Mechanism of electron-irradiation-induced recrystallization in Si

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It has recently become clear that electron irradiation can recrystallize amorphous zones in semiconductors even at very low temperatures and even when the electron beam energy is so low that it cannot induce atomic displacements by ballistic collisions. We study the mechanism of this effect using classical molecular dynamics augmented with models describing the breaking of covalent bonds induced by electronic excitations. We show that the bond breaking allows a geometric rearrangement at the crystal-amorphous interface which can induce recrystallization in silicon without any thermal activation.

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I. INTRODUCTION

Ion implantation is a widely used doping method in the semiconductor industry. It offers several decisive advantages, such as good control of dopant depths and profiles.[1] The main disadvantage of ion implantation is that the energetic ions damage the target material. Due to this, and also to achieve good activation of dopants, one needs to anneal the implanted structures.[2] The method of choice for this has been thermal annealing. However, this method usually broadens the implant profiles, which may become a problem as implant depths become very narrow.[3] Thus there is an interest in alternative annealing methods. One can use different kinds of energetic beams for this purpose. Ion, laser, and electron beams all have been shown to produce recrystallization.[4–7]

For electron irradiation, it has been recently shown that even quite low energy ($\sim$25 keV) electron bombardment can produce recrystallization of amorphous pockets in silicon, germanium, and gallium arsenide.[6–8] This is somewhat surprising, as such low-energy electrons can only transfer a few eV's of energy to target atoms, which is not enough to displace atoms from their sites in a perfect lattice. Even in amorphous zones, the cohesive energy per atom is of the order of 3–4 eV, so it is not likely an atomic displacement can be achieved by an electron transferring only about 1 eV of energy to an atom. Hence some other mechanism for recrystallizing damage needs to be invoked.

Jenčič and co-workers[8] have shown that the explanation which is most consistent with their experiments is the Spaepen-Turnbull model.[9] This model proposes that crystallization (both thermal and that induced by radiation) can be explained by dangling bonds. They are formed at an amorphous-crystalline interface, migrate along it, and find a lower-energy state which is closer to the crystalline one. Although the basic mechanism of crystallization thus appears clear, there are still several issues which are not resolved. For instance, Spaepen and Turnbull suggest that some additional thermal activation may be necessary to induce migration of the dangling bonds. But since recrystallization has been observed at temperatures as low as 30 K,[8] it would seem unlikely this can be an important factor. Furthermore, it is not clear whether a simple bond-breaking event induced by an electron or photon is enough to cause recrystallization or whether some simultaneous transfer of kinetic energy to target atoms is also necessary.

We study this problem with classical molecular dynamics simulations for Si amorphized by ion irradiation. This method allows for both examining how recrystallization proceeds on an atomic level and testing various ways in which bonds can break. Simulations performed at 0 K are used to examine whether any thermal activation for bond migration is necessary in addition to the bond-breaking event itself. It is also straightforward to test whether any transfer of kinetic energy is needed for recrystallization to occur.

II. COMPUTATIONAL DETAILS

We used two different potential models to describe the Si-Si interactions, namely, the Tersoff[10] and Stillinger-Weber[11] models. This was done to rule out any characteristic features that might arise from the model potentials. The forces at small distances and for As-Si pairs were evaluated from repulsive potentials calculated with a DMol program package.[12,13]

At the beginning we had $22\times22\times28$ unit cells (108 416 Si atoms) in the simulation box with periodic boundary conditions in two dimensions. The outermost layers were softly scaled to the heat-bath temperature. The closing of the bottom of the simulation box was done by fixing the two outermost layers and softly scaling the next two layers to the temperature of the surroundings.

Two different amorphous zones were studied, one for the case where the Tersoff potential model was used and one for the Stillinger-Weber potential model. The amorphous zones were produced by giving an energy of 5 keV to an As atom and impinging it to the surface of the simulation box. The resulting amorphous areas consisted of 600–1300 atoms. After the box was relaxed, all atomic layers more than two layers away from the amorphous zones were discarded, to limit the amount of atoms used in the bond-breaking simulations. The final simulation cells used contained 20 000–35 000 atoms. The atoms in the amorphous zones were determined by examining the potential energy of the atoms. All the atoms (excluding the atoms on the surface) with a 0.2 eV higher potential energy than the energy of an atom in a per-

fect diamond lattice were labeled to be in the amorphous phase.[14,15]

To simulate the breaking of a bond between two atoms, two different models were applied. In the first model the interaction between the atoms with a broken bond is purely repulsive, because the attractive part of the model potential is eliminated. The neighboring atoms will interact with the pair in orderly fashion described by the model potential (Tersoff, Stillinger-Weber). In the other, a more sophisticated model, the pair which has undergone bond breaking will interact with a potential which was formed by the repulsive two-body part of the Tersoff potential with the addition of a screened Coloumb potential,[16]

$$V(r)=\frac{1}{2}Ae^{-\lambda(r+r_0)}+\frac{Z^2}{r}e^{-\alpha r},$$

where $A=1.8308\times10^3$ eV, $\lambda=2.4799$ Å^{-1} (Ref. 10), $Z=14$, and $\alpha=4.0$ Å^{-1}. In the original paper where the model was presented two different values for the parameters r_0 were suggested (0.19 Å and 0.065 Å). We used both these values. This parameter is used to adjust the excitation energy at equilibrium internuclear distance.[16] The interaction between the atoms with the broken bond and the neighboring atoms will interact with a potential calculated with *ab initio* simulations,[17] which is slightly repulsive. We shall henceforth call the more sophisticated model the ''antibonding'' model to distinguish it from the simpler, ''nonbonding'' model.

The recrystallization simulations were done by randomly choosing an atom in the amorphous region and one of its neighboring atoms to undergo the bond breaking. The bond was broken in the beginning of the simulation and reformed after 35 fs. This 35-fs interval was used because some experiments[18,19] indicate this is a realistic value for the time in which a bond can reform after an excitation. Intervals of 5 fs and 250 fs were also tested to determine the effect of choice of the interval to the results. Although the excitation effects of one electron in a solid are not known in detail, we observe that the stopping power of the electrons used in the experiments are only of the order of 1 eV/nm (Ref. 8); i.e., the energy deposited in a $\sim$2-unit-cell-depth region is on average less than the energy of one bond. Hence the excitations which lead to bond breaking can be considered to be spatially isolated on an atomistic scale. We further assume that where excitations do occur, it is more likely that they involve the transition of a single electron into an antibonding state rather than several electrons at the same time. The bond breaking and the following reforming of the bond were achieved by scaling the bond-breaking potential with the Fermi function $F(t)$ and the Tersoff–Stillinger-Weber potential with $1-F(t)$. The Fermi function is

$$F(t)=(1+e^{-b(t-t_0)})^{-1},$$

where b was chosen so that the transition from broken to rebonded would take approximately 10 fs, t_0 is the chosen bond-breaking interval time, and t is the time from the start of the simulation event. The simulation was then allowed to thermalize for 500–2000 fs, the last 200 fs of the simulation was used to softly quench the temperature of the simulation cell to the heat-bath temperature. Because of this quench, we cannot directly associate our simulation times to real time. Furthermore, we do not know the real rate of these bond breakings under electron bombardment. The described procedure will later in this paper be referred to as one event. After one event was run, the final positions and velocities of the atoms were saved as the starting state of the next event and a new pair of atoms for the bond breaking were chosen. To determine that a recrystallization really occurred, we simulated at least 4000 bond-breaking events with all different models.

To rule out recrystallization due to thermal effects, a reference simulation, which used exactly the same conditions but left out the bond breaking events, was run.

To calculate the amount of energy inserted into the simulation cell by one event, bond breakings were conducted in a lattice quenched to 0 K. Several different bond-breakings were done in the same lattice to get statistics for the inserted energy.

To further rule out the possibility of recrystallization due to thermal heating, we performed some artificial hot spot simulations. In these simulations, instead of breaking a bond, the atoms around a chosen bond were given energy equal to the energy released in the breaking and rebonding of a bond. The inserted energy was given a Gaussian distribution around the bond. The hot spot size was centered around the bond to be broken and the size of it was chosen so that the nearest neighbors of the pair would be included in it. These simulations were done to see whether the primary recrystallization effect arises from the rearrangement of the atoms during the time the bond was broken or from the local heating (hot spot) created by the bond-breaking event.

Most simulations were carried out at room temperature, where most of the experiments have been performed. In Si and Ge all the amorphous clusters larger than ~2 nm are stable at room temperature.[20–22]

III. RESULTS

We first simulated some bond-breaking events in a crystalline sample. As expected no deviations from the crystalline structure were found. This was done to assure that our choice of limiting the bond-breaking events only to the amorphous zones would not affect the results.

The total simulation time for the Tersoff model is 2 ns (time refers to time in our simulations, not to real time). During this time the recrystallization for the reference run is 2.8%; however, the main recrystallization occurs within the first 0.5 ns (1.6%). Therefore one sees that the thermal recrystallization slows down when the lattice relaxes, as shown before by Caturla *et al.*[14] For the Stillinger-Weber model the total simulation time was 4.5 ns. During this time the recrystallization was 2.6% if the sudden drop is included and about 0% if it was left out. The sudden drop is due to some single amorphous ''knot'' being crystallized. The reference run was also simulated at 1000 K and then a recrystallization rate of 4.2 atoms in a time corresponding to 100 bond-breaking events was observed. To definitely rule out any temperature

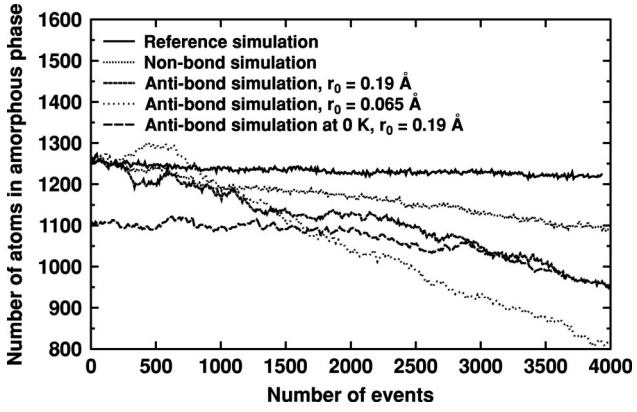

FIG. 1. Number of atoms in the amorphous phase during the simulation for the different models with the Tersoff potential at 0 K and 300 K.

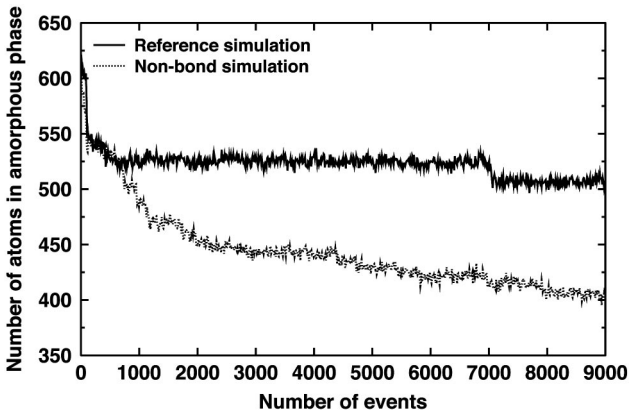

FIG. 2. Number of atoms in the amorphous phase during the simulation for the different models with the Stillinger-Weber potential at 300 K.

dependence at the lower temperatures, the antibonding model simulations were also run at a 0-K heat-bath temperature; the results were practically identical to the results of the 300-K simulations. The only difference in this case was that the analysis gave a smaller size for the initial damage zone due to the use of potential energy analysis.

For the nonbonding model with the Tersoff potential we observed a recrystallization rate of 4.2 atoms per 100 events. For the antibonding model with the Tersoff potential we observed a recrystallization rate of 7.9 atoms per 100 events with a value of 0.19 for the antibonding potential parameter r_0 (Ref. 16). With the r_0 value 0.065 we observed a recrystallization rate of 11.1 atoms per 100 events. The results for the Tersoff potential simulations can be seen in Fig. 1.

Antibonding model simulations with a value of 5 fs for t_0 showed very little recrystallization and a value of 250 fs showed a recrystallization rate accelerated with a factor of 2 compared to the 35 fs value of t_0.

The energies inserted into the lattice by one event for the Tersoff nonbonding model was calculated to be $(1.86 \pm 0.03) \times 10^{-2}$ eV for the 5-fs interval, $(2.4 \pm 0.2) \times 10^{-2}$ eV for the 35-fs interval, and $(5.1 \pm 0.9) \times 10^{-2}$ eV for the 250-fs interval. For the artificial hot spot simulation the energy corresponding to the 250-fs interval value was used to heat a local region. The artificial hot spot simulations showed no observable recrystallization.

Since we used the potential-energy criteria to observe the atoms in the amorphous phase, we wanted to make sure that a real recrystallization actually occurred and not just some internal relaxation of the amorphous areas. The simplest way of doing this is just by looking at the crystal structure. In Figs. 3 and 4, below, the crystal structure is illustrated and one can easily observe the recrystallization. From these figures one can also see that the recrystallization begins from the outer regions of the amorphous zone and continues inwards.

We also simulated the nonbonding model with the Stillinger-Weber potential and found a smaller recrystallization than in the Tersoff case; the recrystallization rate was about 1 atom per 100 events. The results for the Stillinger-Weber potential simulations can be seen in Fig. 2. Figures 3 and 4 show the initial and final lattices for the Stillinger-Weber nonbonding model simulations.

To make sure that the experimentally observed effect is not associated with the displacement of atoms we also simulated recrystallization by displacement. The maximum energy which an electron with the energy of 25 keV can transfer to a Si atom is in the order of eV's. To avoid creating more damage to the lattice but still be able to do some structural rearrangement the displacement simulation energy was chosen to be about the formation energy of Frenkel pairs, which is about 11.7 eV for Si in the Tersoff potential model.[23] We observed no recrystallization in the displacement runs.

IV. DISCUSSION

In previous studies several different mechanisms have been suggested to be the reason behind the recrystallization. These are beam heating, displacement of atoms, bond breaking, displacement of Si interstitials residing at the periphery of the amorphous volume,[24] and local excitations.[25] Beam

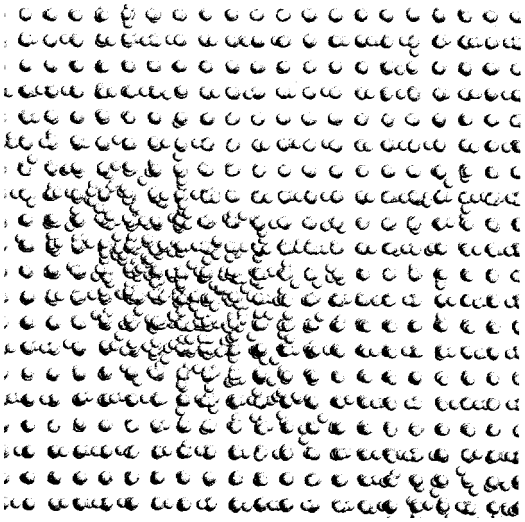

FIG. 3. Initial lattice of the Stillinger-Weber nonbonding simulation. Only a specific part of the whole lattice is shown.

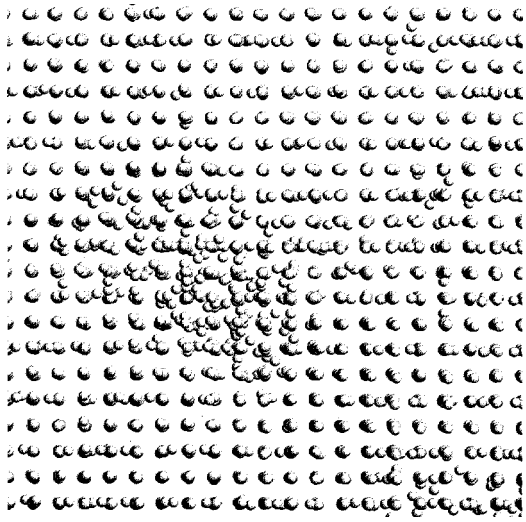

FIG. 4. Final lattice of the Stillinger-Weber nonbonding simulation. Only a specific part of the whole lattice is shown.

heating and displacement processes as possibles solutions have already been rejected by a prior work,[24] leaving bond breaking and local excitations as possible mechanisms.

All models used in these simulations gave similar results, suggesting that bond breaking can successfully be modeled with classical molecular dynamics simulations. The antibonding model is the most realistic model used as it is derived from *ab initio* calculations. However, despite its simplicity, the simple nonbonding model also describes the recrystallization fairly well when compared with this more sophisticated antibonding model and experimental data.[24]

Both model potentials used in this study lead to similar results. However, both the rate of recrystallization and the amount of atoms in the amorphous zones produced by the 5-keV As recoil were considerably lower in the case of the Stillinger-Weber potential than of the Tersoff potential. These differences could arise from the fact that the Stillinger-Weber potential is fitted only to the tetrahedral configuration and thus penalizes nontetrahedral bonding types. The stiffness of this potential has also been found to be too large when comparing it with the tight-binding method.[26]

For the antibonding model the value of the r_0 parameter was found to have a rather large impact on the recrystallization rate. The potential energy difference between the two values of r_0 is 0.6 eV at the nearest-neighbor distance in a crystal, and this is apparently enough to change the behavior. This 0.6-eV potential-energy difference corresponds to the potential-energy difference between the two different values for the r_0 parameter. This does not in any way correspond to the inserted energy of one bond-breaking event. A change in the t_0 parameter also changes the rate of recrystallization. Even though we get different rates with different parameters, it does not change the fact that we see similar recrystallization in all the simulations. Thus, although there clearly are some model dependences in our simulations, they are not so large that they would preclude us from drawing qualitative conclusions on the recrystallization mechanism.

In our models, when the bond is reformed, kinetic energy of the order 10^{-2} eV is inserted into the system. This creates a hot spot around the bond which might lead to reordering of the bonds and recrystallization of the lattice. However, in a prior work[25] a threshold energy of 0.8–1.0 eV has been suggested for recrystallization. Since our simulations only insert a maximum energy of 3.4×10^{-2} eV, it seems very unlikely that the heating alone could be the reason behind the observed recrystallization. This was definitely confirmed by the artificial hot spot simulations (which involve no bond breaking; see Sec. II) we carried out. These showed no recrystallization. Hence we can conclude that the recrystallization in our simulations primarily originates from geometric rearrangement during the time the bond is broken. By geometric rearrangement we mean that after a bond between atoms i and j breaks, the atom i can reform the bond with some other atom k in the local neighborhood (and similarly with j and some other atom l). Although this is quite unlikely to occur in the crystalline state, in an amorphous state produced by irradiation there are weak bonds which are relatively easy to break, and there can be nearby atoms in nonequilibrium bonding configurations, making it much more likely that a new bond forms with another atom. At the amorphous-crystalline interface this process will (on average) induce recrystallization since the more crystal-like bonding configurations lie lower in energy.

The real amount of kinetic energy transferred directly to atomic motion by electronic excitations is not known, so the real ''hot spot'' energy could be higher than in our simulations. However, even if the energy is higher than in our simulations, it would not qualitatively change our observations on the recrystallization. Extra heating could enhance the recrystallization rate, but our results demonstrate that no hot spot effect is necessary to produce recrystallization.

Experiments with electron irradiation also show that recrystallization of the amorphous pockets takes place at the amorphous-crystal interface.[27] Experiments have also shown that the size of the amorphous pockets have a linear dependence on the dose,[24] which is also the trend in our simulations (excluding the short-time scale fluctuations). The experiments also show that the size of the amorphous pockets sometimes even appears to increase in size over short-time scales.[28] However, due to the two-dimensional nature of the transmission electron microscopy imaging used in the experiments, the experiments could not conclusively determine whether this is a real growth or only a rearrangement of some three-dimensional feature which appears as growth in a two-dimensional projection. In our simulations we sometimes observe growth of the amorphous zones (the bumps in the curves in Figs. 1 and 2), strongly indicating that the experimentally observed effect indeed is associated with a real growth.

The Spaepen-Turnbull model of recrystallization at interfaces[9] predicts that recrystallization would occur at interfaces due to bond breaking and migration of the dangling bonds ''with little additional activation.'' Our results are consistent with the basic idea of the model, namely that recrystallization occurs at the interface due to bond breaking. However, the fact that we also observe recrystallization at 0 K shows that no thermally activated migration of dangling bonds is necessary for recrystallization to proceed.

V. CONCLUSION

In this paper we have presented our results for recrystallization in Si utilizing a bond-breaking model. Two different models were used, namely, the nonbonding model and the antibonding model. Both models show similar results. The nonbonding model was tested with both the Tersoff and the Stillinger-Weber potential, which also both gave similar results.

The simulations show that the recrystallization proceeds at about the same pace (within a factor of ~ 2) for several different bond-breaking models, and that it occurs for all four different interatomic force models tested. This fact indicates that the qualitative behavior observed here is very reliable.

We have demonstrated that the recrystallization occurs by the Spaepen-Turnbull mechanism, but contrary to the originally suggested model, no thermally activated dangling bond migration is necessary for recrystallization to occur. Also, no kinetic-energy transfer from irradiating electrons to the target atom is necessary for recrystallization. The bond-breaking and rebonding event itself can supply enough energy to the atoms surrounding the bond for structural rearrangement to occur.

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