–3 GPa, as compared to the bulk value of $P_t = 1.5$ GPa). Therefore, for dots with diameters smaller than 2.5–3.0 nm and prepared in vapor deposition experiments,[16,17] 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-passivated 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). We note that pressure-induced structural transitions in defect-free dots are expected to occur at pressures larger than in the bulk, similar to the case of CdSe nanocrystals.[6]

In order to make direct contact with experiment, we have computed the electron density of valence states (EDOS) of both diamondlike and tetragonal-like nanoparticles and compared it with the results of Ref. 17, where a claim is made about the existence of tetragonal Ge clusters. While the EDOS of tetragonal-like dots is in very good agreement with that measured in Ref. 17, the EDOS of diamondlike dots exhibits a rather different shape in the low-energy part of the spectrum. This agreement between the measured electronic properties and those computed for tetragonal-like particles gives significant weight to the hypothesis that tetragonal particles are indeed present in some of the experiments.

The calculations presented here do not permit quantitative evaluations of optical gaps for Ge dots, due to the LDA. However, it is interesting to note that the difference between the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as obtained for H-passivated clusters is smaller for ST12-like geometries than for DIA-like geometries, when the Ge dot has a diameter smaller than 3 nm.[36] While the energy of the HOMO position is similar in DIA and ST12 clusters, the energy of the LUMO is lower for ST12 than for DIA clusters. If the same trend was to be confirmed for quasiparticle energies, then a measurement 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 to provide more accurate estimates of the 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 $\simeq 1.0$–1.5 nm. We have proposed a mechanism that may be responsible for the formation of metastable ST12 clusters in vapor deposition experiments, by cold quenching of amorphous nanoparticles exhibiting unsaturated, reconstructed surfaces. The pressure exerted on the nanoparticle core by the surface might 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[8,10,11] versus physical vapor deposition methods.[16,17] According to our calculations, chemical methods should always yield diamond structures, consistent with the results of Lee *et al.*[37] Our study indicates that quantum confinement as well as surface effects are both key features in understanding the physical properties of small semiconductor dots, consistent, e.g., with recent findings on CdSe dots.[7] 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.

Helpful discussions with L. Terminello, C. Bostedt, A. Van Buuren, H. Lee, S. Bastea, and E. Schwegler are gratefully acknowledged. We also thank A. Williamson for a critical reading of the manuscript. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory, Office of Basic Energy Sciences, Division of Materials Science, under Contract No. W-7405-Eng-48.

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[23] We carried out total-energy optimizations within DFT-LDA for $Ge_{28}H_{36}$, $Ge_{45}H_{48}$, $Ge_{81}H_{76}$, $Ge_{111}H_{88}$, $Ge_{145}H_{108}$, Ge_{95}, Ge_{145}, Ge_{190}, and Ge_{300}.

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[28] For diameter smaller than 5 nm, nanoparticles are commonly observed with spherical shapes.[8,9,12,14] However, it has been shown that nanoclusters with fewer than 70 Ge atoms (~ 1.4 nm) exhibits a nonspherical shape.[38] Since the focus of our investigation is on the properties of Ge dots in the range 1–5 nm, we considered only spherical clusters in this work.

[29] We computed the minimum-energy volume of the cluster core and then estimated the pressure exerted on the core by using the derivative of the energy/volume $[E(V)]$ relationship (i.e., the bulk modulus) obtained from the bulk. In order to verify that this procedure gives a reasonable estimate of the pressure in the cluster, we compared the bulk modulus obtained from $E(V)$ in the bulk with the corresponding quantity obtained from $E(V)$ for a cluster. The two numbers differed by only a few percent, confirming that the stiffness of the cluster core against isotropic expansion or compression is similar to that in the bulk. The cluster $E(V)$ was computed for the diamondlike Ge_{190} cluster by varying the effective lattice constant of the core and then optimizing the saturated surface structure.

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[34] The vibrational properties of Ge as given by the Tersoff potential are in qualitative agreement with experiments and DFT calculations.[39] 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.

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