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Abstract

The role of entropy in the thermodynamic properties of small interstitial clusters in crystalline silicon is investigated using an empirical potential. It is shown that both vibrational and configurational entropies are potentially important in setting the properties of small silicon interstitial clusters and, in particular, contribute to the formation of “magic” sizes that exhibit special stability, which have been inferred by experimental measurements of dopant diffusion. The results suggest that a competition between formation energy and entropy of small clusters could be linked to the selection process between various self-interstitial precipitate morphologies observed in ion-implanted crystalline silicon.

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Entropic origins of stability in silicon interstitial clusters

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The role of entropy in the thermodynamic properties of small interstitial clusters in crystalline silicon is investigated using an empirical potential. It is shown that both vibrational and configurational entropies are potentially important in setting the properties of small silicon interstitial clusters and, in particular, contribute to the formation of “magic” sizes that exhibit special stability, which have been inferred by experimental measurements of dopant diffusion. The results suggest that a competition between formation energy and entropy of small clusters could be linked to the selection process between various self-interstitial precipitate morphologies observed in ion-implanted crystalline silicon. © 2008 American Institute of Physics. [DOI: 10.1063/1.3042096]

There have been numerous computational and experimental studies aimed at elucidating the nature of self-interstitial clusters in crystalline silicon. These have been motivated by the fact that dopant atom (e.g., boron) introduction during ion irradiation of silicon wafers introduces a large concentration of self-interstitials and interstitial clusters, which lead to undesirable enhancement of dopant atom diffusion, commonly referred to as transient enhanced diffusion.¹ Previous studies suggested that there exist “magic” cluster sizes in the range of $1 < n < 10$, i.e., sizes that are particularly energetically favorable on a per interstitial basis relative to neighboring sizes. These small sizes are presumably the nuclei that lead to the formation of well-identified precipitates such (113) rodlike defects and (111) dislocation loops.^{2–5} Cowern *et al.*,⁶ in particular, applied inverse modeling of boron profile spreading data to infer effective values for interstitial cluster formation energies as a function of cluster size at temperatures in the range of $600 < T < 800$ °C. Strong relative stability was found at $n=4$ and $n=8$ and several subsequent computational studies endeavored to corroborate and explain these findings.

Recently, Lee and Hwang⁷ performed a comprehensive series of density functional theory (DFT) calculations, which provide some indication of energetic favorability at $n=4$ and $n=8$, but the effect shown was quite weak relative to the strong trends observed in Ref. 6, particularly at $n=8$. The building block responsible for the apparent energetic stability at $n=4$ and $n=8$ is a fully fourfold coordinated four-interstitial cluster with D_{2d} symmetry, which has been identified in previous studies on Si (Ref. 8) and diamond;⁹ we henceforth refer to this building block as the “compact” Humble/Arai structure. Thus, the ground-state eight-interstitial cluster identified in Ref. 7 is comprised of two adjacent Humble/Arai four-interstitial units. However, it is well known that there exist multiple structural motifs for building self-interstitial clusters. In addition to the compact four-interstitial building block, various types of elongated (110)-oriented chainlike structures are also favorable. These appear to be nearly degenerate with the compact structures in the size range of $5 < n < 12$.^{7,10} In fact, Kim *et al.*¹⁰ found, also using DFT, that at $n=8$ an elongated chainlike structure

is slightly more favorable than the compact structure, which is in contrast to the predictions in Ref. 7. In either case, it is difficult to infer any significant special energetic stability at $n=8$, especially given the strong apparent stability inferred experimentally in Ref. 6. Other calculations with tight-binding and empirical potentials have also not demonstrated evidence of special energetic stability at these sizes.^{10–12} In this letter, we attempt to explain this discrepancy with molecular dynamics (MD) simulations based on the empirical environment-dependent interatomic potential (EDIP).¹³

We first computed formation energies for the structures identified in Refs. 7 and 10 by periodically quenching (with a conjugate gradient method) atomic coordinates generated by long NVT -ensemble MD simulations at 1100 K and selecting those that matched the structures shown in Ref. 7 (see Fig. 1). The formation energy of an interstitial cluster was defined as $E^f \equiv E_d - (N_d/N_p)E_p$, where d represents the system with the cluster and p represents the perfect reference crystal. The MD simulations were performed using fifth-order Gear predictor-corrector integration with a time step of 0.8 fs. Note that numerous structures corresponding to different local minima in the overall potential energy landscape (PEL) were found at each cluster size, but here we focus on the particular structures identified in Refs. 7 and 10.

The overall energetic trends predicted by the EDIP potential are in excellent agreement with the previous DFT results, although the absolute values are somewhat higher; note that similar differences exist between the two sets of DFT

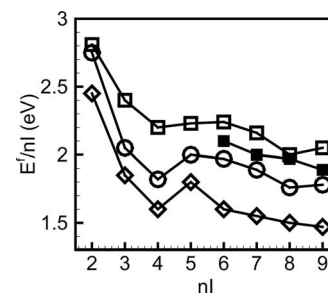


FIG. 1. Formation energies (E^f) per interstitial as a function of cluster size (nI). Squares: EDIP results for the structures corresponding to those identified in Refs. 7 and 10; for $n \geq 6$, formation energies for both compact (open squares) and elongated (filled squares) are shown (see text for definitions). Circles: DFT results from Ref. 7. Diamonds: DFT results from Ref. 10.

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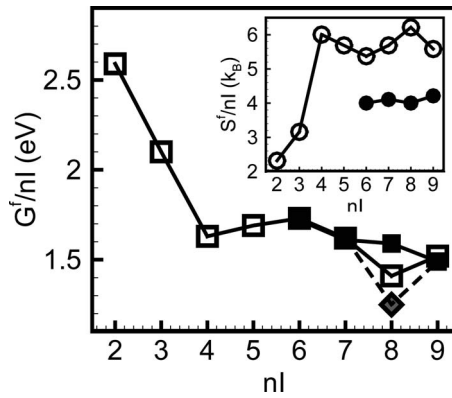


FIG. 2. (a) EDIP formation free energies (G^f) as a function of interstitial cluster size at 1100 K. Open squares: compact structures. Filled squares ($n \geq 6$): elongated structures. Diamond symbol shows free energy including the estimated configurational entropy (see text). Inset: QHA-EDIP formation vibrational entropies as a function of cluster size at 1100 K. Open circles: compact structures. Filled circles: elongated structures.

results. For $n \geq 6$, formation energies for both the compact and elongated chainlike structures were calculated. The elongated structures were found to be slightly more energetically favorable, in qualitative agreement with the results of Kim *et al.*,¹⁰ whereas Lee and Hwang⁷ found the compact structure to be at least as favorable until $n=9$. All three sets of calculations show the same overall trend: some special stability at $n=4$ but very little to none at $n=8$, which is in qualitative contrast to the experimentally regressed energies obtained in Ref. 6.

The above analyses, however, all neglect the role of entropy, which we suggest here can be significant especially in light of the fact that the experimental data in Ref. 6 were obtained at moderately high temperatures ($900 \text{ K} < T < 1100 \text{ K}$). We consider first the vibrational entropy associated with the individual structures discussed in Fig. 1. Formation free energies, defined as $G^f(n) = E^f(n) - TS_{\text{vib}}^f(n)$, were computed at 1100 K within the quasiharmonic approximation (QHA)¹⁴ and are shown on a per interstitial basis in Fig. 2. Increased special stability is now observed at both $n=4$ and $n=8$ for the compact structures (open squares). Note that the free energy of the compact eight-interstitial cluster is significantly lower than that of the corresponding elongated structure (filled squares), while the free energies of the two configurations at the other sizes are comparable. The vibrational entropy is shown explicitly in the inset of Fig. 2 and is substantially higher for the compact clusters (open circles), relative to the corresponding elongated structures (filled circles) for $n \geq 6$. Moreover, the peaks at $n=4$ and $n=8$ show that the perfect Humble/Arai structure is the source of this entropy. It is difficult to precisely identify the features of the compact four-interstitial building block that lead to the increased vibrational entropy, but the unique nature of the near-ideal bond angles associated with the cluster is likely to play a role. Previous electronic structure calculations¹⁵ identified additional vibrational modes that are associated with the compact four-interstitial cluster. In summary, these variations in vibrational entropy imply that selection between compact and elongated morphology during self-interstitial cluster growth at finite temperature cannot be determined solely based on the formation energy.

Vibrational entropy is not the only possible source of entropy for self-interstitial clusters. Configurational entropy

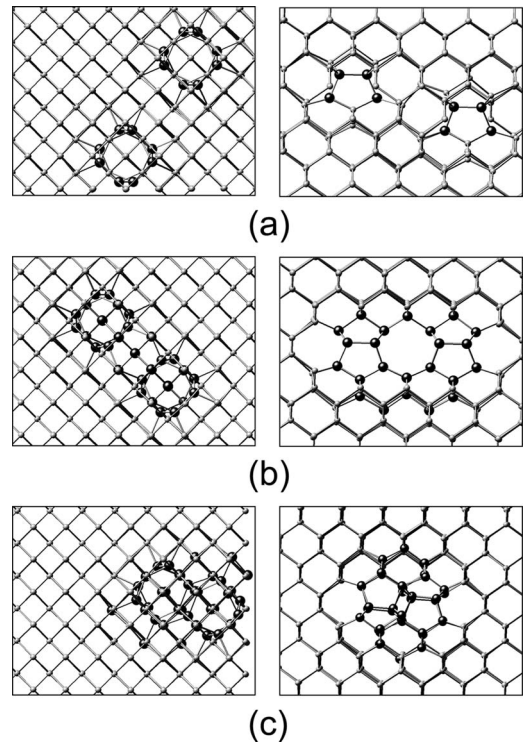


FIG. 3. Nearly degenerate configurations for the compact eight-interstitial cluster based on combinations of two Humble/Arai four-interstitial building blocks. Left-hand panels are projections normal to (100), right-hand panels are projections normal to (110): (a) $E^f = 16.23 \text{ eV}$, (b) $E^f = 15.95 \text{ eV}$, and (c) $E^f = 15.86 \text{ eV}$.

may arise from the presence of numerous mechanically stable configurations of the defect cluster, each of which corresponds to a distinct local minimum in the multidimensional PEL. The notion that a crystal defect can exist in several (not necessarily degenerate) configurations is not surprising, but whether there are enough of these configurations to imply a significant contribution to the defect entropy has only recently been suggested.¹⁶ The rotational symmetry of the D_{2d} Humble/Arai four-interstitial building block is 4, leading to 16 degenerate (rotational) configurations per pair for the eight-interstitial cluster in the compact configuration. Additionally, there are many nearly degenerate ways in which the second Humble/Arai four-interstitial cluster can be placed relative to the first; some of the configurations obtained within our MD simulations are shown in Fig. 3. This large number of translational degrees of freedom is unique to compact structures comprised of multiple Humble/Arai clusters. Clearly, the strong binding between the two Humble/Arai four-interstitial building blocks is preserved over several neighbor shells.

It is difficult to count manually the total number of nearly degenerate possible configurations N_{conf} , which increase the entropy of any cluster according to the relation $S_{\text{conf}} = k_B \ln N_{\text{conf}}$. Nonetheless, based on the configurations in Fig. 3, the eight-interstitial cluster appears to be strongly bound up to the fourth or fifth neighbor shells defined within the (100) projection. Moreover, additional degeneracy is obtained by varying the relative vertical positions of the two four-interstitial clusters (see right-hand panels in Fig. 3). Every 400–500 such configurations (of approximately equal formation energy and vibrational entropy) would lead to a reduction of about 0.1 eV in the per interstitial formation free

energy of the compact eight-interstitial cluster at 1100 K (see diamond symbol in Fig. 2). Note that the special degeneracy for compact eight-interstitial cluster is uniquely large because of high symmetry of the four-interstitial building block and the degeneracy of neighboring sizes is likely to be much lower. The combination of vibrational and configurational entropies favors the compact over the elongated configuration of the eight-interstitial cluster for temperatures above 600–700 K, i.e., the compact structure is likely to be dominant at typical annealing temperatures.

In summary, we analyzed two sources of entropy, vibrational and configurational, that appear to substantially affect the thermodynamics of small self-interstitial clusters at finite temperature. Both entropic sources are particularly large for structures comprised of the Humble/Arai four-interstitial building block, which is the building block for self-interstitial clusters in the compact configuration, and provide a compelling explanation as why very strong stability at $n=8$ has been extracted from experiments at moderate annealing temperatures but not yet confirmed by literature calculations of formation energies to date. It should be stressed that the extracted parameters in Ref. 6 are effective *free* energies rather than simple energies because they are a measure of the overall probability of observing each size. As such, all entropic sources should be considered in calculations attempting to make a direct connection to these data. Finally we note that the temperature dependence introduced by entropic contributions suggests a possible mechanism for explaining the different morphologies that have been observed in self-interstitial clusters at different annealing tem-

peratures. We will address this possibility in a future publication.

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