Electronic properties of Ge–Si nanoparticles

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Abstract. Using a parameterized density-functional tight-binding method we have calculated the electronic and structural properties of Ge–Si nanoparticles. Starting with a spherical part of a zinc-blende/diamond crystal (with the center of the sphere at the mid-point of a nearest-neighbour bond) we have constructed initial structures that subsequently were allowed to relax. Structures consisting solely of Ge atoms or solely of Si atoms were studied, together with core-shell structures for which one semiconductor forms a shell on the core of the other semiconductor. Moreover, homogeneous, ordered SiGe structures as well as structures with a semisphere of one semiconductor and a semisphere of the other were also considered. In analysing the results special emphasis is put on identifying particularly stable structures, on explaining the occurrence of those, on the spatial distribution of the frontier orbitals, and on the variation of the total energy with structure and composition.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Band-structure engineering, i.e., the tuning of the electronic properties of materials through modification of the structure and stoichiometry of semiconducting structures, is an important component of the design of special materials for special purposes. During the last couple of decades another parameter has been added to those that can be varied in order to modify the materials properties, i.e., 'dimensionality' or 'size'. It has been found that materials that can be characterized as being quasi-zero-, one-, or two-dimensional have properties that differ from those of the macroscopic counterparts. For semiconductors, quasi-zero-, one-, and two-dimensional materials are those for which the typical exciton radii are comparable with the spatial extensions of the materials in all, two, or one dimensions. Then, the spatial confinement leads to modified materials properties.

The materials that fall into these categories are clusters, nanowires, and sheets. However, for the typical semiconductors like Si, Ge, GaAs, CdS, InP, ... the interatomic bonds are defined through covalent bonds between nearest neighbours. The covalent bonds are to a large extent formed by sp^3 hybrids on the various atoms. From these directional hybrid orbitals, extended three-dimensional periodic structures like the wurtzite and the zincblende structure can be generated. Therefore, when quasi-zero-, one-, or two-dimensional structures are considered, the periodicity is interrupted in one or more dimensions, and dangling bonds on the surface occur. The dangling bonds are highly reactive and, therefore, in order to stabilize these systems one has to saturate those, e.g., by adding ligands.

Another way of stabilizing the finite systems is to cover the core of one semiconductor with another semiconductor. For quasi-zero-dimensional systems this leads to core-shell nanoparticles, where we for quasi-one-dimensional systems arrive at core-sheath nanowires.

Two of the technologically most important semiconductors are silicon and germanium. For those, experimental realizations of core-shell- or core-sheath-like structures have been reported [1–3]. In order to understand in more details the interplay between the two semiconductors forming an interphase we have performed a set of theoretical calculations on Si–Ge nanoparticles. We have considered both (Si)Ge and (Ge)Si core-shell systems [with (A)B denoting an A-B core-shell nanoparticle] as well as nanoparticles containing two half-parts, Ge|Si, each containing one of the two semiconductors and, finally, mixed GeSi nanoalloys. The purpose of the present work is to describe briefly some of the main outcomes of this study.

2 Computational method

The calculations of the electronic properties for a given structure were performed using the parameterized

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tight-binding density-functional method of Seifert et al. [4–6]. According to this method, the relative total energy of a given compound with a chosen structure is written as the difference in the orbital energies of the compound minus those of the isolated atoms, i.e., as

$$E_e = \sum_i \epsilon_i - \sum_m \sum_i \epsilon_{mi} \qquad (1)$$

(with m being an atom index and i an orbital index), augmented with pair potentials,

$$E_r = \sum_{m_1 \neq m_2} U_{m_1,m_2}(|\boldsymbol{R}_{m_1} - \boldsymbol{R}_{m_2}|) \qquad (2)$$

(with $\boldsymbol{R}_m$ being the position of the mth atom).

In calculating the orbital energies we need the Hamilton matrix elements $\langle \chi_{m_1 n_1}|\hat{H}|\chi_{m_2 n_2}\rangle$ and the overlap matrix elements $\langle \chi_{m_1 n_1}|\chi_{m_2 n_2}\rangle$. χ_{mn} is the nth atomic orbital of the mth atom. The Hamilton operator contains the kinetic-energy operator as well as the potential. The latter is approximated as a superposition of the potentials of the isolated atoms,

$$V(\boldsymbol{r}) = \sum_m V_m(|\boldsymbol{r} - \boldsymbol{R}_m|), \qquad (3)$$

and we assume that the matrix element $\langle \chi_{m_1 n_1}|V_m|\chi_{m_2 n_2}\rangle$ vanishes unless at least one of the atoms m_1 and m_2 equals m. The pair potentials U_{m_1,m_2} are obtained by requiring that the total-energy curves from parameter-free density-functional calculations on the diatomics are accurately reproduced. With these approximations all relevant information on the above-mentioned matrix elements can be extracted from calculations on isolated two-atomic systems, in our case on Si_2, SiGe, and Ge_2. Finally, only the $3s$ and $3p$ electrons of Si and the $4s$ and $4p$ electrons of Ge were explicitly included in the calculations, whereas all other electrons were treated with a frozen-core approximation.

Since we are applying the method on larger systems, we examined its accuracy for infinite, periodic, crystalline systems and found optimized lattice constants within less than 1% of the experimental values. Although the clusters of the present study are neither diatomic molecules, nor infinite crystals, our experience on related systems gives us confidence in using the approach also for the finite-sized nanoparticles.

The structures of the present study were constructed by considering a spherical cut-out of the diamond crystal structure with the center of the sphere at the center of a nearest-neighbour bond. Thereby, concentric atomic shells with 2, 6, 12, 12, 6, 18, 12, 30, 14, 36, 24, ... atoms are obtained, resulting in particles with 2, 8, 20, 32, 38, 56, 74, 86, 116, 130, 166, 190, ... atoms. For the (A)B core-shell systems an inner set of atomic shells were occupied by A atoms and the outer part by B atoms. A special case is the pure Si and Ge clusters for which the core contains no atomic shells. For the Ge|Si systems a plane containing the center of the system splits it into a Si and a Ge part.

Finally, for the GeSi nanoalloys, the atomic positions were occupied alternatingly by Si and Ge atoms.

After having constructed the initial structure (using a lattice constant that is the average of those of crystalline Si and Ge), it was allowed to relax to its closest total-energy minimum.

3 Results

In total we considered 95 different structures, each consisting of $N_{Si,i}$ Si atoms and $N_{Ge,i}$ Ge atoms, $i = 1, 2, \ldots, 95$. Using a least-squares fit we approximated the binding energy of those 95 structures by a sum of atomic energies,

$$E_{b,i} \simeq E_{Si}N_{Si,i} + E_{Ge}N_{Ge,i} \equiv \tilde{E}_{b,i}. \qquad (4)$$

Subsequently, we defined one stability energy for each cluster,

$$\Delta E_1 = E_{b,i} - \tilde{E}_{b,i} \qquad (5)$$

which is the more negative the more stable the cluster is. Finally, we analyse this quantity per atom, i.e.,

$$\Delta E_1/N = \Delta E_1/(N_{Si,i} + N_{Ge,i}). \qquad (6)$$

We also considered the stability energy

$$\Delta E_2/N = E_{t,i}/(N_{Si,i} + N_{Ge,i}) \qquad (7)$$

with $E_t = E_e + E_r$ of equations (1) and (2).

From the fit of equation (4) we found $E_{Si} = -2.37$ eV and $E_{Ge} = -3.58$ eV. That E_{Ge} is more negative than E_{Si} implies that it is energetically more favorable for Ge atoms than for Si atoms to be incorporated into those nanostructures. On the other hand, the cohesive energy of the solids equals 4.63 and 3.85 eV/atom for Si and Ge, respectively [7].

The negative values of E_{Si} and E_{Ge} imply that $\Delta E_2/N$ in general is lower than $\Delta E_1/N$. This is recognizable in Figure 1, where we show these quantities as a function of the number of atomic shell, either in the shell region or in the complete system. The values in Figures 1a and 1b are in general lower than those of the other panels, which first of all can be explained through the negative values of E_{Si} and E_{Ge}. An additional effect is due to the lower surface energy of Ge compared with Si, meaning that naked (Si)Ge particles in general are stabler than the (Ge)Si counterparts.

The presentation in Figure 1 shows that for (Si)Ge core-shell clusters $\Delta E_1/N$ and for (Ge)Si core-shell clusters $\Delta E_2/N$ first of all depends on the number of atomic shells in the shell region. Other representations of these energies show a much less clear correlation between size and stability. Moreover, Figure 1 shows that the homogeneous GeSi alloys are stabler than the Ge|Si systems. Finally, for all systems of Figure 1 the relative total energy is an overall decreasing function of size of the systems.

In an earlier work we have found a close relation between stability (i.e., $\Delta E/N$) and the energy gap between the HOMO and the LUMO [8]. For the present systems we
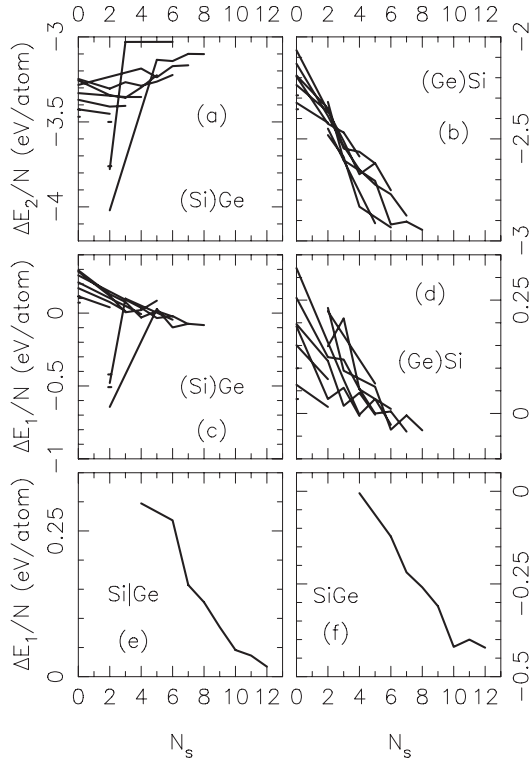
Fig. 1. The variation in the stability energies per atom $\Delta E_1/N$ and $\Delta E_2/N$ as a function of the number of atomic shells for the different systems, as indicated in the panels. N_s is the total number of atomic shells in (e) and (f), whereas it is the number of atomic shells in the shell region in the other panels. Finally, the lines in (a)–(d) connect the values for the systems with the same number of atomic shells in the core region.

Fig. 2. The HOMO-LUMO energy gap as a function of the stability energy per atom $\Delta E_2/N$ for (a, b) the core-shell systems with (a) Ge covering Si and (b) Si covering Ge as well as for (d) the homogeneous GeSi systems and (c) the Ge|Si systems.

do, however, not find a similar correlation. Figure 2 shows one example of this, i.e., the gap vs. $\Delta E_2/N$, but also for the gap vs. $\Delta E_1/N$, no such correlation is observed.

In order to study the charge distribution of the clusters, we first determine the center of the cluster with n Si atoms and m Ge atoms,

$$\boldsymbol{R}_0 = \frac{1}{n+m} \sum_{j=1}^{n+m} \boldsymbol{R}_j, \qquad (8)$$

and, subsequently, for each atom its so-called radial distance

$$r_j = |\boldsymbol{R}_j - \boldsymbol{R}_0|. \qquad (9)$$

Subsequently, we plot the Mulliken gross populations of the individual atoms as a function of the radial distance. Figure 3 shows some few examples of those results that are found for all the systems of the present study: in the outermost parts the atomic populations are much more scattered compared to the inner parts, with both negatively and positively charged Si and Ge atoms. On the other hand, in the inner parts there is a tendency for an electron transfer from Ge to Si. Ge-Si nanowires with a Si sheath covering a Ge core have been of some interest recently (see, e.g., [9]), also as active components in semiconductor devices. In these, it is assumed that a hole gas
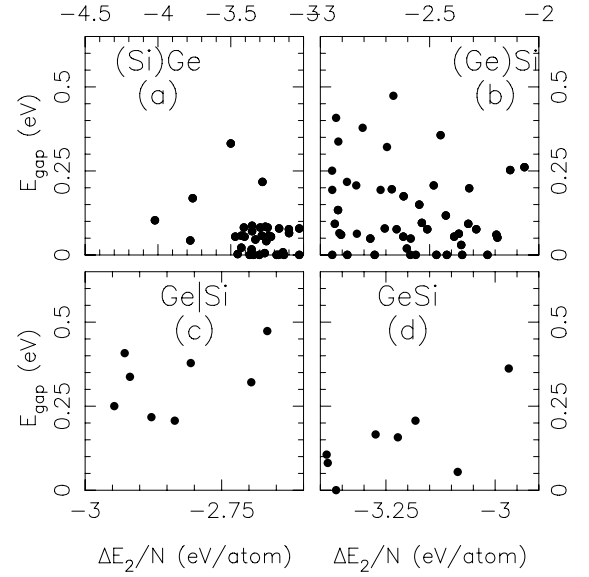
is formed in the Ge wire. If the systems were isolated, this would imply a net electron transfer from Ge to Si, which is in excellent agreement with the findings of the present study.

Finally, we shall study the frontier orbitals. For optical properties, excitons are believed to play a crucial role and these can in turn to a good approximation be described with the HOMO and LUMO single-particle wavefunctions. Therefore, the spatial distribution of these orbitals is important. To this end we construct for any orbital the density

$$\rho_i(\boldsymbol{r}) = \sum_j N_{ij} \left(\frac{2\alpha}{\pi} \right)^{3/2} \exp[-\alpha(\boldsymbol{r} - \boldsymbol{R}_j)^2]. \qquad (10)$$

Here, N_{ij} is the Mulliken gross population for the jth atom and ith orbital, and α is chosen 'reasonably', so that illustrative figures result upon spherical averaging. Typical results are represented in Figure 4, where it is seen that in all cases the frontier orbitals are localized to the surface regions of the nanoparticles. Actually, with no exception this result was found for all the systems of the present study. I.e., in contrast to our findings for certain CdSe-CdS and CdS-CdSe core-shell particles [10] (that the HOMO and the LUMO was localized to different parts of the system), our results do not suggest a charge separation upon excitation.

4 Conclusions

We have presented results of a theoretical study of the electronic properties of roughly spherical nanoparticles
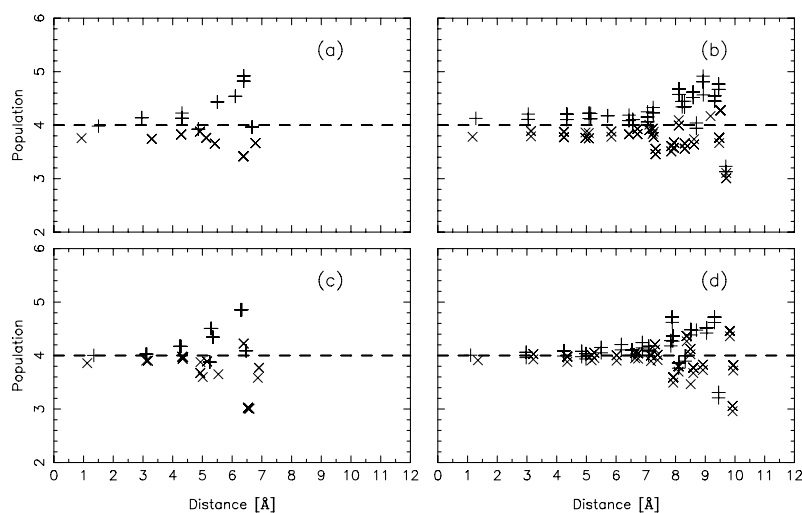
Fig. 3. Radial distribution of Mulliken gross populations of valence electrons of Si (+) and Ge (×) for (upper part) homogeneous GeSi systems and (lower part) Ge|Si systems with (left part) 56 and (right part) 134 atoms. The horizontal solid line marks the value (4) for neutral Si and Ge atoms.
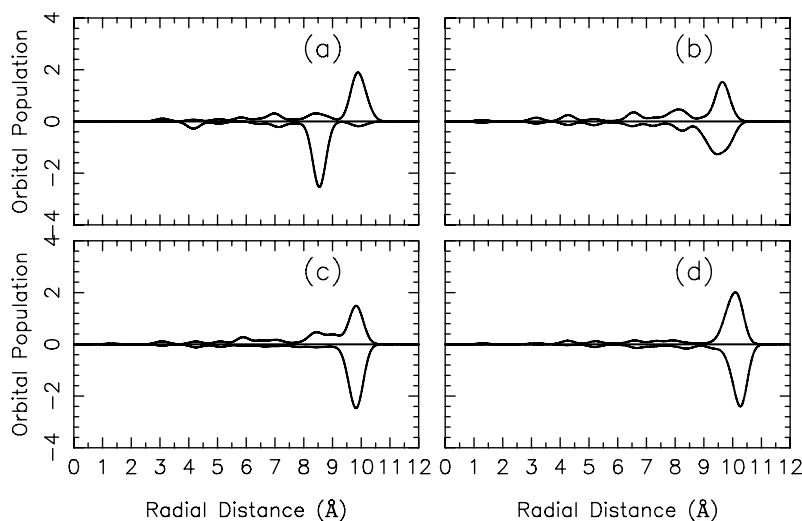

Fig. 4. Schematic presentation of the radial electron distribution of the HOMO (curves pointing upward) and the LUMO (curves pointing downward) for different systems with 190 atoms, i.e., (a) $(Si_{56})Ge_{134}$ and (b) $(Ge_{56})Si_{134}$ core-shell particles, (c) the homogeneous GeSi nanoalloy, and (d) the Ge|Si system.

containing both Si and Ge atoms. We considered various arrangements of the atoms, i.e., a core of one element covered by a shell of the other, systems with two half-spheres each with one element, and homogeneous nanoalloys. No attempt to optimize the structure completely was undertaken.

We found that the stability of the core-shell nanoparticles to a good approximation was dictated by the number of atomic shells in the shell region. This may be related to our finding that the frontier orbitals were localized to the surface regions, and, consequently, the HOMO-LUMO gap was a fairly irregular function of size of the system.

(Si)Ge systems were in general more stable than (Ge)Si ones, and homogeneous GeSi systems more stable than Ge|Si ones.

In the inner parts we observe an electron transfer from Ge to Si, whereas the outermost parts of the clusters, irrespectively of the system, show an increased electron transfer between the atoms.

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