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INFLUENCES OF THERMAL SPIKES IN ION BEAM MIXING*

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ABSTRACT

Guided by the results of molecular dynamics simulations, we develop a thermal spike model for the relaxation of collision cascades in which the hot zone has mobile, reacting defects and cools by thermal diffusion. Marker atoms within such spikes are taken to migrate by radiation enhanced diffusion which is governed by the locally transient temperatures and defect concentrations. The atomic mixing associated with such motions is examined, on the basis of the model, for a variety of ion-target systems. The dependences of spike mixing on diffusion mechanism, irradiation ion and energy, and sample temperature are discussed.

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I. INTRODUCTION

The results of several recent experiments suggest that the mixing of two solid phases during heavy ion irradiation can be influenced by sample temperature and/or chemical effects [1]. Such phenomena would seem to require many-body, collective processes and, therefore, would not be expected to be adequately described by two-body, collisional models. Since most of the theoretical discussion of ion beam mixing to date has been based on some form of a linearized collisional transport approximation [2], an investigation of the relative importance of collective effects appears to be warranted.

Molecular dynamics simulations of energetic collision events hold the promise of providing the most comprehensive picture of what actually occurs in ion beam mixing. Unfortunately, no simulations for either high energy cascades or binary systems are yet available. Nonetheless, simulations for single component targets [3] can guide our understanding. They show the following qualitative features: (1) shortly ($\sim 10^{-13}$ s) after a primary knock-on (PKO) atom is set into motion, a cascade of target atom-target atom collisions is spawned, creating point defects and redistributing the PKO's initial kinetic energy over an extended volume; (2) the very high density of defects after this first phase results in an unstable configuration of atoms (many interstitials lie within the spontaneous recombination volumes of nearby vacancies); at the same time, the average kinetic energy per atom in the cascade greatly exceeds the average potential energy; (3) a second, rapid phase ($\sim 10^{-12}$ s) follows during which the majority of initial defects are removed by spontaneous recombination; the number of point defects left after this occurs is about what would be predicted by Kinchin and Pease calculations; by the end of this phase the average

kinetic and potential energies per atom are roughly equal, though, for the initiating energies studied ($\sim 10^2 - 10^3$ eV), both are considerably greater than typical thermal average values; (4) in a concluding phase, the excess energy remaining in the cascade region relaxes into the surrounding crystal; point defects migrate diffusively and some further recombination occurs; during this period, the vacancy is observed to migrate more rapidly than would be expected from normal, thermally-activated vacancy motions, though nothing particularly unusual is observed about the interstitial atom; (5) essentially no new defects are generated after the first phase and, despite the fact that the instantaneous defect concentration may reach a few atomic percent, the crystal structure within the cascade remains more-or-less intact; the entire event takes place in less than 10^{-11} s.

The atomic motion in the first phase described above is dominated by binary collisions, and that of the second phase by the spontaneous rearrangements. It is not clear whether linearized transport analysis can satisfactorily assess all of the atomic mixing which occurs in these two athermal phases, but we will tentatively assume here that it can. We will refer below to the mixing involved in the first two phases as "ballistic." The third phase obviously involves collective behavior. The approximate local equipartition of energy, during this phase, encourages one to refer to it as a "thermal spike." The thermal spike picture which emerges from the molecular dynamics is one in which the local hot spot in the target remains crystalline, but contains many mobile, annihilating defects. The transport of tagged atoms in the spike presumably is a kind of radiation enhanced diffusion, only at transiently high temperature and defect concentrations.

We exploit this view here in presenting an analytical model, the purpose of which is to try to understand the nature of the contribution of "spikes" to ion beam mixing. As is the case with all thermal spike models, exact values of transport coefficients relevant to the extreme conditions found in spikes are unknown. Nevertheless, useful qualitative information can be obtained by making reasonable guesses. In the next section, we sketch the central features of our model and in the following section discuss some of its quantitative consequences.

II. THE MODEL

The treatment here is limited to the ion beam spreading of a narrow marker layer embedded in a solid host. The restriction to marker configurations permits us to ignore chemical effects (due, for example, to heats of mixing or new phase formation) to a first approximation. A mathematically detailed and more general discussion (one applicable to thick layer geometries) will be given elsewhere.

We start by assuming that linear transport calculations can reasonably describe the initial conditions of a thermal spike. In particular, we use the tabulations of Winterbon [4] to determine the initial geometries and energy densities of our spikes; we employ modified Kinchin and Pease relations [5] to define initial defect numbers.

Our model requires the specification of three instantaneous spatial distributions — for vacancies, interstitials, and temperature. Mathematical tractability is obtained by imposing the condition that the distributions be replaced by uniform spherical distributions of finite extent.

We define the initial vacancy distribution as a uniform sphere with radius obtained from the mean straggling and transverse straggling parameters given by Winterbon [6]. The initial interstitial distribution is taken to be concentric with the vacancy distribution but to extend beyond it (since interstitials are observed, in the simulations, to be somewhat preferentially ejected from the cascade core) by a distance R_p chosen so that a low energy isolated Frenkel pair will have the same mean displacement as that produced by electron irradiation. The initial excess temperature distribution is taken to coincide with the interstitial distribution.

The three distributions are allowed to evolve according to phenomenological kinetic equations, that is, diffusion (in the case of temperature) and diffusion-reaction (defect concentrations) equations. The distributions are maintained as uniform, finite spheres — though with internally changing values and moving fronts — by applying a Koehler-Seitz "trick" [7] to each. Outside of the evolving zones, temperature and defect concentrations are held at fixed ambient values.

Within a spike, a marker atom is assumed to diffuse with a radiation enhanced diffusion coefficient which is proportional to defect concentrations and dependent on spike temperature in an Arrhenius-like manner. If we restrict our attention to experiments in which the energy deposited in the target in elastic collisions is essentially constant over the region of the marker, then (coupled with the approximation of spike uniformity) the marker diffusivity will be spatially independent. It will, however, be a highly nonlinear function of time. The problem of determining the spreading of an initially sharp marker layer can be approximately treated by integrating the marker atom diffusion equation

from one spike to the next, and then summing the result over all spikes which include the atom of interest.

Since the spike temperature enters the calculation nonlinearly, it is important to try to estimate the deposited energy density corresponding to a single damage track rather than that predicted by Winterbon's multitrack average. We do this by performing the calculation outlined above for a spike generated by a single collision event in which the PKO recoils with arbitrary energy P. We then average these results over the primary recoil spectrum [8] of the ion-target system of interest. The experimentally relevant quantity this theory predicts can be expressed as

$$\langle \Delta x^2 \rangle_s = 2\phi \int_{P=0}^{\gamma E} dP \frac{d\sigma}{dP} \int_{t=0}^{t_R} n_0 v_d(t) D(t) dt \quad (1)$$

The following notations are used in (1): $\langle \Delta x^2 \rangle_s$ is the variance associated with the spread marker distribution at the end of the experiment due to spike effects only; ϕ is the total ion dose (ions/area); $d\sigma/dP$ is the differential cross section for a given ion (of energy E at the marker region) to produce a PKO recoil with energy P; γ is the usual kinematic factor; n_0 is the target number density; $v_d(t)$ is the instantaneous damage volume within the spike; $D(t)$ is the instantaneous marker atom diffusivity; and t_R is the mean time interval for two successive cascades to intersect a common volume of the target.

III. NUMERICAL RESULTS

All of the calculations presented below are for metallic hosts. In metals, the energy deposited in nuclear motions by a recoiling PKO is not immediately shared with the conduction electrons. It is estimated that the conduction electron "gas" remains effectively decoupled from the

very short wavelength phonons in the spike for times on the order of 10^{-11} s [9]. After this coupling becomes effective, the thermal diffusivity of the hot zone rises sharply and rapid quenching ensues. Any residual marker atom motions are then activated by the ambient sample temperature and are likely to be considerably limited by intercascade trapping mechanisms at temperatures below 300 K and at the high dose levels of most mixing experiments. Consequently, all of the results cited below were produced from (1) by cutting off the time integration at 10^{-11} s. The thermal diffusivity involved in the thermal relaxation calculations was, in each case, taken to be a constant value, 3×10^{-3} cm²/s (a typical value for the lattice contribution to thermal diffusion).

A. Mechanism

To investigate the relative importance of interstitial versus vacancy associated marker atom motion we assumed $D(t)$, in (1), could be written as $D_0 c(t) \exp [-E_m/k_B T(t)]$ — where D_0 is a spike-independent constant, $c(t)$ an instantaneous defect concentration, and E_m a marker atom migration enthalpy—and calculated $\langle \Delta x^2 \rangle_s$ for typical interstitial and vacancy values of E_m . An illustrative result is given in Table I for Cu as host. The relevant quantity is $\langle \Delta x^2 \rangle_s / 2\phi F_D D_0$, where F_D is the damage energy deposited per ion per unit track length. (Dividing by ϕF_D gives a measure of the effectiveness of a given ion in promoting mixing; dividing by D_0 helps determine the effectiveness of the spike characteristics.) We see that for $E_m = 0.12$ eV (interstitial type motion), the calculated mixing efficiency is 40-50 times larger than for $E_m = 0.71$ eV (normal vacancy

motion). Thus, unless D_0 is much greater for the vacancy mechanism than for interstitial related mechanisms, normal vacancies will not contribute very much to marker spreading during spike cooling.

B. Ion Species

When scaled as in the previous paragraph, spike mixing efficiencies for all ions studied here are remarkably similar. In most instances, He is somewhat less efficient than heavier ions, though for Au as target He is predicted to actually be more efficient at 300 K. (See Table I.)

C. Sample Temperature

For our model, spike temperature, defect concentration, and thermal relaxation time all contribute to marker atom motion. We show in Figure 1 the recoil energy dependence of maximum spike temperatures and thermal decay times for targets of Al and Au (at 0 K); initial defect concentrations are directly proportional to maximum temperature in our model. In Figures 2 and 3 we show, for the same targets, how these parameters influence the time integral in Equation (1) (μ is the time integral divided by D_0). The relatively cool spikes depicted in Figure 1 for Al result in a strong sample temperature dependence at all recoil energies, while, for Au, only the low energy recoil spikes are much affected by sample temperature. To obtain $\langle \Delta x^2 \rangle_s$ from μ it is necessary to average over primary recoil spectrum (that is, do the energy integration in (1)). Since all primary recoil spectra tend to be heavily weighted to the low energy end (see Figure 4 for some examples), $\langle \Delta x^2 \rangle_s$ can be expected to be mildly temperature dependent for Au and strongly for Al. This is seen in Table I. (The interesting reversal of efficiency for He on Au at 300 K is obviously due to the extreme low energy skewing of its primary recoil spectrum.)

It should be noted that no strong temperature dependence has been reported for mixing in Al [1]. This result may raise questions about the importance of the contribution of spike mixing in that material.

D. Ion Energy

Increasing an ion's energy causes its primary recoil spectrum to be increased slightly at both high and low energy recoils and, consequently, decreased slightly over midrange (see Figure 4, curves 2 and 3). Since the extremes of the recoil spectrum tend to produce relatively less mixing than the middle, increasing ion energy may well decrease $\langle \Delta x^2 \rangle_s$. Such is the case for the Cu example in Table I — where not only does $\langle \Delta x^2 \rangle_s$ decrease but so also does $\langle \Delta x^2 \rangle_s / F_D$. Again, the effect is small because the primary recoil spectrum for a given ion-target system doesn't vary much with energy. A recent spike-like model of mixing by Sigmund [10], which does not average over primary recoils, predicts an increase in mixing with increasing ion energy, contrary to some experimental evidence [1].

E. Absolute Values

Lastly, we address the question, What fraction of ion beam mixing might realistically be attributed to thermal spikes? The answer to this question requires us to supply absolute values for D_0 for each marker-target system considered. Unfortunately, we have little guidance in this regard. Tables of trace impurity, thermal diffusion, give, in the vast majority of instances, diffusivities associated with normal vacancy mechanism transport. As we commented in A above, it is very likely that the normal vacancy mechanism contributes little to marker motion in thermal spikes. Let us suppose, for the sake of argument, that normal vacancy mechanism diffusivity preexponentials are representative of those for thermal spike transport. Typical values of D_0 (when

vacancy entropy of formation factors are divided out of the thermal data) are:

for Al, $\sim 5 \times 10^{14} \text{ A}^2\text{s}^{-1}$, for Cu, $\sim 3 - 10 \times 10^{14} \text{ A}^2\text{s}^{-1}$, and for Au, $\sim 2 \times 10^{14} \text{ A}^2\text{s}^{-1}$. In other words, in each case we find values of $\langle \Delta x^2 \rangle_s / 2\phi F_D$ on the order of a few $\times 10 \text{ A}^5/\text{eV}$

(Table I) — very much like what is reported in most metal host-marker experiments [1]. Finally, some values of D_0 for self-interstitial atoms have been deduced from radiation damage experiments [11]. These, too, tend to be in the range

$5 \times 10^{13} \text{ A}^2\text{s}^{-1} - 5 \times 10^{14} \text{ A}^2\text{s}^{-1}$ (with large uncertainties).

Whatever the precise values of D_0 might be, these results suggest that thermal spike effects in ion beam mixing are plausibly at least as important as ballistic effects.

IV. CONCLUSIONS

The model for thermal spike mixing presented here predicts little variation in mixing efficiency from ion-to-ion for a given target, or from target-to-target for metal hosts. Moreover, the mixing efficiency, in this model, scales more-or-less with damage energy. The model does show, however, that the mixing is very sensitive to the defect migration enthalpy. In particular, it predicts that normal vacancies contribute little to the mixing during spike cooling.

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Figure Captions

1. Maximum spike temperature and thermal relaxation times for individual recoil cascades are plotted versus PKO recoil energy.
2. Mixing integrand, μ , for a marker atom in a given recoil cascade versus PKO recoil energy for aluminum as target.
3. Same as Figure 2 except for gold as target.
4. Primary recoil spectra of He and Kr ions on thin copper foils. The areas under the curves shown are normalized to unity.

$$\langle \Delta x^2 \rangle_s / 2 \phi F_D D_0$$

$$\langle \Delta x^2 \rangle_s / 2 \phi F_D D_0$$

Host	Ion	($10^{13} \text{A}^3 \text{s/eV}$)
Al	He	0.32
Migr. En. = 0.12 eV	Ne	0.35
Temp = 0 K	Ar	0.35
Ion En. = 400 keV	Kr	0.32
	Xe	0.32
Al	He	0.72
Migr. En. = 0.12 eV	Ne	0.75
Temp = 300 K	Ar	0.75
Ion En. = 400 keV	Kr	0.73
	Xe	0.73
Cu	He	0.88
Migr. En. = 0.12 eV	Ne	1.08
Temp = 0 K	Ar	1.10
Ion En. = 400 keV	Kr	1.09
	Xe	1.09
Cu	He	1.24
Migr. En. = 0.12 eV	Ne	1.38
Temp = 300 K	Ar	1.37
Ion En. = 400 keV	Kr	1.33
	Xe	1.34

Host	Ion	($10^{13} \text{A}^3 \text{s/eV}$)
Cu	He	0.031
Migr. En. = 0.71 eV	Ne	0.026
Temp = 0 K	Ar	0.022
Ion En. = 400 keV	Kr	0.019
	Xe	0.017
Au	He	0.91
Migr. En. = 0.05 eV	Ne	1.36
Temp = 0 K	Ar	1.33
Ion En. = 400 keV	Kr	1.14
	Xe	1.04
Au	He	1.80
Migr. En. = 0.05 eV	Ne	1.69
Temp = 300 K	Ar	1.52
Ion En. = 400 keV	Kr	1.25
	Xe	1.12
Cu	He	0.81
Migr. En. = 0.12 eV	Kr	0.88
Temp = 0 K		
Ion En. = 2 MeV		

TABLE I. Calculated spike mixing efficiencies for a variety of ion-target, temperature, ion-energy, and migration mechanism combinations.







