



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 an organic film on a gold substrate with Au and Au₂ 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 Au₂, 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.

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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 Au₂ 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

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52 previous simulations demonstrated that when the mass
53 of the atoms in the projectile is close to the mass of the
54 substrate atoms, a greater amount of energy is trans-
55 ferred to the substrate atoms in the top layers close to
56 the organic monolayer, which results in a higher yield
57 of ejected molecules from the surface [6–8].

58 Simulations by Medvedeva et al. have compared the
59 bombardment of a Si(1 0 0)-(2 × 1) substrate with Al_n
60 (n = 1, 2) and Au_n (n = 1, 2) projectiles at an incident
61 energy of 1.5 keV per atom and incident angles of 0
62 and 45° [9,10]. Au₂ showed the greatest increase in the
63 number of high yield trajectories and the largest non-
64 linear enhancement of ejected large Si_n clusters. The
65 Au_n projectiles, which have a lower incident velocity
66 because of their higher mass, stayed near the surface
67 for a longer period of time. The atoms in the Au_n
68 dimer stayed together for a longer time than the atoms
69 in the Al_n dimer, which increased the deposit of energy
70 in the subsurface region.

71 In this paper, we examine the mechanisms for
72 energy transfer that lead to the ejection of species
73 from an organic monolayer on a substrate in which the
74 substrate atoms and the projectile atoms have the same
75 mass. We have performed molecular dynamics simu-
76 lations of the keV bombardment of an organic film
77 with normal incident Au and Au₂ projectiles at
78 2.0 keV per atom. Low yield trajectories occur when
79 the projectile atom or (atoms) lose their energy upon
80 impact of the organic monolayer. When a projectile
81 atom impacts a region of bare substrate, it transfers its
82 energy to the substrate atoms, and collision cascades
83 develop underneath the organic monolayers that result
84 in the ejection of intact molecules from the surface.
85 With Au₂, there is a higher probability that one of the
86 two atoms is able to penetrate into the substrate region
87 with sufficient energy to eject intact molecules from
88 the surface.

89 2. Method

90 The classical method of molecular dynamics simu-
91 lations is used to study the system of interest and the
92 application of this method is explained comprehen-
93 sively elsewhere [11,12]. Briefly, the position and
94 velocity of each atom as a function of time is deter-
95 mined by numerically integrating the classical equa-
96 tions of motion. The force on each atom is calculated

97 from the gradient of the potential energy function,
98 which is a careful blend of empirical pairwise poten-
99 tials and sophisticated many-body potentials. The
100 model system is composed of 13 *sec*-butyl terminated
101 polystyrene tetramers physisorbed on a Au{1 1 1}
102 substrate of 7350 atoms. Simulations were performed
103 with normal incident Au and Au₂ projectiles at kinetic
104 energies of 2.0 keV per atom.

105 3. Results

106 With Au₂ at normal incidence and incident energy
107 of 4.0 keV, there are a few high yield trajectories in
108 which a group of molecules around the impact point
109 are ejected stable and intact from the surface. The only
110 molecule that is ejected as fragments is the target
111 molecule, which is hit directly by the incoming pro-
112 jectile. When Au bombards the same impact point at
113 normal incident at 2.0 keV, no stable molecules are
114 ejected and two molecules are ejected as fragments.

115 Fig. 1 illustrates the mechanism that occurs for a
116 typical trajectory with Au bombardment. Fig. 1a
117 shows a side view of the initial impact of the projectile
118 on the crystal. The Au projectile is presented by a red
119 sphere. Polystyrene molecules that remain intact on
120 the surface are shown by gray lines and balls. The two
121 polystyrene molecules that are fragmented and ejected
122 during the course of the trajectory are shown as green
123 spheres. The positions of the Au substrate atoms are
124 shown as gray points. In Fig. 1b, a lean-on tree
125 illustrates the mechanism for energy transfer during
126 the first 100 fs of this trajectory. In a lean-on tree, the
127 positions of the projectile and the crystal atoms
128 involved in energy transfer are shown as a function
129 of time. The path of the Au projectile is shown by the
130 red spheres. The Au projectile hits a polystyrene
131 molecule upon impact and breaks a carbon–hydrogen
132 bond, producing a hydrogen fragment (orange sphere)
133 that moves downward into the substrate. At 40 fs, the
134 Au projectile has penetrated into the substrate with
135 little energy left because the majority of kinetic energy
136 of the projectile is absorbed in the process of frag-
137 mentation. The paths of substrate atoms with kinetic
138 energy greater than 50 keV are shown by the gray
139 spheres. The projectile and the hydrogen fragment
140 initiate collision cascades in the substrate that move
141 downward deeper into the crystal without producing

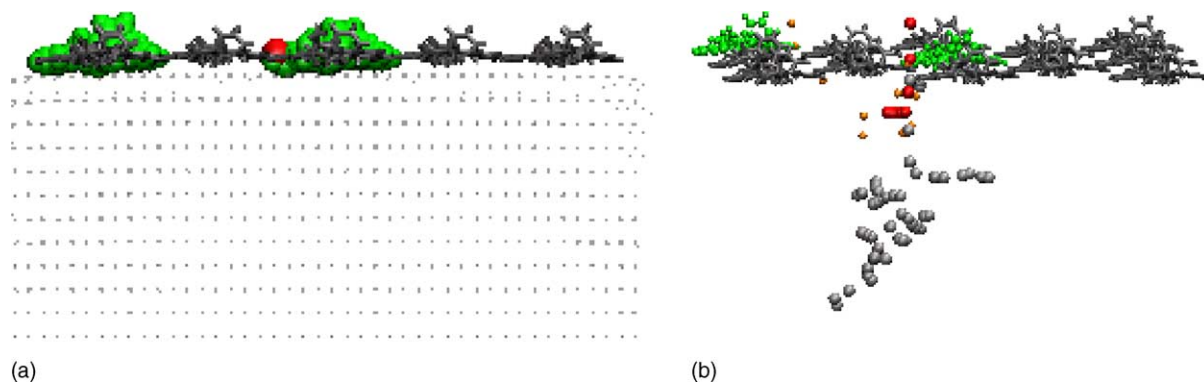


Fig. 1. (a) Snapshot at 10 fs of a trajectory with Au (side view). The incoming Au projectile atom is represented by a red sphere. The green spheres represent the two polystyrene molecules that are ejected as fragments. The Au substrate atoms are represented by gray points and the polystyrene molecules 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

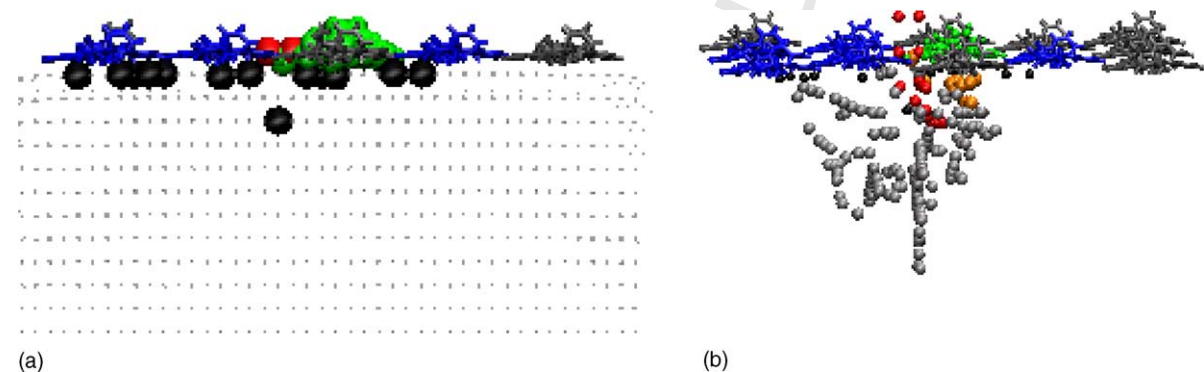


Fig. 2. (a) Snapshot at 10 fs of a trajectory with Au₂ (side view). The color scheme is the same as in Fig. 1a with two additions. The blue spheres represent polystyrene molecules that are ejected intact and stable and the black spheres represent ejected substrate atoms. One of the projectile atoms (red 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 5 intact and stable polystyrene molecules, 1 fragmented polystyrene molecule and 11 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). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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 molecules.

The trajectory at the same impact point with Au₂ 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 in 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{111} substrate with Au and Au₂ 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 Au₂, 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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