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Ge clusters in Si matrix: structure and dynamics

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Abstract. We have determined by computer simulations, some structural properties of Ge clusters embedded 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 ef-

fects, 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) poten-

tials, 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 II we present the model used in this paper and describe the parameters employed in our calculations. In section III, we present and discuss the results obtained. Finally in section IV, 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:

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

(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 $6[110] \times 6[1-10] \times 12[001] = 432$ atoms crystalline supercell and we have introduced at random positions, Ge spherical clusters with sizes varying from ≈ 0.5 to 1.5 nm (see table I) 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 po-

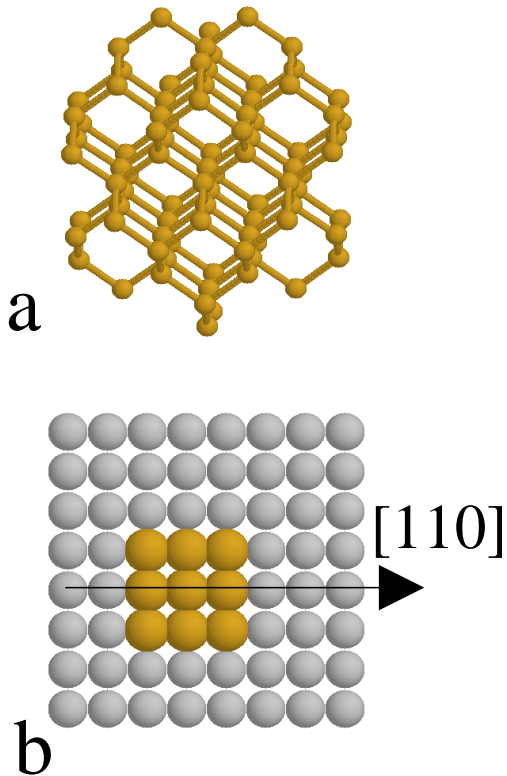


Fig. 1. a) structure representation of a 37 atoms cluster. b) (001) plane of the 1024 atoms supercell, passing through the center of the cluster, darkest and biggest spheres are Ge atoms.

tential in the Martins' harmonic formulation [7]:

$$E_s = \sum_{bonds} k_r (r - r_{bond})^2 + \sum_{bond\ angles} k_\theta (\theta - \theta_0)^2 \quad (1)$$

where r is the actual bond length, r_{bond} is the equilibrium bond length corresponding to the pure materials and we have taken $r_{bond}^{Si-Ge} = (r_{bond}^{Si} + r_{bond}^{Ge})/2$ 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, $k_r^{Si-Ge} = (k_r^{Si} + k_r^{Ge})/2$ and $k_\theta^{X-\widehat{Y}-Z} = k_\theta^{\widehat{Y}}$ ($X, Y, Z = Si\ or\ Ge$).

(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 frequencies spectrum.

3 Structural and dynamical calculations

In this paper, we have focused our computations on the case of a 20% particular concentration of Ge atoms in the Si matrix. In this case, 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 size and number of such clusters(see table I). 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 positive nature of the dynamical matrix in VFF approximation. In other words, our relaxation schema al-

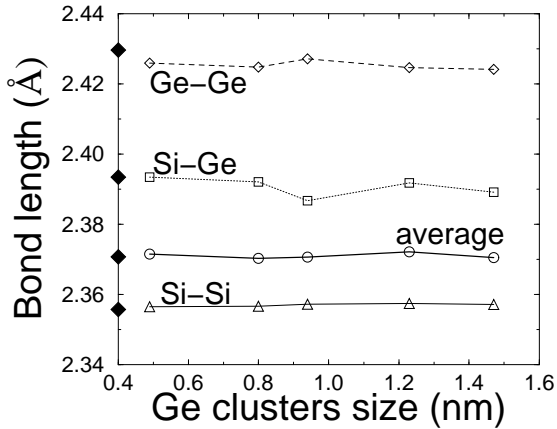


Fig. 2. Average bond lengths of Si-Si, Si-Ge and Ge-Ge types as a function of the clusters size while the total Ge composition is kept constant. The dark diamonds are their values for the calculated $Si_{0.8}Ge_{0.2}$ alloy.

lows 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 of whether inclusions are thermodynamically stable or not can only be addressed through a thermal annealing procedure, both in experimental and simulation grounds. This question is beyond the scope of this paper.

As a first check of our calculations we have calculated the average bond length (noted *average* in fig. 2) over all kind of bonds.

As one can observe, the result is in total agreement with the expected value from the Vegard's law ($L_{average} = 0.2(L_{Ge} - L_{Si}) + L_{Si} \approx 2.37\text{\AA}$). This average value 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 over each specific bond, Si-Si, Ge-Ge and Si-Ge as a function

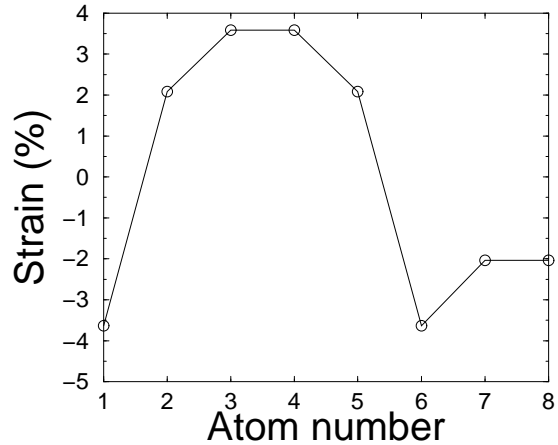


Fig. 3. Strain calculation along the [110] direction passing through the center of a 87 Ge cluster as a function of the atom number along this direction (fig. 1b)).

of the cluster diameter. The calculated bond lengths of a $Si_{0.8}Ge_{0.2}$ 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 for the three kind 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 atoms 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 few number of atoms and the (001) section passing through the center of the 87 cluster (fig. 1a) is a 3x3 atoms square (fig. 1b)).

We have defined this strain at an i site by $\varepsilon_i = (\delta x_i - \delta x_{i+1})/d_{Si}$, 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 due to 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 is made 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 $\approx -3.5\%$ at 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 to the cluster. These results are in quantitative good agreement with calculations made by continuum theory[10].

Next, we are going to discuss the vibrational states of the previous systems. As we are in the supercell method, it would be convenient to define a new wave vector concept related to the new periodicity, leading so 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

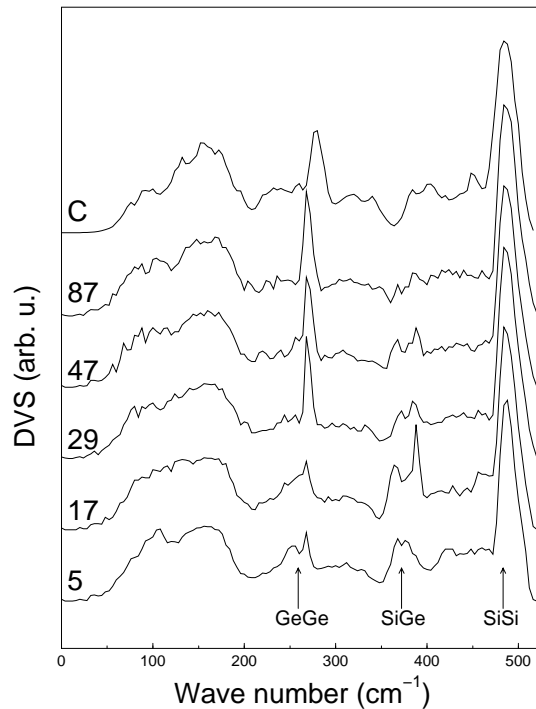


Fig. 4. Calculated DVS for different clusters size, from 5 to 87 atoms. The Ge composition is kept constant to $\approx 20\%$, so the number of clusters varies (see table I). The noted "C" DVS is a linear combination of the pure Ge and Si DVS. Optical bands associated to the Ge-Ge, Si-Ge and Si-Si are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

few wavevectors in the supercell Brillouin zone[6]. We have adopted this second scheme and have used 10 values of the wavevector randomly distributed inside the supercell Brillouin zone. In Fig. 4, we have reported the DVS for different clusters of various sizes, containing from 5 to 87 atoms. The Ge content is kept constant, and equal to 20 of clusters present in the supercell. To compare our results for different distributions of Ge clusters, we have also presented in fig.4 the linear combination of the DVS of pure Si and Ge. Its intensity is given by $I_{combi} = 0.8.I_{Si} + 0.2.I_{Ge}$, this curve is noted C in fig.4. The curve C represents the

DVS of a huge Ge cluster in Si and is used as a reference to observe the size effects, preferably to a pure Ge or Si DVS reference. Concerning the general aspect of the DVS, we observe an important difference between this combination and the DVS for small clusters. This is a consequence of the disorder induced by the dispersion of the Ge atoms in the Si matrix. This lack of symmetries split off the degenerate eigenstates and as a result smoothes the DVS. So, when the cluster sizes become larger, the DVS come closer to the combination DVS, showing a "phase segregation" of Ge and Si species. We can particularly observe in Fig. 4 that the Ge-Ge mode shifts to higher frequencies when cluster sizes increase. A clear shift is seen when 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 modes"[12] behavior, of SiGe compounds for the optical bands(fig. 4). Each optical band is associated with one kind of bond: Si-Si ($\approx 520\text{ cm}^{-1}$), Si-Ge ($\approx 380\text{ cm}^{-1}$) and Ge-Ge ($\approx 270\text{ cm}^{-1}$). 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 bonds are roughly the same as alloy values with the same Ge composition and 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 the Ge pure crystal. Finally, we have discussed the Si-Ge interface effects in the DVS. Actually, we have shown the decrease of the Si-Ge and the 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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