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Capacity of graphite's layered structure to suppress the sputtering yield: A molecular dynamics study

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ABSTRACT

20–120 keV C_{60} bombardment on graphite and 20 keV C_{60} impact on diamond are studied by classical molecular dynamics (MD) simulations. The number of atoms ejected from graphite after a 20 keV C_{60} impact is found to be much smaller than that from diamond. By analyzing the microscopic sputtering process, we find this difference is due to the combined effects of graphite's low number density and layered structure. These two features of graphite make the pressure waves during the spike stage much weaker and the crater rim much more stable, compared to the case of diamond. While the role of atomic density on sputtering has been discussed in previous studies, effect of layered structure has not gained much attention yet. To affirm this effect and exclude the influence of density, we have also simulated C_{60} impact on an amorphous carbon (a-C) target whose density is very close to that of graphite. The yield of a-C is higher than that of graphite, certifying the capacity of graphite's layered structure to suppress the sputtering yield.

1. Introduction

In recent years, cluster ion beams have attracted increasing attentions for their capacity to enhance the ejection of materials in secondary ion mass spectrometry (SIMS) analysis [1–3]. It is also found that nanoscale surface modifications can be realized by energetic gas clusters [4–6]. In the field of ion–solid interactions, cluster bombardment on a solid provides a typical example of nonlinear sputtering, which has many interesting features such as a huge sputtering yield, nanoscale crater production and cluster emission. Developments of surface techniques using cluster beams demand deep understanding of nonlinear sputtering. However, while ion-bombardment-induced sputtering has been clearly elucidated by linear-cascade theory [7], nonlinear sputtering induced by cluster impact is still not fully understood. This issue is not only of high applied interest, but also of fundamental importance in cluster–solid interactions.

Much progress has been made on this topic [8–21] during the last few years. One of the significant advances is that according to MD simulations [10,12] and fluid dynamics calculations [11], the cluster-induced sputtering process can be described as a spike phenomenon in the energized zone under the impact point. In detail, overlap between the collision cascades induced by the constituents of the incident cluster usually introduces a high-energy-density region near surface. Then energy and pressure waves emanating from this spike region are able to drive many hot atoms to leave the surface as a melt (or gas) flow, increasing the sputtering yield greatly [13]. Based on it, Russo et al. [17,18] have developed a mesoscale energy deposition footprint (MEDF) model to predict the sputtering yield induced by cluster bombardment. This model gives a reasonable description of the dependence of sputtering yield on target's number density and cohesive energy. Besides the flow mechanism, large clusters [12,22] or intact molecules [19] ejected from the crater rim also often contribute significantly to the enhancement of sputtering yield, as shown by MD simulations.

While past researches on sputtering are most focused on targets of isotropic crystals like Au [8,9,14], Ag [16], and molecular crystals [19,20], anisotropic targets like graphite attract little attention. Experiments of 50–600 keV C_{60} bombardment on graphite [23] have been carried out, but the authors focused on the damage in graphite rather than sputtering. A number of MD simulations of energetic C_{60} bombardment on graphite have been performed by Webb and co-workers [24–26], but most of them are used to study fullerene fragmentation or cluster ranges. Krantzman et al. [27]

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simulated the bombardment of 20 keV C_{60} on graphite and found that the sputtering yield is negligible. They suggested that this is possibly because the open structure of graphite allows the incident cluster to penetrate deep into the target leaving little energy near surface. However, this reason is somewhat in contradiction to some previous experimental and simulated results [23,28] which imply that 20 keV C_{60} still stops close to the surface. Additionally, the energy (20 keV) is too low to provide a dense energy deposition, and simulations of sputtering on graphite induced by more energetic cluster impact are still absent.

The aim of this work is to provide microscopic insights into nonlinear sputtering on graphite using classical MD simulations and figure out why the sputtering yield is small. For comparison, cluster impact on diamond and a-C are also simulated. These three substrates have similar cohesive energy and melting point, but are different in lattice structure and/or density. C_{60} is chosen as the incident cluster for its wide applications in SIMS experiments [3], and plenty of simulations of C_{60} impact on materials other than graphite have been performed by Garrison and co-workers [16–19]. The present simulations show that the sputtering yield from graphite induced by 20 keV C_{60} bombardment is obviously smaller than that from diamond. We find that besides the low number density, the layered structure of graphite also contributes for this small yield by weakening the outward pressure waves in the heat spike and keeping the crater rim stable. This conclusion is further proved by our simulations of C_{60} bombardment on an a-C target with the same number density as that of graphite.

2. Description of simulation method

MD simulation has been a powerful method to model radiation effects, including sputtering for its capacity to give insights into evolution of atomic displacement cascade within several picoseconds after impacts of particles, which is hard to be detected in experiments. Detailed descriptions of the basic MD algorithms can be found elsewhere [29] and its applications in sputtering have already been reviewed by Urbassek [30,31] and Garrison [32].

In this work, normally incident C_{60} bombardments on carbon material surfaces are performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [33,34]. Information of the three targets are listed in Table 1. A sample of a-C is formed by quenching the liquid, and the resulting structure has been proved to be consistent with experimental properties of a-C [35]. The sample sizes are chosen to make sure that few collision events happen at boundaries. C_{60} molecule is positioned initially at a distance of 3 nm above the surface and has negligible interactions with the substrate. C–C interactions in the whole system are described by the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [36]. We smoothly connected the Ziegler–Biersack–Littmark (ZBL) universal repulsive potential [37] with the AIREBO potential at short interatomic distances using a Fermi-like function [38] to model close collisions between energetic carbon atoms. The X and Y boundaries of the system are periodic and the Z boundaries free. Temperature scaling of 0 K with the Berendsen method [39] is applied at the X and Y boundaries to dissipate the heat. As electronic stopping is not dominant in low energy impacts and graphite is a good electronic conductor, effects of electronic excitations are ignored.

Before performing collision events, we relax the whole system using a conjugate gradient energy minimization algorithm. Incident energies of C_{60} are 20, 60, 120 keV for graphite target and 20 keV for diamond and a-C. Each simulation is run for 5.5 ps, after which no more atoms are found to be ejected. A variable time step is used according to the fastest moving particles in the system. As the large number of atoms and short time step make the simulations computationally demanding, only three simulation runs with different impact points are performed for each energy and target to obtain statistical data. However, previous studies have proved that fluctuations in sputtering yields obviously decrease as incident cluster's size increases [12,9]. For large clusters like C_{60}, a few trajectories are capable of providing representative results [27,17,32].

3. Results and discussion

3.1. Total sputtering yields

Results of the sputtering yields per C_{60} are listed in Table 1. It is obvious that the sputtering yield on graphite increases with cluster energy at first (60 keV) and then decreases at a higher energy (120 keV). It is easy to understand this energy dependence. As incident energy increases, interactions between atoms become stronger, leading to more drastic collision cascades near surface and thus more atoms released to vacuum. On the other hand, projectiles with higher energies prefer to travel deeper into the sample, depositing less energy at surface. These two effects compete with each other and ultimately create a comparatively higher sputtering yield at 60 keV. It can be expected that the yield would continue decreasing if the energy increases after 120 keV. A similar variation trend of sputtering yield along with the cluster energy has also been found in experiments and simulations of sputtering of e.g. Au crystals [14,9].

Table 1 also shows that simulated sputtering yield on graphite due to 20 keV C_{60} impact is much smaller than that on diamond, in line with the results of Krantzman et al. (Y = 254 for diamond and Y = 5 for graphite) [27]. They attributed this difference to graphite's open lattice which allows the incident projectile to penetrate deep into the sample. However, other studies showed that the maximum range of 20 keV C_{60} in graphite is only about 30 Å [23,28,25], implying that the incident fullerene still stops near surface. To resolve this conflict, in the next section we will analyze the microscopic sputtering process and provide a reasonable explanation.

3.2. Sputtering process

3.2.1. Energy deposition

When a high-energy cluster normally bombards solid surface, it will soon fragment into small pieces (usually singe atoms) which are subsequently slowed down in elastic collisions with target

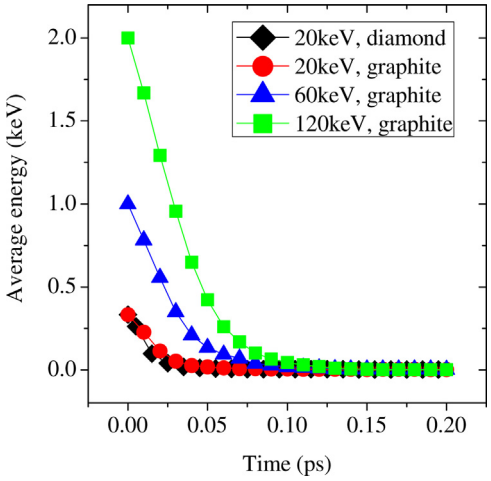

Fig. 1. Average kinetic energy of incident atoms as a function of time after C_{60} bombardment on diamond and graphite at 0 ps. Each curve is an average of three simulation runs.