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## ACCEPTED MANUSCRIPT

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# Influence of helium on the nucleation and growth of bubbles in silicon: a multiscale modelling study

Laurent Pizzagalli<sup>1</sup>, Julien Dérès<sup>1</sup>, Marie-Laure David<sup>1</sup>, and Thomas Jourdan<sup>2</sup>

<sup>1</sup> Institut Pprime - CNRS UPR3346, Université de Poitiers, F-86962 Chasseneuil Futuroscope Cedex, France

 $^2$  Paris Saclay Univ, CEA, DEN Serv Rech Met Phys, F-91191 Gif Sur Yvette, France

E-mail: laurent.pizzagalli@univ-poitiers.fr

Abstract. The formation and growth of helium-filled cavities in silicon have been investigated using both molecular dynamics simulations and rate equation cluster dynamics calculations. This multiscale approach allowed us to identify atomic scale mechanisms involved in nucleation and early growth steps, and to follow their dynamics over experimental timescales. We especially focus our analyses on the influence of helium. Our results first suggest that both Ostwald ripening and migration-coalescence mechanisms are jointly activated during bubble growth. We also discover that an original mechanism, based on the splitting of bubbles, could have a significant contribution. Overall, helium atoms are found to delay growth, proportionally to their concentration. This can be clearly observed at the nanosecond timescale. However, for longer timescales, cluster dynamics calculations also reveal periods of accelerated growth for specific helium concentrations. Finally, it is determined that the main effect of Si interstitials is to impede bubble growth, due to an early recombination with vacancies.

*Keywords*: semiconductors; irradiation; cavities; molecular dynamics; rate equation cluster dynamics

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#### 1. Introduction

The formation of helium-filled bubbles in solids is an ubiquitous and well documented phenomenon [1–5], especially because of its tremendous importance in a nuclear context. In fact, a significant amount of helium can be introduced in structural materials from neutroninduced nuclear reactions or in the presence of plasma in fusion reactors. Because of their low solubility, helium atoms tend to aggregate and promote cavities formation, ultimately leading to pressurised bubbles. Depending on materials, the presence of such bubbles can trigger various mechanisms such as void swelling, embrittlement, surface roughening and blistering, that could significantly degrade mechanical properties.

In a semiconductor like silicon, helium-filled bubbles were also extensively studied as an efficient means to produce voids [6, 7]. Those latter can be used in several materials processes like the gettering of metallic impurities [8, 9], the manufacturing of silicon-on-insulator devices using wafer splitting techniques [10], surface engineering [11], or the control of both point defects concentrations [12] and lifetime of minority carriers [13].

The formation of these bubbles is a complex phenomenon, which is not yet fully understood nowadays. Initial steps depend on how helium atoms interact with the host material, and in particular with structural defects like vacancies or grain boundaries, to form helium bubbles precursors. The next steps are the growth and coarsening of these small aggregates, finally yielding large bubbles. Furthermore, the fact that helium atoms are usually inserted into materials as energetic particles, adds further complication to the whole process.

In silicon, we have at disposal a wealth of information regarding the interaction between few helium and matrix atoms, especially thanks to firstprinciples calculations [14–18]. First, it is commonly agreed that a helium atom tends to preferentially sit in a tetrahedral interstitial site. Counterintuitively, a silicon mono-vacancy is not an attractive centre for a single helium atom. However, the insertion of the helium atom into vacancy aggregates is energetically favourable, starting with the divacancy. The lowest energy diffusion path corresponds to the helium interstitial migrating through an hexagonal site, with an activation energy of about 0.6-0.8 eV [19, 20]. Another well established quantity,

both experimentally [6, 21, 22] and theoretically [23], is the energy equal to 1.7–1.8 eV that is required for the helium atom to effuse out of well formed bubbles.

In comparison, little is known regarding the next steps leading to helium-filled bubbles. Theoretical investigations reveal that bubble formation by helium interstitial clustering, i.e. the self-trapping mechanism originally proposed in metals [24], is unlikely [14, 15, 25]. This obviously suggests that vacancies play an essential role in the case of silicon. Recently. Pizzagalli et al. performed molecular dynamics (MD) calculations in an attempt to unravel the complex interplay between helium atoms and silicon They find that the helium bubble vacancies [26]. precursors are created in a two steps process, with first the fast formation of vacancy aggregates, which are next slowly filled with helium atoms. Little further information could be extracted from these simulations, because of the poor statistics associated to the small computed systems sizes, and the fact that only one set of helium and vacancy concentrations was tested. In the present work, we perform similar MD simulations, with larger systems and for a wide range of conditions, aiming at a better understanding of helium bubble initiation, and in particular of the influence of helium atoms.

Another important aspect concerns the growth of helium-filled bubbles during implantation or annealing. A description of the different proposed mechanisms can be found in [1]. A bubble can grow by the ejection of self-interstitials from the host material, thus increasing the bubble size by vacancies creation. When a single interstitial is involved, this mechanism is usually named trap mutation. A collective ejection of self-interstitials can occur through dislocation loop punching. Other mechanisms assuming interaction between bubbles are migration and coalescence (MC) and Ostwald ripening (OR). With the former, a large bubble is obtained as the product of the coalescence of two smaller migrating bubbles. In the second process, small, energetically less favourable bubbles will slowly shrink, freeing vacancies and helium atoms which will contribute to the growth of the largest bubbles. These mechanisms have been largely investigated in the literature, especially for metals [27]. In silicon, MC and OR are the two most likely mechanisms. On the basis of a theoretical analysis, Evans concluded that OR is unlikely to play any role, at least for temperatures below 1000 °C [28], thus hinting that

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Table 1. Numbers (#) of vacancies, helium, and Si interstitials used in MD simulations, and corresponding concentrations  $(C \times 10^{21} \text{ cm}^{-3})$ .

#	216	692	2162	6920	21626
С	0.05	0.16	0.5	1.6	5

cavity growth is probably driven by MC. Few years later, this conclusion was backed up by Donnelly [29]. Nevertheless, there are conflicting reports in the literature, with experimental evidences in favour of growth by the OR mechanism at temperatures lower than 1000 °C [30, 31]. A possible explanation could come from recent measurements of the helium density in nanometer-scale bubbles in silicon, that reveal surprisingly high values [32–35]. Large helium densities are assumed to significantly influence growth mechanisms, by changing activation energies for resolution during OR [36], or for bubble migration during MC [37], but there are not taken into account in existing models. A connected unanswered question is how such high helium densities could be attained. during bubble growth.

The MD method is not a realistic option for investigating bubble growth occurring during annealing experiments lasting several minutes or even hours [38]. In fact the duration of MD simulations can hardly exceed tens of nanoseconds for systems encompassing millions of atoms on current supercomputers. In addition, the amount of produced data can also become an issue. In the present work, we also perform simulations with the rate equation cluster dynamics (RECD) method since its allows for investigating initial formation of bubbles and their growth at human time scale.

The manuscript structure is the following. In the next section, the models and parameters for MD and RECD simulations are reported. In sections 3 and 4, the results are described and discussed, followed by the conclusion of this work in the section 5.

#### 2. Models and numerical simulations

## 2.1. Molecular dynamics

All the MD simulations reported in section 3 were carried out in the NVT ensemble using the LAMMPS code [39, 40], and the interatomic Si–He potential described in [26]. This potential is specifically designed to model the behaviour of helium atoms interacting with silicon vacancies [26]. Bulk silicon is modeled by a periodically repeated cubic supercell of side length  $30a_0$ , with  $a_0 = 5.431$  Å, encompassing 216000 atoms. Different quantities of interstitial helium atoms (He), of silicon vacancies (V), and of interstitials (I) are randomly introduced into the supercell before each MD run (Table 1). Helium and Si interstitial atoms are initially positioned in vacant tetrahedral sites of the cubic diamond lattice.

Thirty-three different configurations were investigated in this work. Twenty four of those include vacancies (numbers from 216 to 6920) and helium atoms (from 0 to 21626). The nine remaining configurations are selected cases with variable quantities of vacancies (2162 or 6920), helium atoms (692, 2162 or 6920), and interstitials (2162 or 6920). Table 1 shows the concentrations corresponding to these numbers. For helium, they are representative of the amount of atoms introduced at different depths in standard implantation experiments [38, 41]. For each (V, He, I) setup, two MD calculations are carried out with different parameters. In the first one, a temperature of 1000 K, an integration time step of 1 fs and a duration of 3 ns are used. In the second one, the temperature is 1400 K, the time step is 0.5 fs, and the duration is 1 ns. These high temperatures are typical of annealing processes, while helium implantation is usually carried out at ambient conditions. High temperatures are here necessary, in order to enhance thermal activation of growth mechanisms during the limited time span of molecular dynamics simulations.

A structural analysis is performed at frequent intervals during each simulation, allowing for identifying clusters and for extracting their dynamics. Our method is described in details in [26], and only general principles are reported here. First, the location and nature of all point defects (Si and He interstitials, vacancies) are obtained using a procedure similar to a Wigner-Seitz analysis. In a second stage, point defect aggregates are identified according to criteria of minimum separation between species. We considered that He and I interstitials belong to the same cluster when they are closer than 3 Å, i.e. approximately between the first and second neighbours distance in cubic diamond silicon. For V–V and V–I, a separation threshold of 4 Å is chosen. Finally, He and V are assumed to interact only for separations lower than 2 Å. Slightly different distance thresholds have been tested, with no significant changes on the conclusions presented hereinafter.

#### 2.2. Rate equation cluster dynamics

RECD calculations allow for modeling the nucleation and growth of clusters within a mean field approximation, by solving differential equations representing the variations of clusters concentrations as a function of time. A detailed description of the formalism can be found in the literature (see for instance [42] and references cited therein), and only theoretical foundations will be restated in the following.

In RECD, each differential equation describes the concentration evolution of a class of clusters corresponding to defined numbers of vacancies and helium atoms. Assuming that  $V_n He_n$  clusters are all mobile, each equation should include terms corresponding to exchange flux between this specific cluster class and all other classes of clusters with different amount of vacancies and helium atoms. In theory, both OR and MC mechanisms can then be described in RECD calculations. However, the numerical resolution of a large set of coupled differential equations is only feasible if a limited number of exchange terms is considered. Therefore, it is customary to assume that only monomers, i.e. monovacancy and single helium atom, are mobile. Consequently, the MC process is usually neglected in current RECD calculations, although some earlier works have attempted to take this complexity into account [43, 44].

The exchange fluxes between cluster classes depend on the concentration of the concerned species, which are variables in the calculations, and on absorption and emission coefficients. Those latter can be determined from the binding energies of monomers to clusters, as well as from diffusion coefficients of the mobile species. RECD calculations are often used to simulate irradiation processes yielding only vacancies and self-interstitials. In the present work, we also need to consider helium as a third monomer species. Prior to RECD calculations, we have then carried out a large amount of calculations, using LAMMPS and the same interatomic potential than in the aforementioned MD simulations, in order to determine the binding energies for any  $V_n He_p$  cluster. These calculations, and other relevant parameters, are described in the Appendix A.

In this work, we used the CRESCENDO code [42] to perform the RECD calculations. Starting from selected concentrations of monovacancies, helium atoms, and silicon interstitials, the dynamics of cluster populations are calculated at a chosen temperature. No source or sink terms were added in the rate equations, i.e. we simulate the evolution of a closed system, within the same conditions than for molecular dynamics calculations. This allows for a meaningful comparison between the two approaches.

# 3. Molecular dynamics results

#### 3.1. A typical scenario

Figure 1 represents the variation as a function of time of various quantities characterizing the evolution of a representative MD system. At short times, it is

**Figure 1.** Evolution of various indicators during a molecular dynamics simulation (here for an initial configuration of 2162 vacancies and 6920 helium atoms, and T = 1400 K). a) remaining vacancies  $V_1$  (blue), vacancies in  $V_n$  clusters (red), vacancies in  $V_2$  clusters (green), vacancies (maroon) and He atoms (yellow) in  $V_n$ He<sub>p</sub> clusters, expressed as percentages relatively to the initial numbers of vacancies and helium atoms. b) He/V ratio averaged over all formed  $V_n$ He<sub>p</sub> clusters (blue). c) average size of  $V_n$ He<sub>p</sub> (blue) and  $V_n$  (red) clusters, in number of vacancies. d) average numbers of  $V_n$ He<sub>p</sub> (blue) and  $V_n$  (red) clusters. For a color version of the figure, the reader is referred to the online version of the article.

instructive to first focus on the amount of free monovacancies, which decreases according to an exponential law (Fig. 1-a). In fact, after 20 ps only 50% of the initial  $V_1$  remain, and this proportion falls to 20%at 80 ps. Silicon mono-vacancies are highly mobile at the temperatures considered here, due to a low migration energy in the range 0.30-0.45 eV [45-47]. The V<sub>1</sub> species diffuse until they encounter other monovacancies, leading to an increasing number of the energetically favoured V<sub>2</sub> aggregates (Fig. 1-a). A maximum is quickly attained, here at about 11 ps for the chosen example, since larger  $V_n$  clusters also form by further addition of  $V_1$ .  $V_2$  are known to migrate with an activation energy of about 1.2 V [48], meaning that they are nearly static in the time span of the MD simulation. Each  $V_2$  is then potentially a nucleus for a larger  $V_n He_p$  cluster. In this example the mean size of  $V_n$  clusters does not exceed n = 3 (Fig. 1-c). A maximum number of about 250  $V_n$  clusters is reached at about 22 ps (Fig. 1-d), which also corresponds to the maximum proportion of  $V_1$  in  $V_n$  clusters (Fig. 1-a).

After 22 ps, the decrease of the amount of  $V_n$ seen in Fig. 1-d, is correlated to the increase of  $V_n \text{He}_p$ clusters, and is obviously due to the transformation of  $V_n$  to  $V_n \text{He}_p$  by capturing one or more He atoms. A single helium atom is indeed less mobile than  $V_1$ , with a migration energy of 0.68 eV [20], but enough to diffuse during the short MD time span. In contrast with

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 $V_n$ , the mean size of  $V_n He_p$  aggregates continuously increases during the simulation. Due to the large amount of helium in the chosen example, it is indeed unlikely that large  $V_n$  cluster could grow without capturing at least one helium.

At intermediate times and up to the end of the simulation, almost all V<sub>1</sub> can be found in V<sub>n</sub>He<sub>p</sub> clusters (Fig. 1-a). Two different phenomena can also be observed. First, the amount of He atoms in V<sub>n</sub>He<sub>p</sub> increases over time (Fig. 1-a). Although this is a slow process, it is only partially compensated by the growth of the V<sub>n</sub>He<sub>p</sub> clusters, leading to an increase of the He/V ratio (Fig. 1-b). Second, the expansion of V<sub>n</sub>He<sub>p</sub> clusters is accompanied by a decrease of their number, in agreement with the intended growth behaviour. At last, it is noteworthy that pure helium aggregates are not found, as expected [25].

The analysis of all the investigated configurations reveals that three stages can be defined during MD simulations. The first one occurs at the very beginning, with the formation and growth of the slow  $V_n$  clusters (with  $n \geq 2$ ) from the aggregation of the highly mobile  $V_1$ . The second stage is associated to the nucleation of the  $V_n He_p$  clusters and the waning of the  $V_n$  clusters. Finally, a last stage would correspond to the growth of  $V_n He_p$  clusters. These three stages always occur in this specific order, but their duration and starting times greatly depend on the initial amounts of He and  $V_1$ . For instance, for configurations with high initial concentrations of both species, the formation of  $V_n He_p$  clusters, typically  $V_1 He_2$ , can occur almost from the start of the simulation.  $\_Unlike V_1He_1,$  $V_1$ He<sub>2</sub> aggregates are energetically favoured, but they only form when two helium atoms and a vacancy are very close to each other. The three stages scenario applies to all simulations, except for the largest initial V<sub>1</sub> concentration ( $[V_1]=1.6 \times 10^{21} \text{ cm}^{-3}$ ) and 1400 K. In the latter case, the crystalline lattice is progressively destabilised during the calculation, leading to amorphous silicon and the failure of the structural analysis. These runs are then not used in the remainder of this paper.

We have at disposal the evolution of various quantities for all tested configurations, which amounts to a large number of data and makes difficult to go beyond a qualitative analysis. In fact, we have attempted to fit the curves shown in Fig. 1 with mathematical laws corresponding to different coalescence and coarsening models [49–52], in order to evaluate their relevance and to eventually quantify the influence of helium on nucleation and growth processes. Unfortunately, results were not satisfactory, probably because of a significant overlap between the three stages identified in MD simulations. In fact, the evolution of a given quantity often reflects both the initial structuring from the starting random organization of He and V<sub>1</sub> species, and the beginning of bubble growth. Remaining at a qualitative level, the influence of helium during the three stages essentially concerns the transformation of V<sub>n</sub> to V<sub>n</sub>He<sub>p</sub>, which starts sooner and is more intense for high helium concentrations. It also seems that a large amount of initial helium atoms tends to delay the formation V<sub>n</sub> clusters, by restricting the mobility of V<sub>1</sub>. Furthermore, it also makes the direct formation of V<sub>1</sub>He<sub>2</sub> clusters more likely.

#### 3.2. Final states

To circumvent the complexity associated to the large amount of data, we focus the analysis on the final states of the MD simulations. Figures 2 and 3 represent the variation of the quantities defined in Fig. 1, as a function of the initial numbers of He and  $V_1$ , at the end of the MD simulations. Focusing first on the remaining proportion of free mono-vacancies (Fig. 2a,b), it clearly appears that for both temperatures the survival rate of  $V_1$  is inversely proportional to their initial concentration. At 1000 K and low initial  $[V_1]$ , at best 37% of the initial  $V_1$  survive whereas only a few residual percents are found for  $[V_1] \ge 5 \times$  $10^{20}$  cm<sup>-3</sup>. In fact, the probability that a mobile V<sub>1</sub> encounters another  $V_1$  during the simulation time span increases with the  $V_1$  concentration. A similar trend is obtained for 1400 K simulations, except that 57% of  $V_1$  can be found in the most favourable conditions. A thorough analysis of these simulations reveals that at such high temperature, small  $V_n$  clusters like  $V_2$  are less stable than at 1000 K. The latter frequently dissociate, resulting in a significant and constant proportion of free  $V_1$ . Moreover, helium atoms are found to markedly influence the exhaustion of V<sub>1</sub> atoms at low initial  $V_1$  concentrations. At 1000 K, the proportion of remaining  $V_1$  increases with the helium concentration. A possible explanation is that the helium atoms mobility is limited at this temperature, and helium atoms tend to act as obstacle to  $V_1$  diffusion (since a  $V_1$ He<sub>1</sub> aggregate is not energetically favoured), thus preventing the formation of clusters. Conversely, at 1400 K, the amount of remaining free  $V_1$  decreases as a function of helium concentration. On the one hand, helium atoms are more mobile and are less efficient to impede  $V_1$  diffusion. On the other hand, at large He concentration, the probability of forming  $V_n He_p$ clusters increases, and those latter are more stable than  $V_n$  clusters and less prone to dissociation.

Figure 2-c represents the remaining  $V_2$  clusters, and clearly suggests that  $V_2$  is an intermediate species, quickly disappearing in most of cases. Significant proportions are found only for low  $V_1$  and He concentrations, in agreement with the above mentioned



Figure 2. 3D representation of various quantities as a function of initial concentrations of  $V_1$  and of He atoms, at the end of MD simulations: a) free  $V_1$ ; b) free  $V_1$  (1400 K); c) vacancies in  $V_2$ ; d) vacancies in  $V_n$  clusters; e) vacancies in  $V_n$ He<sub>p</sub> clusters; f) He atoms in  $V_n$ He<sub>p</sub> clusters. All quantities are expressed as percentages relative to the initial amounts of either  $V_1$  (for a - e) or He atoms (for f). Colored surfaces are obtained by linear interpolation of the MD data (marked as white circles on surfaces). All curves correspond to simulations performed at 1000 K (3 ns), except b) which is obtained from runs at 1400 K (1 ns). For a color version of the figure, the reader is referred to the online version of the article.

analysis. A similar trend is obtained at 1400 K, overall with lower values (not shown here). When no helium atoms are present, V<sub>2</sub> are progressively transformed to larger  $V_n$  aggregates. This mechanism is more efficient for large initial  $V_1$  concentration, since the probability of a free  $V_1$  to be captured by existing  $V_n$  increases (Fig. 2-d). The final proportion of  $V_n$  decreases as a function of the initial He concentration, which is obviously caused by the transformation of  $V_n$  into  $V_n He_p$  clusters, and the high stability of those latter. Examining Fig. 2-e confirms this mechanism, the final proportion of  $V_n He_p$  increasing with the initial He concentration. The effect is more pronounced at high initial  $V_1$  and He concentrations, and also at 1400 K (not shown here). For instance, almost 100% of  $V_1$ are part of  $V_n He_p$  clusters, when  $[V_1] \ge 5 \times 10^{20} \text{ cm}^{-3}$ and [He]  $\geq 1.6 \times 10^{21}$  cm<sup>-3</sup>, at 1000 K. Finally, the proportion of He atoms contributing to  $V_n He_p$  clusters is shown in Fig. 2-f. We found an almost linear increase with the initial  $V_1$  concentration. Helium atoms are not highly mobile during the time span of the simulation, and their probability to encounter a  $V_n$  cluster increases with the initial  $V_1$  concentration, as will be revealed in the following. At most 42% of the He atoms contribute to  $V_n He_p$  clusters. Conversely, changing the initial He concentration does not seem to markedly influence the resulting value, especially at high initial He concentration. Note that this quantity is expressed as a function of the initial He concentration, and is then a relative value. Nevertheless, we have no explanations concerning the fact that the ratio of He atoms in  $V_n He_p$  is approximately constant for a given initial  $V_1$  concentration. The analysis of 1400 K simulations leads to similar conclusions than from Fig 2-d-f. The proportion of He atoms in  $V_n He_p$  is almost twice than at 1000 K, which confirms the importance of helium diffusion in the bubble precursor formation.

Other important properties for understanding bubbles formation and evolution are sizes and concentrations of both  $V_n$  and  $V_n He_p$  (Fig. 3). Our simulations unsurprisingly show that the highest  $V_n$ concentrations, about  $1.4 \times 10^{20}$  cm<sup>-3</sup> (for  $[V_1] = 1.6 \times 10^{21}$  cm<sup>-3</sup>, at 1000 K), are obtained when many  $V_1$ are initially present, with no He. Such conditions also yield the largest aggregates, composed of about 11.5  $V_1$ on average (Fig. 3-b). Larger sizes and thus lower

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Figure 3. 3D representation of various quantities as a function of initial concentrations of  $V_1$  and of He atoms, at the end of 3 ns MD simulations at 1000 K: a) concentration of  $V_n$  clusters (in em<sup>-3</sup>); b) Mean size of  $V_n$  clusters (in numbers of vacancies); c) concentration of  $V_n$ He<sub>p</sub> clusters (in cm<sup>-3</sup>); d) Mean size of  $V_n$ He<sub>p</sub> clusters (in numbers of vacancies); e) He/V ratio averaged over all formed  $V_n$ He<sub>p</sub> clusters. Colored surfaces are obtained by linear interpolation of the MD data (marked as white circles on surfaces). For a color version of the figure, the reader is referred to the online version of the article.

concentrations are predicted at 1400 K (not shown here). Decreasing the amount of initial V<sub>1</sub> leads to a significant decrease of concentration, towards zero (Fig. 3-a), and of size (Fig. 3-b), with final values about 2-3 vacancies. This is in agreement with the large proportion of V<sub>2</sub> in such conditions (Fig. 2-c). Similar trends are obtained when increasing the number of He atoms, for a given initial [V<sub>1</sub>]. This is obviously due to the transformation of V<sub>n</sub> into V<sub>n</sub>He<sub>p</sub> aggregates.

the transformation of  $V_n$  into  $V_n$ He<sub>p</sub> aggregates. Focusing now on  $V_n$ He<sub>p</sub> aggregates, the highest final concentration, equal to  $2.7 \times 10^{20}$  cm<sup>-3</sup>, corresponds to cases with the largest initial amounts of both  $V_1$  and He (Fig. 3-c). Decreasing any one or both significantly reduces the final  $V_n$ He<sub>p</sub> concentration to about  $2 \times 10^{19}$  cm<sup>-3</sup>. The variation of the average size of  $V_n$ He<sub>p</sub> clusters is different (Fig. 3-d). In fact, largest aggregates, with a mean size equal to about 15 vacancies, are obtained for a high initial amount of  $V_1$ but a low number of helium atoms. Adding more of the latter leads to smaller aggregates, with a mean size of 6 vacancies. For low initial  $V_1$  numbers, the average size is 2 vacancies, again highlighting the role of  $V_2$  as the smallest  $V_n He_p$  cluster. At 1400 K, similar trends are observed, albeit with larger variations (not shown here). The most important result here is certainly that largest clusters are obtained for low initial numbers of helium atoms. It is insightful of the influence of helium on the nucleation and growth of bubbles. It is also in agreement with the fact that  $V_n He_p$  clusters are more stable than  $V_n$  clusters with respect to dissociation, i.e. growth by the OR mechanism is slowed down. Alternatively,  $V_n He_p$  clusters can also be less mobile than  $V_n$ , thus limiting growth by MC.

Finally, Fig. 3-e shows the He/V ratio in  $V_n$ He<sub>p</sub> clusters. The largest values, ranging from 1 to 1.5, are obviously obtained for a high initial number of He atoms. For a given value of the latter it is also observed that the ratio increases when the amount of initial  $V_1$  decreases.

In brief, these analyses yield the following key conclusions: (i) the consumption of  $V_1$  could be either slowed down or accelerated according to the temperature and the initial He concentration; (ii) the  $V_1$  contribute to the growth of both  $V_n$  and  $V_n$ He<sub>p</sub>

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Figure 4. Cumulative numbers of vacancies (orange) and helium atoms (blue) involved in growth processes from 2 ns to 3 ns (1000 K), and from 0.5 ns to 1 ns (1400 K), for an initial configuration  $[V_1] = 5 \times 10^{20}$  cm<sup>-3</sup> and [He] = $1.6 \times 10^{21}$  cm<sup>-3</sup>. Each stacked bar corresponds to a different mechanism, schematically represented in the figure: (1) single He or vacancies gained by clusters, (2) single He or vacancies lost by clusters, (3) Multiple He or vacancies gained by coalescence (4) Multiple He or vacancies lost by splitting. Mechanisms 1 and 2 correspond to OR, whereas mechanism 3 corresponds to MC. For a color version of the figure, the reader is referred to the online version of the article.

clusters, the proportion of each of them being highly dependent on the initial He concentration; (iii) a substantial amount of large  $V_n$  aggregates can be obtained only for low initial He concentrations; (iv) more  $V_n He_p$  clusters are obtained when large numbers of both  $V_1$  and He atoms are initially present; (v) low initial He concentrations yield the biggest  $V_n He_p$ clusters.

#### 3.3. Growth mechanisms

In the section 3.1, we showed that the formation of  $V_n He_p$  aggregates from  $V_1$  and He atoms could be decomposed into three stages, with the last one corresponding to  $V_n He_p$  growth. It is especially important since it leads to the transformation of  $V_n He_p$ clusters into measurable helium-filled bubbles, and as such, has been largely studied [28–31]. However, there is no consensus whether the underlying mechanism ensuring growth is OR or MC.

Here, we analyse our MD simulations aiming at shedding light on this issue. A direct visual inspection of the systems evolution reveals several occurrences of the aggregation of two  $V_n He_p$  clusters, hinting that the MC mechanism is active at both 1000 K and 1400 K. However, the OR mechanism is hardly identified using this naive approach.

We then develop an analysis procedure to extract the relevant information from the MD simulations. First, it is important to use stretches of runs for which there is a minimum overlap between the different stages identified in section 3.1. Ideally, one would like to have a configuration with a high enough number of  $V_n \text{He}_p$  clusters, and with no remaining  $V_n$ . The best case in our MD runs corresponds to an initial setup  $[V_1] = 5 \times 10^{20} \text{ cm}^{-3}$  and  $[\text{He}] = 1.6 \times 10^{21} \text{ cm}^{-3}$ , at 1400 K (whose time evolution is represented in Fig. 1). In the time range 0.5-1 ns, the amount of residual  $V_n$  is low, and significant changes essentially concern  $V_n \text{He}_p$  aggregates.

To uncover growth mechanisms, it is necessary to unambiguously identify each one of the  $V_n He_n$ aggregates during the MD simulation, in order to monitor changes in terms of vacancies (i.e. size) and helium content. It is relatively easy to follow helium atoms, which are labeled in the simulation. Unfortunately, the same is not true for vacancies, and also for vacancy clusters by extension. A way around this issue is to use helium atoms contained in  $V_n$ He<sub>n</sub> clusters as markers for identification. By comparing the helium atoms contained in  $V_n He_p$ clusters between two consecutive snapshots, one can then track changes for each cluster. This approach relies on the assumption that helium exchanges with the silicon matrix or other aggregates remain negligible within the time separation between the two snapshots. To further strengthen the procedure, we impose that at least two identical helium atoms are found for a successful identification. The analysis is also restricted to aggregates composed of at least two vacancies.

For the selected case, at 1400 K, the analysis has been performed on 250 configurations, recorded every 2 ps, in the time range 0.5–1 ns. For comparison, we also studied the same system but at 1000 K, considering 250 configurations recorded every 4 ps in the time range 2-3 ns. The results are reported in Fig. 4. Focusing first on the highest temperature and mechanisms '1' and '2' corresponding to OR, one can see that there are approximately as many single vacancies separating from than aggregating to  $V_n He_p$ clusters. Balance was expected since almost all initial free vacancies were already part of aggregates in the investigated time span (Fig. 1). For helium, there are slightly more helium atoms joining clusters than leaving, in agreement with the low increase rate of trapped helium atoms from 0.5 ns to 1 ns (Fig. 1). Another observation is the lower amount of exchanged helium atoms compared to vacancies for mechanisms '1' and '2'. Although there are more vacancies in aggregates than helium atoms, this might be surprising since binding energies to  $V_n He_p$  derived from formation energies (see Appendix A) tend to be overall lower for helium than for vacancies. Instead, we believe this result is due to the fact that vacancies are highly mobile compared to helium atoms. Those latter are then likely to be recaptured by the same  $V_n He_p$  in the short time

between two snapshots, conversely to vacancies.

The other bars show the amount of helium and vacancies involved in mechanisms '3' and '4' sketched in Fig. 4. The first one corresponds to the coalescence of two aggregates, and is then representative of the MC process. The second one is usually not considered in the literature, and is associated to a fragmentation process, where a  $V_n He_p$  aggregate splits in two (or more) smaller clusters. We find that quantities related to mechanisms '3' and '4' are noticeably comparable, and larger than those corresponding to OR. The ratio of helium atoms to vacancies is about 0.5, which is slightly lower than the average He/V ratio ranging from 0.57 to 0.68 between 0.5 and 1 ns (Fig. 1-b). This would suggest that  $V_n He_p$  aggregates with low helium content are more involved in coalescence and fragmentation mechanisms.

Figure 4 also shows results for the same system, but at 1000 K. All previous mechanisms are found to be active, and in similar proportions. We note that the ratio of helium atoms to vacancies for mechanisms '3' and '4' is now 0.4, thus lower than previously, in agreement with the fact that there are in average less helium atoms in aggregates at 1000 K than at 1400 K.

Performing the analysis for other runs reveals that the mechanisms 1–4 are always active, but different proportions according to the conditions. Therefore an important conclusion is that we identified several growth mechanisms, among which OR and MC. Both have been extensively discussed in the literature, and their respective importance is the matter of debate [28-31]. In this work, we find that they are both active. However we emphasise that one should be cautious in using numbers reported in the Fig. 4, for determining whether OR or MC is the dominant mechanism. In fact, several factors could bias such an analysis. First, even if their number is low for the chosen conditions,  $V_n$  clusters aggregating with  $V_n$ He<sub>p</sub> clusters also contribute as a MC event. Second, the numbers in Fig. 4 depend on distance thresholds in cluster analysis. A third factor is related to the fact that we performed the analysis every 4 ps (2 ps) at 1000 K (1400 K). Multiple events happening on the same cluster between two consecutive snapshots will then not be correctly accounted for.

Comparing numbers between 1000 K and 1400 K indicate that these different processes are thermally activated, as expected. In particular, the contributions to growth by mechanisms '3' and '4' increase more than the two others. On this basis, it is tempting to deduce that their activation energies are lower. However, this would be erroneous since the distributions and sizes of  $V_n He_p$  aggregates are different for the two temperatures.

The second valuable outcome of this section is

the identification of mechanism '4', which significantly contributes to growth. To our knowledge, it has not been taken into account in previous works, probably because the activation energies estimated from the splitting of a large and empty spherical cavity are prohibitively large (using for instance the model described in the appendix). Nevertheless our MD simulations reveal that this process is regularly occurring, in all analyzed cases. We propose the following explanations to this discrepancy. First. the studied  $V_n He_p$  aggregates remain small in our simulations, due to the limited timescale. Furthermore, their morphology could be drastically different from a sphere, and is constantly evolving in MD runs due to the elevated temperature. This tends to facilitate the splitting of the aggregates. Classical models used to describe MC and OR processes are certainly not appropriate for such conditions. Finally, we used systems with high initial densities of helium and vacancies, in order to get a good statistics in the MD timescale. The resulting high concentrations of aggregates lead to small separation distances, which probably facilitates the fragmentation process. However, this does not preclude the fragmentation progress to occur in more realistic conditions.

#### 3.4. Role of Si interstitials

Finally, we also study the role of Si interstitials, which are often neglected in the process of heliumfilled bubble formation, using a limited number of cases. Figure 5 illustrates how the dynamics of aggregation are modified in presence of interstitials. First, the amount of vacancies used up in  $V_n$  and  $V_n$ He<sub>n</sub> clusters is significantly reduced during the simulation, compared to the same system with no interstitials (Fig. 5-a). This can be obviously explained by the recombination of vacancies and interstitials. Both species are highly mobile in silicon, especially the selfinterstitials [53], and we find that recombination occurs from the start of the MD simulations. Figure 5-a also shows that there are slightly less He atoms in  $V_n He_p$ aggregates in presence of Si interstitials. Both  $V_n$  and  $V_n He_p$  clusters become substantially smaller (Fig. 5c), and slightly less numerous (Fig. 5-d). Finally, the He/V ratio in  $V_nHe_n$  aggregates is larger in presence of interstitials. At the end of MD simulations, about 10-20% of the initial interstitials remain, either as single Si atoms, or as small aggregates  $(I_2 \text{ and } I_3 \text{ essentially})$ .

Those results are a clear consequence of the fact that vacancies, either present from the start of the simulation or leaving a cluster after an OR mechanism occurred, can recombine with Si interstitials. The main effect of interstitials is then to reduce the number of available vacancies, thus hindering and delaying the formation of  $V_n$  and  $V_n He_p$  clusters. The interstitials



Figure 5. Influence of Si interstitials on various indicators during a molecular dynamics simulation (here for an initial configuration of 6920 vacancies and 2162 helium atoms, and T = 1000 K). a) vacancies in  $V_n$  clusters (red), vacancies (green) and He atoms (blue) in  $V_n$ He<sub>p</sub> clusters, expressed as percentages relatively to the initial numbers of vacancies and helium atoms. b) He/V ratio averaged over all formed  $V_n$ He<sub>p</sub> clusters (blue). c) average size of  $V_n$ He<sub>p</sub> (blue) and  $V_n$  (red) clusters, in number of vacancies. d) average numbers of  $V_n$ He<sub>p</sub> (blue) and  $V_n$ (red) clusters. Full curves correspond to a simulation with only vacancies and helium atoms, whereas for the dashed ones, 2162 Si interstitials have been introduced at the start. For a color version of the figure, the reader is referred to the online version of the article.

can also interact directly with  $V_n He_p$  aggregates, thus reducing their size. This would explain the higher He/V ratio in presence of interstitials. An alternative explanation could be that  $V_n He_p$  clusters with a high He/V ratio are more stable against shrinking by absorbing an interstitial. This would increase the He/V ratio, which is energetically not favoured at high helium content.

#### 4. Cluster dynamics results

In this section, we describe and discuss the results of RECD calculations, in relation with MD simulations and experiments whenever possible. RECD calculations are done using similar initial conditions than in MD, to ease comparison. In the following, cavities or bubbles are characterised by an equivalent diameter, based on the assumption that they are of spherical shape.

#### 4.1. Empty cavities

We first examine the results of calculations including initially only vacancies  $(V_1)$ . This restricted setup is interesting since there are several investigations reported in the literature to compare with. Those especially concern cavities of diameters larger than



Figure 6. Various outputs of RECD calculations. a) concentration of cavities as a function of their diameter, for different initial vacancies concentrations (in cm<sup>-3</sup>) (1000 K, 1 h). b) concentration of cavities as a function of their diameter, for different temperatures (1 h, initial vacancy concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>). c) concentration of cavities as a function of their diameter, for different simulated times (1000 K, initial vacancy concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>). d) cavity mean diameter as a function of the simulated time for different temperatures and an initial vacancy concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>. d) cavity mean diameter as a function of the simulated time for different temperatures and an initial vacancy concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>. Only cavities including more than ten vacancies are taken into account for determining the average. For a color version of the figure, the reader is referred to the online version of the article.

about 1-2 nm which can be observed using transmission electron microscopy. In the following, we then focus on this size range, and do not discuss variations for cavities formed of less than ten vacancies.

Figure 6 shows the final concentration of cavities versus their equivalent diameter, and the variation of these distributions as a function of different parameters such as the initial vacancy concentration, the annealing temperature, and the simulated time. The cavity distributions are all characterised by a non symmetric hill shape. Although this could hardly be seen in Fig. 6 due to use of a logarithmic scale, the computed average diameter correspond to the maximum concentrations in any cases. In this figure, one can first see that raising the initial amount of vacancies leads to an increase of concentrations for all cavity sizes (Fig. 6a). However the overall distribution shape remains the same, which also means that the average size of cavities is constant. A similar result is obtained when a higher annealing temperature (1400 K) is used (not shown here). In the case of MD simulations, a different behaviour was observed, since the mean cavity size was clearly growing as a function of the initial amount of vacancies (Fig. 3-b). However it is noteworthy that two well different cavity size ranges are studied with both methods. In the short time span of MD simulations, cavities are made up of 4–8 vacancies in

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Figure 7. Mean diameter of cavities as a function of annealing temperature. Orange data correspond to the present RECD calculations (initial vacancy concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>, simulated time of 1 hour), and blue ones to experiments by Raineri et al. [8] (40 keV He implantations, annealing time of 1 hour). For the RECD calculations, the circles show the diameter of the cavities with the highest concentration, while the orange area represents the full width at half maximum (i.e. the vertical boundaries for each temperature correspond to diameters of cavities at half of the highest concentration). Blue symbols show experimental results for different doses:  $1 \times 10^{16}$  cm<sup>-2</sup> (square),  $5 \times 10^{16}$  cm<sup>-2</sup> (diamond), and  $1 \times 10^{17}$  cm<sup>-2</sup> (triangle). The light blue area is only drawn to show the experimental range of cavity diameters. For a color version of the figure, the reader is referred to the online version of the article.

average, while a diameter of 2.3 nm, i.e. equivalent to about 320 vacancies, is obtained with RECD in the case illustrated in Fig. 6-a. Therefore, the cavity growing rate seems to strongly depend on the available amount of  $V_1$ , but only for small sizes. Examining cavity distributions calculated with RECD after few ns confirms this analysis.

The relation between cavity distributions and annealing parameters is also shown in Fig. 6-b,c. Increasing the simulated time leads to an enlargement of the cavity diameter distribution, and yields larger cavities in average. For instance, a mean cavity diameter of 3.5 nm is found after a 10 h annealing at 1000 K. Temperature is found to have a similar effect on cavity size distributions, which significantly widen and shift to larger diameters from 600 K to 1200 K. That both temperature and annealing time have a similar effect is not surprising, since all growing mechanisms modeled in RECD are thermally activated.

The evolution during annealing of the size of cavities initiated by helium implantation was investigated by Raineri and co-workers [8]. We report their data, obtained for different fluences, in the Fig. 7. Note that these cavities are assumed to be empty due to helium desorption for the studied temperature range. We compare measured sizes with our calculated data, considering a diameter range equal to the full width at half maximum of the cavity distributions. We emphasise that this comparison is qualitative, since the initial conditions in our RECD calculations are not fully representative of a post-irradiated state. Bearing in mind this limitation, it appears that calculated sizes are significantly lower than the measured ones, for annealing temperatures lower than about 1400 K. However, a better agreement is obtained for higher temperatures, mainly due to the highest growing rate of cavities in RECD calculations.

Although this agreement is heartening, the discrepancy between experiments and calculations at lower temperatures is disconcerting and calls for clarifications. A first explanation coming to mind could relate to the too simplistic initial conditions in our calculations. In fact, in addition to monovacancies, self-interstitials, and helium atoms,  $V_n He_p$  clusters could readily be present in a post-irradiated state, which may hasten the cavity growth process. A second possible cause could be the parameterisation of the interaction model used in RECD calculations. For instance, the formation energy of empty cavities is obtained from a commonly used but rather simple model (detailed in Appendix A). More refined models for cavity energies have been proposed [54], but it is not clear that they would lead to significant variations. Also, reference data in our model were obtained from 0 K computations, raising questions about their validity at high temperature. Finally, the observed discrepancy could be perfectly explained by the fact that the MC process is missing in RECD calculations. On the one hand, the MD calculations showed that both MC and OR mechanisms contribute to cavity growth, at 1000 K and 1400 K. This also leads to a larger mean cavity size than in RECD calculations after few ns. On the other hand, Hassanuzzaman et al. have investigated the cavity growth [55], using a simpler evolution model than ours, and they have shown that MC has to be taken into account to reach a good agreement with the experimental data. Furthermore, by analysing the theoretical background of MC and OR, Evans [28] concluded that the OR mechanism is not active enough at temperatures below 1273 K to explain reported observations, and that MC was dominant in this regime. Accordingly, in our RECD calculations, a good agreement could only be obtained at the highest temperatures, when OR is expected to dominate.

#### 4.2. Helium influence on bubble growth

The main influence of helium on bubble growth can be seen in Fig. 8-a: increasing the helium concentration makes smaller cavities (for a similar annealing time). The effect is weak when [He] is equal or lower than

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Figure 8. Influence of helium on several cavity properties, from RECD calculations (1000 K, 4 h, initial V<sub>1</sub> concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>). a) concentration of cavities (in cm<sup>-3</sup>) as a function of their diameter (in nm) for several initial He concentrations (in cm<sup>-3</sup>). b) average cavity diameter (in nm) as a function of annealing time (in s) for several He concentrations (in cm<sup>-3</sup>). Only cavities including more than ten vacancies are taken into account for computing the average diameter. c) average He/V ratio as a function of cavity size (in number of vacancies) at different steps of the calculation (in s), initial He concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>. For a color version of the figure, the reader is referred to the online version of the article

 $1.6 \times 10^{20}$  cm<sup>-3</sup>, and becomes significant with a 15% reduction in mean diameter for [He] =  $5 \times 10^{20}$  cm<sup>-3</sup>, and 42% reduction for [He] =  $1 \times 10^{21}$  cm<sup>-3</sup>. The reduction in cavity diameter is accompanied by a rise in concentration, due to the conservation of the total number of vacancies in the calculation. A similar behaviour was obtained in MD simulations.



Figure 9. Concentration of cavities (in cm<sup>-3</sup>) as a function of their size (bottom label: number of vacancies, top label: diameter in nm) from RECD calculations (1000 K, initial V<sub>1</sub> concentration of  $5 \times 10^{20}$  cm<sup>-3</sup>), for three different initial helium concentrations, at different times (from  $3.6 \times 10^{-7}$  s, top graph, to 3600 s, bottom graph). For a color version of the figure, the reader is referred to the online version of the article.

Figure 8-b shows the influence of different initial helium concentrations on the evolution of the average cavity diameter, considering cavities including at least ten vacancies. The mean diameter starts to increase for times greater than about 1 ms, and the influence of helium concentration on cavity growth can clearly be observed. From 0.1 s to 100 s, the largest diameters are surprisingly obtained for intermediate [He] values. For the highest helium concentration  $([\text{He}] = 1 \times 10^{21} \text{ cm}^{-3})$ , the growth is markedly slowed, whereas the lowest one ([He] =  $5 \times 10^{19} \text{ cm}^{-3}$ ) shows little differences with the case with no helium atoms. A behaviour closer to expectations is however recovered for times longer than about 100 s. In fact, the cavity growing rate is then observed to be inversely proportional to the helium concentrations, in agreement with data plotted in Fig. 8-a.

Examining at different times the average He/V ratio as a function of cavity size also reveals unexpected

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features (Fig. 8-c). For short annealing times, clusters formed of few vacancies (typically  $V_1$ ,  $V_2$  and  $V_3$ ), which are the most frequent species, are also those showing the highest values. However, a marked value of about 2 is found for the largest cavities after 0.36  $\mu$ s, while a large ratio can still be found in the remaining  $V_1$  and in aggregates of sizes equal to 6–9 vacancies. Only marginal changes are observed at 1.1 ms. Next, the He/V ratio is slowly decreasing in all cavities up to the end of the calculation. This could be due to helium atoms transferring from small to large cavities, and to the cavity growing with a constant helium content. After 1 h, the helium atoms are essentially present in large bubbles, with only a small proportion included in clusters of few vacancies (here V<sub>3</sub>).

The data presented in Fig. 8 suggest that the influence of helium on the growth of cavities is a complex and rich phenomenon. To further illustrate this point, we represent in Fig. 9 the concentration of cavities as a function of their sizes, at different times, and for three cases: with no helium, with a moderate and realistic helium concentration ([He] = $5 \times 10^{20}$  cm<sup>-3</sup>), and with a large one ([He] = 1 ×  $10^{21} \text{ cm}^{-3}$ ). At 0.36  $\mu$ s, the most frequent cavities are formed of few vacancies, for all helium concentrations. However, the absence of helium favours the growth of larger cavities, compared to the two other cases. This is in agreement with conclusions from the MD calculations, pointing to an enhanced stability of helium-filled cavities compared to the empty ones, that delays bubble growth. This also explains why  $V_1$ ,  $V_2$ and  $V_3$  clusters disappear faster at longer times when no helium is present.

A startling feature, already highlighted in Fig. 8b, is the acceleration of cavity growth between 36  $\mu$ s and 0.36 s for  $[\text{He}] = 5 \times 10^{20} \text{ cm}^{-3}$ . The analysis of the cavity size distributions suggests that this phenomenon is associated to the sudden disappearance of the smallest cavities in the corresponding time span. The freed vacancies can then be captured by the largest bubbles, thus boosting the cavity growth. Conversely, a large proportion of vacancies remain trapped in  $V_{4-5}$ (for [He]=0) or in  $V_{6-8}$  (for [He]=1 × 10<sup>21</sup> cm<sup>-3</sup>). At longer times, these small aggregates also shrink, and released vacancies can accelerate the growth of the large cavities. As a consequence, at 36 s, the cavity size distributions for the three studied cases appear relatively similar, with the presence of highly stable V<sub>9</sub> aggregates (containing a low amount of helium as indicated in Fig. 8-c), and a marked broad peak for large cavity sizes, like in Fig. 8-a. From then on, we find again the behaviour already observed at the shortest timescales, i.e. a cavity growing rate inversely proportional to the total helium concentration.



Figure 10. Concentration of cavities (in cm<sup>-3</sup>) as a function of their equivalent diameter (in nm) from RECD calculations (1000 K, 6 min), for various initial setups (blue: only V<sub>1</sub>, red: V<sub>1</sub> + He, green: V<sub>1</sub> + I<sub>1</sub>, yellow: V<sub>1</sub> + I<sub>1</sub> + He). The initial concentration of each species is equal to  $5 \times 10^{20}$  cm<sup>-3</sup>. For a color version of the figure, the reader is referred to the online version of the article.

## 4.3. Role of Si interstitials

The influence of Si interstitials on the formation of the helium-filled bubbles has also been studied using RECD in selected cases. Our investigations confirm the conclusions drawn from MD calculations. In fact, we find a fast decrease of available vacancies in the RECD simulations, due to the recombination with interstitials. It leads to a significant slowdown of the growth of cavities, which are much smaller and less abundant compared to calculations with no This point is illustrated in Fig. 10. interstitials. However, we note that the maximum concentrations are significantly lower in the presence of interstitials, whereas only a small decrease was observed in MD simulations (Fig. 5-d).

Another similar conclusion is the enhanced stability of the formed cavities because of the presence of helium. This point is clearly visible in Fig. 10, by comparing two simulations including both vacancies and interstitials, one with helium and the other without. Helium thus helps to preserve a significant amount of bubbles.

#### 4.4. Discussion

Comparing available experimental data and RECD calculations shows that with the latter, the cavity size is underestimated. A possible cause, backed up by MD results in similar conditions, is the absence of the MC mechanism in our RECD calculations. As explained in section 2.2, taking into account the mobility of all possible aggregates and not only of simple monomers is

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hardly possible. In addition, it is worth remembering that the mobility of  $V_n \text{He}_p$  clusters is not a well known property. Only an earlier theoretical study by Mikhlin was devoted to this issue [37], and we did not find later confirmations or follow-ups of this work.

Another cause could be the parameters of the RECD calculations. The binding energies between the different species have in fact all been computed at 0 K, thus with no entropic effects, although we aim at simulating high temperature conditions. It is relatively difficult to determine the magnitude of finite temperature contributions, which would require dedicated investigations. Nevertheless, we remark in Fig. 9 that even after an annealing of one hour at 1000 K, a large proportion of vacancies remains concentrated in  $V_9$  clusters, due to the low calculated formation energy of this configuration. In the event that thermal contributions could substantially change the energies, the shrinking of  $V_9$  clusters for the benefit of larger cavities would result in a significant increase of the mean cavity size.

Finally, it is pertinent to discuss the influence of initial conditions on the outcome of RECD calculations. In the present work, we favour similar setups in both MD and RECD calculations, for a meaningful comparison whenever possible.  $\mathbf{As}$ already mentioned, small  $V_n He_p$  aggregates, precursors of large bubbles, could readily form during helium implantation. At first sight, this aspect does not seem very important since both MD and RECD calculations showed that such small aggregates could form in few ns. However, the critical issue is rather the concentration. difference of these aggregates between an implantation and our simulations. In fact, in the former, only a low amount of clusters are expected to form from the start. Those ones will then act as sinks for the helium and vacancies monomers generated by the next cascades, thus yielding fewer but larger bubbles at the end. Conversely, in the present work, starting directly with all needed monomers results in the fast formation of a high numbers of small aggregates. To test this idea, we performed few additional RECD calculations, in which both helium and vacancies are continuously added in the simulation (using realistic dose rates). We find larger and fewer bubbles than in previous RECD calculations, which confirms the importance of initial conditions on the final outcome. This should be a key point for future investigations.

The main objective of the present study is to better understand the influence of helium on the formation and growth of bubbles in silicon. The results from MD calculations tend to suggest that the initial formation of bubbles is relatively independent of the presence of helium, since  $V_n$  are formed before  $V_n$ He<sub>p</sub> clusters. At the ns time scale, both MD and RECD calculations show that helium induces smaller and more abundant aggregates. This trend is also verified at a time scale of the hour, on the This is due to an basis of RECD calculations. enhanced stability of cavities containing helium, which delays growth. Furthermore, a thorough analysis reveals that the dynamics of cavity growth could be relatively complex depending on the concentration of helium. In fact, we found that at the ms time scale, a medium helium content could boost the cavity growth compared to cases with low or high helium concentrations. The influence of helium is therefore probably more subtle than previously thought. It is also worth remembering that MC is not taken into account in RECD calculations. How helium could affect this mechanism and therefore the cavity growth remains a question mark.

#### 5. Conclusions

In this work, we have simulated the formation and growth of helium filled cavities in silicon using both molecular dynamics and rate equation cluster dynamics calculations. The involved mechanisms can be investigated at the atomistic scale with the former method, whereas the latter one allows for modeling the dynamics of cavity growth during a much larger time scale. These simulations bring several new insights about this complex process. Firstly, we find that both MC and OR mechanisms are involved in cavity growth, for different temperatures. It is therefore probably too simplistic to assume that only one of those is active at a given temperature. This aspect is indirectly confirmed by RECD calculations, in which only OR can be activated.

Secondly, the MD calculations reveal that a third mechanism, which could be named fragmentation or splitting, is also active during the growth. We observe that a small fragment can break off from an aggregate, and is next available for migrating and coalescing with another cavity. The splitting mechanism is therefore different from OR and MC, but borrows some of their characteristics. It is clearly evidenced for small aggregates in MD simulations. Its importance for large bubbles remains to be confirmed.

A third point concerns the influence of helium on the bubble initiation and formation. It is shown here that helium tends to delay the growth, resulting in smaller cavities. The dynamics of cavity growth largely depends on helium concentration. At the time scale of MD simulations, we find that three stages can be observed, with first the aggregation of vacancies, followed by the nucleation of  $V_n \text{He}_p$ clusters, and in third their growth. The onset of the last two stages and their duration strongly depend

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## Influence of helium on bubble formation in silicon

on the helium concentration. The initial aggregation is however observed to be weakly dependent on helium, with vacancy clustering always preceding the interaction with helium atoms. At an intermediate time scale, RECD simulations reveal a complex helium dependence, with periods of accelerated growth for certain helium concentrations.

The influence of self-interstitials has also been investigated in selected situations. The results from both methods suggest that the main effect of interstitials is to decrease the amount of available vacancies, following an intense recombination activity at very short timescale. As a consequence, smaller and fewer bubbles are created in presence of interstitials.

This work also allows us for identifying directions for future researches. First, it would be interesting to use more realistic initial configurations, obtained from cascade simulations from instance. Another perspective revolves around the influence of helium on the migration of  $V_n He_p$  aggregates. Monitoring the diffusion of a few clusters with a defined composition in dedicated molecular dynamics simulations should allow to unveil the involved mechanisms as a function of helium content and cavity size. A third direction could concern the splitting process, and in particular whether it could be active for large aggregates. Finally, it would be valuable to refine the interaction model used in RECD calculations, especially regarding finite temperature effects. This could be done by calculating the quantities of interest (see the Appendix A) from molecular dynamics calculations at different temperatures.

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# Appendix A. He–V–I interaction model

Cluster dynamics simulations require energetic parameters governing the rates of the possible mechanisms, e.g. the capture or the emission of an helium atom by an existing  $V_n \text{He}_p$  cluster. Such models have been proposed for helium bubbles formation in metals (see for instance [56, 57]), but unfortunately not in silicon to our knowledge. We propose below such a model, built on atomistic calculations, yielding the formation energies of helium bubbles. From these energies, the binding energies can be easily computed and used as inputs in the CRESCENDO code.

# Appendix A.1. $V_n He_p$ calculations

To determine V–V and He–V interactions, about 30000 atomistic calculations of  $V_n He_p$  clusters are performed, using the same interatomic potential than in large scale MD simulations for sake of consistency. The typical procedure for these simulations is the following. A  $V_n He_p$  cluster is initially generated in the center of a periodically repeated bulk silicon cubic supercell, by removing lattice atoms contained in a sphere of variable radius, and randomly inserting a given number of helium atoms. A supercell size of  $(3a_0)^3$  is used for small bubbles (1–10 vacancies). A NVT simulation with a timestep of 1 fs is next carried out during 10 ps, with a fast annealing to 800 K, followed by a slow quench to 0.1 K. The final energy is then obtained by conjugate gradient energy minimization. For each couple of He and vacancies numbers, 100 simulations with different initial helium arrangements are performed in order to determine the most stable configuration.

For larger bubbles, the calculation procedure is slightly modified. First, the supercell size is increased to  $(5a_0)^3$ . A NVT simulation is performed during 30 ps, the system being first annealed at 1000 K, then slowly quenched to 0.1 K, and a conjugate gradient energy minimization is done at the end. Again, 100 simulations are done for a given composition, and the final energy is computed as the average of the ten lowest energy values. Only bubble sizes corresponding to 13, 23, 35, 50, 100, 150, 200, and 301 vacancies have been computed.

From the computed energies, the formation energy of a  $V_n He_p$  cluster can be calculated according to

$$E^{f}(n,p) = E(n,p) - pE_{\text{He}}^{\circ} - (N-n)E_{\text{Si}}^{\circ}$$
 (A.1)

where E(n,p) is the MD calculated energy,  $E_{\text{He}}^{\circ}$ the energy of an interstitial helium atom in silicon, and  $E_{\text{Si}}^{\circ}$  the energy of a silicon bulk atom. N is the number of silicon atoms in the pristine supercell.

# Appendix A.2. Extrapolation at large sizes

For small clusters, of at most 10 vacancies, and including less than 20 helium atoms, atomistic values can be directly used to determine binding energies. However, for larger systems, interpolation and extrapolation are necessary.

For voids, the formation energy can be efficiently approximated by the cavity surface energy  $4\pi r^2 \gamma$ . Since the cavity volume  $V = 4\pi r^3/3$  is also linearly proportional to the number of vacancies n, the formation energy  $E^f(n,0)$  can be written  $\alpha n^{2/3}$ . Fitting the atomistic data with this expression yields  $\alpha = 3.16$  eV. This corresponds to a surface energy  $\gamma = 1.42$  J.m<sup>-2</sup>, in excellent agreement with available measurements [58].

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For non-empty bubbles, it is convenient to rewrite the expression A.1 as

$$E^{f}(n,p) = \tilde{E}^{f}(n,p) + E^{f}(n,0)$$
 (A.2)

 $\tilde{E}^{f}(n,p)$  is the energy needed to insert p interstitial He atoms into a cavity of n vacancies. Recent investigations revealed that the variation of this term as a function of p is quadratic [59], for a given n. We can then write

$$\tilde{E}^{f}(n,p) = a(n) p^{2} + b(n) p$$
 (A.3)

a(n) and b(n) are calculated for all simulated bubbles with n > 10. We find that both coefficients can then be fitted by the respective expressions

$$a(n) = \frac{0.08}{n} \tag{A.4}$$

$$b(n) = \frac{2.2}{n} - 1.25 \tag{A.5}$$

The formation energy (in eV) of a bubble formed of n vacancies and encompassing p helium atoms is then obtained as

$$E^{f}(n,p) = 0.08 \,\frac{p^{2}}{n} + 2.2 \,\frac{p}{n} - 1.25 \,p + 3.16 \,n^{2/3} \quad (A.6)$$

This expression is used for bubbles of at least 11 vacancies, or containing at least 21 helium atoms. Otherwise, the binding energies are directly calculated from atomistic data.

#### Appendix A.3. I–I interactions

The previous model is restricted to V–V and He–V interactions. Other possible interactions concern Si interstitials and He atoms. Previous investigations showed that the interaction between helium interstitials in silicon is weak and can be safely neglected [20]. We also assume that the combined aggregation of helium and Si interstitials does not play a significant role in the formation of helium bubbles.

For the interactions between silicon interstitials, we use the model proposed by Ortiz et al. to describe {113} extended defects [60]. In the latter, the formation energy of a cluster with q > 9 Si interstitials is given by

$$E_{\rm I}^f(q) = \frac{\mu b^2 L}{2\pi (1-\nu)} \ln\left(\frac{2W}{b}\right) + \gamma q + \frac{\mu b^2 W}{2\pi} \left(\cos^2\theta + \left(\frac{\sin^2\theta}{1-\nu}\right)\right) \ln\left(\frac{2L}{b}\right) (A.7)$$

with the parameters values:  $\mu = 75.5$  GPa,  $\nu = 0.3$ , b = 1.1 Å,  $\theta = 77.8^{\circ}$ ,  $\gamma = 0.38$  eV, W = 40 Å, and L = 2 Å/q. For small interstitial clusters with  $q \leq 9$ , the formation energy values tabulated in [60] are directly used.

 Table A1. Migration energies (in eV) for the species considered mobile in the cluster dynamics calculations.





Although it is theoretically possible to take into account the mobility of all clusters, for practical reasons only the smallest ones are usually considered mobile in cluster dynamics calculations. In the present work, it includes V<sub>1</sub>, V<sub>2</sub>, and single helium and silicon interstitials. The diffusion coefficient is assumed to be equal to  $D = D_0 \exp(-E_m/k_B T)$ , with  $D_0 = a_0^2 \nu = 2.9 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$  ( $a_0 = 5.431 \text{ Å}$ ,  $\nu = 10^{13} \text{ s}^{-1}$ ), for all species.

• The table A1 gives the migration energies used in the calculations, with the appropriate references.

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