Heat spike effect on the straggling of cluster implants

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Recent experiments have shown that when gold atom clusters bombard copper with an energy of 10 keV/atom, the mean range of the gold atoms is independent of the cluster size, but the straggling (broadening) of the depth distribution is an increasing function of the cluster size. The same set of experiments did not show this effect when the target was amorphous Si. Using molecular dynamics computer simulations we have studied this effect by simulating Au cluster bombardment of Cu and Si with energies 1–10 keV/atom. We found that in Cu, the mean range is not fully independent of the cluster size, but the dependence on cluster size is so weak it is hard to observe experimentally. On the other hand, we found a strong enhancement of the straggling in Cu, but not in Si, in agreement with the experiments. By following the time dependence of the straggling we show that this is due to the massive heat spike effects which are present in Cu but not Si.

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I. INTRODUCTION

The use of slow cluster beams, where the energy per atom is a few keV/atom or less, is becoming an important tool in thin film deposition,[1] secondary ion mass spectrometry[2] and shallow junction formation.[3] The implantation of clusters into solids produces different phenomena compared to single-atom implantations, and theoretical knowledge of the subject is very poor because of the complex nature of it.

For slow ions the energy loss is predominantly due to elastic collisions between the atoms. The energy of cluster atoms is deposited in a small volume, and the deposited energy density can be huge. Thus the cluster impact can produce more localized damage than a single ion with comparable energy.[4] During the penetration into the material, the cluster atoms that have a mass greater than the target atoms mass experience nonlinear effects that are usually negligible for single-ion bombardment.[5,6] The nonlinearities arise from the fact that the cluster ions experience the influence of each other during the penetration and thus the environment in the material is different for each ion in the cluster. In implantation, the cluster breaks into single atoms quite rapidly, in tens of femtoseconds in the cases studied in this paper. The single atoms then continue penetrating. Thus the possible difference between the stopping of an atom in cluster and a single atom inside the matrix can cause a difference in the range of the ions compared to a single-ion implantation.

Using molecular dynamics computer simulations Shulga and Sigmund[7] have noticed that the stopping power per gold atom, when bombarding Au_{13} clusters, is noticeably smaller in silicon than for bombardment with single gold atoms. They suggested that this effect is due to the ''clearing-the-way'' effect, where the cluster atoms in the front of the cluster change the target atom configuration for the cluster atoms that come behind. This effect is clearly dependent on the size of the cluster and the mass ratio of the projectile atom and the target atom, so that heavier ions cause more clearing of the light targets. The decrease in the mean energy loss for clusters was also seen using larger Ar clusters.[8]

Recent experiments by Andersen *et al.*[9] show that the mean range of Au ions in copper is the same in Au_1 and Au_2 implantation with an energy of 10 keV/atom but the range profile is broader in the case of clusters; i.e. the straggling is larger. The same experiments show that the range profiles are identical for 44.3 keV/atom Au_1 and Au_7 when amorphous Si is used as a target.

Since the idea behind the ''clearing-the-way'' effect is quite general, it is not clear why this effect is not observed in the experiments of Andersen. One can also ask the question of why the straggling increases with cluster size in Cu, but not in Si. Heat spikes are known to be more long lived in dense fcc metals than in semiconductors,[10] but on the other hand heavy ions such as Pt and Bi clusters are known to produce large liquidlike zones in Si as well.[11,12] Large collision spikes have also been observed to affect the energy loss of ions when implanting Ag clusters in graphite.[13]

In this article we use molecular dynamics (MD) simulations to examine these questions. MD simulations can quantitatively predict range and straggling values, but most importantly allow for following the time evolution of ion movement and heat spikes on an atomic level. This enables definitely recognizing whether the straggling increase is a heat spike effect. Because the energies are such that the nuclear stopping undoubtedly dominates, MD can be expected to correctly describe the physics involved.

Paper is organized as follows. Sec. II describes the simulation method and the results and analysis are divided into Sec. III A for Cu targets and Sec. III B for Si targets. A short summary and discussion is given in Sec. IV.

II. METHOD

Simulations were carried out using a molecular dynamics code developed to treat collision cascades.[10] The target structure was either a copper or a silicon lattice with periodic boundary conditions in the *x* and *y* directions. The atom positions in the last two lattice planes in the negative *z* direction of the box were kept fixed, which mimics an infinite structure that absorbs the pressure and thermal waves. The positive *z* direction of the box was free to simulate the surface of the bulk, and thermal and pressure control were included on the other borders. The lattice constant was set to the 0 K value of the potential model used, and the cell temperature was set to zero. Gold clusters with one to seven atoms were given a qualitatively reasonable configuration, which was first heated and then relaxed to zero temperature. This procedure gives a stable cluster configuration suitable for this study. The size of the lattice varied from 20 000 atoms used for the implantation of 1 keV Au to 350 000 atoms used for the implantation of 5 keV/atom Au_7. For the simulations of 10 keV/atom Au_7 implantation in Cu, the lattice size was 1 048 576 atoms. The range profiles studied were not sensitive to the size of the lattice.

For the actual implantation, the cluster atoms were given the same energy per atom, so that the velocities of the different clusters were the same. The impact point was randomly chosen from the unit cell area of the lattice, and the clusters were randomly rotated before implantation. The direction of implantation was carefully chosen such that channeling effects were minimized. For that purpose we simulated the implantation of one gold atom into copper in several near-normal directions with MDRANGE.[14,15] MDRANGE is a program especially developed for a fast calculation of ion ranges by using simplified MD methods. It has been tested numerous times to give a good description of range profiles both compared to full MD calculations and experiments.[16–18] The direction chosen was the one with the smallest mean range. The direction was such that the polar angle was tilted 25° from the surface normal and the azimuthal angle around the surface normal was rotated 25° from the 001 surface normal of Cu. A polar angle of 25° and an azimuthal angle of 7° were used for implantations in Si. Clusters were then implanted into the target material, and the mean range (projected on the z axis) from the surface and the straggling of the range profile were calculated from a histogram of 90–800 implantations for 1–5 keV/atom Cu target and 5–10 implantations for the 10 keV/atom cases.

The many-body potential that was used for Au-Cu and Cu-Cu interactions was the enbedded-atom-mode (EAM) potential formulated by Foiles *et al.*[19] It has been found to describe the melting properties of Cu decently[20] and is a good choice for describing ion beam mixing,[21] both of which are important for heat spike effects. The potential has been previously found to be good for cascade studies.[10,22,23] For the Au-Si interaction DMol,[24] Au-Au Morse,[25] and Si-Si Tersoff[26] potential models were used. For each potential, the repulsive part describing the energetic short-range interactions was the Ziesler-Biersack-Littmark (ZBL) interatomic potential,[27], which was smoothly joined to the many-body part. The electronic stopping was described as nonlocal frictional force, and the SRIM96 (Refs. 27 and 28) stopping powers were used for this purpose.

III. RESULTS AND ANALYSIS

A. Copper

Results from the implantations are given in Table I. One can see that for the energy of 1 keV/atom, the mean range is an increasing function of cluster size, but the difference between the one-atom and seven-atom cluster cases is less than 5 Å (an about 40% increase over the one-atom case). The straggling increases more rapidly, and the increase is about 130% between these two extremes. For the energy of 5 keV/atom the increase in mean range is about 10% between the extremes and the increase in straggling is about 80%. These results show the same effect in straggling that has been observed in the experiments, although the experiments were done with 10 keV/atom, which is a too high energy for full MD calculations with decent statistics in the range profile. The 10 keV/atom simulations done in this paper are done mainly to compare the effects between different materials as discussed in Sec. III b and have poor statistics.

TABLE I. Mean ranges and stragglings as measured from the surface of Au_n clusters implanted in Cu. MD means a full MD run, and N_{clus} is the amount of ions, n, in the cluster.

E/atom	N_{clus}	Method	$\overline{R}$	Straggling
1 keV	1	MDRANGE	11.5 ± 0.1	1.9 ± 0.1
	1	MD	12.1 ± 0.1	2.9 ± 0.1
	2	MD	13.8 ± 0.1	4.1 ± 0.1
	3	MD	15.2 ± 0.2	4.9 ± 0.1
	4	MD	15.8 ± 0.2	5.0 ± 0.1
	7	MD	17.0 ± 0.3	6.6 ± 0.2
5 keV	1	MDRANGE	24.5 ± 0.1	6.8 ± 0.1
	1	MD	24.8 ± 0.7	6.7 ± 0.4
	3	MD	28.0 ± 0.9	8.7 ± 0.4
	7	MD	28.0 ± 1.4	12.0 ± 0.7
10 keV	1	MDRANGE	29.8 ± 0.1	9.8 ± 0.1
	7	MD	37.0 ± 2.6	18.0 ± 1.3

We calculated the stopping (or the slowing force) $S=F=ma=m\,d^2r/dt^2$ acting on a single atom with an energy of 5 keV and on an atom in the cluster (Au_7) with the same energy and averaging over the ions. The result was that the stopping of an atom in the cluster is about 10–40% smaller than for a free atom. Thus the ions travel longer distances when they are in the cluster. After the cluster breaks down to single atoms, these atoms continue as free atoms. For the 5 keV Au_7 clusters, the breakdown happens within the first 50 f after they hit the surface, but the atoms do not stop penetrating the target material until about 1000 f. As the energy increases, we suspect that this ratio between the two time scales decreases, and so the effect of the different stoppings would be smaller. Thus the mean range would also be close to the same value for small clusters and single atoms. The difference in stopping powers between a cluster atom and a free atom also has an influence on the straggling. If one atom in the cluster gets free at some stage of the penetration, it slows down more rapidly than the atoms inside the cluster, but the cluster atoms affect each other so that the individual atoms can even be temporarily accelerated during the penetration. All together these factors are expected to increase the deviation of the atoms in the early stage of the penetration. This does not explain the large final differences in the straggling (seen in Fig. 2), but shows how complicated the situation is when a cluster is penetrating the material.

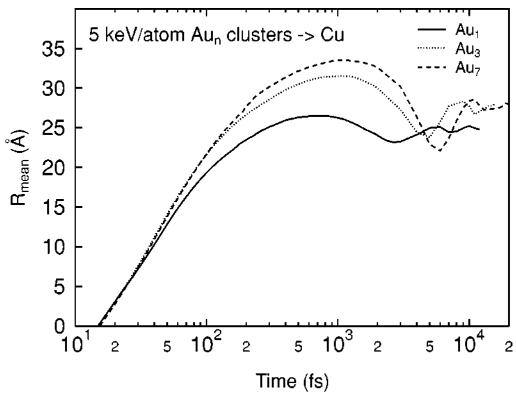

FIG. 1. Mean range values of Au_n clusters implanted into Cu with energies of 5 keV/atom as a function of time.

We studied the time evolution of the mean range and straggling for Au_1, Au_3, and Au_7 with an energy of 5 keV/atom. The results can be seen in Figs. 1 and 2. The fluctuations in the mean range are the results of a liquid volume created by the heat spike, which tries to expand toward the surface. The results for clusters are very much the same as for the implantation of single atoms, except for the slightly larger mean ranges for the clusters. Figure 2 shows that the straggling differences between the clusters compared to the single-atom values, however, start to grow rapidly after the first 100–200 fs and continue growing up to 3000–4000 fs. The straggling is a clearly increasing function of the cluster size.

We looked at the number of ''liquid'' atoms (the atom was labeled ''liquid'' when it had an energy above 0.16 eV) in the simulation box as a function of time and noticed that the time where the straggling saturates is very much correlated to the time where the heat spike starts to cool down. This observation was supported by a visual inspection of the simulation, which showed that the heat spike starts to include a large amount of energetic Cu atoms after 200 fs, reaching a maximum at 400–600 fs. The phase where a liquid volume can be clearly observed starts from 800 fs. The volume of the liquid, surrounding the implanted Au atoms, stays the same until it starts to decrease and cool down at 3000–4000 fs.

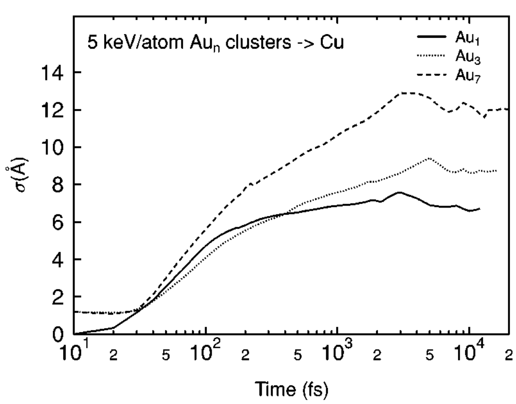

FIG. 2. Straggling values of Au_n clusters implanted into Cu with energies of 5 keV/atom as a function of time.

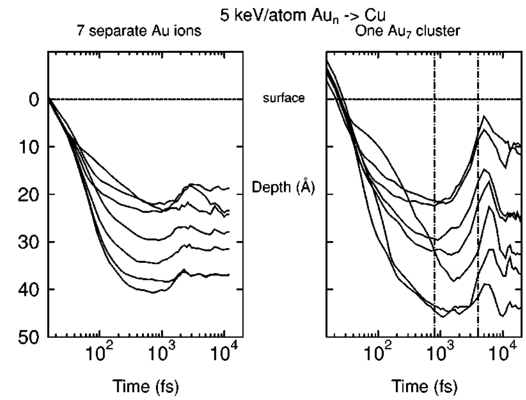

FIG. 3. The time development of z coordinates of Au ions calculated from the surface. The left picture shows implantation of seven independent Au ions, and the right one shows implantation of one Au_7 cluster. The energy per atom is 5 keV. The time where the heat spike starts and the time where it starts to cool down are marked in the right picture. The scaling is the same for both pictures.

The time developments of z coordinates of Au ions are compared in Fig. 3 between the implantation events of seven single Au ions and one Au_7 cluster. The right part of Fig. 3 shows the situation where the implanted Au ions are surrounded by the liquid volume, thus moving upwards during the enlargement of this liquid volume (heat spike). During this heat spike (marked in Fig. 3), the Au ions are spreading in every direction and this results in a growth seen in the straggling curve of Au_7 implants in Fig. 2. The lattice size used in the simulations shown in Fig. 3 was 94 Å in each direction when 5 keV/atom Au_1 was implanted and 159 Å for 5 keV/atom Au_7 clusters. We tested that the size was big enough and did not affect the results.

Combining the results of Figs. 1–3 for Au_7 clusters, during the heat spike time interval 200–4000 fs, the value of the mean range does not change at all compared to its final value and the differences between the mean values do not change. The differences between the straggling values is within the statistical error limits before the spike, but increases clearly during the spike and stays the same to the end. This shows that the increasing straggling is an effect caused by atom mixing in the liquid volume. .

B. Silicon

In Si collisions cascades have been found to break down to subcascades at much smaller energies than those in dense fcc metals. This is in part because of the low mass of Si and in part due to the open crystal structure of Si which makes recoils move farther than in fcc metals, even when the mass is the same.[10,29] Hence, even though liquidlike pockets do form in Si,[30] they are much smaller and cool down faster than in Cu, and there is both little time and space for lattice atoms to move in the small liquidlike zones. Thus it is unlikely that the straggling enhancement observed in Cu would be significant in Si. However, to check this argument we have carried out simulations of the implantation of Au_7 clusters with 10 keV/atom in a nonchanneling direction into

TABLE II. Same as Table I, but for a crystalline Si target.

E/atom	N_{clus}	Method	$\overline{R}$	Straggling
10 keV	1	MDRANGE	145.5 ± 0.4	42.0 ± 0.2
	7	MD	140.3 ± 7.2	37.6 ± 3.6

crystalline Si for a comparison to Cu. Although the experiments used *a*-Si as a target, we want to show the qualitative difference between Cu and Si materials. The situation in a-Si should be the same as in *c*-Si because the densities are about the same and hence the collision cascades similar as well. The implantation angle was again selected to minimize channeling. We simulated only five implantation events, because we are only interested in a comparison of the behavior for same-sized clusters in different materials and do not need accurate statistics for the values themselves. Every event showed the same behavior.

Table II shows the values for mean range and straggling for an implantation profiles of Au_1 and Au_7 clusters. One can see that the values are close to each other, where a large difference was observed contrary to the behavior in Cu.

Figure 4 shows the comparison of mean range and straggling values as a function of time for Au_7 clusters implanted into Cu and Si. The lack of heat spikes in Si shows clearly in Fig. 4, as the mean range does not oscillate. Figure 4 also shows that the growth in straggling has only one phase in Si, but two phases in Cu because of the heat spike. Figure 5 shows the z trajectories of the ions from Au_7 cluster implanted into Si. Comparison of Figs. 3 and 5 shows the reasons for the different straggling curves in Fig. 4. The Au atoms in the clusters penetrate silicon until they have lost all their energy at some depth and stay there.

IV. DISCUSSION AND CONCLUSIONS

For the 10 keV/atom implantations in both Si and Cu we could not perform a complete quantitative comparison between the experimental[9] and simulated range profiles, because the experimental information on depth was only given in units of Ratherfood back scattering (RBS) channels. However, the location of the surface was known from the experiments, and by scaling the areas we found that the shapes of the simulated and experimental ranges profiles were in very good agreement for all cases of single-ion bombardment.

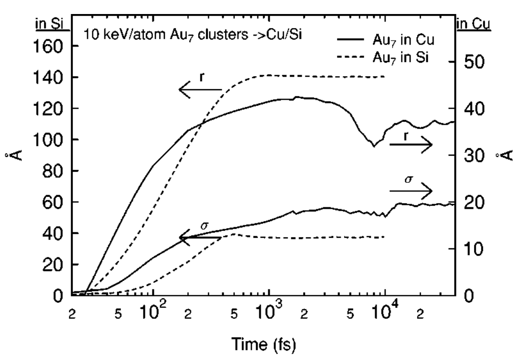

FIG. 4. Mean range values (r) and straggling values (σ) of Au_7 clusters implanted into Cu and Si with energies of 10 keV/atom as a function of time. Note that the curves have different scales on the y axis. The left scale is for the Si target, and the right scale is for the Cu target.

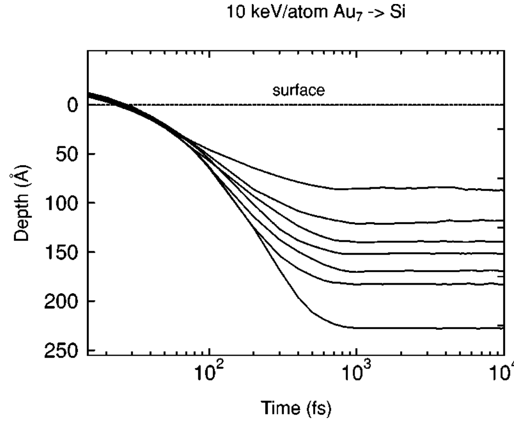

FIG. 5. The time development of z coordinates of Au ions calculated from the surface. The picture shows implantation of one Au_7 cluster in Si. The energy per atom is 10 keV.

Although direct comparison was not possible, in the experiments the broadening was about 20% between Au_1 and Au_2 at 10 keV/atom, while in our simulations it is 30% between Au_1 and Au_3 at 5 keV/atom. This clearly shows that the observed broadenings are of comparable magnitude and, thus, that the heat spike effect we observe explains the experimental broadening.

For the case of 30 keV/atom Au bombardment of Si the experiments report a projected range of 280 Å, and we obtain from an MDRANGE simulation 260 Å. The good agreement in both the shapes at 10 keV/atom and mean range at 30 keV/atom give us confidence that our simulations can predict the ion penetration process well.

Our simulations of implanting small gold clusters in copper, with the same velocity per atom, shows the experimentally observed increase in straggling in the range profile. We have also recently observed the same effect in Au irradiation by 25-keV Au_n ($n = 1-1000$) clusters.[31]

The same simulations show also an increase in the mean range values, which was not observed in the experiments. This increase results from a decrease in the average stopping power per gold atom in clusters, compared to the single-atom value. This could be interpreted as the proposed clearing-the-way effect,[7] but no clear evidence of the reason was found because of the fast breaking down of the clusters. Our result that the ratio between mean energy loss for atomic and cluster bombardment is lower for 5 and 10 keV/atom than for 1 keV/atom is in agreement with the findings of Shulga and Sigmund.[7] Since at 10 keV/atom the difference in the mean range is small, it is not surprising it has not been observed experimentally (note that the experiments in Cu involved 10 keV/atom Au_1 and Au_2,[9,32] so the experimental difference is going to be much less than what we observe between 10 keV/atom Au_1 and Au_7).

Simulations of cluster bombardment of silicon show that the straggling and mean range values are the same for clusters and single ions, as observed in the experiments.[9]

To conclude, our simulations show that the experimentally observed increased straggling of gold cluster implantation range profiles in copper is due to atomic mixing in the heat spike. We also show that in Si no increase of the straggling is expected because the heat spikes in Si are small and short lived.

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