Effect of Viscous Flow on Ion Damage near Solid Surfaces

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Molecular dynamics computer simulations of 10 and 20 keV Au bombardment of Au substrates were performed to elucidate the influence of surfaces on defect production. Nearly all of the damage was due to local melting and viscous flow of hot liquid onto the surface. For the 10 keV event, 554 atoms flowed to the surface, and this led to the formation of a dislocation network that extended ≈ 6 nm below the surface. Only three interstitial atoms and no isolated vacancies or small vacancy clusters were produced. Loop punching and the nature of nonlinear sputtering are also discussed.

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Although the interaction of energetic particles with solids has been studied for over fifty years, a fundamental understanding of the atomic displacement processes in energetic displacement cascades has remained difficult to achieve. In the past few years, progress in developing reliable interatomic potentials [1] coupled with increasing computer capabilities have made molecular dynamics (MD) computer simulation an important tool for studying these displacement processes. An important finding of MD is that thermal spikes, and in particular local melting, play an important role in defect production, defect clustering, and atomic mixing [2–5]. With the exception of sputtering, however, MD simulations of radiation damage have been concerned with cascades in the interior of the solid and have not considered the effects of surfaces, even though nearly all studies of radiation effects using ion beams, and all applications of ion beam modification of solids, involve surfaces. Simulation studies of sputtering have mostly been concerned with the initial phases of cascade development [6], although in one such study, "pit" formation was investigated for a 5 keV event in Cu [7]. In that study, however, the working cell contained only 1745 atoms, which was far too few to properly investigate the full evolution of a 5 keV cascade, as will be realized here. We will show through MD simulations of 10 and 20 keV Au atoms impacting a Au target that local melting in energetic displacement cascades has a far more profound effect on displacement processes near surfaces than in the crystal interior, since the surface provides a mechanism for defect production that does not exist in the interior of a crystal, namely, viscous flow of liquid through the surface. This mechanism, which had not been previously realized, greatly enhances defect production and gives rise to the creation of dislocation loops and a large number of adatoms.

The molecular dynamic simulations were performed using a version of MOLDYCASK [8], which we modified to treat surfaces. For the current simulations, the working cell contained 160000 movable atoms. Three layers of atoms at the boundaries of the cell, but excluding the bombarded surface, were damped to simulate the conduction of heat in a semi-infinite medium. Potentials derived from the embedded atom method [1] were employed to generate the forces. These potentials were modified at close separation to smoothly merge with the universal potential [9]. Possible interactions between lattice vibrations and conduction electrons [10,11] were neglected in these simulations since the phonon-electron coupling time in Au is long, ≈ 64 ps [12]. In some events channeling, or at least quasichanneling, was observed, but these were not investigated in detail.

Many of the important features in the evolution of the cascade structure for a 10 keV Au atom incident on a (001) surface of Au at 0 K are depicted in Figs. 1(a)–1(f). Here, the position of atoms within a (100) cross sectional slab of thickness $a_0/2$ is shown. In Fig. 1(a) it is seen that the cascade begins to evolve much in the way described by Brinkman [13], and noted also by Foreman, English, and Phythian for 2 keV cascades in Cu [5], as many atoms are ejected from the cascade core and a depleted zone begins to develop. Figure 1(b) reveals traces of a replacement collision sequence (RCS) and a much slower moving shock wave which propagates outward at approximately the speed of sound. It is also observed that the size of the disordered zone, which we will refer to as a melt [2], initially increases with time as energy spreads and melts the surrounding lattice. Maximum temperatures in the cascade core exceed 6000 K for times up to ≈ 3 ps, creating extremely high pressures, as seen in Figs. 2(a) and 2(b) where temperature and pressure profiles are plotted at various instants of time. As a consequence of these spike conditions, cavitation occurs below the surface, Figs. 1(b) and 1(c). The cavity contracts by 9.0 ps, and although it does not appear to strongly influence the damage structure in this particular event, it can have greater importance when it intersects the surface, as described below. The most significant influence of the surface is shown in Figs. 1(d)–1(f), where it is observed that hot liquid is forced onto the surface by the pressure in the cascade. This viscous flow of atoms dramatically influences the further evolution of the cascade dynamics and defect structure. As observed in

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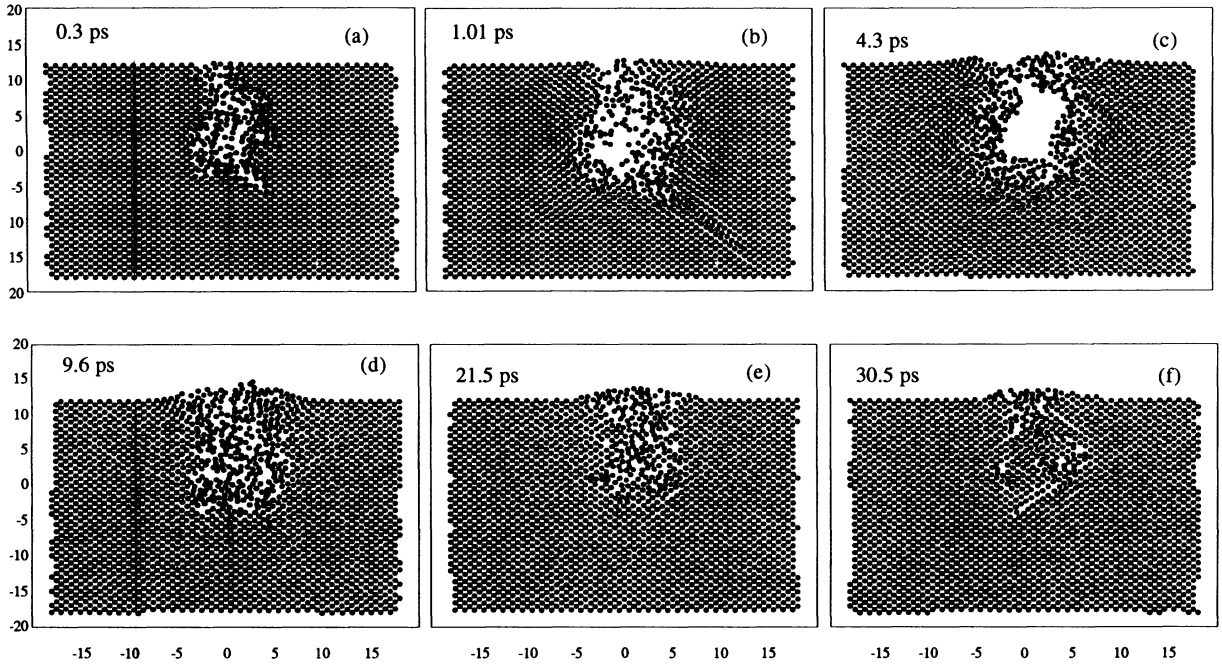

FIG. 1. Locations of atoms within a (100) cross sectional slab of thickness $a_0/2$, viewed along the ⟨100⟩ direction, at various instants of time. The initial velocity of the projectile had polar and azimuthal angles of 160° and 20°, respectively.

these figures, the local melt resolidifies with many atoms left on the surface, approximately 550 in this event; consequently, too few atoms are available to fill the lattice sites below the surface. Thus, as the solid-liquid interface sweeps inward toward the center of the cascade, free volume in the liquid is dragged with the interface until it coalesces to form a complex dislocation structure. This structure is seen clearly in Fig. 3, where the locations of atoms with potential energy greater than 0.4 eV are shown. These sites, which outline the core of the dislocation structure, extend to a depth of ~6 nm, which is approximately the depth of the melt. No isolated vacancies and only three interstitial atoms, which are located at the ends of long replacement sequences, remain at the end of the event. The small number of Frenkel pairs is due to the melt overrunning and absorbing all defects produced on the periphery of the cascade during the earlier displacement phase of the cascade. Thus, the simulations show that the primary defect production mechanism at

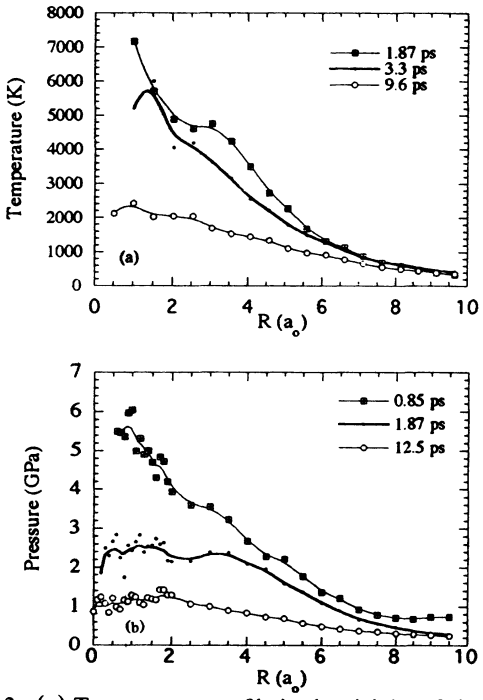

FIG. 2. (a) Temperature profile in the vicinity of the cascade at various times. Distance is measured radially from the center of energy of the damage. (b) Pressure profiles in the vicinity of the cascade at various times. The origin is the center of energy.

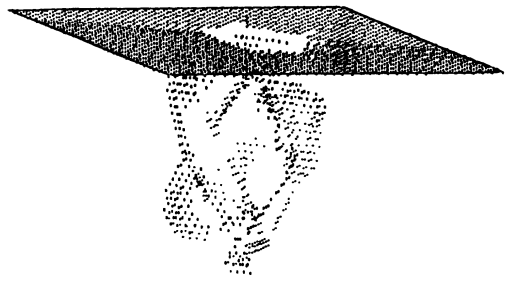

FIG. 3. Structure of the dislocation network as illustrated by the positions of atoms with potential energies ≥ 0.40 eV. The "hole" in the surface indicates the presence of adatoms which are not shown.

the surface can be far different than in the crystal interior, resembling the formation of voids or cracks during chill casting of metals more than the atomic collision processes described by radiation damage theory.

The high pressure in the cavity raises the possibility of defect production in cascades by interstitial loop "punching," as has been recently discussed [3,4]. The minimum pressure required for loop punching is several tenths of the shear modulus [14,15], which for Au is ≈ 28.5 GPa in the ⟨110⟩ direction. Figure 2(b) shows that the pressure in the solid medium surrounding the molten core never exceeds ≈ 2–3 GPa; thus loop punching is neither expected nor found in this event. The absence of loop punching can probably not be attributed to the proximity of the surface since the pressure is only slowly relieved by viscous flow. Moreover, similar pressures and lack of loop punching were observed in a 10 keV simulation event in the interior of the crystal [16].

The sputtering yield for the 10 keV event was four atoms, three surface atoms, and one atom from one plane below, and all sputtered atoms were emitted within ≈ 0.2 ps of initiating the cascade event. The average sputtering yield for 10 keV Au bombardment of Au is 20 [17]; however, this difference is not significant, owing to the large variance in the sputtering yield per ion [18]. The Au atom in this event, moreover, penetrated to a depth of 5.1 nm as compared to the mean range for 10 keV Au of 2.8 nm [19]. Possibly quasichanneling was involved. No influence of the thermal spike on sputtering is apparent in this event. In a 20 keV event the penetration was less deep, and as illustrated in Fig. 4, the cavity intersected the surface and greatly influenced both the sputtering yield and the surface morphology. The sputtering yield was 84 atoms. 52 atoms were emitted within the first 0.2 ps, with 41, 10, and 1 of these coming from the surface, second, and fifth layers, respectively. The remaining 32 sputtered atoms were emitted over the next ≈ 7 ps, and of these, 9 came from the surface and 10, 8, 2, 1, and 2 atoms came from successively deeper layers. Thermal spikes clearly played a role in this event; however, the highly disturbed surface morphology revealed in Fig. 4 indicates that this role is complex and not easily treated by analytical methods. Although the present 20 keV simulation reveals the nature of thermal spike sputtering, many events would be required to determine how typical this event is or other details of the sputtering process.

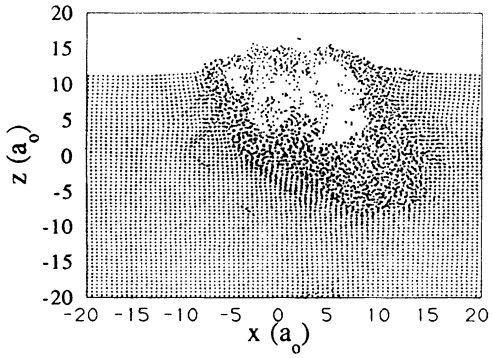

FIG. 4. Locations of atoms within a (100) cross sectional slab of thickness $3a_0/2$, viewed along the ⟨100⟩ direction, 3 ps after the impingement of a 20 keV Au atom. The initial velocity of the projectile had polar and azimuthal angles of 155° and 20°, respectively.

Experimental investigations of 10–40 keV Bi irradiation of Au by Jäger and Merkle, using transmission electron microscopy (TEM) [20], provide strong evidence for the validity of the damage model suggested here. These studies revealed that, similar to the simulations, dislocation loops of vacancy character were produced within ≈ 7 nm of the surface by 10 keV ions. The number of vacancies in the larger loops (these comprise one-third of the loops) was $N \approx 300$ and $N \approx 1380$ for 10 keV Bi atoms and 20 keV Bi_2 molecules, respectively. These yields are much greater than those predicted by the Kinchin-Pease formula, $N_{KP} \approx 100$ for the lower energy cascade and $N_{KP} \approx 200$ for the higher, and they contrast sharply with results on defect production in bulk metals obtained from experiment [21] and from MD simulation [3,4,6,16] for which $N \approx 0.25 N_{KP}$. We obtained $N \approx 0.20 N_{KP}$ in a simulation of a 10 keV cascade in the interior of Au [16]. The present MD simulations provide a simple explanation for the high efficiency of defect production, namely, that the defects were produced by surface melting and viscous flow, as described above, and not by replacement sequences or other recoil events associated with the Kinchin-Pease formula. Since 554 atoms were transported to the surface, a maximum of 561 vacancies (including four sputtered atoms and three Frenkel pairs) can be found in a single dislocation loop. The TEM studies found no evidence for the production of interstitial atoms. The authors concluded that the interstitial atoms must have migrated to the surface [20], but the MD simulations indicate that they were never produced. Finally, the experiments of Jäger and Merkle showed that approximately one-fourth of the 10 keV ions created imagable loops. Why so few ions produced loops is surprising since surface melting, as described here, should have a yield of unity. This discrepancy is not a question of statistical fluctuations, like sputtering yields, since melting is a collective phenomenon involving hundreds of atoms, and all events should behave qualitatively alike. Some ions may have channeled and penetrated too deeply to produce a surface melt, but more likely the unobserved loops slipped to the surface before they could be imaged in the TEM. *In situ* measurements in a scanning tunneling microscope might be able to clarify this point since loops that slip to the surface would image as craters. Recent irradiations of Pt with 5–10 keV Xe ions, in fact, produced such craters with each crater bounded by a ridge of adatoms [22].

The MD simulations have obvious implications for many other studies of radiation damage using keV ion irradiations and for the field of ion beam modifications of

materials. For TEM investigations, the ion energy is usually selected so that the range of the particle is 10–30 nm, presumably so the damage will extend well below the surface, unlike the experiments of Jäger and Merkle. A macroscopic model shows, however, that melting and viscous flow depend predominantly on the square of the ratio of the damage energy deposition near the surface, i.e., on the nuclear stopping power, to the melting point of the material [16]. Therefore, like sputtering [23], the yield will be largest when the nuclear stopping power achieves its maximum, and this occurs approximately at those energies employed for TEM experiments. For the Au event described here, 10 keV was distributed over a depth of ≈ 7 nm, so that the energy per unit length was $\approx 1.5\times10^3$ eV/nm. For 50 keV Kr bombardment of Cu, for which loops were observed *in situ* in a TEM during 10 K irradiation [24], the nuclear stopping power at the surface is nearly twice as high, $\approx 2.5\times10^3$ eV/nm. Viscous flow at surfaces is also important for ion beam modifications of materials. For example, it provides a mechanism for stress relief in irradiated thin films [25], and it is a source of many adatoms, which can subsequently redistribute by surface diffusion or cause surface irregularities.

In summary, the current simulations reveal that defect production near surfaces can be very much different in character than in the interior of a material. Although local melting is important for bulk cascades, we showed here that it has special significance at the surface where viscous flow can lead to the formation of vacancy dislocation loops, stress, and many surface adatoms. As local melting appears to be an important feature of cascades in many materials, we expect that the surface phenomena observed in these simulations are quite common. Extensive cavitation and thermal spike sputtering, on the other hand, may require very high energy densities, and may be restricted to materials like Au.

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