Interaction between a monovacancy and a vacancy cluster in silicon

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The interaction between two vacancies has been investigated in silicon by molecular-dynamics simulations. We introduce the concept of capture radius r_c, according to which the most stable configuration for a vacancy pair is a bound divacancy whenever the two defects are placed at distances smaller than r_c. We also investigate the trapping mechanism of a monovacancy at a vacancy complex and discuss the energetics of early stages of aggregation of small vacancy clusters. [S0163-1829(98)04012-0]

A huge effort has been dedicated in the last two decades or so to understanding and predicting the structural evolution of crystalline silicon under irradiation. Many theoretical investigations, in particular, have been addressed to identify the atomic-scale mechanisms responsible for the formation of point defects as well as for defect-defect interactions.[1] Despite the remarkable improvement in our understanding about how defects diffuse and interact in a crystalline host, a detailed and nonheuristic comprehension of their aggregation features in silicon is still missing. The lack of knowledge about the basic physics of these phenomena is an obstacle for a deeper fundamental description of the amorphous state of matter. In addition, this problem is central to computer modeling of silicon bulk processing, which mostly relies on Monte Carlo calculations or commercial process simulators. In fact, the mechanisms involved at the atomic scale during interaction among like or unlike defects need to be guessed in some way in order to run the simulations. Typically, they are modeled on the basis of physical intuition or simply guessed for numerical convenience, since experiments cannot provide unambiguos information at this level.

Atomistic simulations can be of great help in this field. We can, in principle, follow a given defect or defect complex in whatever thermodynamical or structural condition. Typical finite-temperature properties (say, diffusivity, free energies, migration paths) and ground-state properties (formation energies, equilibrium configurations) can easily be computed, provided that a reliable interatomic potential is available. In this work we have untertaken a critical readdressing of some features of the vacancy-vacancy (V-V) interaction based on molecular-dynamics simulations. In particular, we have studied how two vacancies form a divacancy, and we have characterized the trapping mechanism of an isolated vacancy at a small vacancy cluster (V cluster). Our goal is twofold: (i) to explain the early stages of coalescence of small V clusters, and (ii) to point out the bias effect on the trajectory of a mobile V due to the lattice strain field created by a nearby V cluster.

In the present work, we adopted the Stillinger and Weber[2] (SW) interatomic potential to describe Si-Si interactions. The SW model potential was preferred among others because it correctly describes crystal and amorphous bulk Si properties (e.g., lattice constant, cohesive energy, particle-particle correlation function, and bond-angle distribution function). More importantly, the SW potential has been widely used in computer modeling of phenomena related to silicon bulk processing[3,4] and usually its results are in resonable agreement with more accurate tight-binding and first-principles calculations.[5] It represents, in fact, a sort of reference paradigm in this field and, therefore, we believe that it is worthwhile to carry on the present study using such a model. Finally, we remark that, thanks to the empirical and short-range character of the SW potential, the resulting computational workload is pretty low. This allows for those large-scale simulations really needed to investigate the present problem.

Our molecular dynamics (MD) simulations have been performed in the constant volume, constant temperature (NVT) ensamble using a cubic, periodically repeated simulation cell containing 1000 atoms.[6] Such a large simulation box is mandatory in order to warrant that the lattice strain field created by the defects is well contained in the simulation cell and size effects are negligible. The analysis of the interaction between defect complexes (mono-V and V clusters) has been performed by computing the formation energy of several configurations obtained by placing the mono-V at different lattice sites around the V cluster. The reported formation energies have been obtained after a gentle thermal annealing procedure applied to the initial structure, so that the ground state (minimal energy) configuration is indeed reached by possible particle motion.[7]

The simplest configuration we studied consists in a pair of interacting vacancies. We considered first the relative motion along the bond network distorted by the defects. This network is illustratated in Fig. 1 which shows how the lattice strain field is driven by the bond chains merging into the V site. We simply computed the energetics and stability of a V-V complex by placing the second vacancy in different positions along the distorted-bond network and allowing relaxation. Since the strain field is isotropic, the only parameter governing the energetics of the V-V complex in this case is the relative distance between the two defects. We found that whenever the two vacancies are placed at distance $d_{V\text{-}V}$ above 7.67 Å (corresponding to five bond distances along the bond chains) they behave like independent particles, being the formation energy E_{2V} of the relaxed complex roughly twice the formation energy E_{1V} of a single vacancy. In contrast, when $d_{V\text{-}V} \leqslant 7.67$ Å the complex is unstable against

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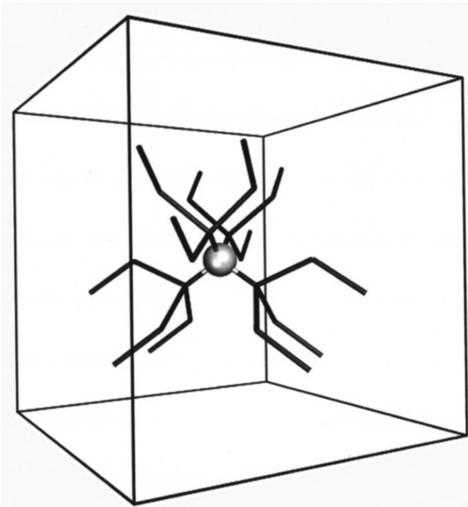

FIG. 1. Lattice strain field created by a monovacancy in silicon. The light-shaded sphere represents the missing atom and the black sticks show the distorted bonds. Distorted bonds link atoms displaced by more than 0.09 Å from their equilibrium positions.

coalescence: during the thermal annealing step the two vacancies collapse and a divacancy is immediately formed. This result is summarized in Fig. 2 where the flat behavior of the formation energy curve below 7.67 Å actually corresponds to a stable divacancy. In other words, there is no way to stabilize two vacancies as separate entities at distances smaller than 7.67 Å. According to this result, Fig. 2 helps in introducing the concept of capture radius r_c: at relative distances smaller than r_c=7.67 Å the most energetically favored configuration for a vacancy pair is a bound divacancy. Our calculations proved that the interaction between the two monovacancies below r_c is driven by the superposition of the strain fields, resulting always in an attractive interaction.[8]

We have then investigated the interaction between two monovacancies displaced along directions other than those ones depicted in Fig. 1, i.e., the two vacancies are not placed on the same distorted-bond network. Even in this case we found that the interaction is short ranged. However the above simple picture is no longer valid since the interaction between the two mono-V strain fields may lead to the formation of V-V stable unbounded complexes different from the collapsed divacancy. A typical configuration belonging to this class consists in two monovacancies placed at opposite vertexes of a six-membered bond ring (see below). This complex has a formation energy of 5.15 eV and a binding energy of 0.15 eV and therefore it represents a $T=0$ K stable aggregate.

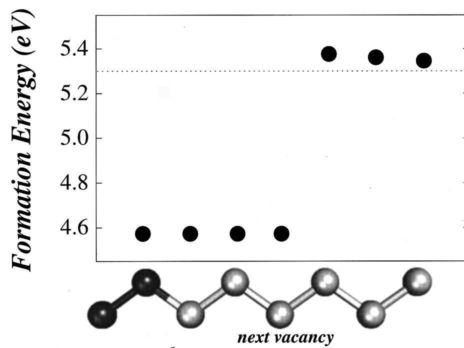

FIG. 2. Formation energy of the V-V complex for different relative positions along the bond chain (light-shaded spheres). The dotted line represents the formation energy of two monovacancies at infinite distance. The flat region on the bottom-left part of the figure represents the formation energy of a bound divacancy (heavy-shaded spheres) obtained during the MD run by coalescence of two vacancies initially placed at a distance smaller than 7.67 Å.

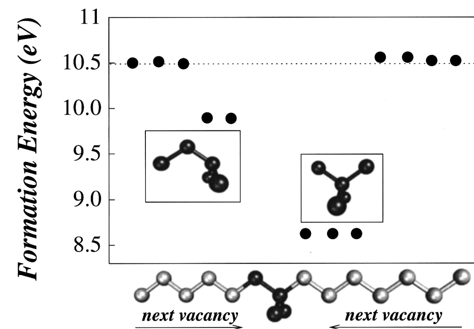

FIG. 3. The same of Fig. 2 for the interaction between a mono-V and a 4-V spheroidal cluster. The mono-V can move along different directions of the same bond chain. Consequently, different complexes can be formed, as shown by the insets. The dotted line represents the formation energy of a monovacancy and 4-V spheroidal cluster at infinite distance.

We extended our analysis to the interaction between an isolated vacancy and an already formed vacancy cluster. Theoretical studies have pointed out that the less energetically expensive way to form a small V cluster consists in extracting neighboring atoms with the constrain to minimize the number of dangling bonds thus created.[9] For clusters with a small number of vacancies (i.e., less than 18 vacancies) the above requirement corresponds to taking atoms away from six-membered bond rings.[9–11] The six-membered ring is the only type of topological bond pattern that is possible to identify in the diamond lattice according to the shortest-path analysis by Franzblau.[12] This growth sequence for small V clusters is energetically favored with respect to forming spheroidal clusters.[13] Our MD study proved that the two kinds of vacancy clusters also differ in their capture mechanism of the next vacancy. This is clearly shown in Figs. 3 and 4 where an isolated vacancy approaches a spheroidal 4-V cluster and a uncomplete six-membered bond ring cluster, respectively, along different directions of the bond network. The main qualitative message is twofold. The first evidence is that for a given cluster structure the capture radius depends now on the approaching direction. This is particularly evident in the case of the spheroidal 4-V cluster where r_c can vary from two to three bond distances according to the final position reached by the fifth incoming vacancy. The capture radius is larger when the next vacancy goes to perfectly complete the spheroidal structure of the cluster (in Fig. 3 this corresponds to move the fifth vacancy from the right). The second result is that different stable V complexes can be formed starting from the same initial configuration (see insets of Fig. 3). These complexes differ in formation energy, despite the fact that they form the same number of dangling bonds in the host crystal. In any case, however, vacancy coalescence into 6-membered rings leads

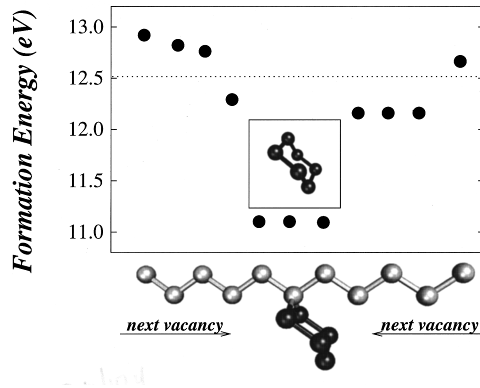

FIG. 4. The same of Fig. 2 for the interaction between a mono-V and an uncomplete six-membered bond ring cluster. The mono-V can move along different directions of the same bond chain. The most stable complete six-membered ring cluster is shown in inset. The dotted line represents the formation energy of a monovacancy and the six-memebred ring cluster at infinite distance.

to a lowest-energy configuration. Most likely V complexes like those depicted in Fig. 3 could form during ion-beam irradiation or Czochralski crystal growth, even if they do not correspond to the lowest-energy $T=0$ K configuration.

In conclusion, we showed that V-V interactions and formation of V clusters are complex phenomena governed by the interplay between the way atoms are extracted from the underlying lattice, the resulting strain field, and the energetics of aggregation of small V complexes. The present investigation was based on model potential molecular-dynamics simulations. We believe that this work, although not predictively quantitative, has pointed out some important qualitative features of V-V interactions which, to the best of our knowledge, have not been previosly discussed. We also think that this problem deserves other investigations, based on more accurate interaction models and where finite-temperature effects are taken into account. Finally, we believe that any accurate and predictive Si-bulk process simulation should include the variety of coalescence states for V complexes that has been only schematically described in this work.

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[6] Possible size effects have been investigated by repeating the calculations for a larger cell, containing 1728 atoms. All the computed energies, and final configurations after annealing have been found nearly identical to the case of 1000-atom simulations.

[7] Special care has been taken to adopt a simulated annealing procedure that allowed lattice rearrangements around the defect, still avoiding the melting of the V cluster. To this end a relatively low temperature ($T=300$ K) was reached during very gentle (i.e., very long) MD simulations. The same procedure was already successfully used to study the structure of vacancy clusters in silicon (Ref. 10). The overall computational effort consisted of several tens of thousands of MD steps.

[8] Just above r_c we can observe a small increase of E_{2V} as compared to $2E_{1V}$ (see Fig. 2), standing for the existence of some small energy barrier for nucleation.

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