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Molecular dynamics simulations to explore the role of mass matching in the keV bombardment of organic films with polyatomic projectiles

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Abstract

Molecular dynamics simulations of the bombardment of a organic film on a gold substrate with Au and Au_2 projectiles have been performed in order to understand the role of mass matching in the mechanisms for energy transfer. There will be an effective energy transfer from the projectile to the substrate atoms if the atom impacts the substrate unimpeded by molecules in the organic film. When a projectile atom hits an organic molecule, the process of fragmentation absorbs its incident kinetic energy and it enters the substrate region with little energy left. With Au_2, there is a higher probability that one or more of the projectile atoms will hit a bare portion of the surface and initiate collision cascades with sufficient energy to result in ejection. Atoms in the top layer of the substrate lift off stable, intact molecules as they move out of the crystal.

Keywords: Molecular dynamics simulations; Organic overlayer; Sputtering

1. Introduction

Secondary ion mass spectrometry (SIMS) experiments have established that polyatomic projectiles have the potential to greatly increase the sensitivity of static SIMS [1–4]. Recently, there has been interest in the use of gold clusters with the goal of increasing the spatial resolution of ToF-SIMS imaging experiments [5]. We have performed molecular dynamics simulations of the keV bombardment of an organic film on a gold substrate with Au and Au_2 projectiles focused on understanding the importance of mass matching for the effectiveness of polyatomic projectiles.

Our previous simulations have provided mechanistic insights into how polyatomic projectiles affect both the yield of desorbed molecules and the damage to the sample as compared to atomic projectiles [7–10]. In order for molecules to be ejected intact, they must be gently hit from underlying substrate atoms that lift the molecule off the surface. For large molecules with multiple contact points to the surface, cooperative lifting in which several substrate atoms hit different parts of the molecule is necessary for the ejection of stable, whole molecules [9]. It is the upward motion of the substrate atoms in the top few layers of the substrate that is responsible for the production of ejected intact molecules. Consequently, the downward momentum of the bombarding projectile must be redirected into the upward momentum of the top few layers of substrate atoms. Our previous

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simulations demonstrated that when the mass of the atoms in the projectile is close to the mass of the substrate atoms, a greater amount of energy is transferred to the substrate atoms in the top layers close to the organic monolayer, which results in a higher yield of ejected molecules from the surface [6–8].

Simulations by Medvedeva et al. have compared the bombardment of a Si(1 0 0)-(2 × 1) substrate with Al_n ($n = 1, 2$) and Au_n ($n = 1, 2$) projectiles at an incident energy of 1.5 keV per atom and incident angles of 0 and 45° [9,10]. Au_2 showed the greatest increase in the number of high yield trajectories and the largest nonlinear enhancement of ejected large Si_n clusters. The Au_n projectiles, which have a lower incident velocity because of their higher mass, stayed near the surface for a longer period of time. The atoms in the Au_n dimer stayed together for a longer time than the atoms in the Al_n dimer, which increased the deposit of energy in the subsurface region.

In this paper, we examine the mechanisms for energy transfer that lead to the ejection of species from an organic monolayer on a substrate in which the substrate atoms and the projectile atoms have the same mass. We have performed molecular dynamics simulations of the keV bombardment of an organic film with normal incident Au and Au_2 projectiles at 2.0 keV per atom. Low yield trajectories occur when the projectile atom or (atoms) lose their energy upon impact of the organic monolayer. When a projectile atom impacts a region of bare substrate, it transfers its energy to the substrate atoms, and collision cascades develop underneath the organic monolayers that result in the ejection of intact molecules from the surface. With Au_2, there is a higher probability that one of the two atoms is able to penetrate into the substrate region with sufficient energy to eject intact molecules from the surface.

2. Method

The classical method of molecular dynamics simulations is used to study the system of interest and the application of this method is explained comprehensively elsewhere [11,12]. Briefly, the position and velocity of each atom as a function of time is determined by numerically integrating the classical equations of motion. The force on each atom is calculated from the gradient of the potential energy function, which is a careful blend of empirical pairwise potentials and sophisticated many-body potentials. The model system is composed of 13 *sec*-butyl terminated polystyrene tetramers physisorbed on a Au{1 1 1} substrate of 7350 atoms. Simulations were performed with normal incident Au and Au_2 projectiles at kinetic energies of 2.0 keV per atom.

3. Results

With Au_2 at normal incidence and incident energy of 4.0 keV, there are a few high yield trajectories in which a group of molecules around the impact point are ejected stable and intact from the surface. The only molecule that is ejected as fragments is the target molecule, which is hit directly by the incoming projectile. When Au bombards the same impact point at normal incidence at 2.0 keV, no stable molecules are ejected and two molecules are ejected as fragments.

Fig. 1 illustrates the mechanism that occurs for a typical trajectory with Au bombardment. Fig. 1a shows a side view of the initial impact of the projectile on the crystal. The Au projectile is represented by a red sphere. Polystyrene molecules that remain intact on the surface are shown by gray lines and balls. The two polystyrene molecules that are fragmented and ejected during the course of the trajectory are shown as green spheres. The positions of the Au substrate atoms are shown as gray points. In Fig. 1b, a lean-on tree illustrates the mechanism for energy transfer during the first 100 fs of this trajectory. In a lean-on tree, the positions of the projectile and the crystal atoms involved in energy transfer are shown as a function of time. The path of the Au projectile is shown by the red spheres. The Au projectile hits a polystyrene molecule upon impact and breaks a carbon–hydrogen bond, producing a hydrogen fragment (orange sphere) that moves downward into the substrate. At 40 fs, the Au projectile has penetrated into the substrate with little energy left because the majority of kinetic energy of the projectile is absorbed in the process of fragmentation. The paths of substrate atoms with kinetic energy greater than 50 keV are shown by the gray spheres. The projectile and the hydrogen fragment initiate collision cascades in the substrate that move downward deeper into the crystal without producing

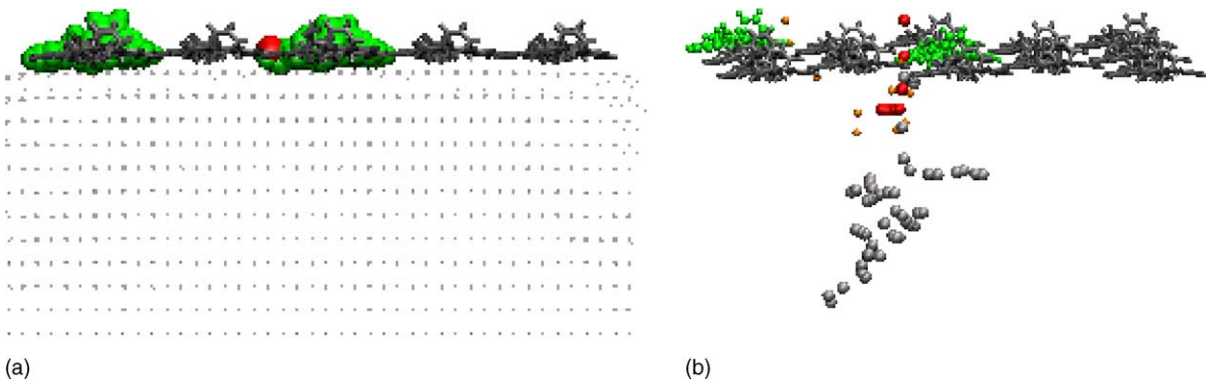

Fig. 1. (a) Snapshot at 10 fs of a trajectory with Au (side view). The incoming Au projectile atom is represented by a red sphere. The green spheres represent the two polystyrene molecules that are ejected as fragments. The Au substrate atoms are represented by gray points and the polystyrene molecules that remain intact on the surface are represented by gray lines and balls. The Au projectile impacts the polystyrene molecule in the target region and breaks it into fragments. (b) The corresponding lean-on tree for the trajectory in (a) illustrates the mechanism for energy transfer that results in the fragmentation and ejection of the two polystyrene molecules (green spheres). The orange spheres show the path of a hydrogen atom, which is produced as the Au projectile fragments the polystyrene molecule upon impact. The gray spheres represent the positions of substrate atoms that have kinetic energies greater than 50 eV. The collision cascades in the substrate do not produce any ejected species. The hydrogen atom eventually recoils in a collision with a substrate atom and moves upward through the crystal, fragmenting a polystyrene molecule (green spheres) as it exits into the vacuum.

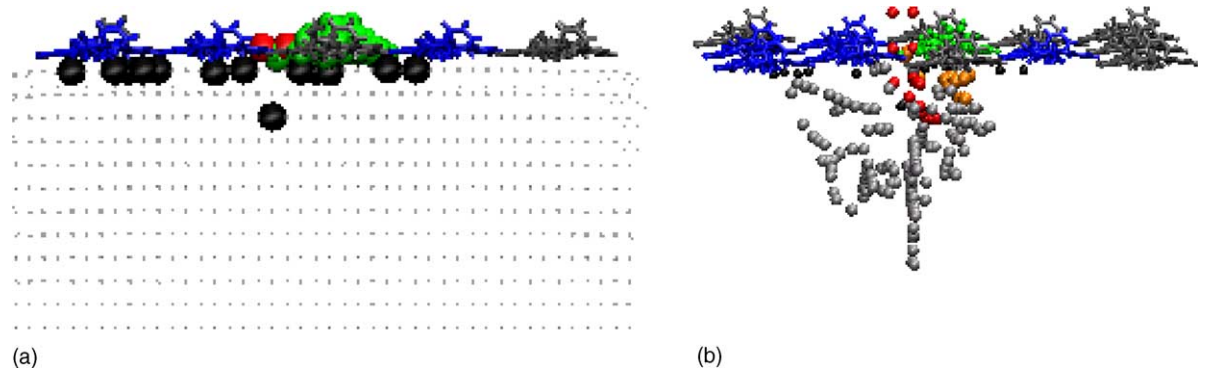

Fig. 2. (a) Snapshot at 10 fs of a trajectory with Au_2 (side view). The color scheme is the same as in Fig. 1a with two additions. The blue spheres represent polystyrene molecules that are ejected intact and stable and the black spheres represent ejected substrate atoms One of the projectile atoms (red spheres) hits a bare substrate atom, while the other projectile atom impacts and fragments the target polystyrene molecule (green spheres). (b) The corresponding lean-on tree for the trajectory in (a) illustrates the mechanism for energy transfer that results in the ejection of results in the ejection of five intact and stable polystyrene molecules, one fragmented polystyrene molecule and eleven substrate atoms. The position of the polystyrene molecules and ejected substrate atoms are shown in the figure at 0 fs. Gray molecules remain intact and whole on the surface, blue molecules are ejected intact and stable and green molecules are ejected as fragments. The black spheres represent substrate atoms that are ejected from the crystal. The position of each of the projectile atoms at 10 fs intervals is shown by the red spheres. One of the projectile atoms hits the target polystyrene molecule and produces a carbon fragment (orange sphere). The path of the carbon atom is shown by the orange spheres. Both the carbon atom and the other projectile atom initiate collision cascades in the substrate. The gray spheres represent substrate atoms that have kinetic energies greater than 50 eV. The collision cascades in the substrate produce ejected substrate atoms (black spheres) and ejected polystyrene molecules (blue spheres).

any ejection from the surface. The hydrogen fragment recoils in a collision with a substrate atom and moves upward through the crystal, hitting and fragmenting a polystyrene molecule (green spheres) as it passes through the organic overlayer into the vacuum. In this trajectory, the projectile does not generate collision cascades in the substrate with sufficient upward momentum to eject intact molecules.

The trajectory at the same impact point with Au_2 is shown in Fig. 2. Fig. 2a shows a side view of the initial impact of the projectile on the crystal. One of the projectile atoms hits a bare substrate atom, while the other atom strikes the target polystyrene molecule. The color scheme is the similar to that in Fig. 1a with additional features. The black spheres represent substrate atoms that are ejected as a result of the impact. The blue spheres represent the five polystyrene molecules that are ejected as intact and stable molecules. In Fig. 2b, a lean-on tree for the first 100 fs illustrates the mechanism for energy transfer. One of the projectile atoms hits the target molecule and produces a carbon fragment. The orange spheres show the path of the carbon atom, which moves downward and initiates collision cascades in the substrate. The other projectile atom passes to the substrate unimpeded and moves downward through the layers of substrate atoms, initiating collision cascades. A sea of energetic substrate atoms, shown by the gray spheres, is created underneath the impact area. Energy from the impact moves upward and initiates the ejection of substrate atoms and polystyrene molecules.

4. Summary

Molecular dynamics simulations to explore the role of mass matching were performed of the keV bombardment of an organic monolayer of polystyrene tetramers adsorbed on a Au{1 1 1} substrate with Au and Au_2 projectiles at 2.0 keV per atom. Lean-on trees are used to understand the mechanisms for energy transfer. Low yield trajectories are produced with Au when the projectile hits the target polystyrene molecule upon impact. The process of fragmentation absorbs the incident kinetic energy of the projectile and little energy is transferred to the substrate atoms. With Au_2, on the other hand, there is a greater probability that one of the two atoms will hit the substrate unimpeded by the organic molecule. Energy from the projectile produces a sea of energetic substrate atoms underneath the target area. Substrate atoms lift off stable, intact molecules as they move out of the crystal into the vacuum. When the projectile and substrate atoms have the same mass, efficient energy transfer from the projectile to the substrate occurs when the projectile atom hits a bare region of the substrate.

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