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Ge clusters in Si matrix: structure and dynamics

J. Dalla Torre[1,2], N. Barriquand[1], M. Djafari Rouhani[1,2], and G. Landa[1,a]

[1] Laboratoire de Physique des Solides[b], Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France
[2] Laboratoire d'Analyse et d'Architecture des Systèmes, CNRS, 7 avenue du Colonel Roche, 31077 Toulouse Cedex, France

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Abstract. We have determined by computer simulations, some structural properties of Ge clusters embeded in a Si crystalline host matrix for cluster sizes varying from ≈ 0.5 to 1.5 nm. In order to describe inter-atomic forces we have chosen a Valence Force Field (VFF) semi-empirical potential. Next we have calculated the density of vibrational states by diagonalization of the dynamical matrix defined with the same potential. The influence of the volume/interface ratio of Ge on the vibrational properties is discussed.

PACS. 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 63.50.+x Vibrational states in disordered systems

1 Introduction

In recent years, an increasing effort has been developed towards the understanding of surprising physical properties of clusters. An example of potential applications for semiconductor clusters is their nonlinear optical properties that usually do not appear in the bulk materials [1]. Many theoretical and particularly "ab initio" calculations have been made in order to determine the structure of these clusters [2,3]. These *ab initio* calculations generally deal with only few atoms. While small semiconductor clusters exhibit particular geometries due to important surface effects, large ones seem to adopt the crystal structure. Otherwise, experimental observations of clusters in a host matrix generally show large cluster (few nanometers) with crystalline structure [4,5]. But the structure, in particular at the interface between the matrix and the cluster, can be strongly modified by the chemical nature of the matrix, the elaboration technique and the elaboration conditions, annealing temperature, etc. Raman spectroscopy can be useful to describe structural and dynamic properties of such clusters [1,5]. Our purpose in this paper is to show that using simple Valence Force Field (VFF) potentials, one may obtain not only the two above properties, but also, the degree of the localization of the states inside the clusters. In this study, we have considered Ge clusters embedded in a Si crystalline host matrix containing 432 atoms. Even if the cluster sizes discussed here can be produced experimentally [4], a more typical size is about 2 to 5 nm [1,5]. So, contrary to the alloy case, the number of atoms in the supercell must be very large in order to describe correctly the large defects. With a 432 atom supercell, we have been able to treat clusters of radius up to 1.5 nm. This cluster sizes are somewhere between the sizes used in *ab initio* models and those in real experiments, but contain the general information, particularly on the localization of the states at the interface. We compare our results to experimental data obtained in a similar case where the Si matrix is polycrystalline [4]. The interface between the Ge clusters and the Si matrix is taken to be perfect with no dangling bonds. The organization of the paper is as follows. In Section 2 we present the model used in this paper and describe the parameters employed in our calculations. In Section 3, we present and discuss the results obtained. Finally in Section 4, we summarize our main conclusions.

2 Model

The frame of our model has been presented before [6] in the case of amorphous Si and we sketch here only the necessary background to understand the procedure. Our simulation procedure can be divided in three main stages:

(a) The first one is the construction of the system under study. The supercell approach is chosen in order to describe the structural and the chemical disorder. Actually, in disordered materials the crystal symmetries are broken due to the introduction of non periodic and extended heterogeneities in the pure crystal. As a result, a disordered material should be modeled by a unique macroscopic cell, but because of the computational limitations, it is approximated by a supercell with periodic boundary conditions keeping in mind that the size and the density of the heterogeneities are limited by this supercell size. So we have defined a $6[110] \times 6[1\bar{1}0] \times 12[001] = 432$ atoms crystalline supercell and we have introduced, at random

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[a] e-mail: `landa@cict.fr`
[b] ESA 5477 associée au CNRS

Table 1. Parameters for the different distributions under study. Number of Ge atoms in a cluster, size of the clusters, number of clusters, and resulting proportion of Ge in the Si matrix.

Number of atoms/cluster	5	17	29	47	87
Clusters diameter (nm)	0.49	0.80	0.94	1.23	1.47
Number of clusters	18	5	3	2	1
% of Ge	20.1	19.7	20.1	21.8	20.1

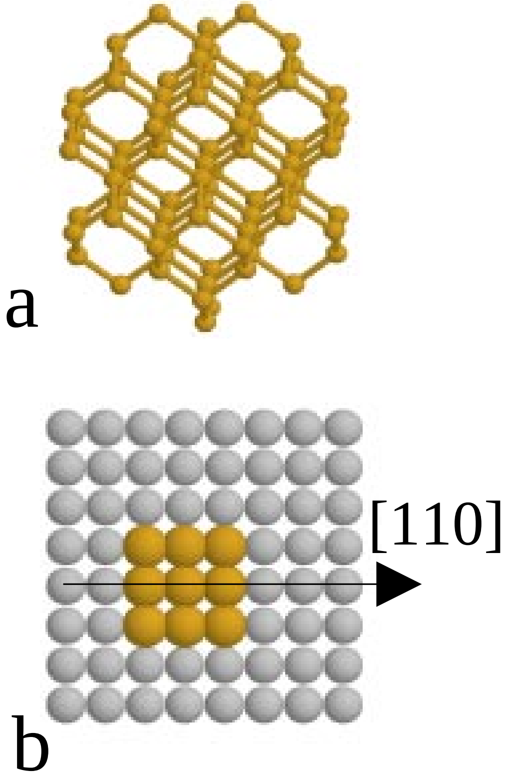

Fig. 1. a) structure of a 87 atom cluster. b) (001) plane of the 1024 atom supercell, passing through the center of the cluster. The darker and bigger spheres are Ge atoms.

positions, Ge spherical clusters with sizes varying from ≈ 0.5 to 1.5 nm (see Tab. 1) with a diamond-like crystalline structure (Fig. 1a).

(b) As the Ge lattice parameter is larger than the Si one, atomic positions must be relaxed. For this, the total elastic energy is minimized and thus the supercell volume is changed. The strain description is made by a VFF potential in the Martin's harmonic formulation [7]:

$$E_{\mathrm{s}} = \sum_{\text{bonds}} k_r (r - r_{\text{bond}})^2 + \sum_{\text{bond angles}} k_\theta (\theta - \theta_0)^2 \qquad (1)$$

where r is the actual bond length, r_{bond} is the equilibrium bond length corresponding to the pure materials and we have taken $r_{\text{bond}}^{\text{Si}-\text{Ge}} = (r_{\text{bond}}^{\text{Si}} + r_{\text{bond}}^{\text{Ge}})/2$ for the heterogeneous Si-Ge bonds. θ is the actual angle between two adjacent bonds and θ_0 is the angle between two adjacent bonds in the diamond perfect structure. k_r and k_θ are the force parameters related to the elastic constants of the pure materials Si and Ge [7], and as a first approximation we have taken for mixed parameters, $k_r^{\text{Si}-\text{Ge}} = (k_r^{\text{Si}} + k_r^{\text{Ge}})/2$ and $k_\theta^{\widehat{X-Y-Z}} = k_\theta^{\widehat{Y}}$ ($X, Y, Z =$ Si or Ge).

(c) After the minimum total strain energy is reached, the vibrational eigenstates or normal mode frequencies are determined by diagonalization of the dynamical matrix obtained with the same VFF inter-atomic potential. Finally, an approximation of the Density of Vibrational States (DVS) is obtained by sampling the vibrational-frequency spectrum.

3 Structural and dynamical calculations

In this paper, we have focused our computations on the case of a particular concentration of Ge atoms in the Si matrix, namely 20%. In this case, the Si character of the matrix is almost preserved and the number of Ge atoms inside is sufficient to introduce different ratios of disorder depending on their relative arrangement. This allows the study of distributions of different sizes and numbers of clusters (see Tab. 1). The center of the cluster is randomly determined at a Si site, a radius is defined with a second Si atom and all the atoms in this sphere are substituted by Ge atoms.

First, we are interested in the structure calculations to evaluate the strain near the cluster boundaries. This is performed through the relaxation of the structure. However, it should be pointed out that the relaxed structure only corresponds to a metastable configuration, *i.e.* a local minimum of the elastic energy. This results from the definite positiveness of the dynamical matrix in the VFF approximation. In other words, our relaxation scheme allows relatively small atomic displacements, but not for atomic migrations along a few interatomic distances.

The result is in agreement with experimental configurations which are also in metastable states. The question whether inclusions are thermodynamically stable or not can only be addressed through a thermal annealing procedure, both in experiments and simulations. This question is beyond the scope of this paper.

As a first check of our calculations we determined the average bond length (noted *average* in Fig. 2) over all kinds of bonds.

The result is in total agreement with the expected value from Vegard's law ($L_{\text{average}} = 0.2(L_{\text{Ge}} - L_{\text{Si}}) + L_{\text{Si}} \approx 2.37$ Å). This average is almost the same whatever is the distribution of Ge atoms, a lot of small clusters or a few big ones. Moreover we have reported in Figure 2 the average bond length for each specific bond, Si-Si, Ge-Ge and Si-Ge as a function of the cluster diameter. The calculated bond lengths of a $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloy where Ge are randomly distributed in the matrix are represented by dark diamonds and are in agreement with previous similar results [8,9]. The interesting point is that as a first approximation, bond lengths are constant and independent of the cluster sizes

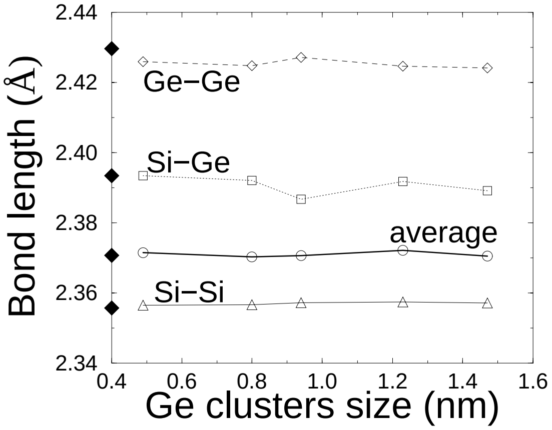

Fig. 2. Average bond lengths of Si-Si, Si-Ge and Ge-Ge as a function of the cluster sizes while the total Ge composition is kept constant. The dark diamonds are the calculated values for $Si_{0.8}Ge_{0.2}$ alloy.

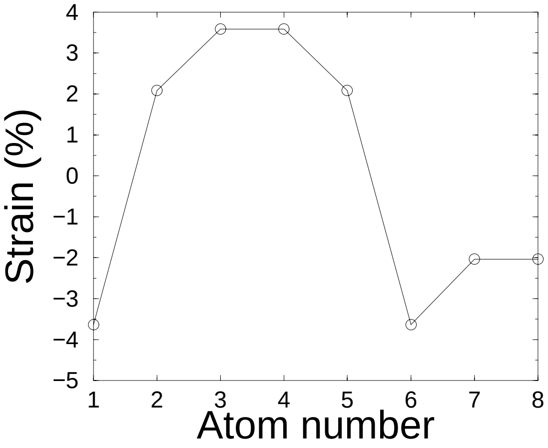

Fig. 3. Calculated strain along the [110] direction passing through the center of a 87 Ge cluster as a function of the atom number along this direction (Fig. 1b).

for the three kinds of bonds. This means that the relaxation for each kind of bond is the same from the alloy case to that of a matrix with a 87 atom cluster. This indicate that due to their covalent nature, each kind of bond keeps its specific character independently of the distribution.

Figure 3 presents the bond strain with respect to Si, along the [110] direction of the supercell passing through the center of the Ge cluster. Because of the discrete and non compact nature of the material at this scale the strain is calculated over a very small number of atoms and the (001) section passing through the center of the 87 cluster (Fig. 1a) is a 3×3 atoms square(Fig. 1b).

We have defined the strain at an i site by $\varepsilon_i = (\delta x_i - \delta x_{i+1})/d_{\mathrm{Si}}$, where δx_i is the variation of the atomic position along the [110] axis (Fig. 1b) and d_{Si} is the distance between two atoms in this direction in the Si pure crystal. In order to evaluate the local strain produced by the cluster in the Si matrix over a larger range, we have enlarged the supercell by few monolayers in each direction. This increase has been limited to keep a low time cost of our calculation. In this calculation the Ge proportion is lower than in the previous cases as this is a 87 Ge atoms in a $8 \times 8 \times 16 = 1024$ atoms matrix ($\approx 8.5\%$). We can observe a rapid variation of the strain from approximately 3.5% to -3.5% which occurs over two atoms. The strain reaches $\approx 3.5\%$ in the Ge cluster, which is 0.5% less than the lattice mismatch between Ge and Si. This corresponds to a residual compression of the Ge cluster by the Si matrix. Otherwise, the strain for the Si matrix reaches $\approx -3.5\%$ in the neighborhood of the cluster which corresponds to a compression of the Si atoms. The absolute value of strain for Si appears to decrease with the distance from the cluster. These results are in quantitative agreement with calculations made using a continuum theory [10].

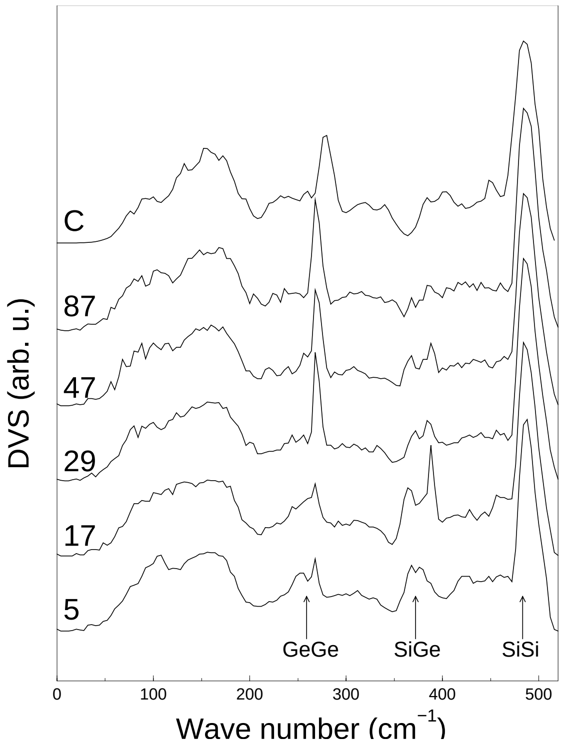

Fig. 4. Calculated DVS for different clusters size, from 5 to 87 atoms. The Ge composition is kept constant to $\approx 20\%$, so the number of clusters varies (see Tab. 1). The noted "C" DVS is a linear combination of the pure Ge and Si DVS. Optical bands associated to the Ge-Ge, Si-Ge and Si-Si are indicated by arrows.

Next, we discuss the vibrational states of the previous systems. As we use the supercell method, it is convenient to define a new wave vector corresponding to the new periodicity, leading to a new Brillouin zone.

In order to obtain a smooth Density of Vibrational States (DVS), we can either average the DVS over a set of different configurations chosen at random [11], or to use few wavevectors in the supercell Brillouin zone [6]. We have adopted this second scheme and used 10 values of the wavevector randomly distributed inside the supercell Brillouin zone. In Figure 4, we present the DVS for different clusters of various sizes, containing from 5 to 87 atoms. The Ge content is kept close to 20%. To compare our results for different distributions of Ge clusters, we have also presented in Figure 4 the linear combination of the DVS of pure Si and Ge. Its intensity is given by $I_{\mathrm{combi}} = 0.8.I_{\mathrm{Si}} + 0.2.I_{\mathrm{Ge}}$, this curve is noted C in Figure 4 and corresponds to the DVS of a very large Ge cluster in Si and is used as a suitable reference to demonstrate the size effects. This reference system is more adequate than pure Ge or Si. Concerning the general aspect of the DVS, we observe an important difference between this combination and the DVS of small clusters. This is a consequence of the disorder induced by the dispersion of the Ge atoms in the Si matrix. The lack of symmetry splits off the degenerate eigenstates and as a result smoothes the DVS. So, when the cluster sizes become larger, the DVS comes closer to the combination DVS, showing a "phase segregation" of Ge and Si species. We can particularly observe in Figure 4 that the Ge-Ge mode shifts to higher frequencies when the cluster sizes increase. A clear shift is seen on going from the 87 atom cluster to the reference curve. The results are in good agreement with experimental Raman spectra of Ge clusters in Si matrix which show a peak at 270 cm^{-1} attributed to the amorphous Ge-Ge mode [1,5]. Moreover, we can see the typical "3 mode" [12] behavior, of SiGe compounds for the optical bands (Fig. 4). Each optical band is associated with one kind of bond: Si-Si ($\approx$ 520 cm^{-1}), Si-Ge ($\approx$ 380 cm^{-1}) and Ge-Ge ($\approx$ 270 cm^{-1}). The effects of the interface/volume ratio of Ge are particularly visible in the different intensities of DVS and should be observed in the corresponding Raman spectra. As the number of clusters decreases, *i.e.* their size increases, the number of Ge-Ge bonds increases which is directly observed in the intensity of the Ge-Ge band. But while increasing the cluster size, the number of Si-Ge bonds at the interfaces decreases and as a result, the Si-Ge signature vanishes.

4 Conclusion

In conclusion, we have calculated some structural and dynamical properties of Ge clusters in an Si matrix by a semi-empirical VFF potential. In this study the number and the size of the clusters are varying in order to keep the Ge proportion approximatively equal to 20%. Despite the small size of the supercell used in the calculations, we have shown that even for large clusters, the average bond lengths are roughly similar to the alloy values with the same Ge composition, in good agreement with experimental observations. We have observed a rapid variation of strain at the cluster interface and we have shown that in the 1.47 nm clusters, the core has a lattice parameter close to pure Ge crystal. Finally, we have discussed the Si-Ge interface effects in the DVS. We have shown a decrease of the Si-Ge and an increase of the Ge-Ge band intensities for large clusters as a result of the interface/volume ratio of clusters. A shift of the Ge-Ge band, close to experimental results, has been obtained.

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