Molecular dynamics simulations of Si/Ge cluster condensation

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ABSTRACT

The condensation of Si, Ge, and Si/Ge nanoclusters in an Ar atmosphere was simulated using molecular dynamics simulations. The clusters formed were made with different Si-to-Ge ratios ranging from 100% Si to 100% Ge. The results indicate that Ge atoms have a tendency to segregate to the surface of the clusters, although the magnitude of this effect depends on the potential used for the simulations. Also, there is a random tendency for the atoms to form non-spherical clusters; this tendency grows with the increased concentration of Ge atoms.

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1. Introduction

Porous silicon has been an object of interest ever since the discovery of its strong visible photoluminescence at room temperature [1]. The luminescent properties of porous or nanocrystalline germanium and Si/Ge have also been investigated and have been found to be at least as attractive as those of porous silicon [2,3]. Porous films are usually made using anodic etching or a similar top-down method, but bottom-up methods such as cluster deposition have also yielded excellent results: e.g. nanostructured silicon films have been obtained by neutral cluster depositions [4] and their optical properties have been investigated [5,6].

To complement the understanding of experimental results, numerical simulations of cluster deposition have also been performed [7,8]. These simulations have shown that the porosities of the deposited layers depend strongly on the deposition energy over a range of about 0.1–1 eV/atom: with the lower energies, the clusters land softly on the substrate, leaving considerable room between themselves, thus increasing the porosity; and with the higher energies, the clusters are flattened upon landing, thus decreasing the amount of empty space and reducing layer porosity.

For the sake of simplicity, simulated cluster deposition typically employs pre-relaxed spherical clusters of constant size. However, it is impossible to experimentally produce clusters with an exact amount of atoms. Similarly, not all real clusters are spherical in shape; in fact, previous studies of structural relaxation in Si and Ge nanocrystallites have shown that relaxation may actually increase deviations from a perfect spherical shape [9]. The problem of the number of atoms can be tackled with the use of variable cluster size in the deposition simulations; however, the effect of cluster shape requires more insight into the formation of the clusters themselves.

Experimentally, there is a number of ways to make atomic clusters. At the newly constructed facility at the University of Helsinki, Department of Physics, the cluster material is sputtered from a magnetron, and the atoms are swept into a condensation chamber by a flow of inert gas (in this case, argon), which cools the vapor, allowing it to condensate into clusters [10]. All components of the machinery, including the argon gas, are kept at room temperature. In this study, we took a step back from the simulations of cluster deposition itself, and we used molecular dynamics simulations to simulate the formation of silicon, germanium, and Si/Ge nanoclusters in an argon atmosphere at room temperature.

The main focus of this study was the structure of the condensed clusters. While sphericity was the most obvious concern, another object of interest was to find out whether or not Ge atoms would

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segregate to the surface of the condensed clusters; this characteristic of SiGe clusters was discovered earlier in our group [11]. The importance of the relative spatial distribution of Ge atoms within SiGe nanocrystals has been investigated and found to affect the optical and electronic properties of the structures [12]. Thus, understanding the formation process of the clusters is an important factor when considering their potential applications.

2. Method

The condensation of Si, Ge, and Si/Ge clusters in Ar was investigated through the use of classical molecular dynamics simulations [13]. To check whether the results were potential-independent, the atomic interactions were realized using both the Stillinger–Weber [14,15] and the Tersoff [16] potentials for Si and Ge. Repulsive potentials, as developed by Ziegler et al. [17], were used for interactions between the semiconductor and Ar atoms, while Ar–Ar forces were modeled by the Lennard-Jones potential [18].

Cells with a random distribution of 2036 atoms consisting of 50% Ar and 50% Si and/or Ge were constructed for the simulations. There were a total of 11 cells, with a Si_xGe_{1-x} ratio ranging from $x = 0.0$ to 1.0 at intervals of 0.1. The cells were run at a constant temperature of 300 K for 50 ns; temperature was controlled using the Berendsen temperature control algorithm [19] with a time constant of 500 fs. For an increased amount of statistics, each run was performed with four different seed numbers for both of the potentials used.

The simulation temperature (300 K) corresponds to the room temperature experiments performed at the University of Helsinki. However, the simulation time scale is too small to yield results directly comparable to experimental clusters; clusters may stabilize into new forms over macroscopic time scales, which cannot be studied using molecular dynamics. Atom mobility may be enhanced by raising the temperature, although the effects of this do not directly correspond to those of a greater time scale. For comparison, one set of simulations was run at 600 K using the Tersoff potential.

3. Results and discussion

Although a perfect sphere represents the most energy-efficient arrangement for cluster atoms, not all simulated clusters were able to reach this form. To devise a method for analyzing this effect, the clusters were ranked according to their sphericity S, which we define as $S = V_c/V_{max}$, where

$$V_c = \sum_i \frac{N_i}{\rho_i} \tag{1}$$

is the total volume taken up by a cluster having N atoms of elements i with densities of ρ_i, and

$$V_{max} = \frac{4}{3}\pi r_{max}^3 \tag{2}$$

is the volume encompassed by a hypothetical spherical cluster with the same radius as the maximum atom distance r_{max} from the center of mass of the actual cluster. This differs from Wadell's original definition, which introduced sphericity as the ratio of the surface area of a sphere to the surface area of a particle having the same volume as the sphere in question [20]; this definition was not used due to the difficulties in determining the surface area of a discrete system such as an atomic cluster. For reference, our definition gives a sphericity of 0.4 for a perfect cube, while Wadell's definition gives 0.8.

As can be seen from Fig. 1, the sphericity of the simulated clusters tends to decrease as the amount of Ge in the cluster increases. This is due to the slower mobility of Ge atoms as compared to Si
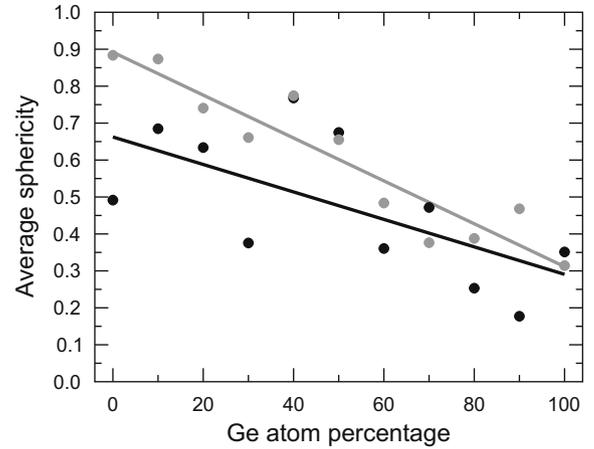
Fig. 1. Average sphericity of simulated clusters as a function of Ge atom percentage within the cluster. Grey dots indicate runs that used the Stillinger–Weber potential and black dots runs that used the Tersoff potential. The lines are linear fits to the data of the corresponding color.

atoms. What is also apparent is that on average, the Stillinger–Weber potential seems to produce clusters with a higher sphericity than the Tersoff potential. Two examples of clusters and their corresponding sphericities are shown in Fig. 2.

To investigate the spatial distribution of the Si and Ge atoms, their average distance from the center of mass of the clusters was calculated. Naturally, the lower the sphericity, the higher the average atom distance becomes — to clean up the data, only clusters with a sphericity of 0.5 or above were considered in the analysis. The remaining results for all runs were averaged, and are shown in Fig. 3.

In the case of the Stillinger–Weber potential, the surface segregation of Ge clusters is clearly visible: at low Ge concentrations, average Ge distances are much higher than average Si distances, which fall below the value for a perfect Si cluster. As the proportional amount of Ge atoms increases, the average atom distances decrease, approaching the value for a perfect cluster. In the case of the Tersoff potential, this effect is also apparent, but at a clearly smaller scale.

Another difference in the results between the two potentials is the distribution of the structure parameter P_{st} in the condensed clusters. The structure parameter is defined for each atom i as

$$P_{st}(i) = \frac{1}{p_u(i)}\left(\sum_j (\theta_i(j) - \theta_i^p(j))^2\right)^{1/2}$$
$$p_u(i) = \left(\sum_j (\theta_i^u(j) - \theta_i^p(j))^2\right)^{1/2} \tag{3}$$

where $\theta_i(j)$ is a list of the $n_{nb}(n_{nb}-1)/2$ angles formed between atom i and its n_{nb} nearest neighbors. The number n_{nb} is determined from the ideal crystal structure, and is 4 for the diamond structure (both Si and Ge). $\theta_i^p(j)$ is the distribution of angles in a perfect lattice and $\theta_i^u(j) = j\pi/n_{nb}(n_{nb}-1)/2$ the uniform angular distribution [21].

The structure parameter can be used to determine how well the atoms in a cluster have settled into a lattice formation according to their relative angles; for reference, $P_{st} = 0$ for all atoms of a perfect crystal lattice. The distributions shown in Fig. 4 indicate that for the Tersoff potential, the condensed clusters are primarily crystalline, since the centroid of the distribution peak of the structure parameter is below 0.2; but there is a number of values above 0.2, implying that the clusters consist of many nanocrystalline regions instead of a single crystal lattice. With the Stillinger–Weber potential, however, the peaks are not as well defined with clusters
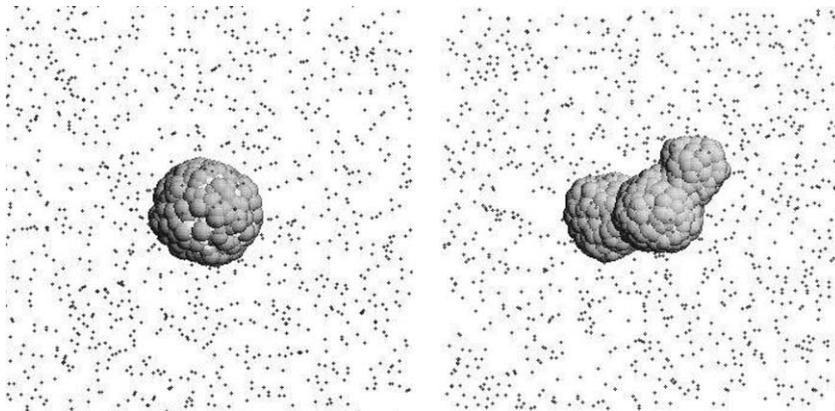
Fig. 2. Clusters of Si_xGe_{1-x} with $x = 0.8$ (left) and $x = 0.2$ (right) condensed using the Stillinger–Weber potential. The sphericities are 0.92 and 0.14, respectively.
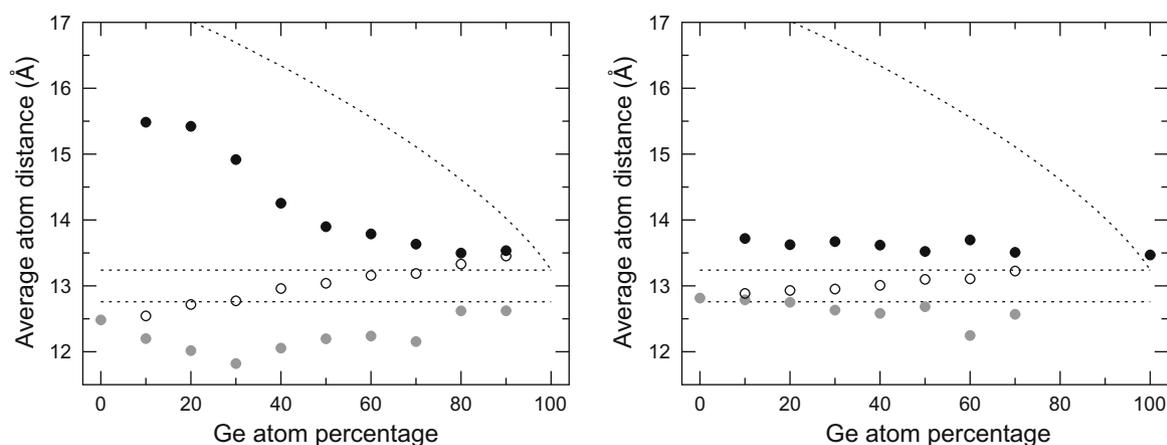

Fig. 3. Average distances of Si (grey) and Ge (black) atoms from the center of mass of the cluster using the Stillinger–Weber (left) and the Tersoff (right) potentials. The empty circles denote average distances of both Si and Ge atoms combined; the horizontal dotted lines represent the average atom distances for perfect clusters of Si (lower line) and Ge (higher line); the curved dotted line represents the average distance of Ge atoms as a function of percentage in a perfect cluster where the Ge atom distribution starts at the surface of the cluster. The results for 80% and 90% Ge for the Tersoff potential are missing because none of the clusters attained a sphericity above 0.5.
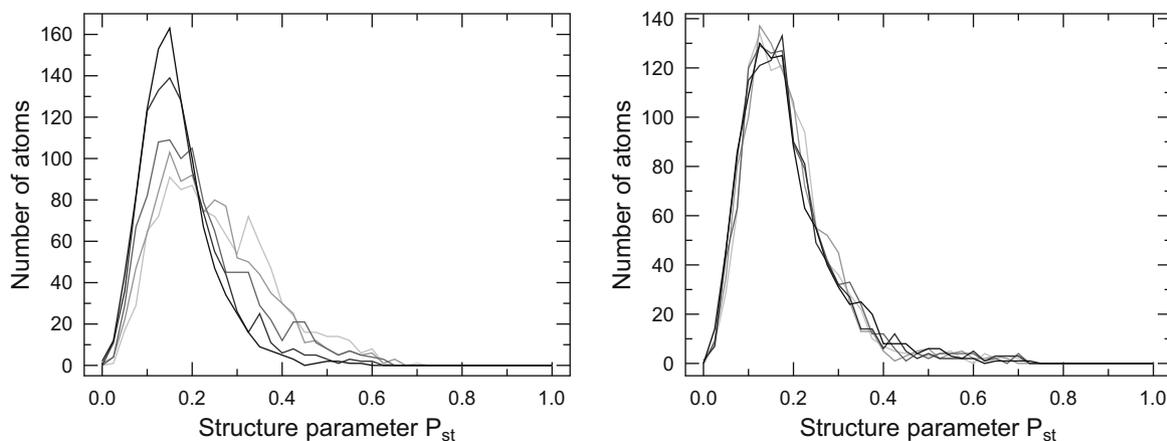

Fig. 4. Distribution of the structure parameter P_{st} in the condensed cluster using the Stillinger–Weber (left) and the Tersoff (right) potentials. The darker the line, the higher the Ge concentration. Only clusters with sphericities above 0.5 were used.

of low Ge concentration, implying that the atoms in clusters consisting primarily of Si have not settled into nanocrystalline regions to as great an extent as with the Tersoff potential. A higher temperature might have caused some annealing to happen, but the simulations run at 600 K did not yield any better results in this respect.

4. Conclusions

Spherical or near-spherical clusters were not obtained in all of the simulations. From these simulations alone, it is impossible to say whether this is an effect of short simulation time, or whether

the acquired statistics are expected to match those of experimentally produced cluster shapes. However, it can be confirmed that increasing the system temperature to 600 K had no visible effect on improving the average sphericity of the condensed clusters. This suggests that there is some degree of stability even in the clusters with low sphericity — those consisting of two or more smaller spherical clusters sticking together, as in Fig. 2.

As for the surface segregation of Ge atoms, the results for the Stillinger–Weber potential clearly support earlier computational and experimental findings. It is curious to note the level at which the results for the Tersoff potential differ; the average Ge atom distances stay close to that of a perfect Ge cluster instead of approaching the upper limit outlined in Fig. 3.

To conclude, all results clearly support the observation that Ge atoms have a tendency to segregate to the surface of the clusters, although the magnitude of this effect depends on the potential used for the simulations. Another finding is that there is a random tendency for the atoms to form non-spherical clusters, and that this tendency grows with the increased concentration of Ge atoms.

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