Heat spike effects on ion beam mixing

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Although ion beam mixing has been studied intensively over the last 20 years, many questions about the fundamental mechanisms involved during mixing remain unresolved. We review here recent simulation and experimental work which provides answers to some of the lingering questions about mixing in elemental materials. The results make clear the specific role which thermodynamic material properties, the nature of atomic bonding and electron-phonon coupling can have on ion beam mixing. Agreement obtained by direct comparison of simulated and experimental mixing coefficients gives confidence in our results, indicating that the experimental mixing values in heavy metals can be understood predominantly on the basis of atomic motion in liquid-like zones, and that the role of the electron-phonon coupling on ion beam mixing is much smaller than previously thought.

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I. INTRODUCTION

The ion beam induced relocation of atoms in a solid is called ion beam mixing. While it has been long realized that ion irradiation of materials could cause some atom relocation, the systematic study of ion beam mixing phenomena is fairly recent. The interest into the mixing accelerated in the late 1970’s driven by interest in applications such as forming metal silicides [1] and supersaturated solid solutions [2] with ion beams. Scientific activity in mixing phenomena peaked in the late-1980’s (see Fig. 1), presumably due to the initial excitement into the potential applications of the effect. Since then the level of mixing work appears to have remained at a fairly constant level of roughly 100 published articles per year, showing that there is a continuing interest into understanding mixing and utilizing it in applications.

Although ion beam mixing is now a part of several applications, there still is good reason to study it scientifically as important aspects remain poorly understood on a fundamental level. Furthermore, as we shall see later in this paper ion beam mixing can also be used as a probe of other physical phenomena occurring during ion irradiation.

Analytical theory and binary collision approximation (BCA) computer simulations [3] have been quite successful at describing ion beam mixing in “linear” cascades, i.e. under conditions when the atomic collisions induced by ion irradiation occur well separated from each other [4,5]. Generally speaking, collision cascades are expected to behave linearly when the atom inducing them is light, and the irradiated material is low in atomic number and mass density. Because of the complex nature of the interactions, it is still not possible to give a quantitative general expression setting limits for when cascades are linear.

![Number of publications in the INSPEC database for 1969 - 1998 with the words “ion”, “beam” and “mixing” anywhere in the title, abstract or keywords. Note that especially some of the early work in the 1970’s may be missing because the use of the concept “ion beam mixing” was not yet well established.](image)

In dense, heavy materials, irradiation can produce a region with numerous low-energy many-body atomic collisions, a so called heat spike. One of the first to describe this concept was Brinkman in 1954 [6], and somewhat later Seitz and Koehler made the first calculations of the atom diffusion which would occur

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in them [7]. Because of the large uncertainties in the parameters at the time, however, Seitz and Koehler concluded that heat spikes are not important.

Although it was early accepted that some sort of 'displacement spike' [8] can be present during heavy-ion irradiation, the question of the nature of a 'thermal spike' (i.e. the displacement spike after all high-energy recoils have thermalized) remained controversial for a long time. In particular, it has been unclear whether the atoms in the spike could be interpreted to have properties of a classical liquid which exists for at least a few ps, and what implications this could have. This was to a large extent because the BCA simulations, which long dominated the theoretical treatment of irradiation effects, were not able to describe regions with overlapping many-body collisions.

In the early 1970's experiments observing sputtering yields which increase nonlinearly with deposited nuclear energy [9,10] were interpreted as evidence for the presence of spikes [11]. Although many later sputtering experiments also were interpreted in terms of heat spikes [8,12,13], other results on quite similar systems were interpreted as evidence against their presence [8,14].

As computers became more efficient, molecular dynamics (MD) simulations became a practical means to fully describe the atom motion in high-energy collision cascades. The MD simulations of Dzie de la Rubia et al. in 1987 [15] demonstrated that local melting was induced by 5 keV cascades in copper, and showed that it strongly affects the mixing.

Several MD studies since then have illustrated local melting in a large variety of other metals (see e.g. [16-19]). In addition to the observations of nonlinear sputtering mentioned above, several other experimental results now also strongly support the existence of heat spikes. The craters that have long been observed at metal surfaces [20] can be described well by MD simulations which also show heat spike behaviour [21,22]. Transmission electron microscope observations of large vacancy loops at temperatures below the vacancy migration temperature provide direct evidence of the original notion of the production of a diluted zone [23], and observations of the decomposition of orthosilicates by heavy ions show that a transient liquid-like zone does indeed form inside materials [24]. Similarly, the direct observations of amorphization by low-dose irradiation of semiconductors are also a strong indication of local melting [25]. Quite recently a direct measurement of the heat spike lifetime in iron has been achieved [26]. Ion beam mixing experiments which find large differences in the mixing in ballistically similar materials [27] also support the idea that significant atom relocation can occur in heat spikes.

Clearly much has thus been learned about ion beam mixing over the years. But in many cases our understanding is either qualitative or simply incomplete. For instance, it has not been clear why mixing in semiconductors tends to be higher than in metals with almost the same mass and atomic density, and thus the same expected ballistic behaviour. Similarly, it is unclear why there are very large differences in the mixing between pairs of metals with identical crystal structures and essentially identical masses and densities.

A particularly elusive issue has been the role of electron-phonon coupling in collision cascades. During a typical collision cascade the high-energy recoils lose their energy primarily by collisions to atoms. If this were the only process involved, the cascade region would cool down only by atomic heat conduction. It has, however, also been proposed that the very hot atoms could lose some of their energy through the electron system [28], the so called "electron-phonon coupling" (EPC) effect. Estimates of the EPC effect have suggested it is particularly strong in metals like Ni, Pd, Pt and Fe [28,29]. The metals Ni, Pd and Pt are interesting in that they exhibit clearly lower mixing than Cu, Ag and Au [30], respectively, even though their ballistic behaviours should be essentially identical. Hence it has been proposed that the low mixing in the former metals is direct evidence of EPC [29]. Studies of mixing in metal alloys have also been used as evidence for EPC [29], as has differences between the damage production in e.g. Cu-Ni and Ag-Pd alloys [31,32]. But these studies can not be considered conclusive; the metals Cu, Ag and Au also have lower melting points than Ni, Pd and Pt, so a simple heat spike mechanism might be sufficient to explain the difference. The damage production studies, moreover, were done at temperatures where defects were mobile and thus could affect the damage, and often under conditions where surface effects in the cascades could have affected the damage production [33,34].

Although MD simulations of high-energy cascades have already shed much light on ion beam mixing mechanisms [15,19,35], computer capacity has in almost all cases limited them from being performed at energies that would allow a direct comparison with experiment. Most mixing experiments have been performed with high-energy beams which produce recoils up and above the subcascade breakdown threshold, which is 10 – 100 keV in typical metals. Only very recently, when massively parallel supercomputers have become available, has it become possible to fully simulate collision cascades produced at these energies.

In this paper we present some recent MD simulation and experimental work shedding light on the open questions discussed above. In section III we provide an explanation for the difference between mixing in semiconductors and metals, and in the following one we discuss mixing mechanisms in common fcc metals. In section V we present a method by which MD simulations of mixing can be used for direct comparison with experiments, and we use the method to simulate mixing
experiments in Ni, Pd, Pt and Si. Finally, we discuss the implications of our results for EPC models.

II. CALCULATION PRINCIPLES

We used classical molecular dynamics methods to simulate full collision cascades. The atoms were arranged in cubic simulation cells, which contained between 20 - 40 atoms for every electron volt of kinetic energy assigned to the initial recoil. Periodic boundary conditions were applied on the cell, and the temperature of the atoms in the outermost atom layers was softly scaled towards 0 K to provide temperature control and ensure that the pressure waves emanating from cascades were damped at the borders.

The forces acting between the atoms were described with different modern many-body interatomic force models. To realistically treat strong collisions the Ziegler-Biersack-Littmark universal repulsive potential [36] or potentials derived from ab initio calculations [37] were smoothly joined to the many-body potential at short interaction distances [38]. The effect of the choice of interatomic potential on the results is discussed in section IV and more extensively in Ref. [39].

We also used range calculations of low-energy self atoms recoiling from an ideal lattice position with the MDRANGE method [40]. The recoil was initially placed on an ideal lattice site (or the site of an existing atom in amorphous material), and given a recoil velocity randomly selected to cover all crystal directions. To obtain a representative picture of ranges from non-equivalent lattice sites in amorphous materials, the range results were calculated as the average over recoils starting from several initial sites. The chord (vector) range [41] was used to quantify the displacement of the initial ion.

Additional details about the simulations are given in the works reviewed here, Refs. [39,42-45].

The simulated mixing parameter $Q$ was determined from the initial $r_i(t = 0)$ and final $r_i(t)$ atom positions using the expression

$$ Q = \frac{\sum_i [r_i(t) - r_i(t = 0)]^2}{6n_0E_{D_a}} $$

where $n_0$ is the atomic density and $E_{D_a}$ the deposited nuclear energy. $E_{D_a}$ was obtained from the difference of the initial recoil energy and the total energy lost to electronic stopping. Following the usual convention within the field, $Q$ is given in units of $\text{Å}^3/\text{eV}$.

The experimentally measured mixing efficiency is usually defined as

$$ Q_{\text{exp}} = \frac{D_t}{\Phi F_{D_a}} $$

where $D$ is an effective diffusion coefficient for mixing, $t$ is the implantation time, $\Phi$ the ion fluence and $F_{D_a}$ the deposited nuclear energy per ion per unit depth [30]. The equivalence between $Q_{\text{exp}}$ and the simulated mixing $Q$ given in Eq. 1 follows from the atomistic definition of the diffusion coefficient [15,46]. The two quantities correspond exactly to each other if the irradiating beam is producing the mixing.

III. DIFFERENCES IN MIXING IN SEMICONDUCTORS AND METALS

A somewhat surprising mixing 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 [27]. 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 [27,47], 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 [47]. 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. Moreover, a-Si is elastically softer than crystalline Si (c-Si), also indicating that thermal spikes may play a larger role in the mixing.

To probe these questions, we studied the difference between mixing in Si and Al on one hand, Ge and Cu on the other hand [42,43]. Since these pairs of materials have almost the same atomic masses, their collisional behaviour is almost the same. Moreover, Si and Al also have similar atomic densities, and Ge and Cu almost identical melting temperatures. The difference between Si and Al is particularly puzzling in that their ballistic behaviour should be almost identical, yet the experimental mixing values differ by roughly a factor of 5 [27]. Since both are low-mass elements, and Al has a much lower melting temperature than Si, it is not likely that the difference could be a heat spike effect either.

Our mixing results for Al, Si, Cu and Ge are summarized in table I. The results in the table show that mixing in amorphous materials is consistently higher than in the crystalline phase of the same material, and that the mixing in semiconductors indeed is larger than in the corresponding metals. Analysis of the atom displacements showed that the reason to the larger mixing in the amorphous state is a large increase in the amount of mixing deriving from atoms moving just a short distance, ~ 5 Å (cf. Fig. 2) [42]. This result
is easily understood, as in the crystalline state a recoil has to overcome the threshold displacement energy in order to produce any permanent atom relocation, which is not the case in amorphous materials. The slower heat conduction in amorphous materials can also increase the short-range mixing.

TABLE I. Average total (Q) and short-range (Q') mixing in cascades in Si, Al, Ge and Cu (Q' is defined as the total mixing from recoils moving less than 10 Å) [43]. E is the energy of the self-recoil producing the mixing and \( E_{D_{\text{r}}} \) the nuclear deposited energy of each cascade.

<table>
<thead>
<tr>
<th>El</th>
<th>Cascade ( E ) (keV)</th>
<th>( E_{D_{\text{r}}} ) (keV)</th>
<th>( Q ) (Å²/eV)</th>
<th>( Q' ) (Å²/eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>10.0</td>
<td>7.5</td>
<td>15 ± 3</td>
<td>3.5 ± 0.5</td>
</tr>
<tr>
<td>a-Si</td>
<td>10.0</td>
<td>7.5</td>
<td>30 ± 1</td>
<td>17 ± 1</td>
</tr>
<tr>
<td>c-Al</td>
<td>10.0</td>
<td>7.9</td>
<td>9 ± 1</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>a-Al</td>
<td>10.0</td>
<td>7.4</td>
<td>41 ± 5</td>
<td>28 ± 4</td>
</tr>
<tr>
<td>c-Ge</td>
<td>10.0</td>
<td>7.6</td>
<td>30 ± 3</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>a-Ge</td>
<td>10.0</td>
<td>7.6</td>
<td>70 ± 5</td>
<td>57 ± 5</td>
</tr>
<tr>
<td>c-Cu</td>
<td>10.0</td>
<td>7.9</td>
<td>13 ± 1</td>
<td>12 ± 1</td>
</tr>
</tbody>
</table>

These results show that the nature of the atomic bonding affects the mixing significantly: the tetrahedral bonding of silicon causes most silicon atoms to have only four nearest neighbours, making it easy for a low-energy recoil to travel beyond its nearest neighbours. Metallic bonding, on the other hand, tends to lead to close-packed crystal structures with 12 nearest neighbours, making a collision with one of them likely. This conclusion is also consistent with our later finding that while interstitials in Si and Al tend to have equal separations with the closest vacancy, those in Al are produced mostly by replacement collisions sequences, while those in Si are produced by long-range recoils [39]. Since mixing is proportional to the square of the atom displacement, the long-range recoils contribute much more to mixing than a replacement collision sequence.

IV. MECHANISMS OF MIXING IN COMMON FCC METALS

In the previous section, we have seen that the crystal structure can have a significant effect on mixing. This, however, can not explain the large differences between pairs of fcc metals like for instance Cu and Ni.

To study how the heat spike affects mixing in fcc metals, we systematically simulated 10 keV cascades in several common fcc metals. The mixing in the heat spike is illustrated in Fig. 3, which shows the formation of a diluted zone at the center of the cascade during the heat spike, and the subsequent recrystallization of the lattice. The final figure shows the atoms that are not at their original positions with open circles, showing that essentially all the atoms in the liquid zone of the cascade relocate during the heat spike.
FIG. 3. Cross sections of the evolution of a 10 keV cascade in Au. The sections show a slice with a size of 30x30x1/4 a₀ in the center of the cell. During the first 3 ps a large, almost void atom region is formed in the center of the cell, but it collapses back and (in this particular z slice shown) regenerates into perfect crystal. In the final 30 ps figure the atoms that are not at their original positions are indicated with hollow circles.
Results for the mixing in 10 keV metal cascades is given in table III (the values are from [39]; Ref. [49] gave slightly different values for some of the events since they had less statistics). The Cu and Pt results in the table are given for two different interatomic potentials. The two Cu potentials [50,51] both have almost exactly the same melting point, which is also quite close to the experimental one. The two Pt interatomic potentials, on the other hand, are both based on the Foiles interatomic potential, but one of them has been modified to reproduce almost exactly the experimental melting point. The original potential has a melting point of about 1500 K, and the modified one of 2100 K. Even though the melting points thus differ only by about a factor of 1.4, the mixing values differ by about a factor of 3.5. This result is in good agreement with the analytical model in Ref. [52], where the melting point difference of ~1.5 between Ag and Pd is also found to lead to a large difference in mixing. This results shows that in MD simulations of mixing it is crucial to use an interatomic potential which reproduces the experimental melting point well.

Another interesting feature in the mixing results is the large difference of a factor of ~3 between mixing in Ni and Cu, a factor of ~10 between mixing in Pt and Au. These ratios between the mixing values compare quite well with the experimental ones. This result is especially interesting because we did not include any model for electron-phonon coupling in our simulations, so the results suggest EPC may not be needed to explain the low mixing in Ni and Pt.

A difference in the lattice thermal conductivity between two materials might also affect the mixing. To determine whether his could affect our results, we determined the lattice thermal conductivity of our Cu and Ni models. We heated up a periodic elongated cell in the center of the elongated dimension, and cooled it down at the edges at the same time. The thermal conductivity was then determined directly from the temperature gradient in the cell after equilibrium had been reached [53]. We obtained lattice thermal conductivities of 3.2 ± 0.2 for Cu and 3.4 ± 0.4 for Ni when the maximum temperature of the cell was about equal to the melting point of the force model. Although the lattice thermal conductivity of metals is difficult to measure directly, these values compare well with rough analytical estimates of the lattice conductivity [53]. Since the conductivities of Cu and Ni in our model are practically equal just below the melting temperature, we conclude that a difference in lattice thermal conductivity cannot explain the large difference in mixing observed in our simulations.

<table>
<thead>
<tr>
<th>Material</th>
<th>$Q_{\text{sim.}}$</th>
<th>$Q_{\text{exp.}}$</th>
<th>Marker element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>4.3</td>
<td>5 - 8</td>
<td>Pt, Au [30]</td>
</tr>
<tr>
<td>Cu</td>
<td>15</td>
<td>23 - 27</td>
<td>Cu [27]; Pt, Au [30]</td>
</tr>
<tr>
<td>Cu</td>
<td>16</td>
<td>23 - 27</td>
<td>Cu [27]; Pt, Au [30]</td>
</tr>
<tr>
<td>Pt</td>
<td>22</td>
<td>14, 24</td>
<td>Fe, Ni [30]</td>
</tr>
<tr>
<td>Pt</td>
<td>6.1</td>
<td>14, 24</td>
<td>Fe, Ni [30]</td>
</tr>
<tr>
<td>Au</td>
<td>60</td>
<td>60, 160</td>
<td>Ni, Cu [30]</td>
</tr>
</tbody>
</table>

a Foiles’ interatomic potential [50]  
\[b\] Sabochick-Lam interatomic potential [51]  
\[c\] Modified interatomic potential with correct melting point

V. DIRECT COMPARISON BETWEEN MD SIMULATIONS AND MIXING EXPERIMENTS

A. Metals

Inspired by the results on mixing in Ni and Pt described in the previous section, we developed a method enabling direct comparison between experimental and simulated mixing coefficients [44].

The method has two steps. Molecular dynamics range calculations [40] are first employed to follow the motion of the implanted ion and obtain the number of primary recoils per incident ion as a function of energy, i.e. the primary recoil spectrum $n(E)$.

Full molecular dynamics simulations are then used to obtain the average atom relocation $R^2_{\text{sim}}(E)$ caused by the primary recoils of different energies. To enable interpolation between the $R^2_{\text{sim}}$ data points, a function $R^2(E)$ is fitted to the simulated data [54]. The function was constructed as follows. At low energies ($\leq 10$ keV) the mixing was of a pure heat spike character, and excellent fits to the simulated data were obtained using a simple power law with an exponent of exactly 1.5, i.e. $R^2(E) = aE^{3/2}$, where $a$ is a fitted constant. At high energies, where cascades are completely broken down into subcascades, it is well known both experimentally and theoretically that the total atom relocation increases linearly with the nuclear damage energy $E_{D_\text{Me}}$ [27]. We used the function

$$R^2(E) = aE^{3/2} + bE^{1/2}$$

which has both the desired low-energy and high-energy...
energy dependence, and only two fitting parameters \( a \) and \( b \) [55].

To obtain a reliable fit for the values with this process, it is necessary to simulate recoils with energies around and above the subcascade threshold energy. In practice this meant simulations of up to 100 keV Ni and Pd recoils, and up to 200 keV Pt recoils. We used simulation cells with up to 4 million atoms, and simulated at least 3 events at each energy in each material.

When subcascade overlap by the mixing beam is negligible, integration of the primary recoil spectrum of the incident ion \( n(E) \), weighted by the primary recoils \( R^2(E) \),

\[
Q_{\text{sim}} = \int_0^{E_0} R^2(E)n(E)\,dE \quad \frac{6\eta E_{D_n}}{\eta_0 E_{D_n}}
\]

yields a mixing efficiency which directly corresponds to the experimental one. Here \( E_0 \) is the initial implantation energy, \( \eta_0 \) the atomic density and \( E_{D_n} \) the deposited nuclear energy of the implanting beam. This simulated mixing can be shown to be equivalent to the experimental one [15,43]. Since the marker layer is broadened during the irradiation, the mixing was calculated in a depth region 200 \( \AA \) above and below the initial location of the marker layer used in the experiments. The exact width of this region did not have a significant effect on the final results.

The calculation process is illustrated in Fig. 4 for Ni, and the results are given in Table IV. The excellent agreement with experiments indicates that the predominant source of mixing in fcc metals is ballistic and heat spike mixing, and that electron-phonon coupling is at most a minor correction on the mixing.

Thus it appears that even in the three fcc metals where EPC has believed to be the strongest, it in fact may not be important at all. We have not simulated mixing in Fe, where EPC also often has been believed to be quite strong. But it is interesting to note that the recent experiments of Studbury and Bezakova give a lifetime of roughly 6 ps for the heat spike in iron, which would seem to rule out strong EPC also in this metal. Thus at least within current experimental and simulation uncertainties it would seem like electron-phonon coupling is not a significant effect.

![Simulated \( R^2 \) values (circles), fit of the function \( R^2(E) \) to the simulated data, and mixing \( Q'(E) \) (dashed line) for the mixing produced by a 600 keV Kr ion in Ni. The total mixing \( Q_{\text{sim}} = Q'(600\text{eV}) \). An excellent fit to the simulated data is obtained over about three orders of magnitude in both energy and mixing.](image)

**FIG. 4.** Simulated \( R^2 \) values (circles), fit of the function \( R^2(E) \) to the simulated data, and mixing \( Q'(E) \) (dashed line) for the mixing produced by a 600 keV Kr ion in Ni. The total mixing \( Q_{\text{sim}} = Q'(600\text{eV}) \). An excellent fit to the simulated data is obtained over about three orders of magnitude in both energy and mixing.

**TABLE IV.** Simulated (sim.) and measured (exp.) values for the mixing efficiency \( Q \). The simulations take into account the mixing beam and the location of the marker layer in the experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Beam</th>
<th>( Q_{\text{sim}} ) (( \text{Å}^2/\text{eV} ))</th>
<th>( Q_{\text{exp}} ) (( \text{Å}^2/\text{eV} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>600 keV Kr</td>
<td>( 5.1 \pm 0.4 )</td>
<td>( 4.8 \pm 0.3 )</td>
</tr>
<tr>
<td>Ni</td>
<td>650 keV Kr</td>
<td>( 5.2 \pm 0.4 )</td>
<td>( 5.0 \pm 0.7 )</td>
</tr>
<tr>
<td>Pd</td>
<td>600 keV Kr</td>
<td>( 9.8 \pm 0.8 )</td>
<td>( 8.4 \pm 0.8 )</td>
</tr>
<tr>
<td>Pd</td>
<td>400 keV Kr</td>
<td>( 9.5 \pm 0.8 )</td>
<td>( 9.1 \pm 1 )</td>
</tr>
<tr>
<td>Pt</td>
<td>1 MeV Kr</td>
<td>( 14 \pm 1 )</td>
<td>( 14 \pm 2 )</td>
</tr>
</tbody>
</table>

\( ^a \) Ref. [44]  
\( ^b \) Ref. [30]  
\( ^c \) Ref. [56]

**B. Silicon**

To further study the relative role of heat spike and ballistic mixing in Si, we repeated the direct comparison with mixing experiments [45]. The approach was basically the same as for the metals, but because of the larger ranges of recoils in the Si lattice the \( R_{\text{sim}}^2(E) \) points were obtained with a two-step process.

The atom relocation by intrinsic recoils in Si up to a recoil energy of 5 keV were calculated by full MD calculations. By fitting an appropriate function,

\[
R^2(E) = aE^b + bE^c,
\]

to the data points we got the atom relocation as a function of energy. At energies higher than 5
keV we used a cumulative method, in which the atom relocation values at high energies were calculated by using the range program and atom relocation values at lower energies. The range calculations were used to get the mixing contribution \( <R^2>_{\text{prim}} \) from primary recoil relocation. The secondary recoil spectrum caused by the primary recoil was obtained from same simulations. The integration of \( R^2(E) \) weighted with the secondary recoil spectrum gave us the atom relocation \( <R^2>_{\text{sec}} \) caused by secondary recoils and the heat spike. The total atom relocation \( <R^2>_{\text{tot}} \) is then a sum of secondary atom relocation and the primary recoil relocation. The total mixing \( Q_{\text{sim}} \) is then obtained using a fit to \( <R^2>_{\text{tot}} \) and Equation (4).

The cumulative method has the disadvantage of increasing the uncertainty in the final result, as small errors at the low energies grow during the cumulative steps increasing the energy. On the other hand many mixing experiments in Si have been performed with relatively low-energy beams, reducing the significance of the problem.

The results are summarized in Table V. Except for the Ne results, all values agree within the error bars. Considering that both the experimental and simulated uncertainties are quite large, the overall agreement can be viewed as quite satisfactory.

TABLE V. Simulated and experimental mixing values in Si.

<table>
<thead>
<tr>
<th>Ion (energy)</th>
<th>( Q_{\text{sim}} ) (A³/eV)</th>
<th>( Q_{\text{exp}} ) (A³/eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne (50 keV)</td>
<td>22 ± 3</td>
<td>40 ± 13</td>
</tr>
<tr>
<td>Ar (110 keV)</td>
<td>33 ± 5</td>
<td>25 ± 9</td>
</tr>
<tr>
<td>Ar (110 keV)</td>
<td>36 ± 5</td>
<td>58 ± 32</td>
</tr>
<tr>
<td>Kr (220 keV)</td>
<td>45 ± 7</td>
<td>34 ± 6</td>
</tr>
<tr>
<td>Xe (300 keV)</td>
<td>52 ± 8</td>
<td>44 ± 7</td>
</tr>
</tbody>
</table>

\( ^a \) Ref. [57]
\( ^b \) Ref. [58]

C. Role of high-energy recoils

We also used the cumulative simulations to determine the relative role of high-energy recoils in the total experimental mixing. Knowing how much they contribute to the total mixing is important because the distribution of recoiled atoms with displacement distance actually falls off as \( 1/r^2 \) [59,43]. Hence the shape of the broadened marker layer will not necessarily have an ideally Gaussian shape [59]. But most experimental mixing values have been obtained from fits to Gaussian distributions, complicating their interpretation.

BCA simulation analysis of mixing experiments in Si has already given evidence that the mixing in Si is dominated by the collisional process [5]. Since these simulations did not, however, include the heat spike phase of the cascade, a re-analysis of the problem by MD methods is justified.

The relative role of the primary recoils to the total atom relocation is shown in Figs. 5 and 6 for a 220 keV Ar beam mixing Si and a 650 keV Kr beam mixing Ni. The squares show the atom relocation caused by primary recoils, and the circles the total atom relocation.

![Fig. 5. Atom relocation \( <R^2> \) and integral mixing \( Q \) as a function of the energy of primary recoils for a 110 keV Ar beam in Si. The squares show the atom relocation by primary recoils and the circles the total atom relocation. The lines are fits to guide the eye.](image1)

![Fig. 6. Atom relocation \( <R^2> \) and integral mixing \( Q \) as a function of the energy of primary recoils for a 650 keV Kr beam in Ni. The squares show the atom relocation by primary recoils and the circles the total atom relocation. The lines are fits to guide the eye.](image2)

The figures show that in Si the primary recoils dominate the mixing, being larger than the mixing by all lower-energy recoils at all energies. Since both MD and BCA simulation analysis of different experiments [5] show that high-energy recoils dominate the mixing in Si, we can with certainty conclude that heat spike mixing in Si is of little importance under usual circumstances.
In Ni, on the other hand, the primary recoils are just a small fraction of the total mixing. This result agrees well with the discussion of mixing in 10 keV cascades in section III, where we also found that recoils traveling far in the lattice dominate the mixing in the diamond, but not the fcc structure.

The Ni figure shows that at the very highest energies, the mixing caused by primary recoils actually exceeds the extrapolated mixing values, indicating that the extrapolation loses some of the mixing contribution of primary recoils. This is because the metal interpolation term (3) does not contain a term accounting for the increase in \( \langle R^2 \rangle_{\text{prim}} \). But since most of the mixing in any case derives from lower energy recoils in the metals, this is not a significant problem for the Ni mixing calculation.

Furthermore, as noted above the role of long-range recoils on the experimental mixing is quite unclear. A worst-case estimate, assuming all of the \( \langle R^2 \rangle_{\text{prim}} \) contribution would be lost in the calculation of \( Q_{\text{prim}} \) (which is highly unlikely since the primary recoils are part of the MD simulations), showed that even this would increase the Ni mixing value only by \( \sim 30 \% \).

In silicon, our cumulative process should account for the \( \langle R^2 \rangle_{\text{prim}} \) contribution correctly. But the fact that the dominant contribution to mixing comes from the primary recoils, whose distribution with displacement distance actually falls off as \( 1/r^2 \), indicates that the fitting Gaussian profiles into marker layer broadening profiles could be an especially serious problem in silicon.

VI. CONCLUSIONS

In this Article, we have reviewed the current level of understanding of the fundamental mechanisms of ion beam mixing. We have demonstrated that using MD simulations it is possible to understand the role that crystal structure, atomic bonding and heat spikes have on mixing. The nature of the tetrahedral atom bonding has been demonstrated to increase the mixing in semiconductors compared to metals. Furthermore, using simulation models with realistic melting points we were able to reproduce experimental mixing values in several fcc metals accurately, demonstrating that the mixing caused by motion of atoms in the heat spikes is the dominating reason for ion beam mixing in dense fcc metals. This also shows that within present experimental and simulation uncertainties, electron-phonon coupling appears to have a negligible effect on cascade development.

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[55] Both MDRANGE and full MD simulations showed that $E_{D_1}$ depends linearly on $E$ in the presently used energy range, whence we can use $E$ rather than $E_{D_1}$ in the function.