International Journal of Thermophysics, Vol. 10, No. 2, 1989

Nonequilibrium Molecular Dynamic Simulation of Rapid Melting and Solidification[1]

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A new nonequilibrium molecular dynamics computer simulation method has been developed for the study of rapid interface kinetics. In this method a strong heat gradient is set up to simulate the action of a laser in a (100) f.c.c. crystalline substrate composed of Lennard–Jones atoms. The substrate is shown to melt partially and then to regrow epitaxially as a crystalline solid. The characteristics of properties such as the melt depth as a function of time, together with the interface temperature and interface velocity as a function of time, are shown to display all the qualitative features of experimental studies of the laser annealing of silicon. The construction of the interface response function (interface velocity versus temperature) is also shown.

KEY WORDS: computer simulation; laser annealing; nonequilibrium molecular dynamics; rapid solidification.

1. INTRODUCTION

In this paper, we use a recently developed nonequilibrium molecular dynamics simulation technique [1] to describe systems subjected to intense and rapid heating, i.e., conditions far from equilibrium. Our goal is to understand both the thermodynamics and the kinetics of the resulting phase transformations that occur in such circumstances. The conditions give rise to interesting physical phenomena which affect the resulting properties of the processed material, for example, directed energy processing is used to anneal implantation damage in semiconductors or to produce new alloys with specialty properties.

Rapid solidification processes take place at such fast rates and over such small time frames that experimental studies of the mechanisms

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[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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involved are extremely difficult. Uncertainties in measuring the most important parameters—the temperature and velocity of the transient solid/liquid interface—prevent direct, reliable calculations of the undercooling–velocity relationship. Thus, there is an incentive to try to predict these properties using theoretical techniques, such as computer simulation. A nonequilibrium molecular dynamics simulation method (NEMD) for the study of laser annealing was developed by Landman and co-workers [2–4], who calculated density profiles during the rapid heating and subsequent cooling for both the hypothetical Lennard–Jones system and a Stillinger–Weber model for silicon. Our method provides a somewhat more realistic model of the method of energy transfer and demonstrates for the first time the calculation of such properties as the interface response function (temperature–velocity), which are of great potential value to those involved in the area of rapid solidification. Full details of this new NEMD method are described in Ref. 1.

In this paper we demonstrate the thermodynamic and kinetic information which can be obtained using the NEMD method in Ref. 1 with results for a system consisting of a single pure component of Lennard–Jones particles.

2. THE NONEQUILIBRIUM MD METHOD

2.1. The Simulation Cell

The initial configuration for the simulation cell (or box) consists of a heterogeneous system of a solid in contact with a vapor. The shape of the box is a square prism of fixed volume, with the length of the box four times its width. In this study, 2744 particles occupy the solid portion of the cell on f.c.c. lattice sites with an exposed (100) face. Roughly 10–15 particles occupy the vapor space. Thus, the overall dimensions of the solid substrate are about $11\sigma \times 11\sigma \times 22\sigma$. Size effects on the results are dealt with thoroughly in Ref. 1, where a description of how the initial configuration is obtained may also be found. Periodic boundary conditions are applied in the two lateral directions (x and y); a reflective wall is employed in the z direction (i.e., that perpendicular to and above the solid/vapor interface). The cell consists of four sections, as shown in Fig. 1. A fixed lattice is imposed at the bottom of the cell, consisting of a few atomic planes whose atoms interact with the rest of the system but are constrained to remain on their lattice sites. This section acts as an external potential stabilizing the system above it. Above the fixed lattice is the heat bath region, again consisting of a few atomic planes. Here the velocities of the atoms are periodically rescaled by a small amount, using Brown and Clark's thermo-

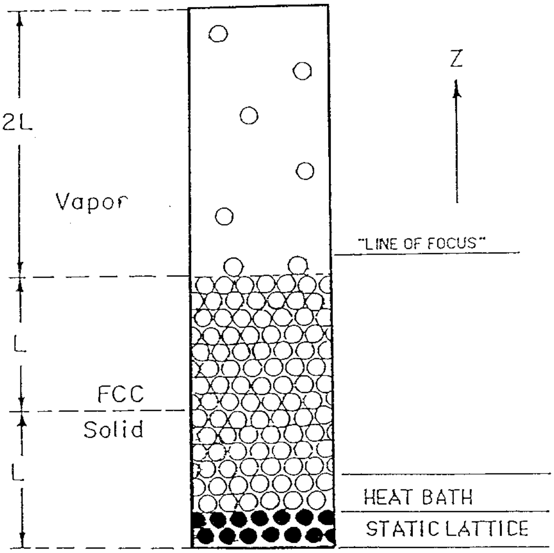

Fig. 1. Schematic diagram of the simulation cell used.

stating method [5], to keep the temperature at a fixed value (the substrate temperature). The heat bath is employed to emulate the heat conducting properties of a deep substrate underlying the physical system in the simulation. Above this is the largest single region, the so-called "dynamic" section, where the particles will interact with the incoming energy "beam." Above that is the vapor.

2.2. Setting Up the Heat Gradient

A real energy beam interacts with a solid to set up a strong heat gradient across the system. In modeling the beam, we assume the following. First, a planar beam impinges on the substrate atoms uniformly, with all affected atoms energized at the same instant. Second, we ignore the plasma formation during the first picosecond or so of interaction with the solid and assume that the incoming energy is immediately converted to kinetic energy. Neither assumption is likely to be too deleterious to the simulation's effectiveness in describing the real physical system. In our NEMD method we need to know only the energy fluence of the beam, its duration, and the shape of its intensity versus time (e.g., Gaussian, triangular, etc.). All of these are readily available as choices of the way in which the experiment will be carried out. We may then predict the behavior of the system under the influence of a chosen energy pulse.

Energy transfer to the system in this NEMD method is made by allowing so-called "energy carrier" particles to interact with the system particles. The energy carriers can be thought of as a very simple model for photons. The only characteristic of the energy carriers is that they carry energy; they possess no other physical properties other than momentum, involving a necessary but tiny mass for the solution of the equations of motion in the molecular dynamics method. This mass of the energy carrier is a parameter in the simulation, but tests described in Ref. 1 have shown that its value can easily be determined in a way which allows the results to be only weakly dependent on its chosen value. For the LJ potential at least, this mass is roughly 10^{-6} that of the argon-like substrate atoms. The available energy from the "beam" at any time instant, ΔE, is distributed among a chosen number of energy carriers, N_c, in the form of kinetic energy only. The energy of a single energy carrier is equipartitioned among all three translational degrees of freedom, giving no directional bias to the carriers. It was shown in Ref. 1 that if N_c is chosen to be roughly half the number of substrate atoms, then the results are essentially independent of N_c. The velocity of the carrier is obtained by a simple energy balance. The energy carrier with this associated velocity collides with the substrate atoms elastically, transfers its energy, and disappears. After the collision, the substrate atoms have an enhanced velocity, which may—depending on the energy of the "beam"—induce a phase transformation in part of the system, for example, melting some fraction of the originally solid substrate. Collisions are carried out only on atoms below a certain value of height in the cell; this is marked as the "line of focus" in Fig. 1, and here is chosen arbitrarily to be 1σ above the original solid–vapor interface. During heating from the influence of the beam, the solid will expand, causing some atoms to lie above the line of focus. Thus these atoms will no longer undergo collisions with the energy carriers. This has been instituted to emulate the focusing action of a real laser, to avoid energizing the vapor particles repeatedly, and most importantly, to provide a way of emulating the change in reflectivity of the substrate upon melting. This is explained in detail in Ref. 1.

After the chosen energy fluence has been transmitted to the system for a specified pulse duration, the beam is "switched off," and the system is allowed to anneal. This annealing is carried out until the temperature of the entire substrate has returned to its original value. This annealing process is not at constant energy, as the heat bath is slowly removing energy from the system to restore the substrate to this temperature. Annealing involves a considerable amount of simulation time; for the simulations involved here, annealing took roughly 10 times the length of the pulse duration.

The NEMD method was developed on a DEC VAX 8250; the calculations described in this paper were made using the IBM 3090 and FPS 264 array processors which comprise the Cornell National Supercomputer Facility. A throughput of roughly 4000 time steps per CPU hour was obtained.

3. RESULTS

The first studies of this new NEMD method have been carried out for a simple hypothetical system, Lennard–Jones atoms, to ensure that the simulation method emulated the characteristics of real physical systems, before extending its use with more sophisticated potential energy functions to model metal alloys and semiconductors and other technologically important materials. Here, we used a truncated Lennard–Jones potential with a cutoff radius of 3.0σ. The mass and the Lennard–Jones parameters for the substrate atoms were chosen to be those commonly used to model argon. A time step of 10^{-14} s (corresponding to $\Delta t^* = 0.0046$) was used to integrate the equations of motion using a modified "leapfrog" algorithm. The result of "irradiating" and annealing the system is analyzed in terms of properties such as the singlet density profiles, $\rho(z)$, and the in-plane radial distribution function, $g(r)$. Again, details of how the time-dependent property evaluations are made for this highly nonequilibrium system are given in Ref. 1. Density profiles were obtained at various times for a system of 2744 solid particles acted upon by a 15-ps pulse with an energy fluence of $25\,\mathrm{mJ\cdot cm^{-2}}$. These values of the fluence and pulse duration are reasonable experimental values. The pulse duration can be as brief as a few femtoseconds or, more commonly, a few nanoseconds. With our choices for the parameters of the "beam," roughly one-third of the solid melts. After the beam has been turned off, melting continues for a short time before recrystallization starts. For the (100) face of an f.c.c. lattice of Lennard–Jones particles, this recrystallization proceeds in a roughened manner, i.e., several layers at a time.

The position of the solid–liquid interface (or melt front) is determined from an analysis of both the layerwise $g(r)$ and the density profiles. In practice, locating the posiotion of this interface is a rather difficult assignation, as described in Ref. 1. The melt depth at time t is defined as the distance of the solid–liquid interface from the location of the original solid–vapor interface; this relationship of melt depth and time is shown in Fig. 2. For qualitative comparison only, the experimental results for silicon [6], for a very different pulse duration, are also shown. It can be seen that all the important features of the experimental results are to be seen in the simulation results. The melt depth rises steeply during the "melt-in" period,

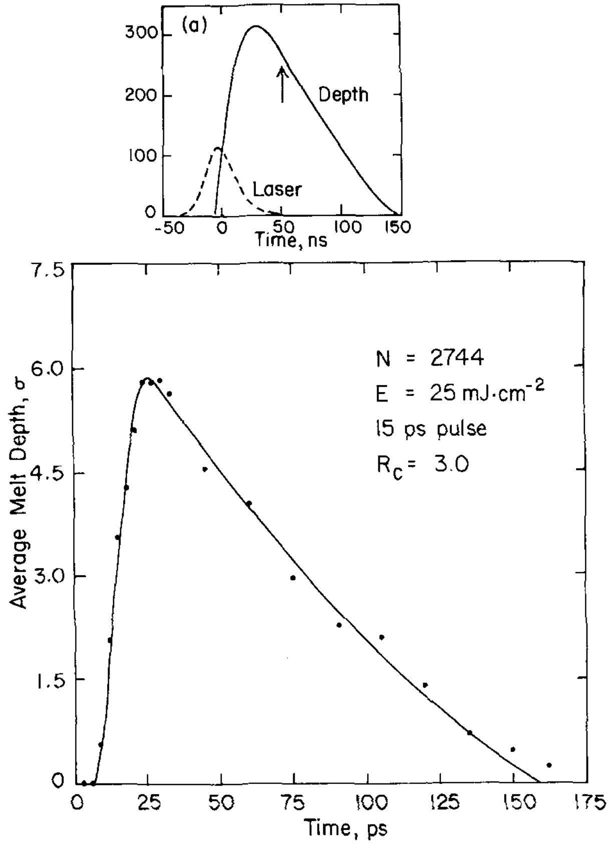

Fig. 2. The average melt depth in units of the Lennard–Jones collision diameter, σ, as a function of time. The solid line represents a polynomial fit to the simulation data (shown as points). The inset above shows experimental results for silicon [6].

and the melt continues to grow for about 5–8 ps after the "pulse" is turned off. The melt depth reaches a maximum value at about 27 ps, followed by a period during which solidification occurs caused by the rapid cooling. As the material cools, the melt thickness decreases at a slower rate until the substrate has resolidified completely.

Once the position of the solid–liquid interface has been determined, the temperature at the interface can be found for a given time, t, from the layerwise temperature profiles produced by the simulation. The resulting interface temperature versus time plot is shown in Fig. 3, together with a corresponding experimental plot for silicon (with a pulse duration of 2 ns) [6]. The scatter in the simulation results, especially at times close to the end

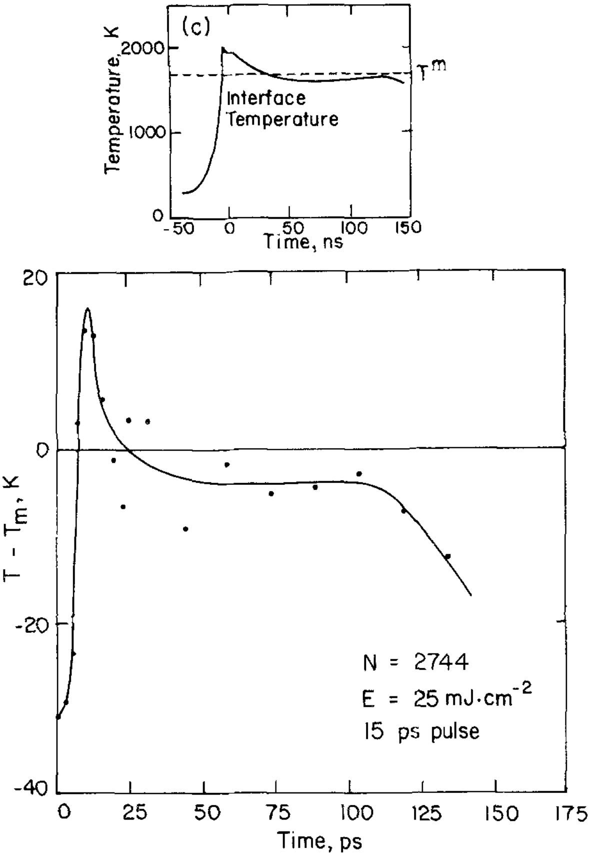

Fig. 3. Interface temperature, as $T - T_m$, versus time, where T_m is the melting point. Key as for Fig. 2.

of the pulse, reflect both the particular difficulty of locating the interface at these times and the relatively poor statistics obtained on averaging the temperature over only 100 or so atoms in the layer. Nonetheless, a mean curve through these points shows the correct qualitative behavior in comparison to experiment. The interface velocity is obtained from the slope of the melt depth versus time plot (Fig. 2); its time dependence is shown in Fig. 4. Knowing both the interface velocity and the temperature as functions of time, one can construct the interface response function, velocity versus temperature, as shown in Fig. 5. This important plot is crucial in ascertaining the kinetics of the rapid recrystallization process, as discussed fully in Ref. 1. As shown in Figs. 4 and 5, it is revealed that during the period of rapid heating, when the pulse is switched on, the interface temperature rises

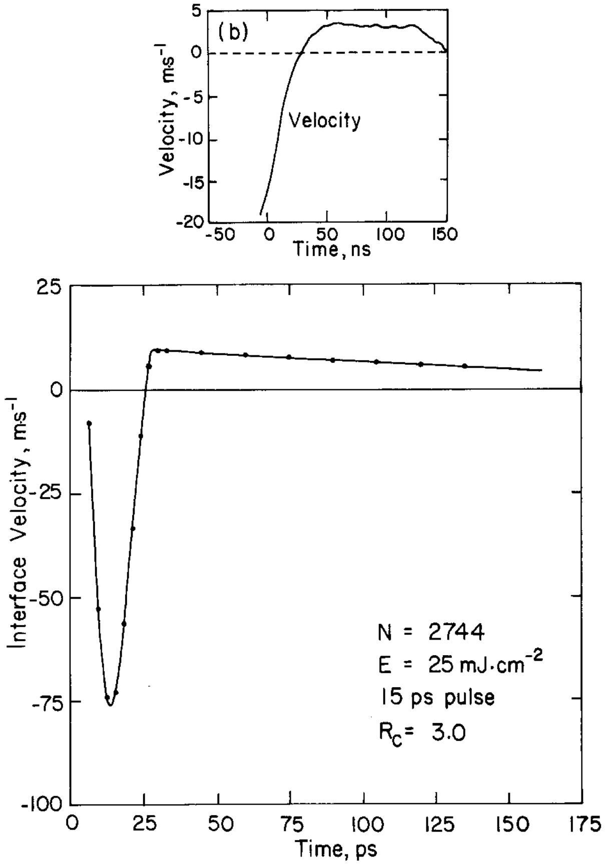

Fig. 4. Interface velocity as a function of time. Key as for Fig. 2.

quickly, superheating to about 20% above the equilibrium melting point, T_m. At the very high velocities involved (in our simulation, up to 75 m · s^{-1}), the rate of atomic rearrangement will be very slow compared to the heating rate, causing the superheating. Once energy input ceases, the temperature at the interface drops rapidly due to the heat conduction to the heat bath. The velocity of the interface also decreases as the temperature drops towards T_m, being zero at T_m. Incidentally, this gives us a prediction for T_m for this system of $T^* = 0.65$. Since T_m^* is 0.62 for a LJ potential cut at 2.5σ [7] and 0.69 for a full LJ potential [8], this result seems to give a good estimate of T_m for the LJ potential cut at 3.0σ used in our present studies. This may prove to be by far the fastest route to an accurate value of T_m, which ordinarily requires data from a number of simulation runs [8].

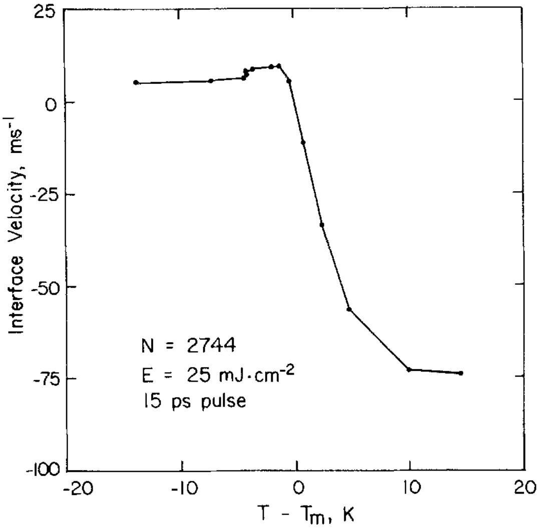

Fig. 5. Interface velocity versus interface temperature. Key as for Fig. 2.

The temperature continues to fall below T_m, thus undercooling the system. This undercooling causes the solid–liquid interface to move in the direction of solidification, as evidenced by the growing positive velocity (the sign of the velocity being a widely adopted convention; positive for solidification, negative for melting). The extent of the undercooling in our system is shown to be the relatively modest value of 8%. A relatively long period of undercooling at a constant value of the velocity then follows, during which steady-state crystal growth occurs. This velocity, 9.5 m · s^{-1} or 0.06 in reduced units, compares well wtih the value of 0.10 obtained by Broughton et al. [9] in steady-state simulations of recrystallization. Eventually, heat conduction into the substrate cools the system to its original temperature and the velocity falls to zero once more. As before, experimental results for silicon acted upon by a 2-ns pulse are shown, for qualitative comparison, in Fig. 4.

4. DISCUSSION

The newly devised NEMD simulation method [1] for the study of rapid solidification processes has been shown to model successfully the qualitative behavior of the thermodynamics and kinetics of a system undergoing both rapid heating and subsequent recooling. The method requires only the knowledge of the energy fluence, pulse duration, and geometry to predict the degree of undercooling and the subsequent kinetics of recrystallization. A relationship between the length and time scales of simulation and experiment is now being determined by performing experimental studies of argon, in collaboration with the laser processing group of Professor Mike Thompson at Cornell, with the goal of refining the simulation method to achieve as close to a quantitative prediction of experimental data as possible.

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