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Molecular Dynamics Simulations of the Effects of Damage Relaxation Following High-Energy Implants

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This work presents a molecular dynamics simulation method designed to describe the processes of electron and lattice relaxation taking place in the typical cascade volumes formed by high-energy implants. The simulation method is based on classical mechanics and includes the motion of electrons and nuclei. The results are in agreement with experimental observations.

INTRODUCTION

In the last few years the research concerning the thermalization of excited electrons have taken the positon of a basic theme in many fields. Excited electrons are, in fact, generated by laser pulses, by high electric fields applied to electronic devices and by the passage of fast, charged particles in solid targets. This study is concerned with this last case.

High-energy irradiations are used in electronic devices fabrication and in superconductors technique and high-energy particles are produced under nuclear reaction conditions. The energy of the irradiating particle spans from few mega electron volts into the Giga electron volts range and the region delineated by the ion path has the dimensions of several μm^3 and contains 10^9 atoms. According to classic theories (for references see [1]) this energy is prevalently conveyed to the electron subsystem and electrons with excitation energies from a few tens to some hundreds of electron volts are formed. Furthermore, if the ion–electron collisions involve the valence gas, as is generally the case, the concentration of excited electrons is larger than, or at least equal to, that of the atomic cores.

For the representation of these regions two different types of problems have to be envisaged. From the point of view of the physical picture there are the traditional concerns of the studies of electronic states, that is, the great diversity of the electronic orbitals within a solid target and the quantistic nature and the long range of the electron–electron interactions. Under the conditions of the simulations these problems are aggravated by effects of electron–lattice interactions. In fact lattice disordering, sometimes of a very conspicuous form, is almost regularly observed on the aftermatch of high-energy irradiations. From the computational side the problem requires a resolution on the atomic scale which can be achieved only with a molecular dynamics simulation scheme. However, evident problems for the application of such method arise from the extremely large size of the volumes involved and from the duration of the transitions. In fact typical values of the times of lattice relaxation are in the range of some picoseconds, or higher, whereas the characteristic times for the loss of energy of highly excited electrons via plasmon excitation fall in the sub-femtosecond scale.

This work presents a molecular dynamic simulation scheme which deals with both the computational and the physical aspect of the phenomena. The method presented here is new and uses the concepts of classical mechanics. The results appear to be in agreement with experimental observations.

DESCRIPTION OF THE MODEL

The Simulation Cell and the Dynamics of the Charges

It is known that the path of a high energy particle is hardly bent from the original direction and consequently consists of a very long projected range R_p and of a lateral straggling parameter R_l of almost one order of magnitude smaller. For this reason the region where the excited electrons are generated is commonly represented (see [1] for references) as a cylinder of dimensions (R_p, R_l) elongated in the direction of the axis R_p (a sketch of a high energy cascade is shown in Fig. 1. In such a figure the crosses indicate the ionization of the target atoms). The values of R_p fall in the range of some micrometers and the cylinder (R_p, R_l) typically contains 10^9 atoms (representative values of R_p and R_l are reported in Table I of the following section). The central problem of the simulation is to reproduce

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the representation of such a volume within a manageable memory occupation.

A first useful simplification is based on a common concept in studies of high-energy particles. In such cases it is generally assumed [1] that the electronic stopping does not change along R_p and the formation of excited electrons is uniform along this axis. Consequently, if the interactions between electrons more distant than the electron mean free path λ are ignored, the cylinder (R_p, R_l) can be considered as formed by the replica of the same cylinder of basis R_l and height λ so that only one cylinder (λ, R_l) is sufficient for characterization of the damaged region (a sketch of the subdivision of a high-energy cascade in elementary cylinders (λ, R_l) is shown in Fig. 1).

Furthermore, according to current concepts, local non-uniformities in a high-density plasma are of scarce relevance and only average features are though to play a significant role. Following this lead a further basic assumption of the simulation is that the spatial behaviour of the charges can be treated with a stepwise approximation and the cascade region can be subdivided into large regions within which spatial uniformity dominates. To this purpose the cylinder (λ, R_l), which is approximated by a parallelepiped with a square basis of linear dimension R_l, is subdivided into concentric parallelepipeds. These parallelepipeds represent the spatial mesh upon which the evolution of the charges is analyzed and the behaviour of the parallelepipeds is determined, at a macroscopic level, by spatial uniformity. Owing to this property each elementary parallelepiped is formed by the repetition of the same basic block and there is one basic block for each parallelepiped (Fig. 2 shows a plane view of the cylinder (λ, R_l), of its subdivision in concentric elements, and of the basic blocks. The basic blocks are indicated by the square hatched areas. Their repetition, for sake of clarity, is indicated only for the more peripheral parallelepiped).

Owing to this periodic structure, one particle (electron or nucleus) leaving the boundaries of the basic block on one side re-enters the block on the opposite side. Furthermore, the locations of the particles are defined by two sets of coordinates; that is, the coordinates within the basic block (x, y, z) and the absolute coordinates (X, Y, Z). The last ones are referred to the central axis of the cascade (indicated by the dot with the cross in the upper panel in Fig. 2) and are constructed by using as translation vectors the dimensions of the basic blocks projected along the (X, Y, Z) axes,

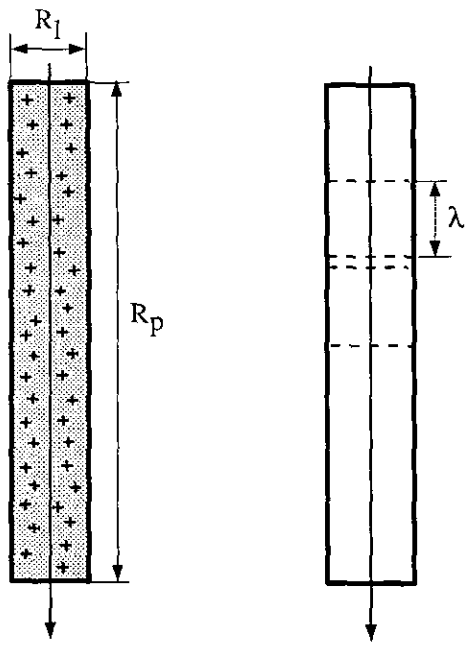

FIG. 1. Damage track of a high-energy particle and subdivision of the cascade volume in elements (λ, R_l).

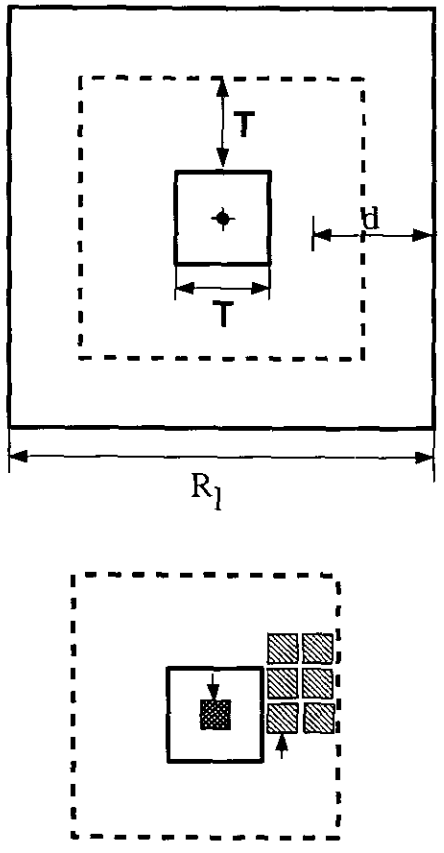

FIG. 2. Structure of the simulation cell. Subdivision in elementary parallelepipeds and repetition of the basic blocks. The cascade axis is indicated by the dot with the cross in the upper panel.

that is, the segments Bx, By, Bz. Consequently the (X, Y, Z) coordinates of a particle which has crossed the block Bj associated to the jth parallelepiped n-times and the block $Bj+1$ associated to the $(j+1)$th parallelepiped m-times are given by an algebraic sum of the type $X = x + nBx_j + mBx_{j+1}$.

The basic block represents the environment in which each charge is moving, and consequently it has the structure of a crystalline solid. In our simulations a simple cubic structure with nodes forming an equispaced three-dimensional array is adopted. The distance between nodes corresponds to a typical nearest neighbour distance in a crystalline solid (that is, 2 Å). The representative character of such a structure is underlined. The basic blocks contain positive and negative charges. The positive charges represent the atomic cores and the inner-shell electrons (in the following such charges will be indicated as nuclei. In the calculations reported below, their atomic mass and number are both equal to one) and they are located at the nodes of the array. In the absence of electrons the force acting on each nucleus is zero for symmetry reasons (for the particles on the peripheral mantle this condition is obtained by applying folding conditions).

To describe the passage of the charged projectile at the beginning of the simulation electrons, endowed with the wanted kinetic energy and with the direction of motion chosen at random, are inserted in equal numbers in each block at a given distance from the nuclei (Fig. 3 shows in a sketchy form a plane view of the charges in the basic block). In a real cascade the most probable initial location of the electrons is the one nearest to the ion track. In our simulation the ion track coincides with the cascade axis and consequently the excited electrons are initially concentrated near this axis (in the lower panel of Fig. 2 these locations are indicated with an arrow).

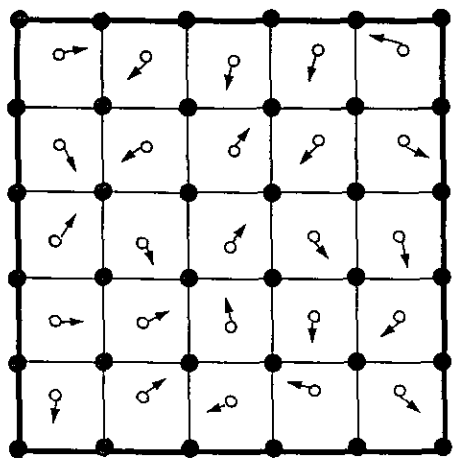

FIG. 3. Charge states in the basic block. Plane view.

The motions of the electrons destroy the equilibrium conditions. Forces appear in the lattice which produce disorder and atomic displacements. The simulation analyzes the evolution of the two subsystems of charges until a stable state is reached. As in [2, 3] (in [3] a preliminary version of this model has been presented) it is assumed that the excited electrons belong to the valence band and, according to a common assumption, can be treated as a gas of free particles. As in [2, 3] for both types of charges a classic representation is adopted. Electrons and nuclei are treated as point charges interacting via an unscreened coulomb potential and their trajectories are evaluated in real space by solving the Newtonian equations of motion.

Generally the electron path exceeds one elementary parallelepiped and involves several basic blocks. Consequently a procedure linking the electron content in the various basic blocks is required. When one electron crosses the boundaries of an elementary parallelepiped a reduction and an enhacement of the negative charge are simultaneously performed in two basic blocks; that is, one electron is removed from the basic block associated with the parallelepiped left by the travelling projectile and one is added to the one associated with the parallelepiped towards which the particle is moving. The freshly injected electron retains the originally velocity and the absolute coordinates, whereas the local coordinates are constructed by using the formula given above. Similar procedure are adopted for nuclei whose motions, however, remain generally confined within the original basic block.

It is underlined that in a real cascade an exchange of electrons among the basic cylinders (λ, R_l) may take place through the interfaces at the λ boundary. To account for this effect electrons crossing the λ boundary of the simulation cell are re-emitted in the damaged volume through specular reflection of their velocity. On the contrary, electrons found at a radial distance from the central axis greater than R_l with an energy above the thermal range are assumed to be dispersed in the cool parts of the target and their simulation is interrupted.

The Thermalization Procedures

Under realistic circumstances the excited region is part of an infinite sample which has a well-defined temperature and acts as a thermal bath. Obviously the energy exchanges with the external reservoir are of fundamental importance for the processes of relaxation and must be accounted for. Several procedures have been so far introduced to describe the equilibration of a system of particles at a given temperature, that is, the Andersen stochastic collisions [4], the Nosé scaling of the velocities [5], and Langevin dynamics. It is known that in equilibrium they all generate configurations belonging to the canonical ensemble. However, outside

equilibrium their applicability is uncertain. Furthermore, test calculations in the conditions of our simulations indicated that complex numerical problems may arise from the application of Langevin dynamics or the Nosé method. In fact, Langevin dynamics requires a complex adjustment of the dissipative force to obtain the wanted temperature. In the case of the Nosé method problems of numerical accuracy and stability arise from the dynamical change of the time-step associated with the method. In our calculations a modified version of the Andersen model [4] has been adopted which has a simple physical meaning and overcomes the computational problems of the other two methods. It is recalled that in [4] the stochastic collisions change the momenta of a particle of an ensemble of N particles to the ones chosen at random in a Boltzmann distribution at a given temperature (in our case 300° K). An adjustable parameter of the model is the mean time interval dt between successive collisions. In our calculations dt is used to account for the fact that, according to normal heat conduction mechanisms [1], the temperature induced by a heat source spatially decays in an exponential manner. If this exponential behaviour is approximated with a linear relationship and the cool boundary is fixed at R_l the heat conduction can be formulated in terms of the Andersen model as a dt value given by the product of a factor (d/R_l) and of a characteristic time for loss of energy T_e. In this evaluation d is the distance of the particle from the cascade boundary (the measure of the d value is indicated in the top panel in Fig. 2). Consequently the time interval $dt = (d/R_l) \times T_e$ leads to a local form of heat exchange and to a more rapid cooling of the regions near the cascade periphery.

Different values of T_e for electrons and nuclei have been adopted. In the case of electrons, owing to their high energies (for references see [1]), it is assumed that the coupling of the damaged region and the surrounding area takes place via plasmon excitation so that T_e corresponds to a typical time of plasmon generation (a representative value equal to 0.1 fs has been used). For the nuclei a representative phonon frequency has been constructed with molecular dynamics simulations of the basic block. In such calculations a small displacement in the thermal range was given to the nuclei and the basic block was then stabilized under the action of the stochastic collisions. This procedure leads to a T_e value around 10 fs.

Parameters of the Simulations: The Size of the Simulation Cell and the Cutoff of the Potential

In all the simulations reported below the size l of the cell (l, R_l) has been kept fixed and its value set equal to 200 Å. Test calculations showed that owing to the reflecting conditions applied to the extremities of (l, R_l) the value of l is not critical.

In the standard running conditions the thickness of the elementary parallelepipeds (such a parameter is defined in the upper panel in Fig. 2, where it is indicated as T) varies between 100 Å and 1000 Å and the larger elements are concentrated at the periphery of the cascade. Furthermore, 15 basic blocks of size $20 \times 20 \times 20$ Å containing 1000 particles for each species have generally been used. Several test calculations were made to assess the effects of the spatial grid. In such calculations a subdivision of (λ, R_l) in elementary parallelepipeds with constant or variable thickness was made and in both cases the thickness was varied between approximately 100 and 1000 Å. No size dependent effect was observed. The linear dimension of the basic blocks was also changed in the interval 20–40 Å. Also in this case no significant size-dependent effect was observed.

As mentioned above, the charged particles are made to interact via an unscreened coulomb potential. Even if very extended interactions may exist in real crystals a cutoff radius must be adopted for computational convenience. For sake of simplicity this parameter was assumed equal for electrons and nuclei and its value was set by the condition that the characteristic time T_e for the thermalization of the nuclei reproduces a typical phonon frequency of a crystalline solid. This leads to a cutoff radius between the second and the third nearest neighbour distances, that is, in the range 4–6 Å. Test calculations showed that the choice of this interval is not critical.

The Numerical Method

An analysis of the numerical methods to be adopted in problems of this type has been made in [7]. In [7] it was shown that a simple mid-point predictor–corrector offers a good trade-off between accuracy and simplicity. Owing to the prolonged duration of the phenomena the evaluation of the time-step has been the object of many test calculations. In these calculations the relaxation of the two systems of charges that were excited to a given ammount of energy was analyzed independently with a representation in the microcanonical ensemble. The results indicated that the adoption of time-steps equal to 0.01 fs and 1 fs for electrons and nuclei, respectively, leads to oscillations of the total energy that are two orders of magnitude lower than the lowest energy of the particles. For the conditions of the simulations, owing to the neat separation of the relaxation of the two subsystems (see below), it was found that the most economical procedure is to use a constant time-step that is equal to 0.01 fs during the transition of the electrons and to 1 fs during the one of the nuclei. In this last case, in fact, the slow motion of the electrons allows the use of a large time-step without loss of accuracy in the representation. Many test calculations using a more gradual transition between the two regimes showed an increase of computational complexity and computer costs without substantial increase of precision.

RESULTS

Typical features of high-energy irradiations are described in Table I. The first case shown in the table, that is, B^+ ions implanted in silicon with an energy of 1 MeV, is representative of the high-energy implants used in electronic devices fabrication and the second one (a fission fragment in an uranium oxide), is of high-energy particles formed under nuclear reaction conditions. Heavy projectiles with energy in the giga electron volt range used in studies of superconductors have properties similar to the ones of a fission fragment.

Table I reports the main parameters of the path of the primary particle (that is, the average in-depth and lateral penetration, R_p and R_l, respectively) and the ones of the electronic excitation, that is, the extent of R_{max} of the region around the ion path, where the hot electrons are generated, and their average energy (details on such calculations are reported in [2]). It is seen that, owing to the small range of R_{max}, the region where the excitation is formed coincides with the one delineated by the ion path and it consequently involves a volume of dimensions (R_p, R_l).

The results reported in Table II illustrate the equilibration of such volumes To briefly resume the essence of such calculations it is mentioned that, in agreement with the Born–Oppenheimer approximation, two phases are identified in the evolution of the damaged region. The first phase is dominated by the rapid scattering of the electrons in the lattice and by their loss of energy and thermalization via coulomb interactions with other particles and heat exchanges with the thermal bath. The second phase is a phase of lattice relaxation. The potential energy due to nucleous–electron interaction is transformed into kinetic energies and displacements of the nuclei. Kinetic energies above the thermal range are gradually reabsorbed by stochastic collisions and their falling values stabilize the displacements. During this transition the effect of the slowly moving electrons on the nuclei is similar to the one of a fixed negative background.

Table II illustrates the state of the two charges at the completion of the respective period of equilibration (a detailed description of the transition has been omitted for sake of brevity). The table shows for the two subsystems of charges the displacements from the initial locations and the times required to achieve thermalization in dependence of the cascade size R_l and of the content of electrons. These two parameters have been found to be more influential in the relaxation processes. In fact, as pointed out in [2, 3], the initial energy of the excited electrons (which in the case of Table II falls in the range indicated in Table I) has only a secondary role as the interparticle field rapidly generates a wide distribution of energies with maxima and minima that are remarkably different from the initial values.

The results of Table II emphasize the role of the cascade size. In fact it is seen that in the case of the larger cascade the displacements are noticeably larger larger than in the smaller cascade. Furthermore in the larger cascade the maximum of the nuclear displacement is well above the extent of the normal values of the lattice thermal vibrations and should appear under experimental conditions. The calculations show that this maximum disorder is limited to the inner parallelepiped and generally involves a thickness around 200 Å.

Under experimental conditions two main modes of lattice damage have been observed. For implants of light and medium mass projectiles with energy of some mega electron volts in Si and GaAs, RBS and X-ray experiments indicate a modest disordering similar to an increase of the lattice thermal vibrations [7]. In the case of fission fragments, visible damage tracks of the lengths of a few micrometers and diameter of some 200 Å are known to be formed [1]. These behaviours are in agreement with the trend of the

TABLE I

Irradiating particle	Projected range R_p [μm]	Lateral straggling parameter R_l [μm]	R_{max} [Å]	Energy per electron [eV]
B^+, 1 MeV	2.6	0.3	~1.0	~40
Fission fragment	~8–10	~1.0	~4.0	~40–100

TABLE II

Molecular Dynamics Simulations of the Electron–Lattice Interactions; Displacements at the Completion of the Thermalization Phase

Electrons		Nuclei		
Time	Displacements	Time	Displacements	
[ps]	Average [Å]	[ps]	Average [Å]	Maximum [Å]
Total electron charge equal to the total nuclear charge				
R_l = 2000 Å				
0.05	500	6.0	0.01	0.05
R_l = 10000 Å				
0.3	~2000	25.0	0.05	0.4
Total electron charge twice the total nuclear charge				
R_l = 2000 Å				
0.1	800	10.0	0.03	0.08
R_l = 10000 Å				
~0.4	~3000	60.0	0.08	1.2

calculations and corroborate the validity of the model. This agreement leads to three important conclusions. In the first place it appears that a classic physics based on the simple concepts of coulombic interaction and heat exchanges may account for phenomena of this complexity. Details of the electronic orbitals, of the interatomic forces, and of the local structure of the charge distribution appear unnecessary. In the second place, the method of stochastic collisions, which is a correct thermalization procedure for near-equilibrium conditions, can be also safely applied to strongly perturbed systems. Finally large volumes can be simulated with a molecular dynamics simulation scheme by using the simple device of periodic conditions. Such conditions are normally applied to infinite samples with a uniform spatial behaviour. Their use for large but nonuniform volumes indicates new potentialities and appears to increase the flexibility of the molecular dynamics simulation methods.

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