Low-energy recoils in crystalline silicon: Quantum simulations

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Tight-binding molecular dynamics has been performed to study low-energy (10–25 eV)-recoil events in Si and to determine the threshold energies of atomic displacement for collision along the $\langle 111\rangle$, $\langle \overline{111}\rangle$, and $\langle 100\rangle$ directions. Since classical molecular dynamics has been widely used to simulate radiation-damage phenomena in Si, we found it of interest to compare tight-binding results with those obtained by classical calculations, using different forms of the empirical potentials. Results show that tight-binding simulations provide threshold energies that are, on average, lower than classical ones, and similar to those calculated with the Tersoff potential. The relevant difference between quantum and classical calculations is that the former systematically provide much larger relaxation energies of the defective configurations left at the end of the thermalization phase. This result may reveal a tendency to further evolution and, possibly, recombination of defects on a time scale relevant for microstructural evolution of implanted silicon.

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A basic concept used to describe the response of crystalline materials to particle irradiation is the threshold energy for atomic displacement (E_d).[1] E_d may be defined as the minimum energy that, when released to a target atom embedded in a crystalline host, leads to the formation of a lattice defect that survives at least the energy thermalization phase, lasting about 10^{-12} s. The quantity E_d has been extensively used in the context of elementary-damage models,[2] or simulations based on the binary-collision approximation (BCA).[3,4] In the past several years there has been increasing awareness that the mechanisms of radiation damage induced by heavy particles (as, for instance, during ion implantation) involve collective lattice properties (see, for instance, Ref. 5), and cannot be accounted for by the simple application of E_d to atoms treated as individuals. Nevertheless, under conditions where particle-target collisions are sufficiently separated in space and time, the process of damage accumulation is approximated by the sum of individual-displacement events, and E_d may be used to estimate the number of radiation-induced defects within the BCA model.

Owing to the huge technological interest in silicon, many studies on radiation damage have been focused on this material. Experimental values of E_d lying between approximately 10 and 40 eV have been reported,[6] depending on irradiation conditions such as crystal orientation[7] and temperature.[8] The experimental determination of E_d is a difficult task, since primary atomic displacements occur during very fast non-equilibrium events. In fact, a defect created and surviving after 10^{-12} s may annihilate at later times due to the long-term relaxation kinetics of the lattice. The experimental detection of defects typically occurs at times much longer than 10^{-12} s after the collision event, when a large part of damage may have annihilated. The measured E_d represents in this case an effective value, which accounts also for the kinetics following the energy-thermalization phase. A chance to investigate the early stages of the displacement process at the relevant atomic scale is offered by molecular-dynamics (MD) computer simulations.

Except for a recent paper,[9] to the best of our knowledge all calculations of E_d in Si reported so far[9–12] have been performed with classical MD.[10–12] It is generally recognized that none of the classical potentials developed for Si can reproduce equally well its different properties and varying atom coordination and bonding.[13,14] Empirical potentials may be inaccurate when used outside the field of properties to which their parameters are empirically fitted. Nevertheless, the strong interest in the study of radiation damage in Si, has led to extensive application of classical MD in this field. In this context it is difficult to understand to what extent the qualitative and quantitative description of radiation effects may be affected by the inaccuracies in the model potential. As a matter of fact, numerical results of E_d in Si so far reported are spread in a wide range, depending on the choice of the interatomic potential. Another critical issue consists in the actual setup of the main parameters governing the simulation, i.e., cell size, temperature control, and time step. The cell size is crucially important: since most of the calculations are typically performed with periodic boundary conditions, the sound wave emitted at the primary knock-on atom (PKA) event may eventually interact with the PKA itself. This possible artifact is prevented either by selecting a large cell, or by providing an efficient mechanism to absorb the thermal spike (like a thermalized boundary wall). As for the computer generation of atomic trajectories, when the displaced atoms are accelerated by the PKA (up to a kinetic energy much larger than the usual thermal one), the choice of the time-step value becomes critical for an optimal integration of the equations of motion.

For covalent materials and interaction energies close to the chemical bonding regime (say $\leqslant 10$ eV), methods that account for the quantum-mechanical effects of valence electrons are expected to be more accurate. Actually, the dynamics of low-energy recoils in Si is a problem where both short-range internuclear forces and chemical bonding are expected

to play a role. A method suitable both to the length scale and time schedule of the problem under consideration, is the tight-binding molecular dynamics (TBMD).[15,16] In this work we report the results of a study on the early-stage dynamics of low-energy (10–25 eV) recoils in Si using the TMBD method. The purpose is twofold. First, we aim to provide a description of the physical mechanisms at the atomic scale more accurate than the one observed with classical MD. Second, we wish to point out the qualitative and quantitative differences between quantum and classical MD results, when the same simulation setup is adopted. The latter aspect is of great interest, considering the large amount of simulation work done in the field of radiation damage with classical MD. To this purpose, the TBMD model by Kwon *et al.*[17] has been applied for studying displacement events in Si along three major lattice directions ($\langle 111\rangle$, $\langle \overline{111}\rangle$, and $\langle 100\rangle$) at a bulk temperature of 0 K. The TB scheme employed here has been successfully applied in several studies on formation, migration, and clustering properties of native defects in silicon and, therefore, represents a thrustworthy theoretical framework. We refer to Refs. 16–19 for further details on the TB model. For comparison, classical MD calculations using different forms of the interatomic potential, namely, Stillinger-Weber (SW),[20] Tersoff (TS),[21] and environment dependent interatomic potential (EDIP),[14,22] have been performed. In all cases no attempt to spline the many-body potentials to a two-body potential for short interatomic separation[23] was done. In fact, due to the low-PKA energies (typically, 10–25 eV) the distances of minimum approach between particles (i.e., displaced atom and its neighbors) are always within the range of applicability of the classical and tight-binding potentials considered here.

The PKA event was simulated as occurring at the center of a periodically repeated cubic cell containing as many as 512 atoms. At variance with previous investigations,[9] we have found that this is the minimum cell dimension assuring no size effect whatsoever. For instance, for both TBMD and EDIP simulations the computed value of E_d for recoils along the $\langle 100\rangle$ direction only varied by about 6% when passing from 216- to 512-atom cells. No further variation was observed for classical potential investigated by even larger cells, containing up to 2744 atoms. On the other hand, problems were always encountered for the smallest (64 atom) cell: in this case TMBD results were found to be sensitive to the thermalization procedure (an exceedingly sizable amount of atoms were actually coupled to the thermostat lying at the boundary wall of the simulation cell). After the initial equilibration at 0 K, one atom at the center of the cell was given the momentum corresponding to the chosen energy and PKA direction. No separate mechanism of inelastic energy transfer to the electronic system (almost in-influent for the dynamics of the system in this PKA energy range[24]) was considered. Atomic trajectories have been aged by means of velocity-Verlet microcanonical evolution. The recovery of the thermal spike occurring immediately after the PKA event and the following sample thermalization was operated through the thermalization of few atomic planes (lying at a boundary wall of the simulation cell) by velocity rescaling. Finally, to obtain the best accuracy in the generation of the atomic trajectories, we implemented a multiple time-step (δt) algorithm, where the actual δt was selected according to the maximum particle displacement and velocity both computed at the previous step. The resulting δt varied in the range 0.01–0.1 fs. Test calculations showed that large errors in the generation of atomic trajectories may arise when using a fixed time step of 0.1 fs, especially under conditions (e.g. PKA in the $\langle 111\rangle$ bonding direction) where the particles experience ''head-on'' collisions. In fact, in the latter case the large steric internuclear repulsion leads to a very fast kinetics, due to the rapid energy exchange between the PKA and the target in the initial phase of the collision. The multiple time-step algorithm here adopted is, of course, much more computer demanding than its fixed time-step counterpart and therefore it results prohibitively expensive for *ab initio* calculations.[9] Under this respect the semiempirical nature of the adopted TBMD scheme has revealed as a breakthrough for this investigation. Nevertheless, such a numerical approach resulted into an heavy computational budget. The work load of TBMD simulations was mastered by means of iterative scalable eigensolvers for matrix diagonalization.[25]

After the PKA event, the evolution of the system is followed for 4 ps and eventually the sample is cooled to 0 K. E_d is defined as the minimum PKA energy for which some defects (i.e., Wigner-Seitz cells of the initial perfect crystal containing zero, or more than one atom) are observed at the end of the final cooling phase.

Table I summarizes the results of the simulations for PKA in $\langle 111\rangle$, $\langle \overline{111}\rangle$, and $\langle 100\rangle$ directions. For each model, the value of E_d and the potential energy variation (ΔE_{pot}) and relaxation energy (ΔE_{rel}) of the cell at the end of the event initiated by the PKA with energy E_d, are reported. The relaxation energy is defined as $\Delta E_{rel}=\Delta E_{pot}-E^f_{vac}-E^f_{int}$, where E^f_{vac} and E^f_{int} are the formation energies of isolated vacancy and interstitial, respectively, calculated with the corresponding model potential. The latter column indicates the mechanism that leads to the formation of the defect. The different mechanisms are described in the figure caption.

E_d values obtained from classical SW and TS calculations are in close agreement with previous reports.[11,12] On the other hand, TMBD value (11.75 eV) found for the antibonding ($\langle \overline{111}\rangle$) direction is 4.5 eV larger (i.e., about 36%) than that of the TMBD value reported in Ref. 9. The discrepancies in TMBD results are most likely due to the different TB models adopted here and in Ref. 9: as a matter of fact, they provide somewhat different values for the formation energies of the different metastable self-interstitial configurations. We also believe that another key point is represented by the temperature-control procedure actually applied. It is, however, hard to further comment on this point since no detail about this feature is offered in Ref. 9. It is, however, worth remarking that our E_d value compares more favorably with the first-principle result of 9.75 eV reported in Ref. 9.

It is apparent from Table I that the values of E_d calculated by the SW potential are the largest for all PKA directions investigated. Moreover the mechanism of defect formation is always different from that observed in TS, EDIP, and TBMD simulations. In fact, for the SW potential the defect formation always involves the displacement both of the PKA and

TABLE I. Results of MD simulations of low-energy recoil events in Si. The labels SW, TS, EDIP refer to classical calculations, made with Stillinger and Weber (Ref. 20), Tersoff (Ref. 21), and EDIP (Ref. 22) potentials, respectively. The label TBMD refers to tight-binding simulations performed with the model of Ref. 17. E_d is the threshold energy of atomic displacement; ΔE_{pot} is the potential energy variation of the cell at the end of the simulation; $\Delta E_{rel}=\Delta E_{pot}-E^f_{vac}-E^f_{int}$ (where E^f_{vac} and E^f_{int} are the formation energies of isolated vacancy and interstitial), is the relaxation energy of the cell. The last column indicates the mechanism leading to the formation of the defect. (a): the PKA becomes an interstitial itself; (b): the PKA displaces the near target and comes back to its original site; (c): the PKA displaces the near target and replaces it; (d): both PKA and near target are found out of lattice sites at the end of the simulation.

PKA direction	Model	E_d (eV)	ΔE_{pot} (eV)	ΔE_{rel} (eV)	Mechanism
$\langle 111\rangle$	SW	20.25 ± 0.25	6.89	-0.18	(c)
	TS	13.75 ± 0.25	7.64	$+0.49$	(b)
	EDIP	18.25 ± 0.25	7.26	-0.01	(b)
	TBMD	13.25 ± 0.25	6.01	-2.34	(b)
$\langle \overline{111}\rangle$	SW	17.25 ± 0.25	7.63	-0.44	(d)
	TS	10.75 ± 0.25	7.87	$+0.72$	(a)
	EDIP	11.25 ± 0.25	7.24	-0.03	(a)
	TBMD	11.75 ± 0.25	6.02	-2.33	(a)
$\langle 100\rangle$	SW	23.50 ± 0.50	7.23	-0.24	(c)
	TS	9.75 ± 0.25	5.67	-1.48	(a)
	EDIP	15.75 ± 0.25	6.12	-1.16	(a)
	TBMD	11.75 ± 0.25	6.51	-1.84	(a)

of the near target. This occurs also for the antibonding ($\langle \overline{111}\rangle$) direction, where the neighbor target is not displaced as a result of direct impact, but as the consequence of the removal of the PKA. These peculiarities of the SW potential lead also to a larger average separation of the self-interstitial/vacancy (I-V) pair, which is in the range of 2.5–3 bond lengths, compared to 0.6–1.6 observed in all other cases. The above features are due to the strong tendency of the SW potential to favor the reconstruction of the perturbed crystal in a tetrahedral configuration.

One reason for which the SW potential has been extensively used for radiation damage calculations in Si is that it reproduces quite accurately its melting temperature, and thus it is thought to better describe the dynamics of hot atoms in cascades induced by heavy-ion bombardment. It must be underlined that these conditions are very different from those encountered in the present simulation, where, due to the low amount of energy/atom introduced in the system, the maximum temperature reached in the simulation cell is about 100 K above the bulk value.

As a matter of fact, it occurs that the E_d values calculated with TS and EDIP potentials are in much better agreement with the results of TBMD simulations, than values obtained using the SW potential. In particular, quantum-mechanical calculations give low E_d values, generally very close to those calculated with the TS potential. It is worth mentioning that the similarity between TS and TMBD results, and their good agreement with *ab initio* calculations, have been previously observed in the study of the structure of the 90° partial dislocation in Si.[26]

TBMD, TS, and EDIP allow a Si lattice ''softer,'' and thus more easily damaged by particle collision, than the one depicted by SW. The same feature has been demonstrated also for MD calculation of cascades initiated by high-energy (2 keV) recoils in Si, where the application of TS potential produces a factor of 2 more defects than those resulting from the use of the SW potential.[5] As EDIP is concerned, it is worth mentioning that, to the best of our knowledge, this is the first time that such potential of relatively recent formulation[14,22] is used to simulate a collision event.

The results obtained by its application are somewhat intermediate between TS and SW ones. This may be explained by the fact that the many-body part of the potential becomes similar to the SW one for structures close to the equilibrium, while it resembles the TS one for highly distorted configurations. The distinctive feature of TBMD results is the strongly negative ΔE_{rel}, with absolute values systematically larger than those found in classical MD calculations. These results are surely related to the specific energy landscape provided by the present TB model for displaced atoms. Nevertheless, we remark that—although single values for formation energies may be affected by the semiemprical nature of the method—when combining our diffusivity and formation[16] data we obtained an overall picture for native defects in silicon that resulted in excellent agreement with recent state-of-the-art experimental data.[27] This makes us confident about the overall reliability of the present picture.

It is rather interesting to observe that large differences in ΔE_{rel} exist between the TBMD and TS results, even if they give very similar values of E_d. Although both classical and quantum-mechanical simulations reported here do not allow to determine the fate of defects at times much longer than 5 ps, the values of ΔE_{rel} may give an indication about their stability. A negative value speaks in favor of defect recombination, since the evolution towards a separate *I-V* pair should be prevented by the fact that the formation energy of

the latter is higher than the energy available in the system. Following such interpretation, it would appear that while in the initial phase of displacement the classical MD with TS potential gives a picture of the event that is most similar to that calculated with TBMD, the description of the subsequent relaxation phase is rather different. In fact, the large negative values of ΔE_{rel} are associated in TBMD results to a large atomic relaxation around defects, especially around the vacancy. This could prelude to *I-V* recombination at later times. An energetically possible alternative to recombination could be the evolution towards a ''bond defect'' complex,[19] characterized by formation energies smaller than the one of the isolated Frenkel pair.

In conclusion, we have shown that the application of TBMD to the simulation of low-energy recoils in Si, gives a picture of the early-stage atomic displacement process that is significantly different from that given by classical MD. Even if E_d values determined with TBMD are close to those obtained by MD with TS potential, the relaxation energies of the defective configurations found by TBMD after 4 ps from the displacement event are much larger than those calculated with any of the classical model potentials. This might prelude to defect recombination at later times, thus leading to ''effective'' E_d considerably larger than values determined on the time scale typical of the energy-thermalization phase.

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