Coulomb Explosion and Thermal Spikes

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A fast ion can electronically excite a solid producing a track of damage, a process initially used to detect energetic particles but now used to alter materials. From the seminal paper by Fleischer *et al.* [Phys. Rev. **156**, 353 (1967)] to the present, "Coulomb explosion" and thermal spike models have been often treated as competing models for describing ion track effects. Here molecular dynamics simulations of electronic sputtering, a surface manifestation of track formation, show that in the absence of significant quenching Coulomb explosion in fact produces a spike at high excitation density, but the standard spike models are incorrect.

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The track of excitations and ionizations produced in a solid by a fast incident ion has been of interest to physicists since the work of Thompson and Rutherford. An incident ion excites the electron cloud producing charge separation along its path through the solid. Fleischer *et al.* [1] (hereafter FPW) proposed that the resulting repulsion between the transiently ionized atoms in the solid, called a "Coulomb explosion," can produce a track of damage in an insulator which may be seen by chemical etching. We refer here to the transiently ionized region produced by an incident ion as an "ionization track" which can produce craters [2] and sputtering [3–5], as well as damage tracks in solids [1,6,7].

In describing track formation by a fast incident ion, FPW compared their Coulomb explosion model to the thermal spike model used to describe defect production in insulators [8]. Such a comparison is not only of historical interest but persists in the recent literature [7,9]. It is somewhat remarkable since Coulomb explosion is a mechanism for coupling of the electronic excitation energy into atomic motion, whereas a thermal spike model [10–13] describes the transport of energy out of a heated region. Here we describe the connection between these models using molecular dynamics (MD) simulations in which the motion of the atoms in a solid is followed in response to an initial excitation. We then examine the possible quenching of the ionization track by the electron cloud.

MD simulations of the response of a solid to an ionization track are compared here to our earlier simulations of the transport of energy from a cylindrical heat spike. We show that when the energy per unit path length along the ionization track is high, the primary effect is the production of a cylindrical spike [14] and differences in predictions between the two models are often due to the use of incorrect spike models. The simulations were carried out for a model solid with a surface because of our interest in the ejection of atoms due to the electronic excitation of a solid [15]. This process, called electronic sputtering, is a surface manifestation of the damage done to the solid by a fast ion. As in the analysis of track data, both spike [13] and Coulomb explosion models [3,14,16] have been employed to explain laboratory data. Although electronic sputtering can occur in response to a number of types of excitations [17], here we describe sputtering by an ionization track. We first review MD results for spikes and then present results for a Coulomb explosion.

In the thermal spike model the energy deposited by a fast ion is described by a radial temperature profile that is assumed to evolve by thermal diffusion. Displacements or ejection from the surface occur if the energy of an atom in the evolving cylindrical spike exceeds a barrier. From such a model, one finds at high energy densities that the yield (Y_S), the number of atoms ejected from the surface per incident ion, is quadratic in the energy per unit path length in the spike, (dQ/dx) [18,19]. Although this result has been extensively used [3,9,13,20,21], it is incorrect. That is, our MD simulations of a cylindrical spike show that at high energy densities, models that include only thermal diffusion fail [22]. Instead, a melted track and a pressure pulse are produced [19] which control the transport of energy and limit the increase of the yield with increasing energy density. Remarkably, a spike model which includes these processes gives a very simple result for the yield at high energy densities [19],

$$Y_S \approx C_S(r_{\mathrm{cyl}}/U)\,(dQ/dx); \qquad (dQ/dx) \gtrsim (\pi r_{\mathrm{cyl}}^2 n U)\,. \tag{1}$$

Here U is the cohesive energy of the solid, n is number density, and r_{cyl} is the initial mean radius of the spike. C_S is $\sim$0.18 for atomic solids and $\sim$0.1 for simple molecular solids. Below we show that the repulsive heating by an ionization track can be well represented by Eq. (1) at high excitation density.

The evolution of an ionization track is simulated in an fcc solid made of atoms interacting via Lennard-Jones (LJ) potentials. Because of our interest in applications in astronomy [15], we use parameters for a condensed gas solid and narrow tracks are used to limit simulation times. These results can be scaled to higher excitation densities

and to refractory materials [19]. In these simulations, interactions occur between all atoms in the solid within a cutoff radius $2.54n^{-1/3}$. MD simulations have been made previously for a few charges in LiF [23] and a distribution of holes in Si [24]. Here we simulate an ionization track in which the holes have low mobility and are not fully screened during the time displacements occur. Even if the holes are neutralized, a track of excited atoms will have overlapping charge clouds that act repulsively [3,20,21]. Therefore, we do not distinguish here between closely spaced, partially screened holes or interacting excited atoms. We describe the repulsion between such excited ("ionized") atoms using $V = (e^2/r)\exp(-r/a)$, with a cutoff at $r_{\rm cut}^{\rm coul} = 7a$, where a is an average screening constant [25]. The interactions of excited atoms with unexcited neighbors are not changed as the polarization potential has a small effect.

The Coulomb explosion produced by an incident ion is described by instantaneously changing from the LJ potentials between those atoms which are ionized to the screened Coulomb potential above. The resulting repulsive forces produce atomic motion, and the velocities and positions of all atoms are then followed [22]. This procedure is carried out for a number of values of "ionization" density, dJ/dx, and screening constant, a. For fast ions ($v > 10^8$ cm/s) dJ/dx is related to the stopping power, dE/dx, and the mean radius of this distribution, $r_{\rm coul}$, depends on v. For each set of track parameters (dJ/dx, $r_{\rm coul}$) excited species are chosen randomly. After exciting the solid, atoms or "ions" sputter if they cross a plane $2r_{\rm cut}^{\rm coul}$ above the surface. The number ejected in each run then gives the yield. Sample sizes ($3 \times 10^{4-5}$ atoms) and simulation times (15–80 ps) were adjusted to the size of a and dJ/dx. Extending times by tens of picoseconds, doubling the thickness, or changing the boundary conditions did not change these results. Yields were averaged over ~10–100 ionization distributions since the spread in the size of the yield is broad, especially for small (dJ/dx) where sputtering occurs only when two excitations are produced close together at the surface [3,4]. In a second set of calculations, the ionized atoms were quenched statistically so that the average number of ionizations decayed as $\exp[-t/\tau]$, where τ is the quenching (neutralization) time.

Average yields for three values of a are given in Fig. 1a vs $l_s(dJ/dx)$, where l_s is the layer spacing for the (001) face. The yield is seen to be *quadratic* in dJ/dx for each a and increases nonlinearly with a. Results for Y vs τ for a fixed (dJ/dx) and a are given in Fig. 1b; these were scaled by the fit in Fig. 1a. Because neutralization is stochastic, the size of the yield only becomes independent of τ for $\tau \gtrsim 10\tau_D$, where τ_D is the Debye period [22]. The average yield is still nearly quadratic in (dJ/dx) for all τ.

Energy transport at the atomic level can be extracted from these simulations. We find that at the highest excitation densities the repulsive energy is transferred to

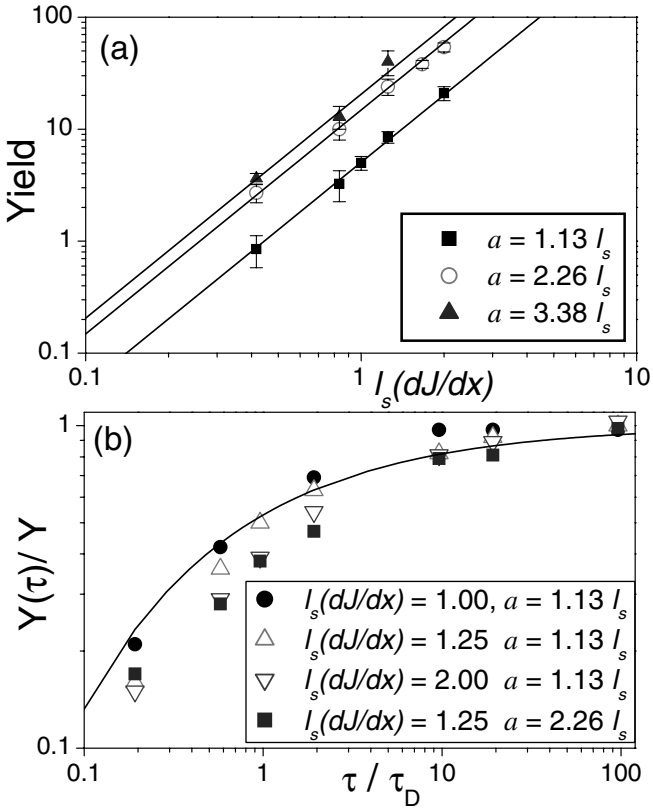

FIG. 1. (a) The sputtering yield from a repulsive track vs $l_s(dJ/dx)$ for $r_{\rm coul} \approx l_s$. The lines are $Y = 14.\ln[1.3(a/r_{\rm coul})][l_s(dJ/dx)]^2$ [4]. Results scale with LJ parameters; here $\varepsilon = 10.3$ meV and $\sigma = 3.405$ Å giving $U = 0.08$ eV and $l_s = 2.66$ Å characteristic of a number of condensed-gas solids. (b) Yield, scaled to the fit in (a), vs τ, the neutralization/recombination time. These are roughly fit by $\exp[-\alpha(\tau_D/\tau)^p]$ with α and p varying slowly with $l_s(dJ/dx)$; the curve shown is for $a = 1.13l_s$; $l_s(dJ/dx) = 1$ with $\alpha = 0.46$ and $p = 0.56$.

neighbors in a very short time, $\sim 0.2\tau_D$, producing a cylindrically heated region. Beyond $\sim 0.2\tau_D$ the evolution of the radial temperature profile in the repulsively energized track is very similar to that in our simulations of a spike. In both cases, the transport is *not* simply by thermal diffusion. From the ejecta energy distributions (Fig. 2), two regions can be seen at high excitation density. At large ejecta energies, $E \geq 10U$, the spectra exhibits peaks due to prompt ejection from the surface layers in the initial track. This includes initially ionized species and accounts for ~20% of the ejecta at large dJ/dx, but dominates at very small dJ/dx. On the other hand, the principal component of the ejecta in Fig. 2 has an energy distribution like that found in our studies of ejection from a cylindrical spike (dashed line) [22]. That is, there is a broad, quasithermal distribution at low ejecta energies, $E < U$, which gives way to a $\sim E^{-2}$ dependence at $E > U$ characteristic of low energy cascades in a solid [19,26] but differs from thermal spike model predictions.

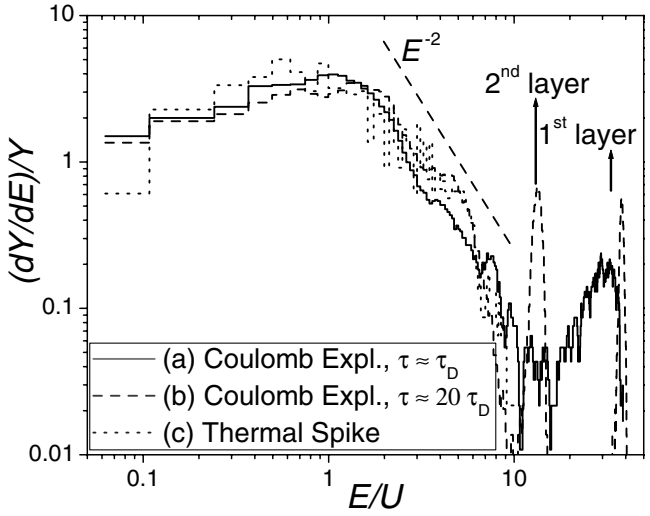

FIG. 2. Energy distribution of the ejecta for $l_s(dJ/dx) = 2$, $a = 1.13l_s$, $r_{\rm coul} \approx l_s$, for $\tau = \tau_D$ (a) and $\tau = 20\tau_D$ (b). Dotted line: energy spectrum from a cylindrical spike in Ref. [19], with $dQ/dx \approx 45U/l_s$ and $r_{\rm cyl} \approx 2.6l_s$. For the Coulomb explosion $dQ/dx \approx 38U/l_s$ and $r_{\rm cyl} \approx 2.6l_s$, while the spike in (b) has a 30% lower dQ/dx. Peaks are prompt ejecta determined by the potential energy between neighbors and U.

Based on these simulations, the primary effect at high dJ/dx is the production of a spike. This is also true quantitatively. That is, from the MD simulations we can determine the amount of repulsive energy which drives atomic motion in times shorter than those for sputter ejection. The energy transferred repulsively to atomic motion by $\sim 0.2\tau_D$ can be approximated by $dQ/dx \approx 0.15e^2(dJ/dx)^2$ for $a = 1.13l_s$ and $r_{\rm coul} \approx l_s$ in a cylindrical region of radius $r_{\rm cyl} \approx 2.6l_s$ [3]. Substituting dQ/dx and $r_{\rm cyl}$ into the new expression for the yield from a cylindrical spike, Eq. (1), gives a result that has the *same dependence* on dJ/dx and the same size (within 10%) as the yield in Fig. 1a. Therefore, at high dJ/dx an ionization track rapidly produces a heat spike which determines the subsequent energy transport, sputtering, and bulk damage. This means that Coulomb explosion and spikes are the *early and late* aspects of an ionization track and differences in predictions occur due to the use of *incorrect* spike models. Below we examine the possible quenching of the ionization track prior to producing a spike.

Neutralization and screening by the electrons can quench the repulsive energy in an ionization track. Therefore, we made a separate set of simulations describing the cooling of the free electrons. Their motion through the solid is calculated in the field produced by the track of positive charges. The lattice structure and excitation densities used are like those in the simulations above. The mean-free paths for elastic, λ_s, and inelastic, λ_{in}, scattering of the electrons by the atoms in the solid were assumed to be isotropic [27]. The interactions between free electrons are Coulombic, as is the interaction between the free electrons and the ions beyond a Bohr radius, a_o. Inside a_o the interaction potentials with the ions become flat with a binding energy of ~ 8.6 eV. The electrons are excited by receiving, on the average, 15 eV [27]. We ignore the very fast electrons which would further slow neutralization. From such simulations, an average a or τ can be estimated and used with the results in Fig. 1. Instead, we give in Fig. 3 the instantaneous total potential energy density in the ionization track vs time. This is the energy actually available for repulsive heating of the lattice. Changing potential forms inside a_o or electron excitation energies did not change the trends in Fig. 3.

The total energy per unit path length in the track in Fig. 3 is, of course, sustained with a large effective a if the electrons scatter only elastically. Examining the radial and time dependence of the electron density, a fraction of the electrons cool rapidly by electron-electron collisions. This partially neutralizes the track and is called dielectronic or Auger recombination. Because of energy conservation and mutual repulsion, the remainder of the electron cloud, now hotter and more fully screened, expands to a *larger* average radius. Varying λ_s affects only the local electron density. Including an energy loss, $\Delta\varepsilon_{in}$, at each collision of an electron with a lattice atom decreases the net potential energy in the track. Inelastic processes also heat the lattice [11]; here we are solely interested in the repulsive energy. Using values of $\Delta\varepsilon_{in}$ and λ_{in} corresponding to electrons in a polymer or ice [27] (dotted curve in Fig. 3), it is seen that most of the initial repulsive interaction is *not* neutralized during the time it takes to produce a spike, $\sim 0.2\tau_D$. Therefore, for reasonable inelastic energy loss parameters, screening and neutralization in the ionized track are not sufficiently rapid to quench the repulsive

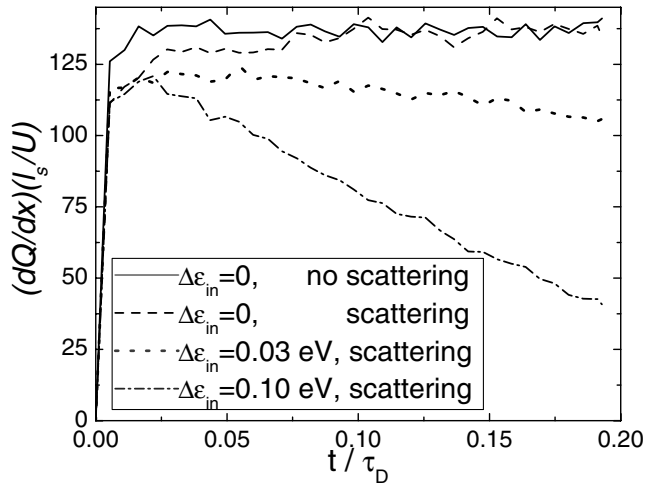

FIG. 3. The change in the total repulsive energy per unit path length in the track of interacting holes and electrons vs time for $l_s(dJ/dx) = 1$ and a dielectric constant $\epsilon = 1.6\epsilon_o$: no scattering (solid line); elastic scattering only $\lambda_s = l$ (dashed line); inelastic scattering $\lambda_{in} = l$ and $\Delta\varepsilon_{in} = 0.03$ eV (dotted line) and $\lambda_{in} = l$ and $\Delta\varepsilon_{in} = 0.01$ eV (dash-dotted line).

production of a spike. Increasing $\Delta\varepsilon_{in}$ (dot-dashed curve) or decreasing λ_{in} leads to more rapid but *still incomplete* quenching. For our track geometry, in Fig. 3, a repulsive energy greater than $\sim 35(U/l_s)$ sustained during $\sim 0.2\tau_D$ will produce a spike satisfying Eq. (1). Since the effects of ionization tracks have also been seen in liquids [28], semiconductors [7] and even metals [6], detailed excitation distributions and specific material properties need to be used.

In this Letter we close the circle on *one aspect* of an old [1] but topical [9] problem, the effect of the track of repulsive energy produced by a fast ion in a solid. We referred to the excited region as an ionization track even though it may be heavily screened. MD simulations of the repulsive ejection of material and heating were carried out and the effects of neutralization and screening were studied. Whereas at low excitation densities ejection can occur if neighboring excited species are formed near the surface [3,4], at the higher excitation densities the repulsive energy in the track produces a spike [14]. Therefore, Coulomb explosion and spikes refer to the early and late aspects of the ionization track produced in a solid by a fast incident ion. The resulting damage can lead to an etchable track or to ejection, the process examined here. If the track is not rapidly quenched (Fig. 3) or dispersed by hole diffusion [17], the principal contribution to the yield at high excitation densities can be estimated by substituting the track repulsive energy into the new expression for spike sputtering [Eq. (1)]. For very energetic heavy incident ions, electron cooling to the lattice can also contribute to the spike [11], and at low excitation densities individual excitonic decays can produce sputtering [17]. Work should now focus on fully calculating the distribution of excitations and ionizations produced by a fast ion for times $\lesssim 0.2\tau_D$, in order to separate such effects from the track of repulsive energy described here.

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