Atomic displacement processes in irradiated amorphous and crystalline silicon

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Ion beam mixing was investigated in crystalline and amorphous Si using molecular dynamics simulations. The magnitude of mixing was found to be larger in amorphous Si by a factor of about two. The difference is attributed to local relaxation mechanisms occurring during the cooling down phase of the cascade. Comparison of mixing between Si and Al shows that short range structural order also has a significant influence on mixing.

Irradiation of solids with energetic particles leads to the local rearrangement of atoms, a process usually referred to as ion beam mixing. Ion beam mixing, or simply “mixing,” has been measured in many solids representing all classes of materials. A surprising result is that the amount of mixing per unit dose (measured in deposited damage energy per unit volume) is larger in Si than in most metals and ceramics [1]. In fact, mixing in several semiconductors, like Ge, GaAs, and InP, seems anomalously large. These observations persist to very low temperatures, in some cases less than 30 K, and they are independent of the type of irradiation particle [1,2], indicating that neither radiation enhanced diffusion nor electronic excitation are likely explanations for these results.

One of the differences between mixing in metals and semiconductors is that semiconductors become amorphous upon irradiation, whereas metals do not, and there is some indication that mixing in the amorphous structure is larger than in the crystalline one [2]. This is expected within thermal spike models of mixing since the thermal conductivities of amorphous materials are much less than those of their crystalline counterparts. Since it is not possible to measure mixing of a material in both the crystalline and amorphous states, we use molecular dynamics computer simulations to examine this question in Si and Al. We show that for cascades between 400 eV and 10 keV mixing in a-Si is about twice that in c-Si. We also show that local atomic coordination plays an important role in the displacement process.

We used classical molecular dynamics (MD) methods to simulate full collision cascades. The atoms were arranged in cubic simulation cells with periodic boundary conditions, and the temperature of the atoms in the outermost atom layers was scaled towards 0 K to provide temperature control. The forces acting between the atoms were described by many-body interatomic potentials fitted to a repulsive potential at short interaction distances to realistically describe energetic collisions. For Si we used the Stillinger-Weber three-body potential and a repulsive potential derived from ab initio calculations [3,4] and for Al we used an EAM-type potential and the ZBL universal repulsive potential [5,6].

The amorphous Si structure was created by first equilibrating liquid Si at 3000 K for 10 ps, then quenching it to 0 K at a rate of 0.05 K/fs for 300 ps [7]. The collision cascades were initiated by giving one atom in the cell a recoil energy of 400 eV, 2 keV or 10 keV. Electronic stopping powers [8,9] were included in the simulations as a non-local frictional force affecting all atoms with a kinetic energy higher than 10 eV.

To obtain the time dependence of mixing the positions of all atoms were output at 10-15 instants during an event and the squares of the atomic displacements \( r(t) - r(t = 0) \) were summed over all atoms in the simulation cell. The mixing parameter was determined using the expression

\[
Q = \frac{\langle r_{t}(t) - r_{t}(t = 0) \rangle^{2}}{6 \pi n_{0} E_{D_{n}}}
\]

where \( n_{0} \) is the atomic density and \( E_{D_{n}} \) the deposited nuclear energy. \( E_{D_{n}} \) was obtained from the difference of the initial recoil energy and the total energy lost to electronic slowing down.

The mixing results are summarized in Table I and Figures 1 - 3. Table I contains both the total mixing \( Q \), as defined in Eq. 1, and the mixing \( Q' \) which represents the contribution from atoms that have moved less than 10 Å from their initial locations. The latter quantity disregards the movement of energetic recoils. The choice of 10 Å for the cut-off was motivated by plotting the integrated relative mixing

\[
Q_{1}(r) = \frac{\int_{0}^{r} Q(r') dr'}{Q_{TOT}}
\]

as a function of the atom displacement distance for all atoms in the cell (Fig. 1). The leveling-off of the mixing between 5 Å and 10 Å makes \( Q' \) reasonably insensitive to the cut-off distance in this region. The results presented in Table I and Fig. 1 clearly show that mixing is larger in a-Si than in c-Si. The added mixing, moreover, derives almost entirely from the difference in the short range mixing parameters \( Q' \). The long range mixing, \( Q - Q' \), is the same for the crystalline and amorphous targets to within the uncertainties.
The difference in the mixing behavior can also be seen in Fig. 2, where the number of atoms that have been displaced from their initial locations a distance between $r$ and $r + dr$ is plotted as a function of $r$. The far greater number of displaced atoms in the amorphous target at small $r$ is readily apparent, whereas beyond about 10 Å only minor differences are found between a-Si and c-Si.

The result that short range mixing is substantially larger in a-Si than in c-Si might, at first glance, suggest that thermal spikes have greater influence in amorphous targets. A plot of the time dependence of mixing, however, indicates otherwise. Fig. 3 shows that at 0.3 ps most of the mixing is complete and the magnitudes of the mixing in the two structures are very similar at each of the recoil energies examined. Following this initial displacement process, however, mixing in the amorphous phase creeps upward over the next few ps, whereas in the crystalline phase it creeps downward. The difference in mixing, therefore, derives from an atomic relaxation process that follows the collisional phase of the cascade. For the crystalline matrix, many atoms displaced short distances from their lattice sites return to them during the relaxation. For the amorphous phase, memory of the original site locations is lost as the local atomic configurations are rearranged, and so excited atoms randomly fall back to sites representing local minima in the potential energy. Thus, the atomic motion during the relaxation process adds to the mixing in a-Si but deducts from it in c-Si.

Whether the mixing in the later stages of the cascade in a-Si event should be referred to as thermal spike mixing is arguable. While no extended spike was seen, it is likely that the local relaxation process is stimulated by the thermal agitation of the lattice in the vicinity of the cascade. Evaluation of the local temperature in the region of the cascade showed that it remains above the melting temperature for about 0.6 ps following the initiation of the cascade event in both structures. It is interesting to note that mixing associated with relaxation occurs while the atomic energies are a few tenths of eV, and its magnitude is about the same as that for collisional mixing. This suggests that in systems where chemical forces are involved, the movement of atoms during relaxation might be biased toward more or less mixing depending upon these interactions.

A direct comparison of the mixing data obtained here with experiments is not possible since most irradiations have been performed using ions with energies over 100 keV [1]. Nevertheless, if we assume that subcascade formation begins not far above ~ 10 keV, a rough comparison can be made. Note that since the energy dependence of the mixing parameter is relatively weak, the mixing value for 10 keV should be representative of the mixing in the experiments. The range of experimental mixing values is between 20 Å⁵/eV (W-marker) and 110 Å⁵/eV (Au marker) with the value for Ge being 80 Å⁵/eV [1]. If we assume that Ge markers most closely represent self mixing then the simulations yield a value that is roughly a factor of 2 too small. The most likely sources of this discrepancy are inadequacies in the Stillinger-Weber potential in describing Si and assuming that the quenched and irradiation induced amorphous structures are the same. The main point here, however, is that the mixing parameter calculated here for a-Si is significantly larger than it is in c-Si. Mixing is also large with respect to collisional models of mixing and to mixing in metals, which we now consider.

Since Al has nearly the same atomic number and atomic density as Si, but different bonding and cohesive properties, a comparison of mixing in Si and Al further elucidates the bonding effect on mixing. The results in Table I show that the mixing parameter is smaller in Al than in both a-Si and c-Si. Moreover, the smaller mixing derives predominantly from the long range mixing,
as the short range mixing is close to that of c-Si. This result may at first seem surprising since no difference was observed in the long range part of the mixing for a-Si and c-Si. Apparently the short range order associated with covalent bonding plays a role in the mixing beyond 10 Å. This can be understood by noting that the cross section for Si recoils with energy less than 400 eV to scatter by more than 30° in subsequent collisions is 2 Å². Since this is comparable to the atomic size of Si atoms and to unfilled spaces in the open tetrahedral structure of a- and c-Si, there is some transparency to low energy recoils. In the close packed FCC structure, the dimensions of open spaces are much smaller so the transparency is reduced.

We tested this idea by calculating ranges of low-energy self atoms recoiling from an ideal lattice position in Si and Al with the MDRANGE method [10]. The results show that both the range and straggling are larger for Si than for Al (see Table II). The larger number of long-range recoils produces a significant increase for the mean square atom displacement $<R^2>$ relevant for mixing. The results for a-Si are quite close to those of c-Si. Range calculations in artificial

![Graph showing fraction of atoms displaced](image1)

**FIG. 2.** Fraction of atoms that have been displaced a certain distance in cascade events in amorphous (a-) and crystalline (c-) Si.

![Graph showing mixing vs time](image2)

**FIG. 3.** Mixing as a function of time for individual representative cascade events in amorphous and crystalline Si.

<table>
<thead>
<tr>
<th>Element</th>
<th>$E$ (eV)</th>
<th>$R$ (Å)</th>
<th>Straggly (Å)</th>
<th>$&lt;R^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>100</td>
<td>9.0 ± 0.1</td>
<td>2.6</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>13.0 ± 0.2</td>
<td>4.9</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>21.0 ± 0.3</td>
<td>10.0</td>
<td>530</td>
</tr>
<tr>
<td>a-Si</td>
<td>100</td>
<td>9.6 ± 0.1</td>
<td>3.4</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>14.3 ± 0.2</td>
<td>5.6</td>
<td>195</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>21.3 ± 0.2</td>
<td>8.7</td>
<td>530</td>
</tr>
<tr>
<td>c-Al</td>
<td>100</td>
<td>6.8 ± 0.1</td>
<td>1.8</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>9.2 ± 0.1</td>
<td>2.7</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>14.5 ± 0.1</td>
<td>5.4</td>
<td>240</td>
</tr>
</tbody>
</table>

Table II. Range results for low-energy self-ions in crystalline Si and Al at a temperature of 77 K. The results for each case are averages over 2000 events.

$^a$ Ab initio amorphous Si structure from [11].

FCC Si (not shown) verified that this is not a consequence of the 20% difference in atomic densities.

The present work has shown two important aspects of mixing in Si that were not previously recognized. First, mixing in the amorphous structure of Si is larger than in the crystalline structure primarily due to relaxation effects following the ballistic phase of the cascade. The effect enhances mixing by a factor of two. Second, the role of the local structural order on the range of low-energy particles is revealed. Since the tetrahedral bonding of Si leaves many open spaces in the structure, low-energy particles can traverse much further than they can in close-packed structures.

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[7] We checked that this was the lowest-energy amorphous structure of the potential with annealing steps.