Applied Surface Science 435 (2018) 65–71

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Molecular dynamics simulations with electronic stopping can reproduce experimental sputtering yields of metals impacted by large cluster ions

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ARTICLE INFO

Article history:
Received 23 September 2017
Received in revised form 2 November 2017
Accepted 9 November 2017
Available online 11 November 2017

Keywords:
Molecular dynamics
Sputtering
Cluster ions
Electronic stopping

ABSTRACT

An unsolved problem in research of sputtering from metals induced by energetic large cluster ions is that molecular dynamics (MD) simulations often produce sputtering yields much higher than experimental results. Different from the previous simulations considering only elastic atomic interactions (nuclear stopping), here we incorporate inelastic electrons–atoms interactions (electronic stopping, ES) into MD simulations using a friction model. In this way we have simulated continuous 45° impacts of 10–20 keV C_{60} on a Ag(111) surface, and found that the calculated sputtering yields can be very close to the experimental results when the model parameter is appropriately assigned. Conversely, when we ignore the effect of ES, the yields are much higher, just like the previous studies. We further expand our research to the sputtering of Au induced by continuous keV C_{60} or Ar_{100} bombardments, and obtain quite similar results. Our study indicates that the gap between the experimental and the simulated sputtering yields is probably induced by the ignorance of ES in the simulations, and that a careful treatment of this issue is important for simulations of cluster-ion-induced sputtering, especially for those aiming to compare with experiments.

1. Introduction

When bombarding a solid, large cluster projectiles (*e.g.* C_{60} or Ar_n ions) can induce a drastic ejection of materials from the solid surface. This phenomenon, usually termed spike sputtering [1,2], has attracted increasing attentions in recent years for its great potential applications in chemical analysis based on secondary ion mass spectrometry (SIMS) [3–5] and nanoscale surface modifications [6–8]. Developments of these microscopic surface techniques based on cluster ion beams demand a comprehensive and deep understanding of cluster–surface interactions. However, as sputtering usually occurs at a space–time scale of nm–ps which is still inaccessible with current experimental techniques, the atomic-level dynamics of the sputtering process is still not fully understood.

In recent decades, MD simulation has been widely used [9–18] in research of sputtering for its capacity to provide single-atom level information of the whole sputtering process, and many insightful results have been obtained using this method. Many simulations [9–13,18] have shown that a cluster ion produces a high sputtering yield mainly by introducing a high-energy-density zone (spike) near the surface. More specifically, the incident cluster usually fragments into single atoms immediately after bombarding the surface [18], and each of these energetic components is able to introduce an atomic collision cascade along its trajectory. Then these cascades overlap with each other, causing a local melting and sometimes even a "microexplosion" [9] near the surface, which finally leads to a violent ejection of materials. However, the aforementioned investigations only simulated single cluster bombardments on a flat surface (sputtering yield was calculated as an average of independent bombardment events), while in experiments the surface would actually experience countless ion impacts (usually 10^{12}–10^{16} ions/cm^2). To address the influence of this discrepancy, Russo et al. [19] established a novel protocol to model multiple cluster impacts on a solid in MD simulations. Using this method, Paruch et al. found that for large clusters like C_{60}, with an increasing projectile dose the sputtering yield would increase or decrease depending on the incident angle. This outstanding study, which shows that the development of the surface topography has a significant influence on the calculated sputtering yields, reminds researchers that in order to compare with experiments, multiple impacts rather than a single impact should be simulated.

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https://doi.org/10.1016/j.apsusc.2017.11.080
0169-4332/

Although MD simulation has been a powerful tool to investigate spike sputtering, there still exist some obvious discrepancies between simulated and experimental results, especially in sputtering yields. For instance, Sun et al. [20] experimentally measured the sputtering yields of Ag bombarded by 10, 15 and 20 keV C_{60} projectiles. The results were 47, 98 and 144, respectively, much smaller than the corresponding simulated yields (174, 327 and 482, respectively) [21]. The authors mainly attributed this discrepancy to two factors [20]: (1) in the simulations the clusters normally (0°) bombarded the metal whereas the experiments were performed at an incident angle of 40°, and studies of C_{60}–Ag sputtering system [21,22] have shown that the sputtering yield decreases with an increasing incident angle as more energy are reflected. (2) In the simulations only one single impact on a flat surface was modeled and the sputtering yield was an average of tens of independent impacts, whereas in the actual experiments the final sputtering yield was a result of continuous multiple bombardments which would inevitably make the surface quite rough. However, these two reasonable factors are not sufficient to explain the aforementioned discrepancy, as implied by a further study. MD simulations [22] showed that the sputtering yields of Ag induced by multiple 20 keV C_{60} bombardments at 0° and 70° were 342 ± 17 and 258 ± 14, respectively. We can infer that the yield at 45° should locate between these two values, *i.e.* ~300, which is still much larger than the experimental result (144). This gap means that even the two factors (impact angle and multiple impacts) mentioned above have been adequately addressed, simulations still cannot reproduce the experimental yields, implying that some important factors are missing in the previous simulations of C_{60}–Ag sputtering system.

We suggest that taking electronic stopping (ES) into account in MD simulations of spike sputtering might provide results closer to the experimental yields. ES refers to the energy loss through inelastic interactions between the electrons and the atoms in the materials under irradiation. It is a subtle but important issue in ion–solid interactions [23], but nearly all the previous simulations of keV large cluster (like C_{60} or Ar_{100}) bombardments on metals [15–17,21,22] have ignored it. Our idea was inspired by the previous works on spike sputtering of Au induced by small Au clusters [11,13,24], which showed that MD simulations with ES were able to produce sputtering yields close to the experimental findings. On the contrary, if ES was not considered, the simulated yields were much higher than the experimental results [13,24], quite similar to the case of C_{60}–Ag sputtering system.

In this paper, we use MD simulations with ES to model multiple 45° 10–20 keV C_{60} impacts on a Ag crystal, exploring whether the difference between the experimental and the simulated sputtering yields is caused by ES. The influence of ES on the atomic motions was introduced by a simple friction model [25]. The calculated yields are reported and compared with the experiments. To verify the universality of the effect of ES on spike sputtering, we further expand our research to sputtering systems of C_{60}–Au and Ar_{100}–Au, and obtain quite similar results. Additionally, although our simulations focus on spike sputtering from metals, the cases of linear sputtering and nonmetals are also discussed.

2. Method

We display our simulated model in Fig. 1. All the snapshots of the atoms in this paper were obtained by the visualization tool OVITO [26]. All the MD simulations were performed with LAMMPS [27]. A simulation box (the black box in Fig. 1(b) and (c)) containing a crystal of fcc (111) Ag with a size of $202 \times 200 \times 99$ Å^3 (~235,000 atoms) was created. The sample size was large enough to contain all the atomic collisions beneath the surface during the whole process. (111) face instead of (100) was chosen for coincidence with the experimental setup [20]. The *X* and *Y* boundaries of the system were periodic and the *Z* boundaries were free. C–C, C–Ag, Ag–Ag interactions were modeled by the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [28], the Ziegler–Biersack–Littmark (ZBL) universal repulsive potential [29], and the highly optimized embedded-atom-method (EAM) potential for Ag [30], respectively. As the energies of the Ag atoms knocked out by the incident C atoms (0.17–0.33 keV) were not very high and hence drastic Ag–Ag collisions were very rare in our simulations, we did not connect the EAM potential with the ZBL potential to model short-distance Ag–Ag interactions. This connection is usually required when the atoms are very energetic and the atomic distance can be very short, such as the case of MeV Au_n cluster bombardment on Au [10,11,13].

To compare with the experiments, we simulated tens of continuous 45° bombardments of keV C_{60} on the 202×200 Å^2 Ag surface. The protocol was inspired by the work of Russo et al. [19], but we used a simpler MD setup. First, a thermodynamic-equilibrium sample was prepared by relaxing the whole Ag system at 300 K for 10 ps using a Nose–Hoover thermostat [31]. Then, a C_{60} molecule (the white ball in Fig. 1) was created at a distance of 3 nm above the surface and had no interactions with the substrate. Before initiating a sputtering event (*i.e.* a bombardment), an impact point (x_0, y_0) was chosen randomly and the C_{60} was moved close to this location (but still above the surface), see Fig. 1(a). Then the C atoms in the C_{60} molecule were given a specific velocity at an angle of 45° according to the cluster's energy. This energetic cluster would bombard the sample and induce an intense ejection of materials.

Like the previous simulations [10,11,13,19,22], we applied a temperature scaling of 300 K with a Nose–Hoover method [31] at 4 "constant-temperature walls" (CTWs) to dissipate the heat, see the green region in Fig. 1. Each CTW contains 6 layers of atoms and is parallel to the *Z* direction. Different from the previous simulations [10,11,13,19,22], our CTWs were not fixed at the *X*–*Y* boundaries of the box but were dynamically located about 10 nm (half of the sample size) away from the impact point. For every new bombardment, a new impact point was chosen and the CTWs were moved to new positions. Thanks to the periodic boundaries, the spike sputtering always occurred at the center of the region surrounded by the CTWs (see the periodic images in Fig. 1(c)), no matter where the impact point was. Another important issue was the movement of the entire sample under continuous impacts (this movement is ignorable for one single impact), so we set the atoms in the 2 bottom layers along the *Z* direction to be rigid (red region in Fig. 1(a)) to prohibit the whole displacement.

Each sputtering event was simulated for 20.5 ps, with a timestep of 0.1 fs for the first 0.5 ps and another of 1 fs for the left 20 ps. This choice of timesteps was based on the velocities of the atoms during the sputtering process. We performed test simulations with a timestep of 0.1 fs for the whole 20.5 ps, and found no obvious differences in the results. Spike sputtering in our simulations usually peaked at ~2 ps and would completely end before 10.5 ps. The left 10 ps was long enough for the CTWs to cool down the free region (which received much energy from the incident C_{60}) to 300 K, as shown by Russo et al. [19]. For 20 keV impacts, another 5 ps was added to ensure a sufficient relaxation. When a sputtering event ended, the ejected atoms were removed and the process mentioned above was repeated, until a total of 40 (or 80) events were simulated.

The novelty of our work compared to the previous simulations [21,22] is that we have taken ES into account in the MD simulations. ES is a subtle topic, and how to accurately deal with it in atomistic simulations still remains an open challenge [23]. In this work we employed Nordlund's friction model [25] to incorporate ES into the simulations of spike sputtering. In detail, each atom with a kinetic