Surface reconstruction effects on atomic properties of semiconducting nanoparticles

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Abstract

We have performed first-principles and empirical molecular dynamics calculations of the effect of size and surface reconstruction on the atomic structure properties of small Ge nanoparticles (1–2.5 nm). Systems with ideal H-passivated surfaces, or bare reconstructed surfaces have been considered. We show that the surface reconstruction leads to a very strong volume contraction of the nanoparticles, equivalent to an applied pressure of 4 GPa for a 2 nm nanoparticle. We also found that the surface reconstruction shifts significantly the optic mode peak of the vibrational spectrum, thus preventing a straightforward size determination from Raman spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

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Interest for nanoparticles has considerably grown recently, in particular because the luminescence properties obtained for selected materials are promising for technological applications[1–7]. However, the mechanisms responsible for these effects are not completely understood for several reasons. First, the very small sizes of these physical objects is a challenge for most of the experimental techniques. It is also difficult to prepare these nanoparticles with a controlled and narrow size distribution, except in specific case such as CdSe [8]. Hence, theoretical studies are difficult to perform, because of the large number of atoms in the nanoparticles. In this domain, up to now most of the efforts have been focussed on electronic properties, rather than on the atomic structure, which is always supposed to be bulk-like. However, the surface may have a crucial importance. Under some specific preparation conditions, it is reasonable to assume that perfect and passivated nanoparticles surfaces could be obtained. But in general, the surface will reconstruct prior to passivation, or in the case of embedded nanoparticles, the interface with the matrix may be disordered. The importance of surface reconstruction or

disorder on the nanoparticles properties are not completely understood. Here we have investigated how the reconstruction of the nanoparticle surface affects the atomic properties. We have performed ab initio and empirical molecular dynamics calculations for Ge nanoparticles, with either a H-passivated ideal surface, or a bare reconstructed surface. We have analyzed the atomic structure, separating quantum confinement and reconstruction effects, and showed how the calculated contraction is equivalent to an applied pressure. Finally, we report surface effects on the vibrational properties.

In our calculations, both non-reconstructed H-passivated, and reconstructed Ge nanocrystallites were represented by free-standing clusters in a large supercell (60 a.u.). We considered nanoclusters with spherical shapes [9], the number of Ge atoms ranging from 28 to 300 [10]. For large cluster sizes, the number of metastable configurations with reconstructed surfaces is extremely large, and the exploration of such a configuration space is still out of the reach of ab initio molecular dynamics. Instead, we have performed classical molecular dynamics calculations [11] with the potential of Tersoff [12] to relax the surface. Only the outer shell of the cluster was allowed to relax, while the inner shell remained fixed for conserving the core crystalline structure. The system was relaxed by combining several annealings and quenches, a typical run

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during about 1 ns. The minimal energy configuration obtained with several runs was then selected as the starting structure for ab initio calculations. For both non-reconstructed and reconstructed clusters, the final atomic structure was computed within the Density Functional Theory (DFT) in the Local Density Approximation (LDA), all the atoms being allowed to relax. 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 [13].

First, we focus on the H-passivated non-reconstructed nanoparticles. The average first neighbor distances for several sizes are represented on the Fig. 1. One can see a continuous decrease of the atomic separation when nanoparticles become smaller. For the smallest one ($Ge_{28}H_{36}$), the bond length is 1.2% lower than the LDA bulk value. This is clearly a quantum confinement effect, due to the small size of the nanoparticles. We also tried to investigate the atomic separation variation from the center to the surface. The strongest reduction occurred in the outer shell, in the vicinity of the surface, whereas the atomic separation is close to the bulk value in the inner shell, for the biggest cluster ($Ge_{145}H_{108}$). It is interesting to note that for small clusters, atomic separations in both inner and outer shells become very close. We also analyze the variation of the angles between first neighbor bonds. We found a well-defined maximum at 109.4° and an angular dispersion ranging from 6° for the biggest cluster to 11° for the smallest one. This angular variation is required for accomodating the cubic diamond structure in the spherical cluster shape.

The reduction of the atomic separation can be viewed as a contraction of the nanoparticles volume. However, it is difficult to extract this volume reduction directly from the atomic separation value, since the angle between nearest neighbors is not constant. Instead, we determined the volume reduction using the following procedure: For each cluster with the radius R, we compute the function $V(r) = 4/3\pi r^3/n(r)$, with $n(r)$ the number of atoms included in the sphere centered on the cluster and of radius r, with $r \in [0, R]$. Using a reference $V_0(r)$, computed for a perfect non-relaxed spherical cluster, we have determined the average volume reduction V/V_0. The results are represented on the Fig. 2. As expected, the largest volume reduction occured for the small nanoparticles, but even for the biggest one ($Ge_{145}H_{108}$), it is still around 98.5%. This is an effect of quantum confinement, but alternatively, it could also be viewed as the result of an applied hydrostatic pressure on the clusters. We used the calculated relation between atomic volume and pressure in bulk germanium [14], to obtain an estimate of this pressure[15]. We found values ranging from 2 GPa for small nanoparticles to 1 GPa. By extrapolating the calculated size-volume relation, we noted that the volume contraction is vanishing slowly as the size increases.

For nanoparticles with reconstructed surfaces, in addition to quantum confinement effects, we expect the surface to change significantly the atomic properties of the nanoparticles. By construction, the investigated clusters retain the cubic diamond structure in their core, while the surface is reconstructed. A cross-section view of the reconstructed Ge190 is shown on the Fig. 3. One can see the appearance of several dimers at the surface, the reduction of dangling bonds by dimerization being known as the main driving force to reconstruct Ge surfaces. Our molecular dynamics treatments lead to a dangling bonds reduction of about 40–50% in surface, and to an average energy reduction of about 75 meV per
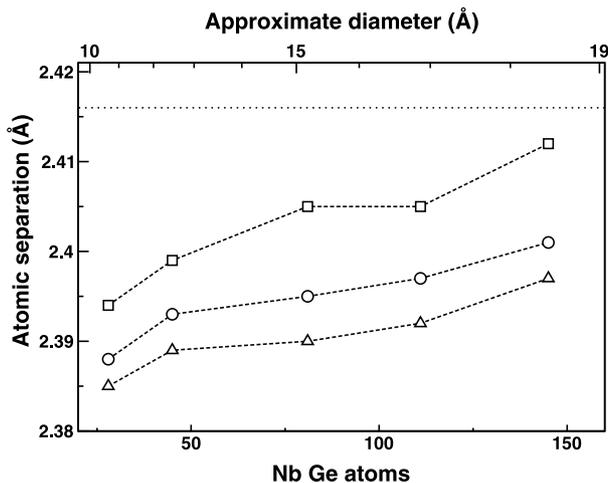

Fig. 1. Calculated first nearest neighbors distance (circle) as a function of the nanoparticle size. The square (diamond) symbols show this variation in the inner (outer) shell of the spherical nanoparticles. The dotted line marks the LDA first neighbor distance in cubic diamond bulk germanium.
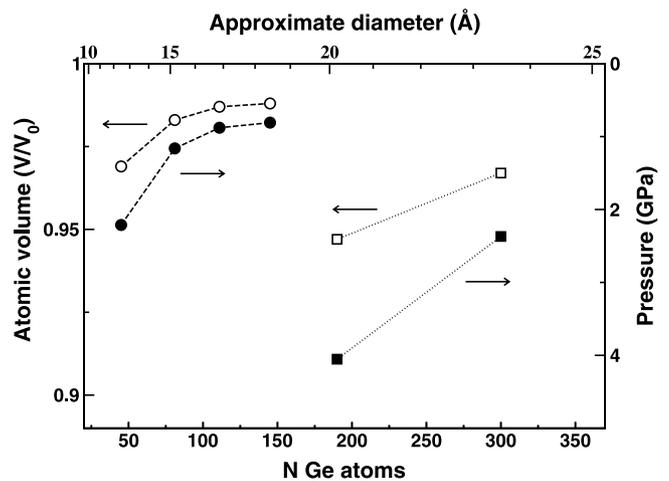

Fig. 2. Atomic volume reduction (open symbols) and internal pressure (filled symbols) as a function of the size for H-passivated non-reconstructed (circles) and clean constructed (squares) Ge nanoparticles.
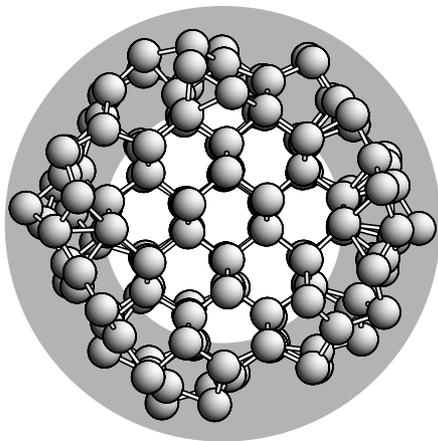
Fig. 3. Cross-section view of Ge_{190}, with a crystalline diamond inner shell, and a reconstructed disordered outer shell (grey).

at for the first step (classical potential) and 90 meV per at for the second step (ab initio). The disordered character of the surface is clearly visible on the Fig. 3. An analysis of the bond length in the surface shell reveals an average value of 2.46 Å, i.e. equal to the amorphous Ge atomic separation [16], and the bond angles range widely from 63 to 144°. We also note the presence at the surface of atoms with coordinations 3 and 5. A disordered surface for spherical clusters is not surprising, since a perfect ordering, with a maximal reduction of dangling bonds, will occur mainly in the presence of facets [17], which are not observed for nanoparticles in this size range.

With the procedure described for the H-passivated nanoparticles, we have determined the volume contraction and the corresponding internal pressure in the crystalline core of the clusters with a reconstructed surface. The results are shown for two sizes (Ge_{190} and Ge_{300}) on the Fig. 2. For the smaller nanoparticles, the crystalline cores were too limited to allow for a non ambiguous calculation. We observed a very strong volume reduction, up to 95% for a 2 nm nanoparticle. The corresponding pressure is 4 GPa. Comparing with the results for the non-reconstructed clusters, it is clear that quantum confinement can not completely account for such a strong effect. Actually, the surface reconstruction is the main factor. Shortening of the atomic separation between surface atoms during dimerization, leads to a reduction of the surface area, and a contraction of the core volume. This is equivalent to the well-known situation for semiconducting surfaces: the dimerization lowers the chemical energy by the formation of bonds, at the expense of the strain energy required to stress the surface and bring the atoms closer. Here, the stress of the spherical surface is responsible for the volume contraction. We have recently proposed that this effect is responsible for the formation of metastable structure in Ge nanoparticles [14]. Indeed, a denser

crystalline structure could be more stable in a smaller available volume.

We have also investigated the vibrational properties of the nanoparticles. The vibrational frequencies ω_i have been computed[18] using the Tersoff potential [19], because of the huge computational effort required to obtain these frequencies within a first-principles calculation. Here, the surface hydrogen atoms were removed for the non-reconstructed clusters. The ω_i spectrum is then convoluted with Gaussian functions centered on each ω_i, in order to compare more easily with experiments. For non-reconstructed nanoparticles, we obtained similar densities for each size with a well-defined peak at 301 cm^{-1} corresponding to the bulk silicon optic mode frequency. No peak frequency shift was observed with varying sizes, as experimentally observed and predicted from quantum confinement theories [20,21]. Such subtle quantum effects can not be correctly reproduced using a classical potential. For nanoparticles with reconstructed surfaces, we found an optic mode peak which is not clearly defined (Fig. 4), associated with a shift to lower frequencies. The general shape of the vibrational density is very close to the one calculated for an amorphous bulk germanium, confirming the disordered character of the reconstructed surface. Raman spectroscopy is often used to estimate the size of the nanoparticles [22,23], the optic mode peak shift being related to the size [20,21]. However, our results show that the disorder at the surface, or at the interface with a surrounding medium, could significantly act on this frequency shift and may lead to an erroneous estimation of the size.

In this paper, we have reported results about the atomic properties of Ge nanoparticles in the size range 1–2.5 nm, with surfaces either ideal and H-passivated, or bare and reconstructed, using first-principles calculations. We observed a contraction of bond lengths and
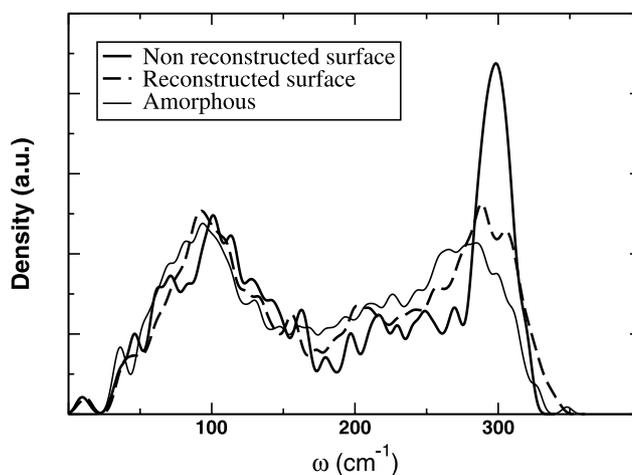

Fig. 4. Calculated one-photon density of states for perfect (thick line), surface re-constructed (dashed line), and amorphous (thin line) Ge_{190} nanoparticles.

volumes, as a result of quantum confinement effect, for the non-reconstructed nanoparticles. Using a combination of empirical and first-principles molecular dynamics, we have reconstructed the surface of the clusters. The stress associated with the reconstruction is responsible for a large volume contraction, which corresponds to an applied pressure of about 4 GPa for a 2 nm cluster. Finally, a vibrational properties analysis reveals how the surface reconstruction can significantly shifts the optic mode peak, preventing an easy determination of the nanoparticle size from Raman spectroscopy.

Acknowledgements

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