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Investigation of helium interstitials aggregation in silicon: Why bubbles formation by a self-trapping mechanism does not work

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ABSTRACT

First-principles calculations of the aggregation of helium interstitials in silicon have been performed to determine whether the first steps of helium-filled bubbles formation could occur by a self-trapping mechanism. These simulations show that the interaction between helium interstitials is repulsive, of low magnitude, and that this effect will saturate for a large number of interstitials. Considering the relaxation of the computational cell only leads to a small reduction of the binding energy. These results imply that the aggregation of interstitial helium atoms is highly unlikely in silicon, which allowed us to conclude that a self-trapping mechanism can not occur, and that an initial amount of vacancies is required for helium-filled bubbles formation.

1. Introduction

It is well established that helium implantation in silicon could lead to the formation of helium-filled extended defects such as platelets or bubbles, depending on the experimental conditions [1–5]. These defects have been found useful in electronics applications, for gettering or as one of the key ingredient in SOI fabrication by the layer splitting process. However, what is less known is the sequence of elementary mechanisms that are successively activated during the creation and evolution of these defects. Self-trapping of helium atoms is one of these, which could occur during the initial steps of formation, as proposed in the case of metals [6,7]. In the latter, the energetically favored clustering of helium interstitials leads to the spontaneous creation of vacancies by expelling lattice atoms. Therefore, helium-filled bubbles formation is possible with no need of an initial population of vacancies.

It is not clear whether such a process could occur in silicon, especially because there is a serious lack of information regarding the aggregation of helium interstitials. In fact, most of the available data concern the structure and stability of a single helium atom, in interstitial configuration or interacting with mono and divacancies [8–13]. It seems that only Alatalo and co-workers have studied the interaction between two interstitial helium atoms [8]. Their first-principles calculations indicated an energy gain of 0.08 eV when the two helium atoms are brought in neighboring interstitial sites. From this result, it was proposed that the self-trapping mechanism could occur in the He:Si system. However, the authors also suggested that further investigations considering more than two helium atoms were needed before drawing definitive conclusions.

In this paper, we report first principles calculations of the aggregation of helium atoms in silicon. Our results show that the interaction is always repulsive, in contradiction with the aforementioned work, which suggests that the self trapping mechanism proposed by Wilson et al. [6] is not relevant for helium in silicon. Instead, we conclude that silicon vacancies are needed for helium-filled bubbles to form.

2. Methods

To model the helium aggregation in silicon, we considered a $3a_0 \times 3a_0 \times 3a_0$ supercell, a_0 being the lattice constant of silicon, periodically repeated along all directions. This amounts to 216 silicon atoms. Our calculations were performed in the framework of density functional theory, using the Perdew–Burke–Ernzerhof exchange correlation functional [14], the PWscf code [15] from the Quantum-ESPRESSO project [16], and ultrasoft pseudopotentials [17]. Wave functions were expanded on a plane-wave basis, with an energy cutoff of 15 Ry. a_0 was computed to be equal to 5.468 Å, in good agreement with the experimental value of 5.43 Å. The Brillouin zone sampling was made with a $\frac{1}{2}$-shifted 2^3 Monkhorst–Pack grid of k-points [18], equivalent to a set of 4 irreducible k-points. Finally, each configuration was relaxed using the Broyden-Fletcher-Goldfarb-Shanno quasi-Newton algorithm, with

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a force criterion of 10^{-3} eV Å^{-1} to ensure well converged final structures.

This computational setup has been validated by calculating silicon vacancies. For the monovacancy, a formation energy of 3.33 eV was obtained, and the relaxed structure exhibited the correct D_{2d} symmetry, in excellent agreement with previous calculations [19,20]. For the divacancy, the calculated formation energy of 5.05 eV yields a binding energy of 1.61 eV for two monovacancies, again in agreement with previous works [21].

In this work, the formation energy E^f associated with the insertion of n helium atoms in silicon is computed according to the usual definition $E^f = E(\text{bulk} + n\text{He}) - E(\text{bulk}) - nE(\text{He})$, where $E(\text{bulk} + n\text{He})$ is the energy of the configuration of interest, $E(\text{bulk})$ the silicon bulk energy, and $E(\text{He})$ the energy of a single helium atom. All energies are computed in the same reference cell. The binding energy E^b of a cluster of n helium atoms is then obtained as the formation energy differences using as a reference a dilute configuration, in which the n helium atoms are well separated and in interstitial positions. Then $E^b = E^f(n\text{He}) - nE^f(\text{He})$, with $E^f(\text{He})$ the formation energy of a single interstitial helium atom.

3. Results

The most stable interstitial configuration for a single helium atom in silicon is the tetrahedral site, so called because it is surrounded by four silicon neighbors with a distance equal to the first-neighbor distance of the cubic diamond lattice. This is confirmed by previous investigations [8–11,13], although the reported formation energies vary from 0.77 eV [8] to 1.28 eV [9]. Possible other locations are the hexagonal and bond-center sites. Both are higher in energy than the tetrahedral site [11,13], and in the following only tetrahedral interstitials will be considered. The formation energy E^f of a single interstitial is 0.992 eV as computed with our computational setup.

First insights about interstitial helium aggregation are obtained by adding a second helium. Initially positioning this atom to the first neighbor tetrahedral site leads to a stable structure (Fig. 1). The distance between the two helium atoms after relaxation is found to be 2.304 Å, i.e. 3% lower than the initial tetrahedral sites separation. We found that the formation energy of this configuration is 2.028 eV, which is 0.044 eV larger compared to two infinitely separated interstitials. Thus the interaction between two first neighbors helium interstitials is repulsive, in disagreement with the interaction energy of −0.08 eV described in the earlier work of Alatalo and co-workers [8]. To understand this difference, we have performed calculations using a relatively similar computational setup than in this work, i.e. with a cell including 64 silicon atoms and a Brillouin zone sampling restricted to the Gamma point. In that case, the result of Alatalo et al. is partially recovered since the interaction between the two helium atoms now becomes attractive with an energy of −0.011 eV. Then the apparent disagreement is likely due to the limited accuracy and cell size used in this pioneering work.

Note that additional calculations were performed starting with the second helium atom closer to the first one, but the structure previously described was always recovered after relaxation. Instead, another stable configuration was obtained only when the two helium atoms were initially located at a second neighbors separation (Fig. 1). The corresponding binding energy, 0.02 eV, was lower than previously but remained positive. This was expected since the interaction should decrease as a function of the helium interstitials separation. Relaxation tends to slightly enlarge the distance between the helium atoms, but by less than 1%.

Next we considered structures including larger compact interstitials clusters, with respectively five and eight helium atoms initially located in first-neighbor tetrahedral sites (Fig. 2). In the first case, after relaxation, we found a positive binding energy of 0.096 eV, indicating a repulsive interaction between helium atoms. The aggregated configuration is then energetically less stable than the dilute one. Analysis of the final structure revealed that the interstitials cluster has lost its initial symmetry during relaxation. In fact, the central helium atom slightly shifted along a ⟨111⟩ direction, resulting in three helium-helium distances shortened by 1%, and the last one enlarged by 5%.

In the case of the eight helium atoms cluster, the initial interstitials configuration is overall retained after relaxation (Fig. 2). The separation between the two central helium atoms is shortened by 3%, while the other distances are slightly enlarged by about 1%. Regarding the interaction between helium atoms, the computed binding energy of 0.128 eV again points to a repulsive behavior.

The Fig. 3 shows the variation of the calculated formation energy as a function of the number of clustered helium atoms, which is almost linear. The computed binding energy is also increasing, highlighting the repulsive interaction, but with a rate seemingly decreasing. This would suggest that for a large number

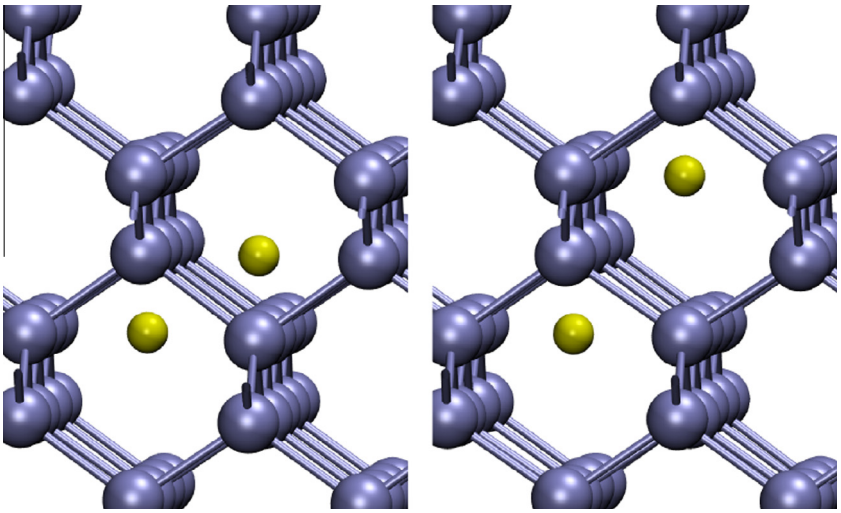

Fig. 1. Relaxed structures for two interstitial helium atoms (yellow spheres) initially located at first neighbor (left) and second neighbor (right) separations in silicon (blue spheres). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

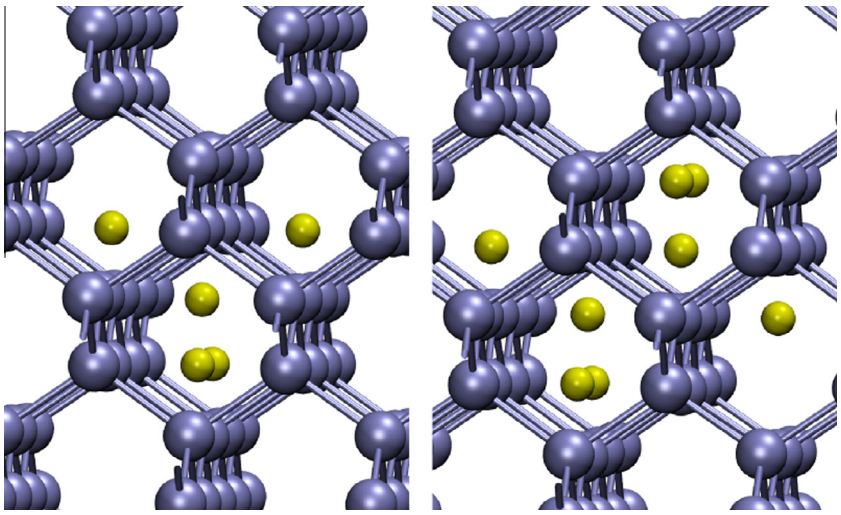

Fig. 2. Relaxed structures including five (left) and eight (right) clustered interstitial helium atoms (yellow spheres) in silicon (blue spheres). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

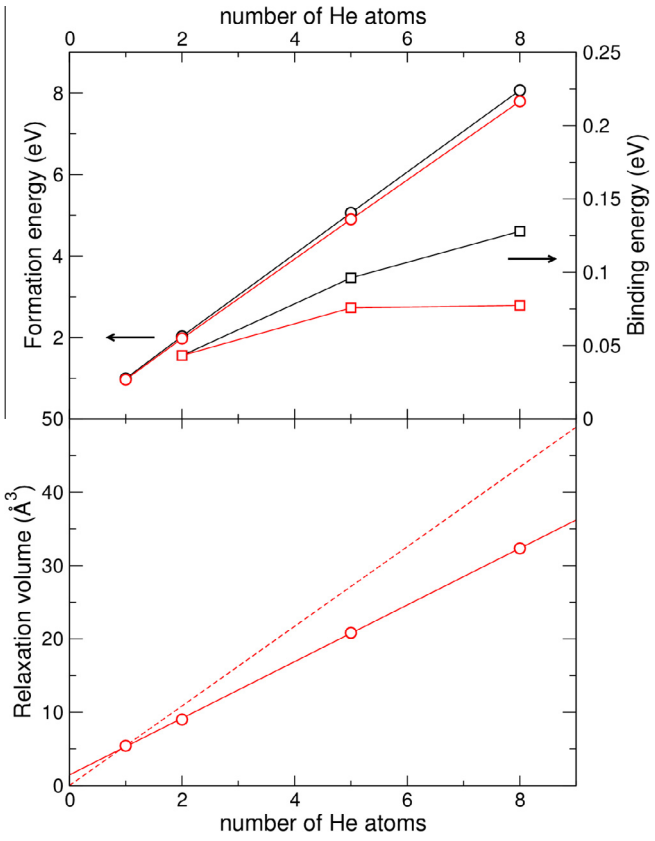

Fig. 3. Top panel: Formation and binding energies of clustered interstitial helium atoms, red curves corresponding to values calculated with relaxation of the cell. Bottom panel: Relaxation volume defined as the volume change upon cell relaxation for the clustered interstitial helium atoms (full line), and for a dilute configuration (dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of helium atoms, the binding energy will converge to a constant value. At this stage, there would be neither loss nor gain in energy by adding an interstitial helium atom to an already formed large clusters. An important point is that this threshold value is relatively low. In fact, even if the cluster sizes selected here are too small to reach an asymptotic behavior, one can safely assume that the binding energy will remain lower than + 0.2 eV.

First-principles calculations are typically limited in dimensions, and a potential issue is the artificial constraint associated with a fixed computational cell size. It has been investigated here by performing variable cell calculations [22]. In that case, the increase of the formation energy as a function of the number of helium atoms is now slightly lower (Fig. 3). As a consequence, the binding energy is also lower, and tends to converge faster to a constant value of about + 0.08 eV. Finally, the volume change due to the relaxation of the cell is represented in the bottom part of the Fig. 3. This relaxation volume is positive, in agreement with the experimental observations of a swelling phenomenon when helium is inserted into materials. Furthermore, it follows an almost perfect linear variation, with a slope coefficient of 3.86 $Å^3$/He. It is noteworthy that in the case of a single helium atom, the computed relaxation volume is larger and equal to 5.43 $Å^3$. In the case of a dilute configuration including spread interstitial helium atoms, the relaxation volume should be proportional to this value (dashed curve in Fig. 3), leading to much higher dilation of the system. Then the clustering of the interstitial helium atoms would result in a softening of the swelling effect.

To examine further the influence of the limited system size on the results, we have also performed calculations using a classical interatomic potential [12]. Comparing formation energies computed in $3a_0 \times 3a_0 \times 3a_0$ and $4a_0 \times 4a_0 \times 4a_0$ supercells for the previous configurations, differences of at most 0.03 eV were obtained with or without cell relaxation. This suggests that the system size used for first-principles calculations is appropriate for the small interstitials clusters considered here.

4. Discussion

Our calculations revealed that the interaction between interstitial helium atoms in silicon is repulsive and of low magnitude. When the size of the cluster increases by adding extra interstitial helium atoms, the binding energy seems to converge to a constant value. The fact that the interaction is repulsive for small clusters indicates that the aggregation of interstitial helium atoms is highly unlikely to occur in silicon. Note that in our calculations, finite temperature effects were not considered. Those have been shown to slightly change the formation energies in specific situations. Given the low magnitude of energy differences involved in our investigations, one could not exclude the possibility that considering these finite temperature effects might in fact lead to a reverse

of the sign of the binding energy, and thus a weak attraction for small clusters. In any cases, however, the low magnitude of the interaction will be of the same order than thermal energy at temperatures relevant for helium bubbles formation. Then the lifetime of such a cluster of helium atoms would be extremely short. It is then reasonable to conclude that helium interstitial aggregation in silicon does not occur.

This has obvious consequences regarding the possible occurence of a self-trapping mechanism for initiating the formation of helium-filled bubbles. In this mechanism, a cluster of interstitial helium atoms becomes unstable, compared to the formation of a vacancy accommodating the helium atoms. To estimate the feasibility of such a process, one has to compare the formation energy of a cluster of n helium interstitials and a He_nV complex. Unfortunately, there are no published data regarding the formation energies of He_nV complexes in silicon for $n > 2$. We have recently performed calculations, to be published elsewhere, which suggest that the instability is reached for $n = 11$ helium atoms. Since the clustering of as many helium atoms is not possible according to the aforementioned conclusion, it results that a self-trapping mechanism can not occur in silicon. Obvious consequences are that helium filled bubbles can form in silicon only if a certain concentration of vacancies is present. This is in agreement with experiments showing that bubbles appear at places of maximum vacancy concentration [3].

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