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Stability of defects in crystalline silicon and their role in amorphization

Luis A. Marqués, Lourdes Pelaz, Jesús Hernández, and Juan Barbolla
Departamento de Electrónica, Universidad de Valladolid, E.T.S.I. de Telecomunicación, 47011 Valladolid, Spain

George H. Gilmer
Agere Systems (formerly Bell Laboratories), 600 Mountain Avenue, Murray Hill, New Jersey 07974
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Using molecular-dynamics simulation techniques, we have investigated the role that point defects and interstitial-vacancy complexes have on the silicon amorphization process. We have observed that accumulation of interstitial-vacancy complexes in concentrations of 25% and above lead to homogeneous amorphization. However, we have determined the basic properties of the interstitial-vacancy complex, and showed that it is not as stable at room temperature as previously reported by other authors. From our simulations we have identified more stable defect structures, consisting of the combination of the complex and Si self-interstitials. These defects form when there is an excess of interstitials or by incomplete interstitial-vacancy recombination in a highly damaged lattice. Unlike the interstitial-vacancy complex, these defects could survive long enough at room temperature to act as embryos for the formation of extended amorphous zones and/or point defect clusters.

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I. INTRODUCTION

The transformation of crystalline silicon into the amorphous state has attracted much interest in the last two decades. The study of the ion-irradiation-induced amorphization of Si is of particular importance due to the use of increasingly high ion implantation doses in the microelectronics industry. When energetic ions strike a silicon substrate, they create zones of disorder, populated by interstitials (I) and vacancies (V). The lattice in these disordered regions exhibits different damage configurations going from isolated point defects and point defect clusters in essentially crystalline silicon (c-Si), to continuous amorphous layers, as the dose of the implanted ions increases and damage from the ions accumulates. Experiments show that amorphization starts near the ion end of range,[1,2] where lattice damage and a net excess of Si interstitials coexist.[3] Under conditions where defect production (influenced by ion flux and mass) and dynamic defect annealing (influenced by temperature) are nearly balanced, damage accumulation is extremely nonlinear with ion fluence.[4] If defect production is faster than its annealing, damage accumulates linearly until the amorphization level is reached. Conversely, if defects anneal as they are produced, they do not survive between successive cascades. Therefore, damage cannot accumulate and amorphization does not take place.

It was proposed that excess interstitials could have an influence on the amorphization process, perhaps through their interaction with lattice defects created by irradiation or by forming interstitial clusters that would act as amorphous embryos.[5] This idea was also suggested to explain the recently achieved amorphization of Si by electron beams.[6] There has also been some discussion about whether the Si amorphization process takes place by lattice collapse due to the accumulation of individual point defects (homogeneous amorphization) or by superposition of amorphous zones (heterogeneous amorphization). In spite of all the aforementioned experimental evidence, these questions have not yet been conclusively answered, and the microscopic details behind the crystal-to-amorphous transition of Si are not fully understood.

Some simulation work was done on the Si amorphization process as well. Wooten, Winer, and Weaire (WWW) developed an algorithm for the generation of random-network models for amorphous silicon (a-Si).[7] It consisted of a local rearrangement of bonds (bond switching) which introduced five- and seven-membered rings into the crystalline lattice without the presence of dangling bonds. These authors observed that the pair correlation function of the generated amorphous network was almost identical to the one determined experimentally. The WWW algorithm does produce a good-quality amorphous structure, but the generation scheme is not based on a real physical process such as ion implantation. Motooka proposed a more realistic model for describing the silicon amorphization process.[8] It consisted of the accumulation of divacancies and di-interstitials (DD pairs) in the crystalline lattice. Using a Monte Carlo code and the Tersoff potential for the force calculation, Motooka observed that the introduction of 21% DD pairs in the crystalline lattice produced complete amorphization. However, no dynamic annealing effects were taken into account.

Tang *et al.* studied the self-diffusion and I-V recombination in Si using tight-binding molecular-dynamics (TBMD) techniques.[9] They found that when a vacancy approaches a $\langle 110 \rangle$ dumbbell interstitial, a metastable defect structure is generated instead of immediate I-V recombination. This defect, that they called an *I-V complex*, consists of a local distortion of the crystalline lattice without any excess or deficit of particles. These authors also studied the stability of the defect, showing that its lifetime could be in the range of hours at room temperature. Consequently, the I-V complex could play an important role in the amorphization of silicon by ion bombardment. This I-V complex was also studied by Cargnoni *et al.* using *ab initio* Hartree-Fock calculations.[10]

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They showed that the *I-V* complex consists of a large nuclear distortion compensated by electron charge rearrangement, and confirmed its stability.

Recently, Stock *et al.* showed that the bond switching of WWW, the DD pair of Motooka, and the *I-V* complex of Tang *et al.* are indeed the same bond defect.[11] This implies a unified picture for the introduction of topological disorder into the Si lattice. These authors observed that the bond defect can be generated not only by incomplete *I-V* recombination, but also as a result of a pure ballistic process. Thus the *I-V* complex can be a primary defect generated by irradiation, with no need of pre-existing interstitials and vacancies in the lattice for its formation. They showed, as well, that the *I-V* complex is a characteristic structural feature of the *a*-Si/(001)Si interface.[11,12] Ishimaru *et al.* also observed this defect, combined with vacancies, in their simulation studies of the liquid-crystal transformation in silicon.[13] Consequently, the *I-V* complex could play as well an important role for the understanding of the solid-phase epitaxial growth.

In this paper we will try to induce the role that incomplete *I-V* recombination has on the amorphization process by the use of molecular-dynamics simulation techniques. For the sake of clarity, throughout this study we will use the term *IV pair* instead of *I-V* complex, since we will use the word *complex* to describe several structures which involve the combination of IV pairs and point defects. In Sec. II we give a description of the simulations we have carried out, with special emphasis on the motivation behind the selection of the interaction potential. In Sec. III we overview the configurations of the IV pair predicted by the chosen potential. In Sec. IV we present our results on the simulations of the Si amorphization process by IV pair accumulation. In Sec. V we discuss on the stability of the combination of IV pairs with point defects. Finally, in Sec. VI we summarize our findings.

II. MOLECULAR-DYNAMICS SIMULATIONS

The molecular-dynamics (MD) technique[14] is a powerful tool that can be readily employed to explore the underlying atomic mechanisms involved in the amorphization process. In this type of simulations, the interactions among the atoms determine the dynamics of the system. Consequently, it is important to use an interatomic potential that represents as closely as possible the interactions in the real material. In this way the results obtained from the simulation may be extrapolated to the phenomenon under study. It would then be desirable to use first-principles (or at least tight binding) methods to obtain the forces among the atoms. Unfortunately, these calculations require a large amount of CPU time, and are thus limited to systems of relatively few particles and very short total simulation times. In our case, even though no large systems are necessary, we have to simulate very long times. We resorted to the use of an empirical interatomic potential, which is less computationally intensive. Among the several potentials developed for silicon, the most frequently used in MD simulations are the Stillinger-Weber[15] (SW) and the Tersoff[16] potentials. We have chosen to use the Tersoff 3 (T3) parametrization in our simulations, for reasons we shall explain later.

The Tersoff potential takes into account many-body interactions, needed to successfully simulate covalent materials, through the use of an effective coordination term that depends on the bond lengths and their relative orientations. The potential parameters were fitted to experimental and *ab initio* data such as cohesive energies and bond lengths for different structures: diatomic molecule, graphite, diamond, etc. The T3 potential was successfully used to describe the liquid phase of silicon and its direct transformation to *a*-Si upon quenching.[17] In addition, the overall properties of the *a*-Si simulated using T3 coincide very well with real *a*-Si. This potential also gives a fairly good description of point defect formation and migration energies.[18] Lately it was successfully applied to study several phenomena in Si related to ion irradiation, such as stress relaxation[19] and induction,[20] point defect movement and annealing,[21] and crystal growth from the amorphous phase[22] and the melt.[13] All of these results make suitable the use of the T3 potential in our study of the silicon amorphization process. Another promising feature is the fact that the IV pair structure predicted by T3 is very close to the one found in TBMD and *ab initio* calculations,[9,10] as we shall see in Sec. III. Conversely, the IV pair structure predicted by the SW potential has a lifetime that is far too short: it recombines after a few femtoseconds at temperatures as low as 10 K. This makes the SW potential unsuitable for our study.

However, the T3 potential also has its limitations. The melting point temperature it predicts is claimed to be well above the value found in the experiments: 1685 K.[23] The initial estimation of Tersoff set this melting temperature around 3000 K,[16] but recently other authors, using different approaches, determined that the T3 transition from crystal to liquid takes place near 2000 K,[18,21] much closer to the experimental value. Cook and Clancy carried out MD simulations to determine the T3 melting point, but obtained two different values in two different runs: 2744 and 2547 K.[24] Since there appears to be some discrepancy on the melting point temperature given by T3, we decided to calculate it by ourselves. This temperature can be easily determined by simulating the coexistence of the two phases (liquid and crystal) at constant pressure and energy. If the system temperature is below the melting point, some of the liquid will transform into the crystalline phase with the release of latent heat. The released heat will increase the system temperature. Conversely, if the temperature is above the melting point, part of the crystal will melt with the absorption of latent heat. As a consequence, this process produces a decrease of the system temperature. During the simulation the system temperature will approach the melting point temperature. At this time the equilibrium of the two phases is reached, with no net phase change, and the temperature remains constant. We have followed this scheme for MD simulation times as long as 2 ns, and determined a melting temperature of 2396 ± 5 K. Effectively the temperature scale is not well predicted by the T3 potential, but at least it is possible to infer useful information by comparing our results to TBMD and *ab initio* calculations.

In our simulations of amorphization we have used a system consisting of 576 Si atoms in a computational cell whose dimensions were $4a\times3\sqrt{2}a\times3\sqrt{2}a$, a being the basic unit-cell length (5.43 Å). The cell, of approximately the shape of a cube, was bounded by two (100) planes in the X direction and by four (110) planes in Y and Z directions. To minimize finite-size effects, we used periodic boundary conditions along the three axes. We solved the classical equations of motion using the fourth-order Gear predictor-corrector algorithm,[25] with a variable time step. All simulations were performed at constant temperature by rescaling the atom velocities every 1000 simulation steps. This is necessary, since the heat released when a-Si transforms into c-Si accumulates in the MD simulation cell, and could even lead to the vaporization of the system. We have carried out all MD simulations at temperatures between 1000 and 2000 K, as high as possible to accelerate the system dynamics but always below the melting temperature predicted by the T3 potential.

III. IV PAIR

The formation scheme of the IV pair is depicted in Fig. 1(a). In the undamaged crystal lattice atom A moves toward atom B and atom A' moves toward atom B' following the $\langle 110\rangle$ chain, as indicated by the arrows. The formation of the IV pair involves the breaking of bonds A-B' and A'-B, and the creation of the new two bonds A-B and A'-B'. As mentioned above, the formation of IV pairs was reported as a consequence of incomplete I-V recombination[9] or as a result of a pure collisional process,[11] but no spontaneous generation of an IV pair from the undamaged lattice was observed. Therefore, the described formation process (the bond-switching method described in Ref. 7) is rather artificial, but gives the structural rearrangement that takes place in the Si lattice to accommodate the IV pair.

In order to obtain the IV pair structure given by the T3 potential, we carried out MD simulations in a perfect crystal lattice, where we slightly displaced two neighboring atoms following the scheme of Fig. 1(a). In order to find the system energy minimum, we allowed the system to relax at a finite temperature for several picoseconds, and afterward we cooled it down to absolute zero. Figure 1(b) shows the structure obtained for the IV pair, where the typical amorphous feature of five- and seven-membered rings[26] can be clearly observed. The gray scale denotes atom potential energies, where darker tones correspond to higher energies. As can be seen, the higher potential energies correspond to atoms A and B (0.39 and 0.32 eV above the ground state, respectively) and, by symmetry, atoms A' and B'. The displacement of these atoms with respect to the perfect crystal positions perturbs as well atom pairs C, D, and E (and C', D', and E'), having their potential energies increased around 0.1 eV above the ground state. The bond lengths of the structure are displayed in Table I, along with the results from tight binding and *ab initio* calculations. The agreement is very good. The formation energy of the IV pair is determined by subtracting the system total energy from the energy of a perfect crystal at 0 K, with the same number of atoms. The value

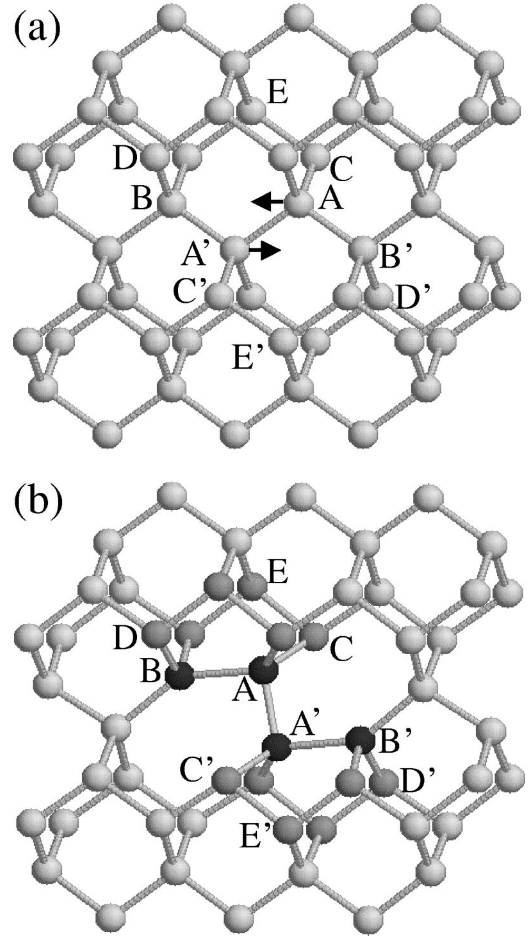

FIG. 1. Formation scheme of the IV pair. In (a) we show several $\langle 110\rangle$ chains in a perfect crystal lattice. Atoms A and A' move along the directions indicated by the arrows and switch their bonds with atoms B and B', giving rise to the IV pair displayed in (b). The gray scale indicates the atom potential energies, where darker tones correspond to higher energies.

obtained is 3.01 eV, which compares with the 3.51 eV obtained from the TBMD calculation,[9] and the 3.26 eV obtains from the *ab initio* calculation.[10] This suggests that the T3 potential describes well the configuration of the IV pair.

Next we study the stability of the IV pair. The reverse path to the IV pair formation scheme depicted in Fig. 1 constitutes an I-V recombination sequence, which is expected to be a thermally activated process: the higher the temperature, the more likely the structure will relax to the perfect crystal lattice due to wider atomic vibrations. The stability of the IV pair, i.e., the average lifetime of the defect structure, is re-

TABLE I. Lengths of the bonds involved in the IV pair, expressed in Å. Letters refer to the corresponding atoms in Fig. 1(b). For the sake of comparison, we show as well results from TBMD (Ref. 9) and *ab initio* (Ref. 10) calculations.

Bond	This work (T3)	TBMD	*Ab initio*
A-A'	2.28	2.28	2.27
A-B	2.51	2.46	2.46
A-C	2.35	2.38	2.39

lated approximately to the saddle point energy E_A for *I*-*V* recombination by

$$t = t_0 \exp(E_A / k_B T). \quad (1)$$

In order to calculate the recombination times, we have carried out MD simulations of the IV pair recombination sequence at different temperatures: 1000, 1200, 1400, 1600, and 2000 K. The initial system consists of a perfect crystal lattice at 0 K, where we introduce an IV pair. The initial velocities are chosen from a Maxwell-Boltzmann distribution corresponding to each temperature. Velocity rescaling is needed to compensate for the exchange between kinetic and potential energies. Due to the statistical nature of the IV pair recombination process, it is necessary to run several simulations for each temperature. This is done by giving different initial velocities to the atoms. In this way, even though the initial spatial configuration is always the same, the time evolution of the system is totally different due to the chaotic nature of the atomic interactions.

The time needed for IV pair recombination can be easily computed by following the evolution of the potential energy of one of the atoms that form the IV pair, for instance atom *A* in Fig. 1(b). Figure 2 shows the time evolution of this potential energy for a pair of simulations done at 1000 K. When the atom overcomes the recombination barrier, the IV pair disappears. Then the atom potential energy decreases to a value corresponding to the perfect lattice at that temperature. We have carried out a total of 20 simulations for each temperature. In all cases, we observed that the logarithm of the recombination times followed a Gaussian distribution. The mean values of the different recombination times are represented in the Arrhenius plot of Fig. 3. Error bars represent the 95% confidence interval. The fit gives a prefactor of 162 ± 8 fs, and an effective activation energy of 0.43 ± 0.03 eV. The prefactor defines a frequency of 6.2×10^{12} s^{-1}, of the order of the vibrational frequency of Si.

The value of the activation energy for IV pair recombination is low in comparison with the 1.23 eV obtained from the TBMD method,[9] and the 1.32 eV from the *ab initio*[10] method. This difference implies a lifetime of only 3 μs at room temperature instead of several hours, as suggested by Tang *et al.* The discrepancy can be explained if we take into account that the scheme followed in those calculations was a static relaxation procedure: the two atoms that form the IV pair were moved systematically towards their final positions, and were constrained to relax only in the [110] plane.[9] Consequently, it was assumed that during the recombination process the two atoms maintained symmetry, breaking and forming bonds simultaneously. Doing a similar calculation with the T3 potential we found a higher value for the barrier, 1.05 eV. When the system is allowed to evolve freely at a finite temperature the IV pair recombination sequence can differ from the symmetric path, and thus find one with a lower-energy barrier. This can be deduced by inspection of Fig. 2, where the insets show an enlargement of the transitions at 1000 K. The potential barriers (saddle-point energies) overcome by the atom are different in each simulation, 0.63 eV in one case and 0.75 eV in the other. This was also

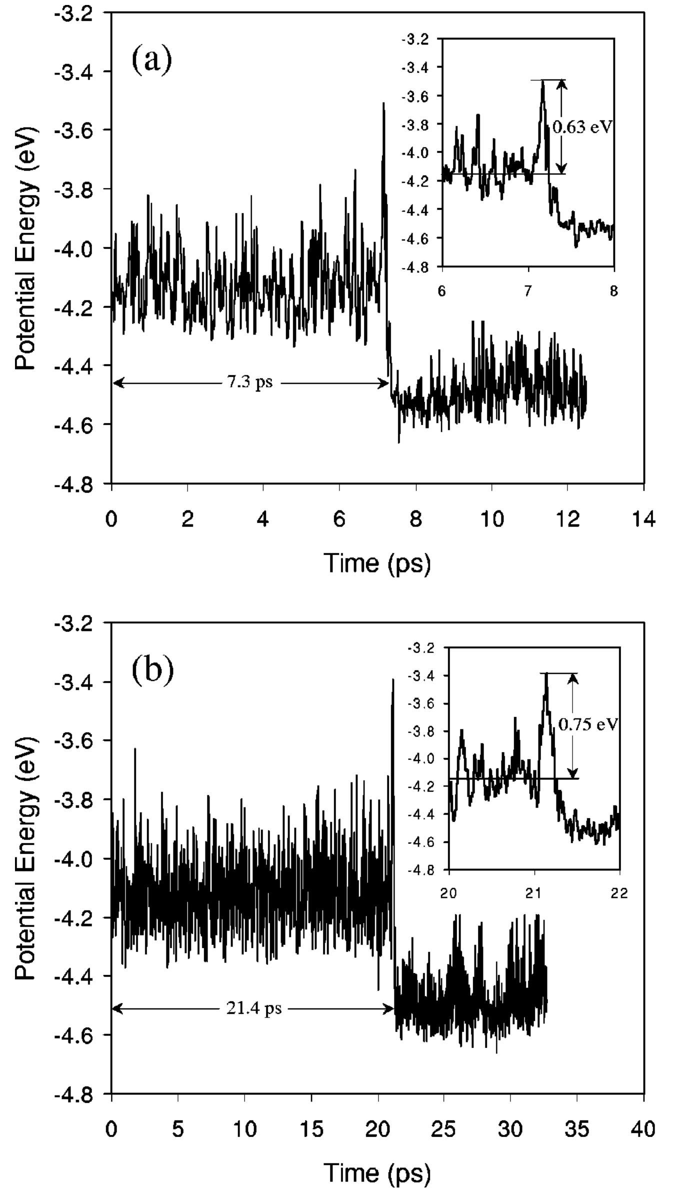

FIG. 2. Evolution of the potential energy of one of the atoms that form the IV pair in two different runs at 1000 K. The insets show an enlargement of the transition regions. Times for recombination and barrier heights are different in each simulation due to the stochastic nature of the IV pair recombination process.

noted by Tang *et al.*[9] By choosing a different annihilating (nonsymmetric) path, they found that the energy barrier decreased to a value of 1.13 eV. The assumption of annihilating paths *a priori* is not needed in our MD simulations, since it is possible to obtain the recombination times directly. The energy barrier implied by the Arrhenius plot can be calculated as a nice side effect. Obviously, this procedure is not feasible for TBMD and first principles calculations, since it would require prohibitive run times. If in this type of simulation the recombination barrier were the critical quantity to be calculated, it would be necessary to use techniques such as the nudged elastic band method.[27] However, it should also be taken into account that the saddle-point energy may

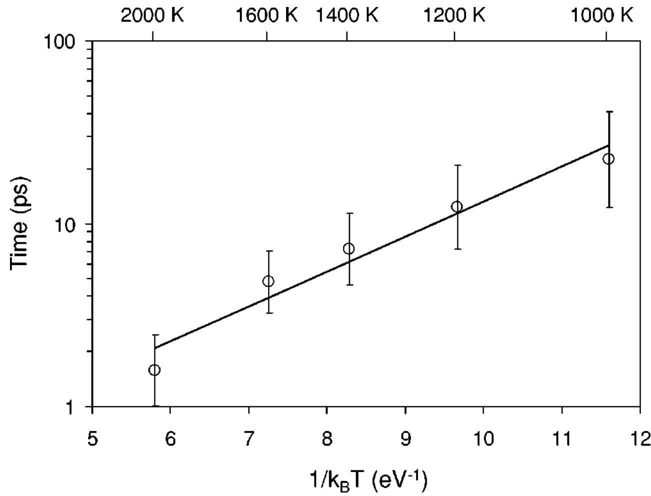

FIG. 3. Arrhenius plot of the time needed for I-V recombination. Each data point represents the mean value from 20 different simulations. The line is the best fit to the data, which determines an activation energy of 0.43 ± 0.03 eV.

change with temperature, giving a false Arrhenius slope and thus inexact lifetimes.

IV. AMORPHIZATION SIMULATIONS

We simulate the damage accumulation corresponding to increasing irradiation doses in c-Si by introducing different concentrations of IV pairs in a perfect crystal lattice. This is done by randomly selecting pairs of neighboring atoms and displacing them, as shown in Fig. 1, until the desired final concentration of IV pairs is reached. After that, the system is allowed to relax at low temperature for several time steps in order to dissipate the unphysically high potential energies that can be present due to atoms too close to each other as a consequence of their displacements to create the IV pairs. This stabilization process is particularly needed in samples with high concentrations of IV pairs. After that, the system samples were heated to different temperatures in order to simulate the dynamic annealing that takes place during the irradiation process.

We carried out simulations with IV pair concentrations of 10%, 20%, 25%, 30%, and 40%, and temperature annealings of 1000, 1200, 1600, and 2000 K. The time evolution of the potential energy per atom is displayed in Fig. 4. For the sake of clarity, results for samples with concentrations of 40% are not shown, because the potential-energy evolution was virtually identical to the one obtained in samples with concentrations of 30% for all the temperatures considered here. The mean potential energies that an atom has in the amorphous phase, E_{AM}, and in the crystal, E_C, at each temperature are indicated by solid lines in Fig. 4. As can be seen, samples with starting concentrations of 10% and 20% of IV pairs recrystallized for temperatures between 1000 and 2000 K. On the other hand, the samples with 30% and 40% of IV pairs remained amorphous for all the simulated temperatures. The pair correlation functions for these two samples were identical to the ones calculated from amorphous samples obtained by directly cooling from the melt. It is interesting to note that the behavior of the sample with an initial concentration of 25% depends on temperature. For $T=1000$ K the sample returns to a perfect crystal, though initially the potential energy per atom is higher than E_{AM}, while it amorphizes for $T=1600$ and 2000 K. In the case of $T=1200$ K, the potential energy per atom stays between the levels corresponding to a-Si and c-Si. In this simulation the sample started to recrystallize, but with a small misorientation with respect to the original crystal lattice due to thermal agitation. Since the rotated crystal was not consistent with the boundary conditions of the computational cell further crystallization was prevented. In real silicon, such a situation would correspond to the formation of low-angle grain boundaries, as observed in experiments.[28,29]

As can be deduced from Fig. 4, the higher the temperature, the higher the recrystallization velocity for the same concentration of IV pairs. For samples with a concentration of 10%, the energy decay is exponential, which suggests a single activation energy. Effectively, we observed that decay times in these samples followed an Arrhenius behavior with an activation energy of 0.45 eV, very close to the barrier obtained for IV pair recombination. This means that 10% is a concentration so low that the IV pairs do not interact strongly with each other; they recombine one by one, and the overall crystallization behavior is the same as when there is just one IV pair. On the other hand, for higher concentrations the evolution of the potential energy per atom shows plateaus followed by steep decreases, indicated by arrows in Fig. 4. Caturla *et al.* observed the same type of behavior in their MD study of the recrystallization kinetics of amorphous pockets created by ion irradiation.[30] In these cases, IV pairs interact with each other and form more stable structures, responsible for the plateaus in the curves of Fig. 4. The crystallization then requires the collective movement of several atoms, which produces a sudden decrease in the potential energy per atom. The interaction of IV pairs when their concentration is relatively high makes the characterization of the recrystallization process difficult, since there is not a single activation energy. This could be the reason why different authors found different experimental values for the activation energy, and why it is difficult to assign a particular defect as being responsible for the recrystallization process.

There exists some discussion about whether the amorphization process takes place homogeneously or heterogeneously. In a homogeneous process, the ion irradiation increases the defect density to a level where the damaged crystal becomes unstable and spontaneously transforms to a-Si. In the heterogeneous case, amorphous pockets accumulate with increasing ion dose, eventually overlapping and giving rise to a continuous amorphous layer. Lewis and Nieminen proposed a microscopic model of Si amorphization using MD techniques.[31] From their simulations they concluded that amorphization can only take place heterogeneously, from defect clusters surrounded by damaged crystal. They also observed that uniform distributions of point defects did not produce amorphization. However, our results suggest that homogeneous amorphization can take place by uniform accumulation of IV pairs when a critical concentration (which depends on temperature) is reached. These re-

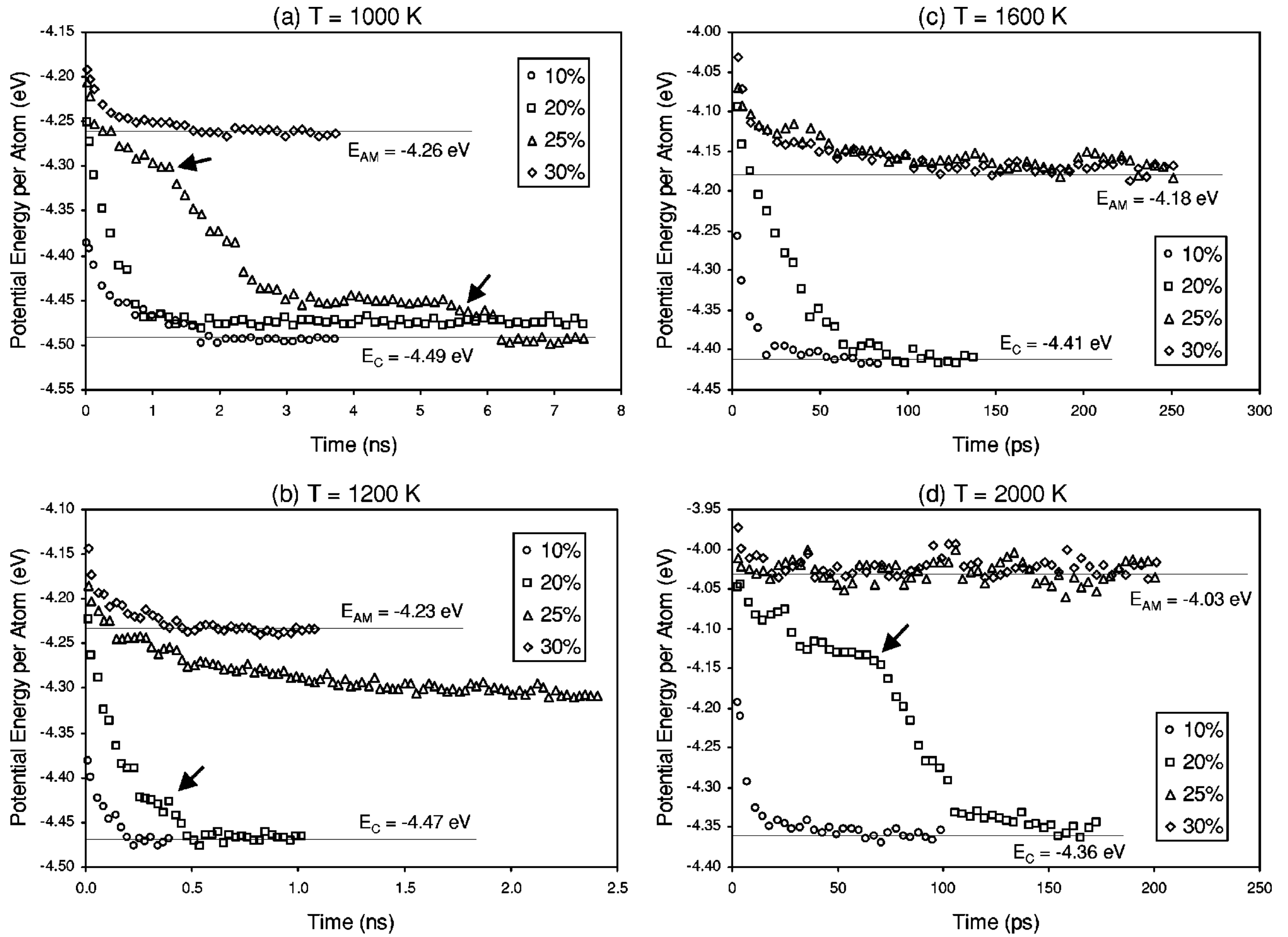

FIG. 4. Time evolution of the potential energy per atom in samples with 10%, 20%, 25%, and 30% of IV pairs during the annealing at different temperatures. Solid lines indicate the mean potential energy per atom in a-Si and c-Si at each temperature E_{AM} and E_C, respectively. Arrows indicate plateaus followed by steep decreases, due to the more stable structures formed by the interaction of several IV pairs.

sults may explain why it is possible to achieve Si amorphization by electron irradiation at very low temperatures and high fluences.[6] Electrons are very light particles which presumably create isolated IV pairs and point defects. As we have proven, the IV pair lifetime is very short at room temperature, but at low temperatures IV pairs could survive and accumulate as the electron irradiation dose increases. When the IV pair concentration reaches a critical value (around 30%), the lattice collapses spontaneously to an amorphous state (homogeneous amorphization). The critical concentration can also be reached locally in the amorphous pockets produced when irradiating silicon with heavy ions,[30] such as arsenic. During the collisional phase, the ion produces highly damaged zones which, as previously mentioned, are similar to regions with high concentration of IV pairs. These amorphous zones, or a part of them, can survive between successive cascades and act as a nuclei for damage accumulation (heterogeneous amorphization). The amorphization process is favored if the surrounding crystal lattice is already distorted by the presence of point defects.[31]

Figure 5 shows the atomic structure and pair correlation function $g(r)$ of the sample with 25% of IV pairs at several times during its annealing at 1000 K. For $t=0$ the atomic structure and $g(r)$ correspond to an amorphous sample. Previous simulations done by Motooka showed that complete amorphization of the Si lattice takes place when introducing 21% of DD pairs,[8] which are structurally equivalent to the IV pairs.[11] In his simulations, performed using Monte Carlo techniques, no dynamic temperature effects were taken into account. In our simulations, even though the initial concentration of IV pairs is higher than in the case of Motooka's, the sample recrystallizes when annealed at $T=1000$ K. For higher temperatures, $T=1600$ and 2000 K, this sample becomes amorphous. Evidently, after introducing 25% of IV pairs, there are some traces of crystallinity left which act as a seed for crystal recovery at 1000 K, but further thermal agitation at $T=1600$ K dissolves these traces and amorphization takes place. These findings are in agreement with the classical theory of nucleation and growth.[32] In the case of microcrystals of spherical shape embedded in the amorphous matrix, this theory predicts that there exists a critical radius r_C, given by

$$r_C=\frac{2\sigma}{\rho\Delta g}, \tag{2}$$

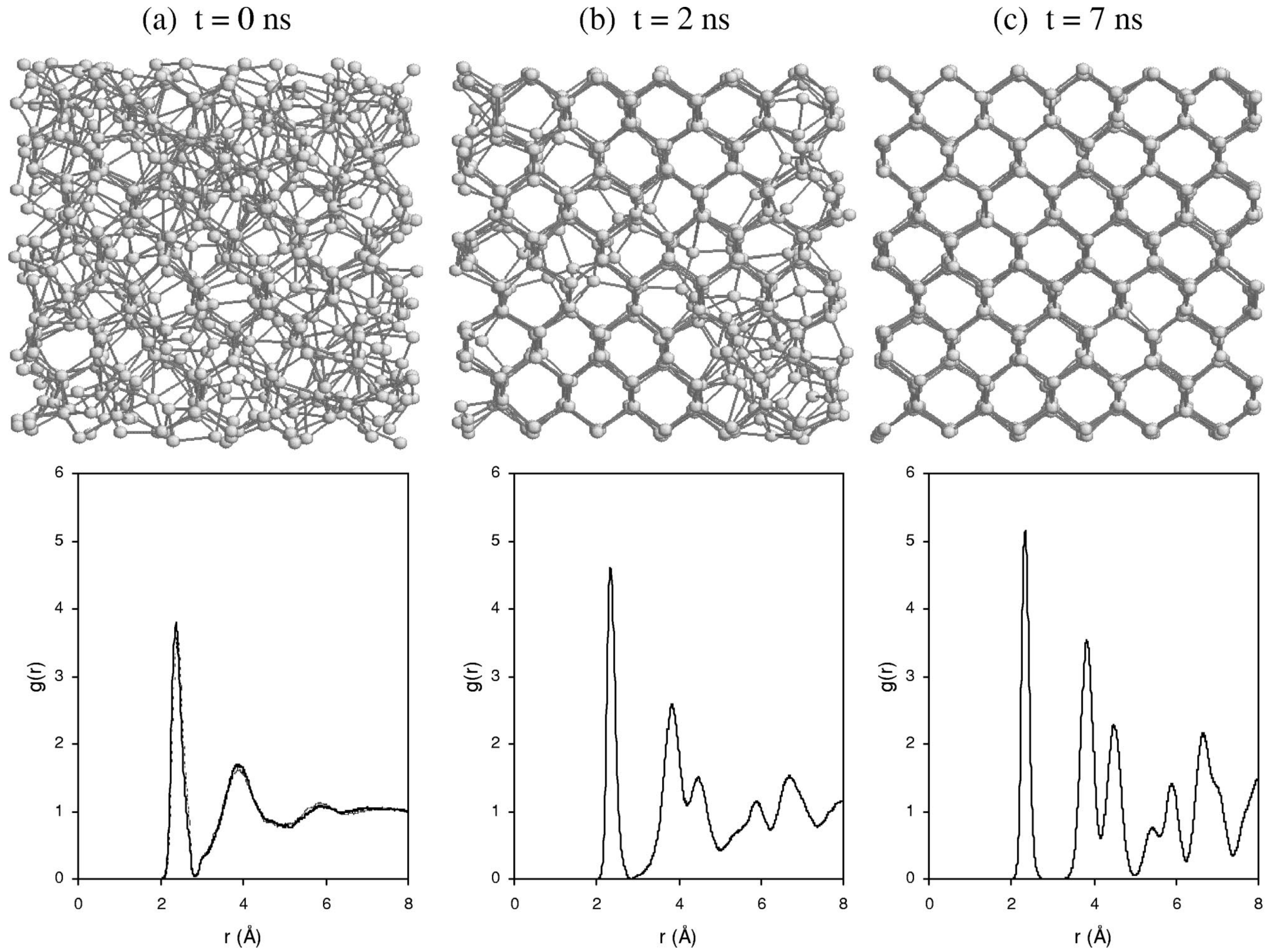

FIG. 5. Snapshots of the sample with 25% of IV pairs, and the corresponding pair distribution function $g(r)$ during the annealing at 1000 K: (a) at the beginning of the annealing, (b) after 2 ns, and (c) after 7 ns. The dashed line in the $g(r)$ graph (a) corresponds to an amorphous sample generated by cooling from the melt.

where σ is the interfacial free energy per unit area, ρ the atomic density, and Δg the free-energy difference between a-Si and c-Si in a per atom basis. Δg is positive due to the lower free-energy content of the crystal. σ represents the free energy necessary to maintain an interface between the crystalline and amorphous states, and is also positive. Microcrystals having a radius larger than r_C tend to grow spontaneously, and shrink otherwise. With increasing temperature the free-energy difference between amorphous and crystal Δg diminishes, and consequently r_C increases. This is probably the reason why at 1000 K the sample with 25% of IV pairs recrystallizes, and why at 1600 K and above it amorphizes. Temperature then plays an important role in the amorphization process. Higher temperatures favor the recombination of the defects produced during the irradiation, and thus prevent the damage accumulation. However, our simulations show that if the defects have accumulated and are interacting strongly, higher temperatures favor amorphization.

V. IV+2I COMPLEX

As we pointed out earlier, during our simulations we observed the formation of structures (similar to amorphous pockets) more stable than the IV pair. When recrystallization took place, these structures annealed out and disappeared, except in the simulation with 20% of IV pairs at 1000 K. In that case, as can be seen in Fig. 4(a), the potential energy per atom does not reach a level corresponding to a perfect crystal. After 5.22 ns the lattice was mostly recovered, leaving a divacancy and the defect shown in Fig. 6(a). It is formed by the combination of an IV pair [atoms A and B, which are equivalent to atoms A and A' in Fig. 1(b)], and two tetrahedral interstitials (C and D). We observed that this defect, that we will refer to as the *IV+2I complex*, is mobile. Its displacement through the Si lattice takes place following the scheme depicted in Fig. 6. Atom D moves down a little, and atom E is displaced toward atom B, forming the configuration shown in Fig. 6(b). Atoms A-B-D-E form a complex with an excess atom, since atoms A and D share the same lattice site (dashed circle). Structurally this can be described as a combination of an interstitial with two IV pairs. This complex is different from the usual $\langle 110\rangle$ interstitial, where atoms A and D would be closer and not bonded with atoms B and E, respectively. Atom C is just a tetrahedral interstitial bonded to the previously described complex. From this intermediate structure, the defect evolves to the configuration

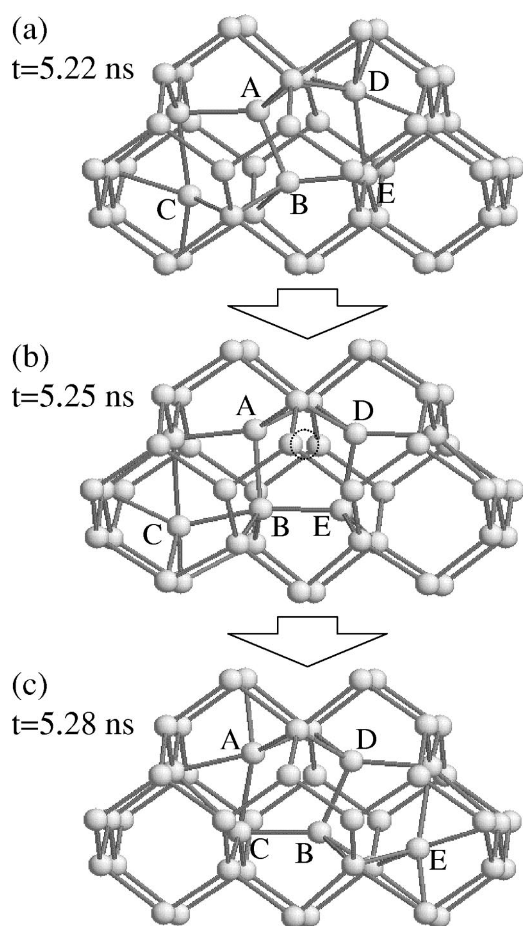

FIG. 6. Atomic pictures showing the time evolution of the defect complex structure formed during annealing at 1000 K of the sample, with an initial concentration of 20% (explanation in the text). Bonds are displayed when atom distances are less than 2.84 Å, the first minimum in $g(r)$.

shown in Fig. 6(c), where atom E has been pushed to a tetrahedral interstitial site and atom C comes to a regular lattice site. Again we have a combination of an IV pair (atoms B and D) and two tetrahedral interstitials (A and E), but with a net displacement of atoms with respect to Fig. 6(a). In principle, it may seem surprising that a complex that involves two extra atoms could diffuse so easily through the Si lattice, but recently *ab initio* MD simulations showed that interstitial clusters of two and three atoms diffuse extremely fast.[33]

In order to study the stability of this defect complex, we continued the simulation at 1000 K for several nanoseconds. In its movement through the MD cell during the simulation, the IV+2I complex approached the divacancy. After 10 ns, one of the interstitials in the structure recombined with one of the vacancies, leaving behind the other vacancy and the five-ring structure shown in Fig. 6(b) (atoms A, B, D, and E), which constitutes a net interstitial. This structure remained stable for 0.4 ns. After this time, the structure reacted with the remaining vacancy creating an IV pair which finally disappeared after 60 ps more. Even though the IV+2I complex moved along the simulation cell, no interstitial emission took place. This suggests that the defect complex is fairly stable unless it encounters vacancies.

To further check the stability of the IV+2I complex, we tried to apply the same scheme used for the IV pair, with no vacancies in the computational cell. However, the characterization of the dissolution process turned out to be very difficult due to the change of the IV+2I atomic configuration during its movement through the lattice at temperatures above 1500 K. In any case, in all the simulations that we carried out at 1000 K the complex remained stable after 10 ns. This implies a lifetime at least two orders of magnitude longer than that of the IV pair. This fact means that Si self-interstitials can stabilize the lattice disorder represented by the IV pair.

We also studied the relationship between this complex and the Si di-interstitial. The lowest-energy configuration for the di-interstitial consists of two adjacent tetrahedral interstitials.[34] There is very little difference between the formation energy of the IV+2I complex (3.16 eV per extra atom) and the ground-state di-interstitial (3.13 eV per extra atom). These findings are in agreement with the results obtained by other authors using TBMD and *ab initio* techniques,[35,36] who observed that the atomic structure corresponding to the IV+2I complex is stable. This fact demonstrates that the IV+2I complex it is not just an artifact of the T3 potential. In our simulations we have found that the di-interstitial is stable at room temperature (for time scales accessible to MD), but spontaneously transforms to the IV+2I complex at temperatures around 800 K. Once the complex is formed, it remains in the lattice even if the temperature comes down to 300 K again. This implies that local heating (which can be induced by the irradiation) could transform the di-interstitial into the IV+2I complex, which introduces more disorder into the lattice (four atoms out of place instead of two), as well the five and seven-membered rings characteristic of the a-Si phase.[26] When the complex is formed, it may survive between successive cascades, and thus act as the nucleus for the generation of extended defects and/or the amorphous phase.

VI. SUMMARY

We have studied the influence that IV pair accumulation may have on the amorphization process in Si. We have carried out MD simulations using the Tersoff 3 potential. First we studied the properties of the IV pair based on this potential. The formation energy and bond lengths are in very good agreement with TBMD and first-principles calculations. However, the energy barrier for IV pair annihilation, estimated by an Arrhenius plot of the recombination times for different temperatures, is only one-third the value given by the TBMD and *ab initio* calculations. We have explained this discrepancy by showing that these calculations used relaxation procedures that restricted the recombination path, while in our case the system was allowed to move freely according to its own dynamics during the recombination process. The claimed stability of the IV pair is then questionable, since the effective barrier for recombination is 0.43 eV, giving a lifetime of only $\simeq 3\,\mu$s at room temperature.

We have simulated the accumulation of damage during

the implantation by introducing different fractions of IV pairs into the Si lattice. We have observed that concentrations of 10–20 % do not produce amorphization in the temperature range between 1000 and 2000 K. On the other hand, concentrations of 30% and above gave rise to the destabilization of the crystal lattice, and homogeneous amorphization took place. For a concentration of 25% of IV pairs, we observed that the evolution of the system depended on temperature: at $T=1000$ K, recrystallization occurred; $T=1200$ K produced polycrystalline material; and for $T=1600$ K an amorphous matrix was generated. These results are in agreement with the predictions of the classical theory of nucleation and growth.

We have observed that when the concentration of IV pairs is relatively low (around 10%), recrystallization takes place by direct *I-V* recombination. However, for higher concentrations, IV pair interactions produce more stable defect structures similar to the amorphous pockets generated by direct irradiation with heavy ions. In these cases, the recrystallization process becomes more complicated, since it takes place due to collective movement of atoms. This explains why it is difficult to assign a particular defect as being responsible for the recrystallization.

Even though the IV pair lifetime is very short at room temperature, we have shown that its combination with Si self-interstitials gives rise to much more stable defect complexes. These complexes could accumulate during irradiation, and thus act as the embryos for interstitial clusters or extended amorphous pockets. The formation of these complexes is favored when excess interstitials coexist with the lattice damage, as in the case of ion irradiation. However, we have also shown that they can be formed when there is no excess atoms, just by incomplete *I-V* recombination in a highly damaged zone.

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