Defect structures in ion beam amorphized Si, Ge and GaAs

J. Nord, K. Nordlund and J. Keinonen
Accelerator Laboratory, P.O. Box 43, FIN-00014 University of Helsinki, Finland
(March 30, 2001)

We use molecular dynamics simulations to study ion irradiation induced amorphization in Si, Ge and GaAs using several potential models. The amorphization in Si is shown to proceed via growth of amorphous regions during self-ion irradiation. Although the ions produce damage everywhere, low-energy recoils recrystallize some of the isolated point defects, but can not recrystallize larger amorphous pockets, which thus grow to induce full amorphization. We further find that the density of irradiated amorphous silicon depends strongly on the energy distribution of recoil atoms. The simulations also show that the coordination number is higher and average bond length is longer for irradiated than melted structures in Si and Ge. Three and four membered rings are found in irradiated Si. For irradiated amorphous GaAs, we suggest that long, weak Ga-Ga bonds (about 2.8 Å), also present in pure Ga, are produced during irradiation.

PACS numbers: 61.72.De,61.72.Ji,61.72.Lk,61.82.Fk

I. INTRODUCTION

Ion implantation of semiconductors at doses high enough to introduce significant amounts of electrically active dopants leads normally to amorphization of the implanted volume. Although the material is subsequently recrystallized by annealing, the mechanisms leading to amorphization may affect for instance dopant clustering.

The amorphization mechanisms have been intensively studied in the literature, see e.g. Refs. 1–13. Still, the mechanisms leading to amorphization even in very common semiconductor materials such as Si and GaAs remain subject to debate. Also, it is not clear whether the structure of the amorphous material produced by irradiation corresponds to that produced by other means such as quenching, some experiments indicate that at least the density of ion-beam amorphized Si (a-Si)14 is always the same (even after annealing) or smaller than that of crystalline Si16, yet other experiments and computer simulations observe an a-Si phase denser than crystalline Si16,17. Custer et al. conclude that this indicates that at least the computer models describing Si only by tetrahedrally coordinated atoms must be erroneous15, implying that the presence of over- and undercoordinated Si atoms in ion-beam-amorphized Si may be responsible for the discrepancy.

Since it appears likely that defects smaller than those visible in transmission electron microscopy (TEM) experiments play a significant role in the amorphization process, atom-level computer simulations can play a significant role in understanding the pathway to amorphization. Numerous computer simulation studies have examined the amorphization or recrystallization mechanisms of Si from different viewpoints6,8,10,12,13. However, only a few have produced amorphous Si by multiple recoils in crystalline Si and studied the structure and density of amorphous Si, and these studies have usually been limited to using only one interatomic potential, or the results have been partly dependent on simulation parameters with no experimental correspondence3,12,18.

In this paper we study the amorphization of Si, Ge and GaAs by amorphizing the sample with energetic self-recoils starting from pristine crystal. We use three different interatomic potentials for Si and two for Ge to enable deducing which results can be considered reliable.

The paper is organized as follows. First the simulation methods are explained is section II. The results in section III are divided in general results for different recoil distributions, and a more detailed analysis for Si, Ge and GaAs materials, along with results on the stability of irradiated amorphous material.

II. METHOD

To study the properties of amorphous semiconductor materials we amorphized samples of the medium by successive energetic recoils starting from initially perfect crystal. Monoenergetic recoils consisting of 100 eV or 1 keV recoils and a more realistic simulated recoil energy distribution were used. Periodic boundaries were used in three dimensions in all simulations. The number of atoms was 22000 for 1 keV recoils, 4000 and 8000 for 100 eV recoils and 40000 atoms for variable energy.

In the first phase an energetic recoil was started at about the middle of a simulation cell, which was initially at 0 K temperature. The cell was cooled down towards 0 K at the borders using Berendsen temperature control. Simulation times varying between 6000 ps and 10000 ps were used for 1 keV energy to test whether this affects the final results. In all cases the temperature after the recoil event was below 80 K and no difference was seen between the final structures generated with different simulation times. In the simulations with varying recoil energy the simulation times depended linearly on the recoil energy. The minimum simulation time was set to 500 ps. At this stage the size of the cell was held constant and a variable time step was used to speed up the simulations.

In the second phase the cell was relaxed to 0 K and average zero pressure in either all or in the z-direction using Berendsen pressure control. Relaxation times varied between 2000 ps and 3500 ps. In the varying energy cases, the cell was relaxed after every 100 eV
recoil dose. After relaxation the atoms were displaced a random distance in x, y and z directions and the positions of the atoms corrected by periodic boundary conditions. This way all the positions were equal and the generated amorphous material homogeneous. The procedure was then iterated until full amorphization was achieved, i.e. the average potential energy and volume of the cell leveled at some constant value.

This way the simulations had no dependency of parameters with no experimental correspondence. The simulation scheme is suitable for light ion irradiation ($Z \leq 15$), since recoils are uncorrelated.

Monoenergetic 100 eV and 1 keV recoils were used to see whether the recoil energy affected the final structure or amorphization doze. Also a random energy scheme with an energy distribution produced by 500 keV Si bombardment of Si simulated with the MDRANGE method was used. Because low energy recoils are dominant in cascades, only recoils with energies higher than either 3 or 15 eV were used. The latter value was chosen because this is about the threshold displacement energy in Si (at least in our models). so recoils with energies below this do not affect the damage structure in initially perfect crystal regions. However, in Si it is possible that even lower-energy recoils cause some dynamic recrystallization of the material (see below), so we also used the threshold value of 3 eV in some simulations. This value was chosen because it is less than the strength of two bonds in Si, so recoils below this value should not cause significant structural change even in a-Si. In simulations with a cutoff of 3 eV the sample amorphized somewhat slower, but the final a-Si structure was practically identical to the simulations with a 15 eV cutoff. Since the total computing time needed to achieve full amorphization was very much longer for the 3 eV cutoff because of the large number of low-energy recoils, most simulations used the cutoff value of 15 eV.

Recoils with more than 2 keV energy were not used, which allowed us to use smaller simulation cells. This is not a severe approximation, since recoils with more than ~2 keV energy break into sub-cascades with similar secondary recoil energy distributions as the initial recoil$^{19,20}$.

The angular distribution was simulated for both 100 eV and 1 keV recoils, and the amorphizations were done both by using a simulated angular distribution and random directions of recoils. The distributions were simulated with the MDRANGE method by 500 keV Si bombardment of Si and selecting 80 - 120 eV and 800 - 1200 eV recoils. In the relaxation phase the cell size was let to change only in z-direction or in x, y and z-directions. Several of the runs were repeated starting from scratch to be sure statistical fluctuations do not affect our conclusions.

Amorphous material was also generated by melting and quenching. First the material was held at a temperature much higher than the melting point for 50 - 100 ps. The cell was then cooled down to 0 K not faster than 0.01 K/fs. The starting temperature was then about halved and the procedure repeated until temperatures lower than 400 K were used. The quenching ratio is still high compared to experimental conditions, and the effect of simulation time was estimated by running a quenching simulation for longer than 3 ns for comparison purposes. The differences between quenched and radiated materials remained qualitatively same. 8000 atoms were used in quenching simulations to acquire sufficient statistics.

The forces between the atoms were described by semi-empirical many-body potentials. Stillinger-Weber$^{21}$, Tersoff III$^{22}$ and EDIP$^{23}$ were used for Si, SW$^{21}$ and Tersoff$^{24}$ for Ge, and a potential by Albe et al.$^{25}$ for GaAs.

The melting point for EDIP, which to our knowledge has not been reported before for bulk melting, was determined by liquid-solid equilibrium. A cell with 2744 atom liquid phase and 2744 atom solid phase was equilibrated at 1400 K. The system was then simulated at several temperatures. Simulations were continued until either crystallization or melting was observed, which usually took about 1 ns. Berendsen pressure control to zero pressure was used in x, y and z-directions. The observed melting point was 1550 ± 50 K, which compares very well with the experimental value of 1685 K.

The structure of amorphous materials was characterized by the distribution of bond lengths, potential energies of atoms and angles between bonds. The pair-correlation function seemed to give little difference between different models and could not be used to judge which one described the real amorphous material best. The amorphization doze for different cases could easily be extracted, as well as the density of amorphous material.

### III. RESULTS

#### A. Effect of recoil impact vector

The angular and energy distribution dependencies were only tested for Tersoff III potential for Si, since no dramatic dependence of the main results on the impact vector were found, while the differences between the potentials were much bigger. The effects of recoil impact vector were studied mono-energetic recoils of 100 eV and 1 keV energy with two different angular distributions. The dependency on the recoil energy distribution was also studied by simulating amorphization by variable energy recoil distribution simulated by MDRANGE. The other distribution used the same probability for all directions, while the other was a typical distribution of secondary recoils obtained by simulations. No difference was seen between the materials produced by angular dependent and random direction recoils. Amorphization doses were the same, as well as the volume-dose and potential energy-dose dependencies.
TABLE I. Amorphization doses for different materials and Si potentials. \( E_{\text{dose}} \) is the dose needed to reach saturation potential energy level and \( V_{\text{dose}} \) is the dose per atom needed for final volume. Relaxation corresponds to the pressure relaxation method in all directions (3d), one direction (x) or to an annealing temperature. \( V/V_0 \) is the volume of amorphized material compared to perfect crystal.

<table>
<thead>
<tr>
<th>Method</th>
<th>Relaxation</th>
<th>( E_{\text{dose}} ) (eV)</th>
<th>( V_{\text{dose}} ) (eV)</th>
<th>( V/V_0 )</th>
<th>( E_{\text{potential}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDIP</td>
<td>100 eV irr.</td>
<td>z</td>
<td>6.5</td>
<td>10</td>
<td>1.035</td>
</tr>
<tr>
<td></td>
<td>100 eV irr.</td>
<td>3d</td>
<td>6.5</td>
<td>2</td>
<td>1.035</td>
</tr>
<tr>
<td></td>
<td>1 keV irr.</td>
<td>3d</td>
<td>6.5</td>
<td>3</td>
<td>1.022</td>
</tr>
<tr>
<td></td>
<td>Variable E irr. (^a)</td>
<td>3d</td>
<td>6.5</td>
<td>2</td>
<td>1.029</td>
</tr>
<tr>
<td></td>
<td>quench</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.035</td>
</tr>
<tr>
<td></td>
<td>Variable E irr. (^a)</td>
<td>900 K</td>
<td>-</td>
<td>-</td>
<td>1.036</td>
</tr>
<tr>
<td>Tersoff</td>
<td>100 eV irr.</td>
<td>z</td>
<td>8</td>
<td>12</td>
<td>1.093</td>
</tr>
<tr>
<td></td>
<td>100 eV irr.</td>
<td>x</td>
<td>8</td>
<td>13</td>
<td>1.093</td>
</tr>
<tr>
<td></td>
<td>1 keV irr.</td>
<td>3d</td>
<td>8</td>
<td>7</td>
<td>1.047</td>
</tr>
<tr>
<td></td>
<td>Variable E irr. (^b)</td>
<td>x</td>
<td>8</td>
<td>13</td>
<td>1.045</td>
</tr>
<tr>
<td></td>
<td>Variable E irr. (^b)</td>
<td>3d</td>
<td>8</td>
<td>8</td>
<td>1.089</td>
</tr>
<tr>
<td></td>
<td>quench</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.019</td>
</tr>
<tr>
<td>Stillinger-Weber</td>
<td>1 keV irr.</td>
<td>3d</td>
<td>8</td>
<td>11</td>
<td>1.084</td>
</tr>
<tr>
<td></td>
<td>quench</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.944</td>
</tr>
<tr>
<td>expit</td>
<td>12</td>
<td>1.018^(a)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Cutoff energy is 15 eV.
\(^b\) Cutoff energy is 3 eV.
\(^c\) Ref.1
\(^d\) Ref.15

B. Effect of pressure boundary conditions

Another condition which might generate direction dependency in the structure was pressure relaxation. In the relaxation phase, the pressure was set to relax to zero in x, y- and z-directions separately, or in the z-direction only. The latter condition is significant, because experimentally the pressure relaxation during ion beam irradiation is limited in x- and y-directions. While the development of average potential energy with amorphization dose was unaffected by the condition, the volume changed slower in the latter case. When the pressure was only relaxed in one direction, the average potential energy reached the saturation level at the same dose as in the free case, but more irradiation was needed for the pressure to relax in the x- and y-directions. For most cases the volume and average potential energy did not saturate at the same dose. Therefore, the volume is not a good measure of whether the material is amorphized. The final potential energy and volume were the same in both relaxation schemes.

FIG. 1. Development of volume and potential energy compared to perfect Si crystal in 100 eV or 1 keV monoenergetic irradiation, and variable energy irradiation with 15 eV lower recoil energy cutoff as a function of irradiation dose. Values for quenched amorphous material are included for comparison purposes. The Tersoff III potential model was used.

FIG. 2. Development of volume and potential energy compared to perfect Si crystal in 100 eV or 1 keV monoenergetic irradiation, and variable energy irradiation with 3 or 15 eV lower recoil energy cutoff as a function of irradiation dose. Values for quenched amorphous material are included for comparison purposes. The Tersoff III potential model was used.

The volume change was found to depend strongly on the energy of the recoil atoms. For monoenergetic 100 eV recoils the volume change was bigger than for 1 keV recoils. The final potential energy of the 100 eV cases is slightly above the 1 keV ones.

A realistic simulated recoil energy distribution was also used in simulations with EDIP and Tersoff III. With a
15 eV lower energy cutoff value, the potential energy development is very similar to the 100 eV monoenergetic case. For Tersoff III this is also true for the development of the volume, whereas for EDIP the volume with realistic distribution saturates to a smaller value.

Two different lower energy cutoffs, 3 and 15 eV, were used for variable recoil energy simulations for the Tersoff III potential model. The final volume and average potential energy of amorphized material was the same for both cutoffs, but the 3 eV case amorphized slower. The dose needed for the average potential energy to saturate was the same for variable energy scheme with 15 eV cutoff as for all tested monoenergetic cases, but for 3 eV cutoff the dose was somewhat bigger. The reason is that low-energy recoils with about 3 eV energy may recrystallize the material\(^{26}\) (see section IV).

### C. Amorphization in Si

Since semi-empirical interatomic potentials have different functional forms and are fit to different sets of properties, it is not clear which, if any, of the potentials is suitable for simulating a certain phenomenon not part of the original fitting database. The problem is especially important when simulating disordered phases, since functional forms are often built on the basis of favoring some bond-angle in well defined and ordered crystal lattice. Simulations were therefore repeated with Tersoff III\(^{22}\), EDIP\(^{23}\) and Stillinger-Weber\(^{21}\) for Si. The reliability of the results between potentials could be estimated by comparing the experimental values for amorphization dose and density of the material to those obtained by simulations.

Big differences between potentials were found in the density of amorphous Si. The EDIP and Tersoff potential models were able to reproduce the positive volume change observed in experiments\(^{15}\), whereas for SW the amorphous material was denser than crystalline Si. The volume-dose dependency for different potentials for 1 keV monoenergetic recoils is shown in Fig. 3.

![Figure 3](image)

**FIG. 3.** Development of volume and potential energy compared to perfect Si crystal during ion irradiation for different Si potential models as a function of irradiation dose. 1 keV monoenergetic recoils were used.

For all potentials the amorphization was done both by repetitive melting-quenching and irradiation. The distribution of potential energy of atoms is illustrated in Fig. 4. The difference between production methods was largest for EDIP and smallest for SW. The average potential energy for all three potential models is higher for the irradiated case than for quenched one. This indicates that defects in the amorphous structure are present in the irradiated samples.

![Figure 4](image)

**FIG. 4.** Potential energy distribution for different Si potential models. The dotted line represents the distribution for amorphized material produced by 1 keV monoenergetic recoils, and solid line the distribution for quenched amorphous material.

Because the quenching method may be sensitive to the quenching ratio and simulation time, this procedure
was repeated for different time-scales. Longer simulation times only increased the difference between the structures of molten and radiated materials, ensuring the difference exists regardless of the quenching ratio. The longest quenching simulation time was about 3 ns.

For all tested Si potentials and irradiation conditions the average coordination was bigger and average bond lengths longer in irradiated than in quenched cases as shown in table II and Fig. 5. The average bond lengths for different irradiation conditions are about 2.47 Å for EDIP and about 2.43 Å for Tersoff and Stillinger-Weber. Over 90% of atoms in the quenched amorphous structures described by EDIP and Tersoff potential models have a coordination of four, and the average coordination number is a little higher than four. For irradiated structures described by EDIP the most common coordination is five. For Tersoff there are much more five-fold and three-fold coordinated atoms in the irradiated structure. Stillinger-Weber produced a very similar structure for both irradiated and quenched samples.

The bond-angle distributions of irradiated and molten structures are illustrated in Fig. 6. Once again Stillinger-Weber has about the same distributions for both production methods. However, EDIP shows sharp peaks near 60° and 75°. Tersoff III also shows a small increase near these values. The 60° peak is associated with a Si-Si-Si triangle with all angles near 60°. There are much more 3-rings in irradiated structures, as shown in Table II. The peak near 75° is associated with four membered rings, which often have two 75° angles.

The amorphization doses needed to saturate both the volume and potential energy vary between 6 and 17 eV/atom for different Si potential models and amorphization methods. These values are in reasonable agreement with the experimental value of about 12 eV/atom determined at low temperatures, where defect migration is not important.

![Figure 5](image1.png)  
**FIG. 5.** Bond length distributions of amorphous materials for different Si potential models. The dotted line represents the distribution for amorphized material produced by 1 keV monoenergetic recoils, and the solid line the distribution for quenched amorphous material.

![Figure 6](image2.png)  
**FIG. 6.** Distribution of angles between bonds for different Si potential models. The dotted line represents the distribution for amorphized material produced by 1 keV monoenergetic recoils, and the solid line the distribution for quenched amorphous material.

---

### TABLE II. Amount of three membered rings, coordination distribution and average bond length and coordination for different Si potential models and amorphization methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>3-rings/at.</th>
<th>Z=3</th>
<th>Z=4</th>
<th>Z=5</th>
<th>&lt;Z&gt; bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDIP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irr. 100 eV</td>
<td>0.137</td>
<td>0.5</td>
<td>34.0</td>
<td>65.3</td>
<td>4.67</td>
</tr>
<tr>
<td>Irr. 1 keV</td>
<td>0.108</td>
<td>0.2</td>
<td>44.8</td>
<td>54.8</td>
<td>4.55</td>
</tr>
<tr>
<td>Irr. variable energy</td>
<td>0.137</td>
<td>0.5</td>
<td>39.1</td>
<td>60.0</td>
<td>4.60</td>
</tr>
<tr>
<td>Quenched</td>
<td>0.005</td>
<td>0.1</td>
<td>93.9</td>
<td>6.0</td>
<td>4.06</td>
</tr>
<tr>
<td>Tersoff III</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irr. 100 eV</td>
<td>0.013</td>
<td>10.9</td>
<td>64.3</td>
<td>22.8</td>
<td>4.15</td>
</tr>
<tr>
<td>Irr. 1 keV</td>
<td>0.010</td>
<td>7.6</td>
<td>65.3</td>
<td>24.8</td>
<td>4.21</td>
</tr>
<tr>
<td>Irr. variable</td>
<td>0.014</td>
<td>10.2</td>
<td>64.9</td>
<td>22.9</td>
<td>4.16</td>
</tr>
<tr>
<td>Quenched</td>
<td>0.001</td>
<td>0.5</td>
<td>91.4</td>
<td>8.1</td>
<td>4.08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Stillinger-Weber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irr. 1 keV</td>
<td>0.0003</td>
<td>0.9</td>
<td>53.8</td>
<td>43.1</td>
<td>4.46</td>
</tr>
<tr>
<td>Quenched</td>
<td>0.0003</td>
<td>0.7</td>
<td>56.5</td>
<td>41.1</td>
<td>4.43</td>
</tr>
</tbody>
</table>
D. Amorphization in Ge

FIG. 7. Development of volume in different Ge and GaAs potential models as a function of the irradiation dose. Monoenergetic 1 keV recoils were used to produce irradiated amorphous material. Values for quenched material are included for Ge models.

Stillinger-Weber\(^{27}\) and Tersoff\(^{24}\) potential models were used for Ge. The irradiated amorphous Ge described by Stillinger-Weber potential was less dense than molten amorphous Ge, and crystalline Ge was denser than both of them. The increase in density is explained by longer bonds, which were about 3\% longer in irradiated material than in crystalline Ge as seen in Table III. The average coordination number was very close to that of crystalline Ge, 4.04 for irradiated and 4.02 for molten sample.

The behavior of Ge during ion irradiation described by Tersoff potential is more complicated. First the volume grows, but then it decreases almost back to the level of crystalline Ge. The bonds are about 4\% longer than in crystalline Ge, but highly coordinated atoms compensate the change in volume. After the material was fully amorphized by irradiation, the average coordination was 4.93. Molten amorphous Ge has a lower coordination of 4.21 and is slightly less dense than crystalline Ge.

Experimentally the coordination number of irradiated amorphous Ge is found to be close to four\(^{28}\). The ab initio calculations predict that the coordination number of molten amorphous Ge is 4.05\(^{29}\). These are in good agreement with our amorphization simulations modeled by the Stillinger-Weber potential, which predict a small increase in coordination number. The simulation with the Tersoff germanium potential show more increase in coordination number for both molten and irradiated amorphous materials. The bonds are found to be longer in irradiated samples than in quenched ones. This is in agreement with experiments, where the bond length is found to decrease during annealing\(^{28}\). Our simulations predict longer bonds than experimental measurements. However, the experimental bond length increased with ion dose\(^{28}\).

<table>
<thead>
<tr>
<th>Material</th>
<th>Z=3</th>
<th>Z=4</th>
<th>Z=5</th>
<th>Z=6</th>
<th>&lt;Z&gt;</th>
<th>bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Ge</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>4.00</td>
<td>2.45</td>
</tr>
<tr>
<td>irr. SW Ge</td>
<td>2.4</td>
<td>91.5</td>
<td>6.07</td>
<td>0.0</td>
<td>4.04</td>
<td>2.52</td>
</tr>
<tr>
<td>melt SW Ge</td>
<td>1.1</td>
<td>96.2</td>
<td>2.8</td>
<td>0.0</td>
<td>4.02</td>
<td>2.50</td>
</tr>
<tr>
<td>irr. Ter Ge</td>
<td>1.7</td>
<td>33.8</td>
<td>40.3</td>
<td>18.4</td>
<td>4.93</td>
<td>2.56</td>
</tr>
<tr>
<td>melt Ter Ge</td>
<td>0.3</td>
<td>80.0</td>
<td>17.4</td>
<td>2.1</td>
<td>4.21</td>
<td>2.50</td>
</tr>
</tbody>
</table>

For molten amorphous Ge described by the Stillinger-Weber potential the angles between bonds are distributed near 108.6° with 10.8° standard deviation. The average angle for irradiated material is 108.3° with standard deviation of 13.1°.

The amorphization dose for the Tersoff Ge potential model is 9.1 eV/atom in good agreement with experimental value of about 13 eV/atom (calculated with TRIM from irradiation parameters in Ref.\(^{28}\)). The Stillinger-Weber Ge overestimates the amorphization dose probably because it has a too high melting point\(^{20}\).

<table>
<thead>
<tr>
<th>Material</th>
<th>E-dose (eV)</th>
<th>V-dose (eV)</th>
<th>V/V(_0)</th>
<th>E(_{pot})</th>
</tr>
</thead>
<tbody>
<tr>
<td>irr. Tersoff Ge</td>
<td>9.1</td>
<td>9.1</td>
<td>1.000 -3.42</td>
<td></td>
</tr>
<tr>
<td>melt Tersoff Ge</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-3.58</td>
</tr>
<tr>
<td>irr. Stillinger-Weber Ge</td>
<td>36</td>
<td>36</td>
<td>1.067 -3.48</td>
<td></td>
</tr>
<tr>
<td>melt Stillinger-Weber Ge</td>
<td>-</td>
<td>-</td>
<td>1.049 -3.54</td>
<td></td>
</tr>
<tr>
<td>irr. GaAs</td>
<td>13</td>
<td>12</td>
<td>1.045 -2.89</td>
<td></td>
</tr>
<tr>
<td>annealed GaAs</td>
<td>-</td>
<td>-</td>
<td>1.029 -2.98</td>
<td></td>
</tr>
</tbody>
</table>
E. Amorphization in GaAs

Amorphization in GaAs was modeled by the potential by Albe et al. We do not present the values for molted amorphous GaAs, because the cell recrystallized almost perfectly in melting simulations (the total simulation time was about 10 ns). Therefore we compare the irradiated amorphous GaAs before and after annealing at a temperature much lower than the melting point for the used potential model.

In GaAs amorphization simulations we used 1 keV monoenergetic recoils (randomly chosen as Ga or As). The amorphization dose was about 13 eV/atom, in reasonable agreement with the experimental value of about 10 eV/atom (obtained from the low temperature values from Fig. 5 in Ref. 30). Crystalline GaAs was about 4.5% denser than irradiated amorphous GaAs.

The distribution of Ga-Ga, As-As and Ga-As bonds before and after annealing is shown in Fig. 8. Most of the bonds are between Ga and As atoms. The fraction of wrong bonds before annealing is 37%. About 73% of the wrong bonds are Ga-Ga bonds with an average length of 2.81 Å. These bonds are longer versions of the metallic bonds present in pure GaAs. The amount of covalent wrong bonds is about 14%. If the cutoff value for the coordination number calculation is selected as 2.7 Å (cf. section IV.C), the average coordination is 3.45. If also longer Ga-Ga bonds are counted, the coordination number is 4.64.

The amorphized cell was annealed at 900 K for 400 ps and then cooled to 0 K. During the annealing, the amount of Ga-As bonds increased about 2.5%. The amount of Ga-Ga bonds near 2.8 Å decreased about 16%, indicating that the defect is not stable at high temperatures. There were some more As-As bonds after annealing and As segregation was observed. However, simulations at 1300 K and 1500 K temperatures (still below the melting point of about 1900 K for the potential model) show that the As regions are not stable and can be annealed at longer time scales. Because the As regions are eventually annealed, it is also possible that all Ga defects with 2.8 Å bond length are converted to Ga-As bonds during high-temperature annealing.

During annealing the Ga-As bonds were shortened from 2.51 to 2.48 Å. At the same time the length of As-As bonds increased from 2.44 to 2.46 Å. The amount of covalent bonds shorter than 2.7 Å was increased during annealing.

F. Stability of amorphous material

The stability of the structure of amorphous Si produced by irradiation was tested by heating a few amorphous cells up to 300, 600, 900 and 1200 K. The cells were held at each temperature for about 4 ns and then quickly cooled down to 0 K. The initial cell for annealing simulations was amorphized by variable energy recoils with 15 eV lower energy cutoff. We focused on the Tersoff and EDIP potentials in this analysis, as the Stillinger-Weber potential gave a density of the amorphous material in clear contradiction to experiments.

| Table V. Percentage of most common coordinations and average bond length and coordination of irradiated amorphous silicon modeled by EDIP or Tersoff and variable energy recoils with 15 eV lower cutoff before and after annealing. Values for quenched amorphous silicon are included for comparison purposes.

<table>
<thead>
<tr>
<th>Anneal</th>
<th>Z=3</th>
<th>Z=4</th>
<th>Z=5</th>
<th>&lt;Z&gt;</th>
<th>bond length</th>
<th>d_{potential}</th>
<th>V/V0</th>
<th>EDIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>before</td>
<td>0.45</td>
<td>39.1</td>
<td>60.0</td>
<td>4.60</td>
<td>2.47</td>
<td></td>
<td>-4.26</td>
<td>1.028</td>
</tr>
<tr>
<td>300 K</td>
<td>0.06</td>
<td>66.9</td>
<td>33.0</td>
<td>4.32</td>
<td>2.43</td>
<td>-4.36</td>
<td>1.099</td>
<td></td>
</tr>
<tr>
<td>600 K</td>
<td>0.08</td>
<td>91.0</td>
<td>9.0</td>
<td>4.09</td>
<td>2.40</td>
<td>-4.42</td>
<td>1.032</td>
<td></td>
</tr>
<tr>
<td>900 K</td>
<td>0.06</td>
<td>96.1</td>
<td>3.8</td>
<td>4.04</td>
<td>2.39</td>
<td>-4.45</td>
<td>1.037</td>
<td></td>
</tr>
<tr>
<td>1200 K</td>
<td>0.21</td>
<td>73.5</td>
<td>26.7</td>
<td>4.26</td>
<td>2.43</td>
<td>-4.36</td>
<td>1.012</td>
<td></td>
</tr>
<tr>
<td>quench</td>
<td>0.05</td>
<td>93.9</td>
<td>6.0</td>
<td>4.06</td>
<td>2.40</td>
<td>-4.44</td>
<td>1.035</td>
<td></td>
</tr>
</tbody>
</table>

After annealing in 600 or 900 K the structure of the cell modeled by EDIP was very close to the quenched amorphous structure as seen in table V. The average coordination number, potential energy and volume are almost the same for annealed and quenched materials. Also the number of three or four membered ring are at the same level and qualitative differences are not present in bond angle distributions. At 1200 K the fraction of five-fold coordinated atoms suddenly increases to about 26%. This is probably because 1200 K is above the
glass temperature of EDIP-Si, which we determined to be $\lesssim 1200$ K. The glass temperature was obtained by simulating a 2000 atom cell with disordered structure at temperatures between 100 and 1600 K with 20 K interval. At $1200$ K the thermal expansion coefficient changed dramatically (and even changed sign), which is a signature of the glass temperature$^{32}$. However, because of the limited time scale of the equilibration runs at each temperature, this can only be considered to be an upper limit for the glass temperature.

The number of coordination defects in annealed cells modeled by Tersoff decreases during annealing. The coordination number distribution after $1200$ K annealing of irradiated sample is similar to the quenched sample. Also the bond angle and potential energy distributions are similar. However, the amorphous structure produced by quenching is about 1.6 % denser than the annealed sample, and has 2.4 % less four membered rings.

IV. DISCUSSION

The results for amorphization mechanisms during ion irradiation presented here are directly relevant to low-temperature experiments (less than 150 K) only, because at higher temperatures defects in highly irradiated Si are mobile$^{33-35}$.

A. Amorphization mechanism

Our simulations show that at least self-ion irradiated silicon amorphizes via growth of amorphous regions. Because the recoil spectra of ions with similar masses do not differ strongly, this conclusion can be expected to also hold for other ion in the same mass range as Si. In the amorphization simulations with simulated recoil energy distribution and 3 eV lower recoil energy cutoff, most recoil atoms have less than 10 eV energy. These low energy recoils effectively recombine defects. If the defect concentration at some region is high enough, an amorphous region is formed. The region then starts to grow, because defects are more stable inside amorphous zones. In the intermediate state between crystalline and fully amorphized sample, the material then contains amorphous regions with some isolated defects between them. This is consistent with experiments, where amorphous zones are found to grow preferentially at crystalline-amorphous interface$^{36}$ or at pre-existing defects$^{37}$. The amorphization process is illustrated in Fig. 9. This amorphization mechanism is not homogeneous, because clear amorphization centers exist. On the other hand, the mechanism requires multiple ion passes in a spatial region before full amorphization. The amorphous centers may also move by recrystallizing from one interface and amorphizing from another. We thus interpret the mechanism to be a combination of heterogeneous and homogeneous mechanism.

![FIG. 9. Evolution of Si during ion irradiation. The doses are about a) 0.005 eV, b) 0.15 eV, c) 3.0 eV and d) 14 eV/µ. The Tersoff III potential model and simulated recoil energy distribution with 3 eV lower energy cutoff were used.](image)

In the simulations with realistic recoil energy distribution and 15 eV lower recoil energy cutoff, the damage is not recombined as much, and the amorphization proceeds via frozen-in damage accumulation. This was also true for all monoenergetic simulations. For heavier ions or target materials this mechanism may be favored, since the damage is more concentrated.

The recrystallization efficiency can be estimated by the amorphization process theory of Wang et al.$^{38}$ The theory predicts that the amorphous fraction $f_a$ can be expressed as a function of a normalized ion dose $D_n$ and crystallization efficiency $A$:

$$f_a = 1 - \frac{1}{\sqrt{A + (1 - A)\exp[2(1 - A)D_n]}}. \quad (1)$$

We fitted the parameters $A$ and $k = D_n/D$, where $D$ is the irradiation dose, for both 3 and 15 eV cutoff cases to see how the crystallization parameter is affected by low energy recoils. The normalized change in average potential energy of atoms was used as a measure of amorphous fraction. We obtained a recrystallization parameter $A$ of $0.48 \pm 0.02$ for 3 eV case and $0.16 \pm 0.05$ for 15 eV case, so there is more recrystallization with the lower energy recoils included. The $k$ parameter was $(0.59 \pm 0.03) \, 1/\text{eV}$ for 3 eV and $(0.49 \pm 0.04) \, 1/\text{eV}$ for 15 eV cutoff. Plots of the fits and original values are shown in Fig. 10.
B. Structure of amorphous Si and Ge

Because the volume changes for different potentials of the same material had big variation, we cannot predict the density of amorphous material conclusively. Moreover, the final volume of irradiated samples was found to depend strongly on the recoil energy distribution. Monoenergetic 100 eV recoil distribution produced a very similar structure as the variable energy distribution, whereas monoenergetic 1 keV distribution produced slightly denser material. Nevertheless, the coordination numbers and bond lengths were very close for each distribution and different to molten ones. The amorphization doses were in reasonable agreement with experiments.

The initial direction distribution of recoil atoms had no effect on the final structure of irradiated samples. Also the relaxation method, either 3d or z-direction only, did not affect the final structure. However, a bigger dose is needed until the volume of the z-relaxed samples reach a steady state, because it takes longer for the amorphous material to flow and relax the pressure induced in the cell by the phase transition.

Custer et al. report that the density of the amorphous structure they produce by irradiation does not change during annealing, and is about 2 % larger than the density of the crystalline phase. In our annealing tests, the EDIP potential and Tersoff potentials both had a fairly stable volume (about 2-3 % higher than that of the crystalline phase) during annealing between 600 and the melting point, and a similar volume in the quenched samples. The density for no annealing and low-temperature anneals was different, but this is probably because very unstable defects can be present in samples simulated only for short time scales at low temperatures, and these would anneal out on any experimental timescale. Thus we can consider the results of the Tersoff and EDIP potential to be in good agreement with experiments. The fact that both the quenched and ion-beam amorphized and annealed a-Si we observe with these potentials still contain coordination defects strongly supports the suggestion by Custer et al. that a-Si cannot contain tetrahedrally coordinated atoms only.

High energy defects, not appearing in quenched amorphous material, were present in irradiated samples for all tested potential models and materials. In irradiated amorphous silicon much more three and four-membered rings were present than in molten amorphous silicon. These rings were associated with peaks near 60° and 75° in the bond-angle distributions. Also the average bond lengths and coordination number were bigger in irradiated than melted structures at least for Si and Ge. In most cases the amorphized material (formed either by irradiation or quenching) is less dense than crystalline matter.

Ab initio simulations of the structure of amorphous Si frequently find a much larger fraction of defects (~ 10 %) than observed experimentally (both < 1 %)[30-41]. The defects in these simulations take the form of e.g. 3-fold and 5-fold coordinated atoms, as well as 3-membered, 4-membered etc. atom rings[40,41]. The a-Si structure in ab initio simulations was usually created by extremely rapid quenching, typically over ~ 1 ps, due to the limited time scale available to quantum mechanical simulations. Since the cooling in collision cascades in semiconductors also occurs over 1-2 ps, it is not surprising that the defects observed in the ab initio modeling are similar to those we observe in irradiated Si. The fact that we observe similar defects as the ab initio calculations gives us confidence that the defects we observe can indeed be expected to be at least metastable. Since we observe much less defects in the quenched a-Si samples, it also seems clear that the predominant reason to the presence of high defect concentrations in irradiated Si is the very rapid cooling of the amorphous zones produced.

C. Structure of amorphous GaAs

The volume of our amorphous GaAs (4.5 % less dense than crystalline GaAs, in good agreement with the experimental value of about 4 % (Ref. 42).

It is not clear experimentally whether wrong bonds (i.e. bonds between like atoms) are present in amorphous GaAs. The fraction of wrong bonds has been experimentally measured to be between 0 and 12 %[43,44]. It has been suggested that wrong bonds could not be present in a-GaAs because of the energy cost associated with them[45]. However, irradiated amorphous structures do contain high energy defects, which might contain wrong bonds.

The comparison of the bonding structure with experiments is complicated by the presence of the 2.8 Å "metallic" Ga-Ga bonds in our simulations. We do not know whether such bonds, if present in experimental samples, would contribute to the measured numbers of bonds. At least the experiments by Ridgway et al. do.
used a 2.7 Å cutoff in the analysis of the structural parameters
so presumably 2.8 Å bonds would not be observed in these experiments.

Assuming only bonds shorter than 2.7 Å should be
counted, the fraction of wrong bonds we observe before
annealing is 14 %, which is slightly more than the 0–
12 % observed in the experiments.\textsuperscript{35,42,44} Moreover, we
observed that the number of wrong bonds decreases
during annealing, so we do not think the discrepancy
between 14 % and less than 12 % is a serious one.

The coordination number (again with 2.7 Å cutoff)
of 3.45 we obtained for irradiated amorphous GaAs is
smaller than experimental value of 3.85 measured by
EXAFS\textsuperscript{42,11} An increase in nearest neighbour distance
was observed in the EXAFS measurements, from 2.445
Å in the crystal to 2.452 Å in the amorphous phase.
We observe the same effect in our simulations (2.45 Å
in the crystal vs. 2.51 Å in the amorphous zone), but the
experimental increase was much smaller.

Since both deviations from the values of perfect crystals
all GaAs are smaller in experiments, our simulated
\&GaAs sample is concluded to have more defects than
the sample used by Ridgway \textit{et al.}\textsuperscript{35} This difference may,
again, be related to annealing effects. In the experiments
sample was not held at low temperatures before analysis.
It is known that structural changes can occur in GaAs
even at room temperature\textsuperscript{46,47}, so it is likely that some of
the defects in our simulated samples would vanish
during experimentally accessible timescales. We can not
perform MD simulations for more than \textsim{} 10 timescales,
but during our high-temperature annealing tests the Ga-
As bonds were shortened from 2.51 Å to 2.48 Å.

To summarize our discussion of the structure of a-
GaAs, we have found that our simulations reproduce
at least qualitatively correctly several experimentally
observed features (density change, coordination number
less than 4, average bond length, presence of wrong bonds
in some samples). The fact that we observe a large
number of weak “metallic” Ga-Ga bonds around 2.8–
2.9 Å, which to our knowledge can not necessarily be
observed in experiments, leads us to propose that such
bonds may have a significant role on the structure of a-
GaAs at least at low temperatures.

\section*{V. CONCLUSIONS}

We have studied ion irradiation-induced amorphization
of Si, Ge and GaAs by simulating the entire amorph-
sification process starting from perfect crystal until a
stable amorphous state is reached. Comparison of results
obtained with different interatomic potential models in
the same material and comparison to experiment allowed
us to deduce which features observed in the simulation
can be considered reliable.

From the development of volume and potential energy
during irradiation we deduced that the volume of the
material is not a good measure of whether the material is
amorphized. Our structural results showed that both in
Si and Ge the average coordination number of amorphous
material produced by irradiation was higher than in
molten structures. Also bond lengths were longer in the
irradiated samples. The recombination of defects by low
energy recoils was found to be significant during light ion
irradiation of Si.

In the amorphous zones produced during irradiation
coordination defects were very common. During an-
nealing most of these defects, but not all, were quickly
removed even at low temperatures.

We also observed a large fraction of topological defects,
such as 3-, 4- etc. membered atom rings in the amorphous
network. In particular, in irradiated amorphous Si
triangles with all angles close to 60 % are very common.
During annealing the majority of the topological defects
are removed. Our results thus strongly indicate that
topological defects have a central role in the structure
of amorphous Si produced by irradiation.

We propose that these remaining coordination defects
are those suggested to be present in ion beam amorphized
Si by Custer \textit{et al.}

Our results also suggest that weak Ga-Ga bonds with
length near 2.8 Å are present in irradiated amorphous
GaAs.

\section*{ACKNOWLEDGMENTS}

We thank Prof. M. Bazant for useful discussions on the
EDIP interatomic potential, and Mr. J. Peltola for
calculating the recoil spectra of high-energy ions. The
research was supported by the Academy of Finland under
project No. 44215. Grants of computer time from the
Center for Scientific Computing in Espoo, Finland are
gratefully acknowledged.

\begin{thebibliography}{99}
\bibitem{1} J. R. Dennis and E. B. Hale, J. Appl. Phys. 49, 1119 (1978).
\bibitem{2} J. Namyan, D. Fath, O. S. Oen, and O. W. Holland, J. Vac. Sci.
\bibitem{3} M. O. Ruaul, J. Chaumoit, J. M. Penisson, and A.
\bibitem{4} T. Motooka and O. W. Holland, Appl. Phys. Lett. 58, 2360
\bibitem{5} S. U. Campisano, S. Coffs, V. Rainieri, F. Priolo, and E.
\bibitem{6} M. J. Caturla, L. A. M. T. Dias de la Rubia, and G. H.
\bibitem{7} L. J. Lewis and R. M. Nemenov, Phys. Rev. B 54, 1459
  (1996).
\bibitem{8} K. Nordlund and R. S. Averback, Phys. Rev. B 56, 2421
  (1997).
\bibitem{10} A. Gaber, H. Zillgen, P. Erhardt, P. Partyka, and R. S.
\bibitem{11} M. C. Ridgway, C. J. Gloer, E. Bezkova, A. P. B. G. J.
\bibitem{12} K. M. Beardsmore and N. Gronbech-Jensen, Phys. Rev. B
  60, 12610 (1999).
\end{thebibliography}

14 When we talk about amorphous Si (a-Si) in this paper, we mean any Si structure which lacks long-range order, regardless of the detailed short-range structure of the material.


18 In the study by Bearmore et al the density of the amorphized material depends on the pressure coupling constant $\tau_p$.


