Vacancy Interaction with Dislocations in Silicon: The Shuffle-Glide Competition

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Competition between the two alternative positions (shuffle and glide {111} plane subsets) for the core of a 30° partial dislocation in Si is examined. Using a combination of *ab initio* total energy calculations with finite temperature free-energy calculations based on an interatomic potential, we obtained free energies for the relevant vacancy-type core defects. Generally, the free energy of vacancy formation in the core of a 30° glide partial dislocation is considerably lower (by more than 1 eV) than in the bulk. However, even at high temperatures, the predicted thermal concentration of the shuffle segments comprised of a row of vacancies in the core is low, placing the 30° partial dislocation in the glide subset position.

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Because of their involvement in the processing and operation of electronic devices, dislocations in semiconductors have attracted considerable attention over the past two decades [1]. In all zinc-blende semiconductors, dislocations move in the {111} planes. However, due to the nonprimitive unit cell, there are two distinct sets of {111} planes: the closely spaced *glide* subset and the widely spaced *shuffle* subset [2]. *A priori*, it is not clear which of the two subsets is more important for dislocation mobility [3]. Initially it was thought that dislocations should be confined to the shuffle planes, since the lattice resistance, or Peierls barrier, to dislocation motion between the widely spaced atomic planes is generally lower. On the other hand, high resolution electron microscopy (HREM) images showed that perfect dislocations are, in fact, dissociated into Shockley partials separated by a ribbon of stacking fault [4]. Since stable stacking faults can exist only in the glide subset, it seemed straightforward to conclude that dislocations should belong to the glide planes, both in motion and at rest. Subsequently, theoretical work has been almost exclusively focused on the glide partial dislocations.

An alternative view on the shuffle-glide competition has been proposed [5], where it was shown that dissociated dislocations can exist both in the glide and in the shuffle subsets. In the latter case, shuffle partials can be formed by removal/insertion of a row of atoms from/into the core of the glide partials. It was also suggested that the partials can simultaneously exist in both subsets, with shuffle and glide segments alternating along the dislocation. Surprisingly, this idea of "shuffle-glide coexistence" was largely ignored in the literature as if the exclusive role of the glide partials were well established. Yet, HREM observations indicate a significant concentration of intrinsic defects in the core of partial dislocations [4] leaving open the fundamental issue of shuffle-glide competition.

In this Letter we examine the energetics of glide and shuffle partial dislocations in Si in a series of calculations in which the concentration of vacancies in the core of a 30° partial dislocation varies from zero for a pure glide core to 100% for a pure shuffle core. Our approach is a combination of *ab initio* calculations for the zero temperature energetics with classical molecular dynamics (MD) simulations for the temperature-dependent free energies of the relevant core configurations. The results provide the first direct theoretical evidence for a predominant role of the glide partial dislocations in Si, justifying the recent flourish of theoretical work on the core structure and mobility mechanisms of the glide partials [6–9].

Of the two most important dislocations in Si, 90° and 30° partials, our focus is on the latter, for the following reasons. First, core structure of the 30° glide partial is reasonably well established [9], whereas the same is not the case for the 90° glide partial [6,8,10]. Second, both theoretical and experimental data suggest that the overall mobility of the dissociated perfect dislocations in Si is controlled by the slower 30° partial [11]. Finally, there is considerable evidence linking the electrically active centers, observed in the electron paramagnetic spin resonance (ESR) measurements, to vacancies in the core of 30° partial dislocations [12,13].

For *ab initio* calculations, we constructed orthorhombic supercells containing 144 or 192 atoms, in order to have three and four core atoms per dislocation line, respectively. A dipole of 30° partial dislocations was introduced by displacing the atoms according to the known solution for the displacement field of a dislocation dipole [2]. The cell geometry was such that dislocations of the dipole were no closer than 13.2 Å from each other, which was far enough to prevent the core-core overlap. Figure 1 shows a schematic representation of the 30° partial dislocation

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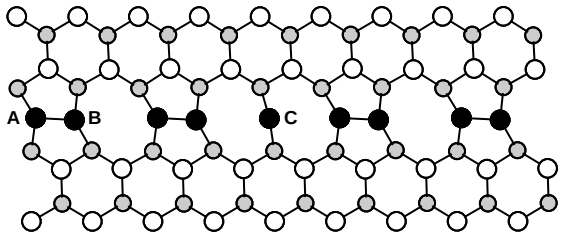

FIG. 1. Atomic structure of the 30° partial viewed from above the {111} glide plane. White and gray atoms lie above and below the glide plane, respectively. Core atoms are shown in black.

core in the {111} glide plane, after 2×1 core reconstruction. There are two types of atoms in the core: fourfold coordinated "reconstructed" (atoms A and B) or threefold coordinated "unreconstructed" (atom C). Positions of all atoms were initially relaxed by a conjugate gradient algorithm using a newly developed environment-dependent interatomic potential (EDIP) for silicon [14]. In the initial relaxation procedure, the shape of the supercell was adjusted using the Parrinello-Rahman method. The final relaxed structures obtained with EDIP were then used as the initial configurations for subsequent relaxations with the *ab initio* forces. The latter were evaluated within the local density approximation (LDA) of the density-functional theory (DFT) [15]. The Kohn-Sham equations were solved within the Car-Parrinello approach using pseudopotentials [16]. The valence electron wave functions were expanded in a plane-wave basis set, with kinetic energy cutoff of 10 Ry. Sampling of the Brillouin zone was performed using the $(0, 0, 1/2)$ point. Relaxation was performed until the Hellmann-Feynman forces on all atoms were smaller than 0.001 Ry/a.u.

First, we consider a single vacancy in the dislocation core, using a supercell of 192 atoms. In Fig. 1, atoms A and B of the reconstruction dimer maintain the usual fourfold coordination, although the reconstruction bond between them is 5% longer than the perfect bulk bond. By removing atom A and relaxing the resulting structure, a vacancy is created in the dislocation core. The formation energy of this vacancy is 2.36 eV and should be compared to 3.64 eV for the formation energy of a vacancy in the bulk. This latter value was obtained after introducing a single vacancy in the same supercell, but without the dislocation dipole. This bulk vacancy features a nearly perfect D_{2d} symmetry, in agreement with an earlier calculation [17]. The difference of 1.28 eV between the two formation energies is consistent with another earlier calculation [18] and represents the binding energy of a vacancy to the core of a 30° partial dislocation. This core defect has been identified by ESR measurements, and is usually referred to as the Si-$K1$ center [12]. By removing the second atom B, a di-vacancy is created in the core. This defect has a formation energy of 3.74 eV (1.87 eV/vacancy), which is only slightly higher than the formation energy of a single vacancy in the perfect crystal, at 3.64 eV. The di-vacancy defect can be related to the so-called Si-$K2$ center identified in ESR experiments with a row of n vacancies ($n \geq 2$) in the core of a 30° partial dislocation [12]. By further removing all atoms from the dislocation core, a shuffle-vacancy (S_V) partial dislocation is created. For this case, we obtain formation energy of 1.95 eV/vacancy, which is only slightly different from that for the di-vacancy, indicating that interaction between neighboring di-vacancies in the core is weak.

Two centers discussed so far, Si-$K1$ and Si-$K2$, are associated with the vacancies in fourfold coordinated core atoms. However, a core atom can also be threefold coordinated (atom C in Fig. 1), which is usually referred to as a reconstruction defect (RD). A threefold coordinated vacancy is created by removing atom C from the core. Such a configuration has been identified in ESR measurements and labeled the Si-Y center [12]. From our *ab initio* calculations, using a supercell with 144 atoms, we find that the formation energy of a vacancy in the RD center is 0.89 eV. This is markedly lower than the formation energy of a fourfold coordinated core vacancy. The formation energies of all vacancy-type defects are significantly lower than the corresponding formation energy of a vacancy in the bulk, indicating that the glide dislocation core provides a center of preferred sites for vacancy nucleation. These results are consistent with recent calculations which show that the stacking fault also provides preferred sites for defect nucleation [19]. From the point of view of equilibrium thermodynamics, our results imply that the concentration of vacancies in the glide core should be higher than in the bulk.

In principle, in order to compare the relative concentrations of bulk and core vacancies at finite temperatures, one has to calculate free energies of the relevant defect configurations. Mindful of the fact that free-energy calculations are almost prohibitively expensive when used in combination with the total energy DFT methods, we chose to carry out the necessary finite temperature simulations using the computationally inexpensive semiempirical EDIP model [14]. First, as a consistency check, we determined the zero-temperature formation energies of the relevant defect configurations and compared them with the corresponding DFT/LDA values reported above (Table I). The good agreement between the EDIP and the *ab initio*

TABLE I. Per-vacancy formation energies and entropies of various vacancy-type defects in the core of a 30° partial dislocation. For reference, the values for a vacancy in the bulk are also shown.

	LDA (eV)	EDIP (eV)	Formation entropy (k_B)
Bulk	3.64	3.25	4.3
Si-Y	0.89	1.45	1.6
Si-$K1$	2.36	2.11	2.9
Si-$K2$	1.87	1.79	2.2
S_V	1.95	1.79	2.2

results provides some assurance that the EDIP model can give equally accurate description of the energetics of partial dislocations at finite temperatures.

For the finite temperature simulations, we employed a bigger, 864 atom periodic supercell containing a dipole of fully reconstructed 30° glide partials of length 45.7 Å ($[\bar{1}10]$ direction), separated by a stacking fault ribbon 20.0 Å wide ($[11\bar{2}]$ direction). As earlier, the initial configurations of the Si-$K1$ and Si-$K2$ defects were obtained by removing, respectively, one (atom A in Fig. 1) and two adjacent atoms (A and B) from one of the glide partials in the dipole. For the Si-Y defect, the initial configuration was obtained by removing one atom from the dislocation core (atom C in Fig. 1). For the complete S_V partial dislocation, all the core atoms of both glide partials in the dipole were removed. The resulting defect structures were relaxed using a combined simulated annealing/conjugate gradient minimization scheme.

In order to determine the free energies of the vacancy-type defects, or shuffle segments in the glide partial core, we applied the recently developed reversible-scaling (RS) method [20], which allows efficient calculation of free energies using Monte Carlo (MC) or MD techniques. The method is based on a dynamical scaling of the potential energy function, implemented through the adiabatic switching method [21]. This particular approach allows the determination of free energies as a function of temperature using a single constant temperature run in a MC or MD simulation.

Figure 2 shows formation free energies (per vacancy) as a function of temperature for the Si-Y, Si-$K1$, and Si-$K2$ centers, the S_V partial, and the single vacancy in the bulk crystal. The symbols show the data determined using the RS method. For comparison, we also evaluated the free energies within the harmonic approximation (HA) [22], using the partition function based on the "frozen" phonon frequencies of the relaxed defect structures. The HA results are represented by the lines. The agreement between the RS and HA values suggests that anharmonic effects are minor and that the formation entropies are essentially temperature independent. The values of the EDIP formation entropies are listed in Table I. The formation entropy of $4.3k_B$ for the single vacancy in bulk crystalline Si is in good agreement with an earlier *ab initio* value [23] of $5k_B$. For all vacancy-type defects in the 30° glide partial core the formation entropies are found to be lower than in the perfect crystal.

Assuming that the values for formation entropies obtained with the EDIP function are reliable, we now combine the LDA formation energies E_f with the EDIP formation entropies S_f. The relative equilibrium concentration C_V of thermally nucleated vacancies in the reconstructed core, defined as the fraction of sites in the core occupied by vacancies, is then determined by

$$C_V = \exp(S_f/k_B)\exp(-E_f/k_BT)\,. \qquad (1)$$

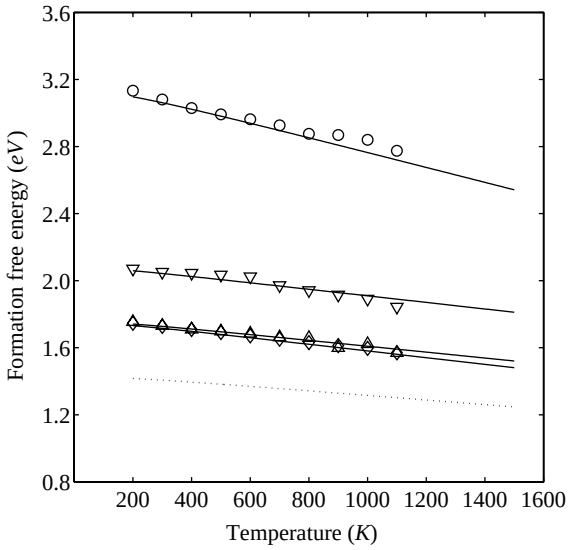

FIG. 2. EDIP formation free energies per vacancy as a function of temperature for several vacancy-type defects in the 30° glide partial core. Symbols indicate RS values calculated for Si-$K1$ (▽), Si-$K2$ (△), and S_V (◇). Lines are formation free energies calculated within the harmonic approximation. For Si-Y defect only HA results are shown (dotted line). For comparison, RS (○) and HA formation free energies of a vacancy in the perfect crystal are also shown.

For the Si-Y center, we included an appropriate prefactor in the C_V expression to account for the concentration of RD centers in the dislocation core. For that we used the RD formation energy of 0.65 eV reported earlier [9], and the entropy of $0.3k_B$ computed here for the EDIP model using the HA method.

Figure 3 shows the contributions of the Si-Y, Si-$K1$, and Si-$K2$ centers to the equilibrium concentration of vacancies in a 30° glide partial dislocation. The relative equilibrium concentration of single vacancies along a bulk $[\bar{1}10]$ atomic row is also shown. The predicted concentrations of Si-Y and Si-$K1$ defects are much higher than the corresponding vacancy concentration in the bulk $[\bar{1}10]$ atomic row. At $T = 1600$ K, for example, the concentration of vacancies in the glide core due to the Si-Y defects is about 10^{-4}, while the corresponding value in a bulk $[\bar{1}10]$ atomic row is roughly 10^{-9}. Consistent with the experimental findings, the concentration of the Si-Y center is the largest of all the vacancy core defects [1], much higher than the predicted concentration of the Si-$K1$ and Si-$K2$ defects.

Although the equilibrium concentration of vacancies in a glide partial core is considerably higher than in the bulk, it is still rather low. Even at temperatures around the melting point, only one in each 10^4 sites is expected to be occupied by a vacancy. This suggests that the concentration of thermally nucleated shuffle sections is small and that 30° partial dislocations in Si should belong to the glide set. Strictly speaking, this conclusion pertains only to the partial dislocations at rest and in local thermodynamic equilibrium. This is because vacancy defects can be introduced

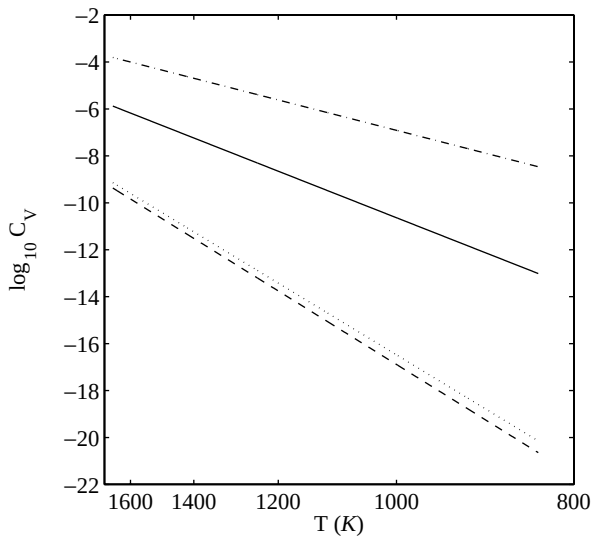

FIG. 3. Concentrations C_V of vacancy-type defects in the 30° glide partial core as a function of temperature: Si-Y (dot-dashed line), Si-$K1$ (full line), and Si-$K2$ (dashed line). The corresponding equilibrium concentration in a $[\bar{1}10]$ atomic row in the bulk crystal is also shown (dotted line).

in the core when the partials move under stress, especially under conditions of vacancy supersaturation. Whether or not this principal possibility is in fact realized in Si remains an issue for further study.

In summary, we have investigated the interaction of vacancies with the core of a 30° partial dislocation in Si. The predicted thermal concentrations of several vacancy-related centers in the core are considerably higher than in the bulk crystalline environment. Still, these concentrations are too low to expect that shuffle-vacancy segments of appreciable lengths will be present in the core. Therefore, our results support the view that Shockley partial dislocations in Si belong to the glide subset.

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