Stability and Dynamics of Frenkel Pairs in Si

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(Received 20 August 2007; published 20 November 2007)

Extensive experiments and calculation have shown that interstitials in *p*-Si diffuse athermally, leading to the conclusion that vacancy-interstitial pairs, or Frenkel pairs (FPs), either rapidly recombine or dissociate, even at cryogenic temperatures. More recent experiments, however, suggest that FPs persist to 150 K. Here we report first-principles calculations of FP properties and resolve the apparent conflict between experiments by showing that athermal interstitial diffusion is suppressed in proximal FPs due to vacancy-interstitial interactions.

DOI: 10.1103/PhysRevLett.99.215503 PACS numbers: 61.72.Ji, 61.72.Yx

The Si lattice vacancy and self-interstitial are prototype point defects in semiconductors and have been extensively studied. In a series of experiments dating to the 1960s, Watkins and co-workers used an electron beam at cryogenic temperatures to produce vacancies and interstitials in bulk Si [1–4]. Only EPR signals identified as arising from *isolated* vacancies (V_{Si}) and interstitial impurities were subsequently observed, leading to the conclusion that Si interstitials (I_{Si}) are highly mobile, even at 4.2 K [2,3]. This large low-temperature mobility has been attributed to athermal, recombination-enhanced diffusion pathways according to the Bourgoin-Corbett mechanism [5]. In this mechanism, the successive capture of electrons and holes by a defect overcomes the barriers to defect diffusion. Bourgoin-Corbett pathways have been identified for *both* isolated I_{Si} [6,7] and V_{Si} [5,8,9].

It has, therefore, been widely believed that high V_{Si} and/or I_{Si} mobilities necessarily lead either to the rapid dissociation or recombination of Si vacancy-interstitial pairs, or Frenkel pairs (FPs), at any temperature [2,3]. This conclusion was recently challenged by results of x-ray scattering experiments that show paired positive and negative strain centers in electron-irradiated *p*-Si separated by ~10 Å [10,11]. These spatially correlated strain centers have been identified as FPs and persist to temperatures beyond 150 K. As recently noted by Watkins [3], this result necessitates a reexamination of the fundamental interactions between V_{Si} and I_{Si}.

In this Letter, we report results of extensive first-principles density-functional calculations of the properties of FPs in *p*-Si and reconcile the seemingly conflicting experimental data on Si FPs. We demonstrate that athermal diffusion is suppressed in *proximal* FPs, because the interaction between component vacancy and interstitial defects removes the charge-state dependence of the interstitial configuration. Thus, though no chemical bonding occurs between nearby V_{Si} and I_{Si}, proximal FPs are stabilized by migration energy barriers, which are gradually overcome at high temperatures. We find that while FPs with *V*-*I* separations smaller than ~5 Å are unstable and recombine spontaneously, FPs with larger separations are stable. In addition, we show that the vacancy components of FPs in *p*-Si would be indistinguishable in EPR experiments from isolated V_{Si}. This analysis is corroborated by the fact that both the paired strain centers (FPs) observed by x-ray scattering and the EPR observed V_{Si}^0 anneal in the same temperature range [1,10,11].

Total energies, relaxed geometries, and valence electron densities were calculated using density-functional theory and the local density approximation as implemented in the VASP program [12]. Core-electron interactions were modeled using Vanderbilt ultrasoft pseudopotentials [13]. The electronic wave functions were expanded in plane waves with a kinetic-energy cutoff of 188 eV. Reciprocal-space summations were performed using a $3 \times 3 \times 3$ Monkhorst-Pack mesh [14] of special *k* points centered at the Γ point. Defects were studied using periodically repeated cubic supercells containing 216 ± 1 atoms. Convergence test results and calculation parameters for this study are consistent with the extensive and systematic analysis of Ref. [15] for point defects in Si.

Fifteen different FP configurations and the isolated V_{Si} and I_{Si} were studied. The atomic positions were relaxed according to the calculated forces until the total energy was converged to within 10^{-5} eV. After relaxation, residual forces were less than 0.02 eV/Å. Results for isolated defects were consistent with previous results [8,15,16]. The nudged-elastic-band method was used to calculate minimum energy pathways (MEPs) and migration energy barriers (MEBs) for a number of diffusion related transitions between FP configurations. A uniform background charge was introduced in calculations of charged defects to give net neutral cells.

Starting atomic geometries for FPs included hexagonal and tetrahedral I_{Si} in various configurations within ~8.1 Å of a V_{Si} and at various net charge states. All hexagonal interstitial configurations spontaneously relaxed to tetrahedral interstitial configurations, implying that FPs with hex-

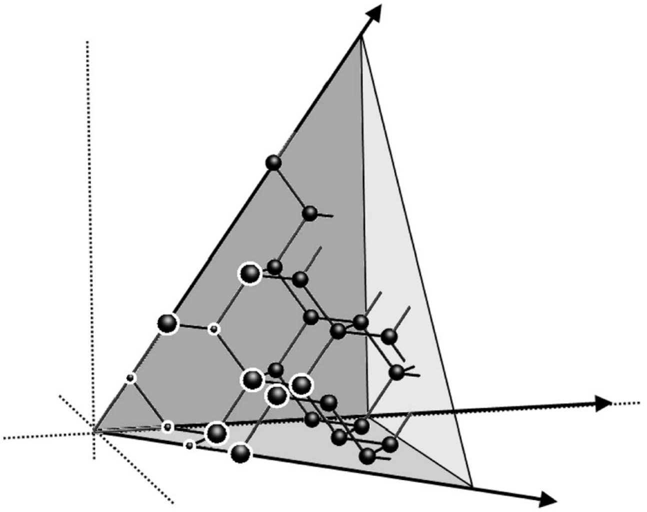

FIG. 1. Symmetrically distinct FP configurations in Si. Each ball indicates a different position for a tetrahedral I_{Si} relative to a V_{Si} at the origin. Large and small balls in white circles indicate stable and unstable, respectively; remaining balls are FPs with larger V-I separations. Sticks connect FP configurations that are related by a single vacancy-diffusion hop. Bold arrows define the minimum volume containing the set of symmetrically distinct FPs.

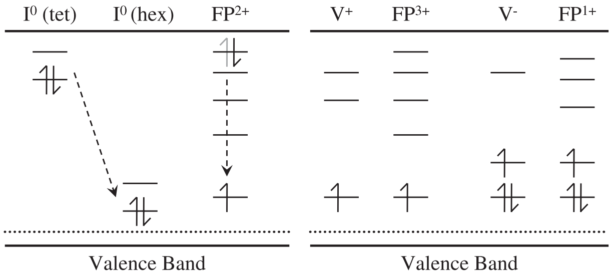

FIG. 2. Relative positions of I_{Si}, V_{Si}, and FP defect levels in the Si band gap at the Γ point. Dotted line indicates expected Fermi level for B-doped Si. The left panel depicts expected behavior after electron capture in shallow defect levels, while the right panel highlights similarities between EPR-active FPs and V_{Si} in p-Si.

agonal interstitial components are never stable structures, regardless of charge state. A subset of tetrahedral interstitial configurations are unstable and relaxed directly to defect-free bulk Si, indicating the absence of any energy barrier to V-I recombination. For large enough distances between the V_{Si} and I_{Si} (generally >5 Å), relaxed, globally metastable FP structures, separated from the global ground-state structure (undefected bulk Si) exist for all considered charge states. The minimum separation distance for stable FPs increases with the addition of electrons, as noted previously [17]. Figure 1 presents a schematic of the set of possible, symmetrically distinct positions for a tetrahedral I_{Si} within $\sim$17 Å of a V_{Si} located at the origin. In Fig. 1, FP^0 configurations found to be stable (unstable) are indicated as large (small) spheres highlighted with a white outline. The remaining medium spheres indicate configurations with larger V-I separations.

The previously studied athermal diffusion pathways for both isolated I_{Si} and V_{Si} rely on the remarkable fact that changing the local defect charge state by capturing available electrons or holes results in a barrierless relaxation from one defect configuration to another. Alternating the charge state of a V_{Si} from negative (where V_{Si}^{2-} has the ground-state semivacancy, or split vacancy, configuration) to neutral or positive (where the D_{2d} vacancy configuration is stable) results in barrierless diffusion of V_{Si}. This process is active in n-Si and is not active for the defect charge states considered here in p-Si.

On the other hand, an athermal I_{Si} diffusion mechanism is active in p-Si. While the ground state I_{Si} in B-doped p-Si has charge $q = +2$ (see Fig. 2 and, e.g., Ref. [8]) and is tetrahedrally configured, the neutral I_{Si}^0 has lower energy in either the hexagonal or split-$\langle 110\rangle$ configuration [8]. Therefore, repeated capture and recombination of electrons on an I_{Si}^{2+} allow athermal diffusion from a tetrahedral site, through a hexagonal or split-$\langle 110\rangle$ interstitial site, and back to a tetrahedral site [6]. The enabling capture and recombination processes are highly efficient due to the position of the I_{Si} defect states high in the band gap for the tetrahedral I_{Si} and low in the band gap for the hexagonal I_{Si} (see Fig. 2). The net effect is fast, athermal diffusion of isolated I_{Si} in p-Si, given the presence of a nontrivial population of electrons and holes (generated, e.g., by carrier injection, or illumination with band-gap light).

The analogous process for *proximal* FPs in p-Si, involving electron capture at shallow FP defect states, *does not* activate the athermal diffusion of the interstitial defect component. FPs in B-doped p-Si have a ground-state local charge of $q = 4+$ (see Fig. 2) and a tetrahedrally configured interstitial component. After adding *either* one *or* two electrons (giving a net local charge of $q = 3+$ or $q = 2+$) to *either* of the two highest FP defect energy levels in the Si band gap, the tetrahedral interstitial in the FP remains stable and must overcome a nonzero energy barrier in order to transition to a hexagonal or split-$\langle 110\rangle$ configuration. Therefore, while entropy contributions to the defect-free energy at finite temperature may alter the quantitative details of the energy barriers, there exists a temperature range within which FPs are stable. Both the interaction of the component defect strain fields and the overlap of defect wave functions for proximal V_{Si} and I_{Si} contribute to the stabilization of the tetrahedral interstitial. Electrons captured in shallow FP states are trapped and may subsequently fall into deeper gap states before recombining (see Fig. 2). This process is facilitated by wave function overlap between the shallow FP states (centered on the interstitial) and deep FP states (centered on the vacancy) due to the proximity of the vacancy and interstitial.

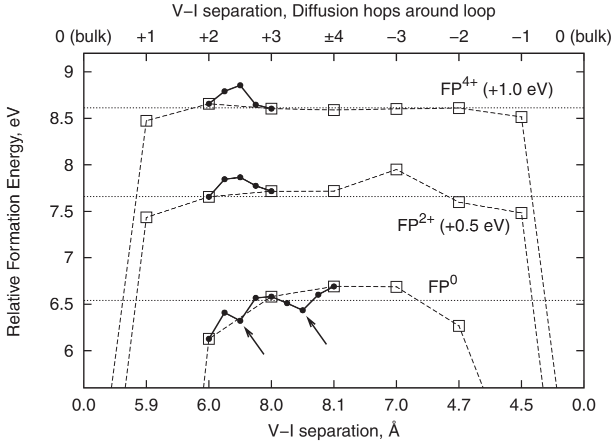

FIG. 3. Relative formation energies of FPs along a loop of vacancy-diffusion hops (open squares, dashed lines). Dotted horizontal lines indicate net formation energy of dissociated components. Black points connected by solid lines are calculated energies along MEPs. Formation energies for FP^{+2} and FP^{+4} have been shifted up by 0.5 and 1.0 eV, respectively.

Given that *athermal* motion of V_{Si} and I_{Si} is suppressed in proximal FPs, we next consider the MEBs to the motion of the FP components—that is, the barriers to FP dissociation or recombination. Dissociation (or recombination) of a FP is accomplished by successive individual diffusion "hops" of either the vacancy or interstitial component of the FP increasing or decreasing the vacancy-interstitial separation. For a sufficiently large separation (the value of which would depend on the local dielectric properties, and is likely on the order of nanometers) there is no interaction, either electronic or strain mediated, between the defects. The now isolated vacancy and interstitial are free to diffuse according to the previously described athermal mechanisms. Similarly, for a sufficiently small separation (~6 Å), no barrier remains to FP recombination and the component vacancy and interstitial annihilate each other. Individual diffusive events within a FP are equivalent to FP configuration changes (see, e.g., Fig. 1).

We calculated representative MEBs for FP configuration changes to be 0.86 eV for interstitial diffusion and 0.20 eV for vacancy diffusion. These barriers are quantitatively similar for all FP charge states $q \geq 0$ and indicate that FP dissociation or recombination is vacancy-diffusion mediated. The large barrier for interstitial diffusion is consistent with the calculations of Car *et al.* [6] for I_{Si}^{2+}. The barriers for vacancy diffusion within a FP (0.20 eV) are similar to the barrier calculated in the present work for diffusion of an isolated V_{Si}^{0} (0.17 eV). Based on the experimentally determined annealing curves of Watkins for V_{Si}^{0} (see, e.g., [1]), these quantitatively similar MEBs indicate that FPs should be expected to anneal at the same temperature as V_{Si}^{0}: ~150 K. This is consistent with the x-ray scattering observed FP annealing behavior [10,11].

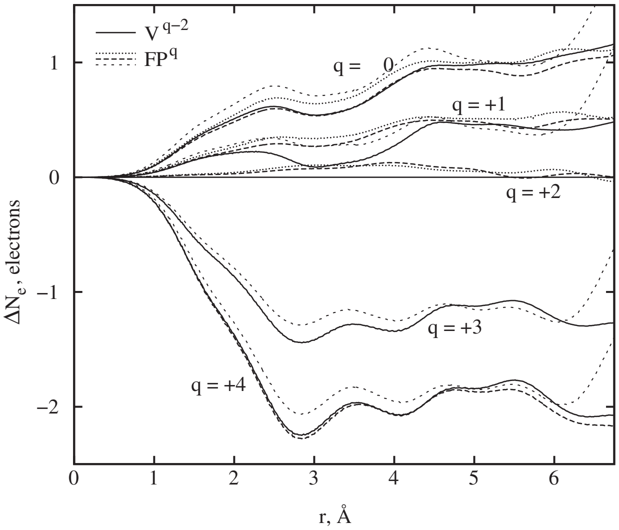

FIG. 4. The difference as a function of radius, $\Delta N_e(r)$, of the spherically integrated valence electron density around isolated and FP vacancies at various charge states relative to the spherically integrated valence electron density around a neutral, isolated V_{Si}^{0}. Solid lines are ΔN_e for isolated V_{Si} with charges $q - 2 = -2$, -1, 0, $+1$, and $+2$. Dashed lines are ΔN_e for vacancies in different FP configurations with net charges $q = 0$, $+1$, $+2$, $+3$, and $+4$.

To assess the binding energy of vacancies and interstitials in FPs we have considered a vacancy-diffusion "loop", in which a vacancy first travels away from an interstitial and then returns towards the interstitial by a different path. For each tetrahedral FP configuration in the loop, the formation energy was calculated at various charge states, and is shown in Fig. 3. To aid readability, plotted values for FP^{2+} and FP^{4+} formation energies has been shifted up by 0.5 and 1.0 eV, respectively. Calculated energies along MEPs for vacancy diffusions connecting a subset of FP configurations are plotted as small solid circles connected by solid lines in Fig. 3.

The FP binding energy is the difference between the FP formation energy and a component defect reference energy. For all calculations conducted in equivalent cells and with identical settings, this reference energy is the sum of the isolated V_{Si} and isolated I_{Si} formation energies. As it has previously been suggested that Si FPs are donor-acceptor pairs [8], it is important to specify the correct charge states of the isolated V_{Si} and I_{Si} when calculating reference energies. Figure 4, showing the difference in the spherically integrated density of valence electrons around isolated and FP vacancies relative to the spherically integrated valence electron density around a neutral, isolated V_{Si}^{0}, demonstrates that FPs are, in fact, donor-acceptor pairs in intrinsic Si. Figure 4 shows that the charge distribution in ground-state Si FPs obeys the rule $\mathrm{FP}^{q} = V^{q-2} + I^{2+}$ for $q \geq 0$. This is further supported by the fact that the MEPs calculated for neutral FPs (which are unlikely to be present in B-doped Si, as they would represent equilibrium FPs which have captured *four* electrons) have local energy minima lying at the halfway point for vacancy diffusion between two standard FP configurations (see Fig. 3, points indicated with arrows). These halfway configurations correspond to FPs containing semivacancies, in agreement with the previously noted behavior of isolated V_{Si}^{2-}. Variations in charge state among FPs and their reference isolated components result in a small deviations of reference energy from the asymtoptic "infinitely separated" FP formation energy (see Fig. 4). This deviation represents a measure of the errors in defect formation energies induced by finite system size and the uniform background charge employed for charged defects, and it suggests that the current system sizes are sufficient to give formation energies accurate to within ~0.1 eV.

Neutral FPs with a small radius of separation, e.g., configurations labeled +2 or −2 in Fig. 3, have a positive binding energy of about 0.5 eV. These same configurations have effectively zero binding energy for $q = 4+$. This result is generally consistent with a simple Coulombic argument, where the vacancy and interstitial of a FP^0 have opposite local net charge ($\mathrm{FP}^0 = V^{-2} + I^{+2}$), while the components of a FP^{+4} have local net charges of the same sign. The lack of a negative binding energy (a repulsion) within FP^{+4} indicates the relative strength of electronic and strain-mediated defect stabilization.

It is certainly necessary to comment on the fact that EPR characterization of electron-irradiated *p*-Si has not identified any specific signal associated with the FP. In the ground state, the electronic and atomic structure of vacancies in FPs greatly resembles that of isolated V_{Si}. The defect levels low in the Si band gap (and therefore observable in *p*-Si) calculated here for FPs and isolated V_{Si} are quantitatively similar. This is highlighted in Fig. 2 for EPR-active V_{Si} and FPs likely present in *p*-Si. The atomic structure of vacancies in FPs (that is, the arrangement of atoms which are nearest neighbors to the vacant lattice site) is also extremely similar to the atomic structure of isolated V_{Si}, with near-vacancy bond lengths in FPs varying by <0.05 Å from those in isolated V_{Si}. In addition, Fig. 4 shows that the spherically integrated valence charge distribution around FP vacancies is nearly identical to those of isolated V_{Si}. Therefore, no specific EPR signal from FPs, as distinct from those due to free, isolated V_{Si}, should be observed in *p*-Si.

Based on first-principles calculations of the properties of Si FPs, we have demonstrated that the known athermal diffusion pathway for I_{Si} in *p*-Si is suppressed in proximal FPs. This suppression results in energy barriers to the diffusion of interstitial and vacancy components of proximal FPs. We have also shown that FPs in intrinsic Si are donor-acceptor pairs, and that a charge-state dependent binding energy is present between vacancies and interstitials. Based on analogy to the calculated diffusion barriers and EPR-observed annealing behavior of isolated V_{Si}^{0}, the 0.20 eV diffusion barrier calculated here for FP component vacancies correlates well with the x-ray scattering observed annealing temperature for FPs of ~150 K. The quantitative similarities between FP and isolated V_{Si} properties (including defect energy levels, atomic structure, and valence electron charge distribution) imply that FPs and isolated V_{Si} are likely indistinguishable in EPR experiments on electron-irradiated *p*-Si samples. Finally, the present results highlight the fact that the properties of compound defects in semiconductors—including, e.g., divacancies, defect clusters, and impurity complexes—are generally not a direct superposition of the component defect properties.

This work was supported in part by AFOSR under MURI Grant No. FA9550-05-1-0306 and by the McMinn Endowment at Vanderbilt University. We would like to thank D. M. Fleetwood, R. D. Schrimpf, and L. C. Feldman for useful discussions.

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