Surface Sensitivity in Cluster-Ion-Induced Sputtering

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(Received 17 February 2006; published 1 June 2006)

The ion beam-induced removal of thin water ice films condensed onto Ag and bombarded by energetic Au, Au_2, Au_3, and C_{60} projectiles is examined both experimentally and with molecular dynamics computer simulations. For water overlayers of thicknesses greater than 10 Å, the yields of sputtered Ag^+ secondary ions decay exponentially with increasing ice thickness, revealing characteristic decay lengths of 24, 20, 18, and 7.0 Å, respectively. It is shown that these values manifest the characteristic depths of projectile energy loss, rather than escape depths of the sputtered Ag atoms through the water ice overlayer. Computer simulations show that the mechanism of ejection involves the sweeping away of overlayer water molecules, allowing for an unimpeded escape of ejected Ag atoms. The relevance of these data with respect to surface sensitivity in secondary ion mass spectrometry is discussed.

DOI: 10.1103/PhysRevLett.96.216104 PACS numbers: 68.49.Sf, 61.80.Jh, 79.20.Ap, 79.20.Rf

Bombardment of surfaces by energetic particles leads to atomic motion in the solid, followed by the emission of atomic and molecular species from the top layers of the sample. Detection of the sputtered ions constitutes the technique of secondary ion mass spectrometry (SIMS), which has become a powerful tool for the analysis of complex organic and biochemical materials [1]. Since secondary ion emission occurs from the top few layers, sputter-induced erosion of atomic solids is possible with layer mixing and depth resolution as low as a few nm [2]. For molecular solids, beam-induced damage generally destroys the chemical integrity of the sample, making these types of experiments problematic, at best [3].

The landscape of this field has changed dramatically in the last few years with the introduction of cluster ion projectiles to initiate sputtering and depth profiling [4–6]. Since each atom in the cluster contains a proportionately smaller kinetic energy than those in an atomic projectile, the incident energy is deposited in a concentrated region near the sample surface. This effect has led to a number of new observations including the formation of mesoscale craters of several nm in diameter [7], reduced physical damage in the vicinity of the crater walls [8], and the observation that molecular ions of thermally labile biomolecules can be desorbed intact with orders of magnitude greater efficiency than with atomic projectiles [9,10]. Clusters such as C_{60} yield particularly intriguing physical phenomena during collisions with surfaces and have opened the door to smoothing of surfaces [11], thin film synthesis [12,13], molecular depth profiling [14–20], surface characterization via SIMS, and most recently, bioimaging [21–24].

For atomic bombardment, many of the details of the energy deposition process are understood, with molecular dynamics computer simulations and collision cascade theory providing the insight. The new physical properties associated with cluster bombardment still present a number of challenges which are important to resolve in order to maximize the value of the emerging applications noted above. An interesting dichotomy lies in the relationship between the degree of surface damage and interlayer mixing and the range of deposited energy. For example, a 15 keV Ga projectile penetrates about 7 nm into a Ag substrate before coming to rest, whereas a C_{60} molecule with the same energy stops within about 2 nm of the Ag surface [8]. Yet, for Ag, about 80% of the sputtered atoms originate from the top one layer of Ag when bombarded by an atomic projectile such as Ga^+ or Au^+, but for bombardment by C_{60} with the shallower energy deposition range, about 80% of the particles originate from the top three layers [8]. Even though the particle flux removed by an atomic projectile appears to be more sensitive to the surface composition, the depth resolution achieved during depth profiling experiments is dramatically improved when using cluster projectiles at comparable total kinetic energy [14,16,17].

To elucidate the basis for this apparently contradictory behavior, we have examined experimentally the response of a Ag substrate covered with water ice overlayers of 5 to 225 Å that is bombarded by 25 keV Au^+, ${Au_2}^+$, ${Au_3}^+$ and 20 keV ${C_{60}}^+$, and have provided corresponding molecular dynamics computer simulations to interpret the information. The ice system is chosen as a model since it has a low cohesive energy comparable to many molecular solids of practical interest and it is the matrix within and surrounding targeted biological cells in bioimaging experiments.

A detailed description of the water ice deposition is described elsewhere [25]. Briefly, water ice films were prepared by dosing 2×10^{-7} torr water vapor onto a modified Ag-coated quartz crystal microbalance (QCM) from Maxtek. The temperature of the substrate was held at 100 K to ensure that the ice film deposits in an amorphous state [26].

The mass spectra of these water ice films were recorded using a SIMS instrument described elsewhere [27]. Primary projectiles of Au^+, ${Au_2}^+$ and ${Au_3}^+$ at 25 keV were produced with a liquid metal ion gun [6] and ${C_{60}}^+$ ions were produced at 20 keV by a new buckminsterfullerene ion source of similar design to that reported previously [9], except that it is equipped with a Wien filter for mass selection of the ${C_{60}}^+$ ions. The angle of incidence was 40° in all cases. Mass spectral data were collected using a conventional time-of-flight analyzer, and consisted of a series of major peaks assigned to water clusters $(H_2O)_nH^+$ with $n = 1$–8, and ${Ag(H_2O)_n}^+$ clusters with $n = 0$–6. Only the $^{107}Ag^+$ integrated peak area was necessary for this study.

The molecular dynamics (MD) scheme utilized here has been described elsewhere [28]. Simulations were performed using Au, Au_2, Au_3, and C_{60} projectiles to bombard a substrate of 25 Å of amorphous water ice on a Ag microcrystallite that measures $278 \times 278 \times 100$ Å. The sample required 432 048 Ag atoms and 62 780 water molecules to contain all of the relevant motion. The forces among the atoms within the substrate were described by a mix of several different empirical potential functions with water molecules constrained to be rigid through the use of the RATTLE algorithm. The descriptions of these potentials along with their parameters have been described elsewhere [29]. By fitting to electronic structure calculations [30], parameters for the Ag-O Morse interaction were determined to be $D_e = 0.0868$ eV, $r_e = 2.28$ Å, and $\alpha = 1.3$ Å^{-1}. The Ag-H interaction is purely repulsive with $V(r) = 2000\ \text{eV} \exp(-17\ \text{Å}^{-1} r)$. For the incident clusters, all interactions with substrate constituents were modeled using a Molière potential. For the Ag-Ag and Au-Au interactions, we employed an embedded atom method many-body potential [31], and for C-C we made use of the reactive bond order potential [32].

Integration of the equations of motion for very energetic collisions of a projectile with a rigid water molecule is numerically challenging. Consequently, we chose an initial kinetic energy of 15 keV, which represents a balance of maintaining an energy close to the experimental value and one that is numerically tractable. The particles were directed at an angle of 40° with respect to the surface normal and were randomly oriented. Two different trajectories were performed for the cluster projectiles Au_3 and C_{60}, each extending to 20 ps. Ten different trajectories were required for Au and Au_2 since the course of the trajectory depends upon the coordinates of the projectile-surface collision. For these studies, there is only a weak dependence of the dynamics of the water overlayer subsequent to impact. The nature of the Au-Ag dynamics depends more strongly upon the impact point.

In the experiment, water films were deposited in 5 or 10 Å increments, beginning with a sputter-cleaned Ag substrate. The integrated peak intensity of the $^{107}Ag^+$ secondary ions were recorded after each increment, utilizing a primary ion fluence of approximately $10^8/\text{cm}^2$ to avoid observable beam-induced damage. Log/linear plots of the $^{107}Ag^+$ secondary ion integrated peak intensity vs deposited film thickness for each primary projectile are summarized in Fig. 1. These data show that, regardless of projectile type, there is a region where the $^{107}Ag^+$ ion yield decreases exponentially with increasing ice film thickness. This dependence suggests that the overlaying water film attenuates the $^{107}Ag^+$ ion intensity according to a simple relation $\exp(-z/\lambda)$, where z is the ice film thickness, and λ is a decay length parameter reported in Table I and is dependent upon the nature of the incident projectile and the overlayer material.

These results are striking since the data show it is possible for Ag^+ ions to eject from the surface initially covered with a water ice overlayer of up to 225 Å. Moreover, the amount of Ag signal attenuation is considerably greater for C_{60} than for any of the other projectiles, suggesting it is most sensitive to the presence of water overlayers. The MD simulations provide a definitive explanation. Shown in Fig. 2 are time snapshots at 1, 3, and 5 ps of the simulations of Au_3 and C_{60} bombardment of a 25 Å ice film on Ag. The simulations clearly show that in 1 to 3 ps after the projectile impact, most of the water molecules near the impact point have been removed from the Ag substrate for both projectiles. This configuration opens an unimpeded ejection pathway for Ag atoms that have acquired sufficient kinetic energy from the incident projectile to eject. Similar behavior is observed for the Au and Au_2 simulations (data not shown). Hence, the experimental value of λ is a direct measure of the ability of the overlayer ice film to absorb the incident ion energy. In effect, it is the characteristic depth of projectile energy loss and provides a measure of the relative depth of origin of Ag atoms from within this specific multilayer structure.

These results are consistent with MD simulations of C_{60} and Au_3 bombardment at 5 keV of a bulk water ice substrate [33]. Within the first ps, both projectiles deposit all of their kinetic energy into the top 40 Å and top 100 Å, respectively. In both cases, crater formation and ejection of material from within the crater are predicted. Similarly, MD simulations of 15 keV Ga and C_{60} bombardment of three layers of benzene on Ag result in nearly complete removal of benzene molecules from the Ag surface near

TABLE I. Characteristic depths of projectile energy loss, λ, in the water ice film as measured by the $^{107}Ag^+$ intensity. Y_{eq} represents the number of removed water molecule equivalents for each respective projectile. The energy loss in the water ice overlayer is determined from the MD simulations. Standard deviations are included for the Au and Au_2 projectiles since the energy loss is dependent upon the incident trajectory.

	Au	Au_2	Au_3	C_{60}
λ/Å	24	20	18	7.0
Y_{eq}	94	570	1200	1830
Energy loss/keV	4.7 ± 1.8	4.8 ± 0.8	7.3	14.5

the point of impact [34]. However, as reported in Table I, additional simulations show that C_{60} deposits 97% of its incident energy in the 25 Å water ice overlayer, while Au_3 deposits just 49%, Au_2 32%, and Au 31%. These values further illustrate the surface sensitivity of the water ice/Ag system when interrogated by each of the four projectiles as shown in Fig. 1. From Fig. 2 and Table I, it is clear that the water ice film is most effective at stopping the C_{60} projectile and there is little displacement of Ag atoms in the Ag substrate relative to the Au_x projectiles. The C_{60} cluster, with the lowest energy per particle and the best mass match with the water ice molecules, most efficiently loses its energy in the overlayer, as is shown by the results in Fig. 1 and Table I.

The observation of metal atoms ejecting in the presence of a thick organic layer is not unprecedented [35]. Bolbach *et al.* [36] deposited Cd stearate Langmuir-Blodgett layers on Au and Ag substrates and measured the substrate ion signal due to 21 keV Cs^+ bombardment as a function of coverage. They found that there is a measurable Ag^+ ion signal to 8 layers or about 200 Å. Wong *et al.* [37] measured the emission of Au^-, $Au_2{}^-$, and $Au_3{}^-$ from thiolate layers adsorbed on a Au substrate due to 25 keV Ga^+ bombardment. For the Au^- emission, they find a depth of origin of 70 Å and see emission of all three ions up to a depth of 10 layers or 160 Å. These values are comparable to those found in this study as shown in Fig. 1. Moreover, the mechanism presented here suggests that the metal ions are not ejecting through the organic overlayer but rather the overlayer is swept away providing an unimpeded path for ejection.

This picture of cluster bombardment provides insight into related phenomena. Experimentally, it is possible to determine the number of water molecule equivalents that are desorbed from a thick film of water ice per incident projectile, Y_{eq}, using a QCM and a strategy similar to that described earlier. These yields are reported in Table I. Note the inverse relationship between Y_{eq} and λ and the direct relationship between Y_{eq} and energy loss of the projectile. When the energy loss to the overlayer is highest, Y_{eq} is also highest. Hence, the C_{60} beam is most sensitive for removing material closest to the surface while also removing the most total material. With the energy deposition region severely confined, it is not surprising that a projectile such as C_{60} provides depth resolution of a few nm during depth profiling of metal multilayer structures. Moreover, since this energy confinement also applies to weakly bound molecular systems, it is reasonable to expect there will be little damage accumulation during bombardment and that residual damage will be removed during the impact event. Hence, the observation that molecular depth profiling is feasible with cluster sources, but not atomic projectiles, seems reasonable. The water ice/Ag system may be contrasted with a strongly bound material such as a clean Ag crystal. For cluster bombardment, the crater formation process appears to be quite similar to that found for water ice, with Ag atoms ejecting from layers extending to near the bottom of the crater, or about 2 nm [8]. For atomic

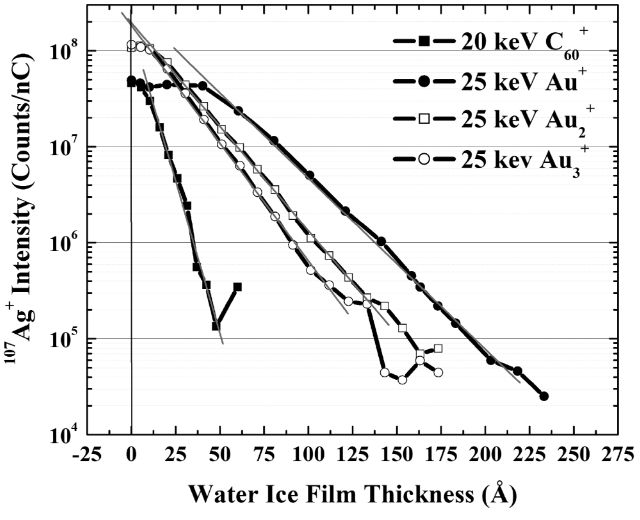

FIG. 1. Integrated peak intensity values for $^{107}Ag^+$ vs water ice film thickness for the four primary projectiles being studied. Linear regression lines for the central portion of each curve are included to show the data used for determining the λ values.

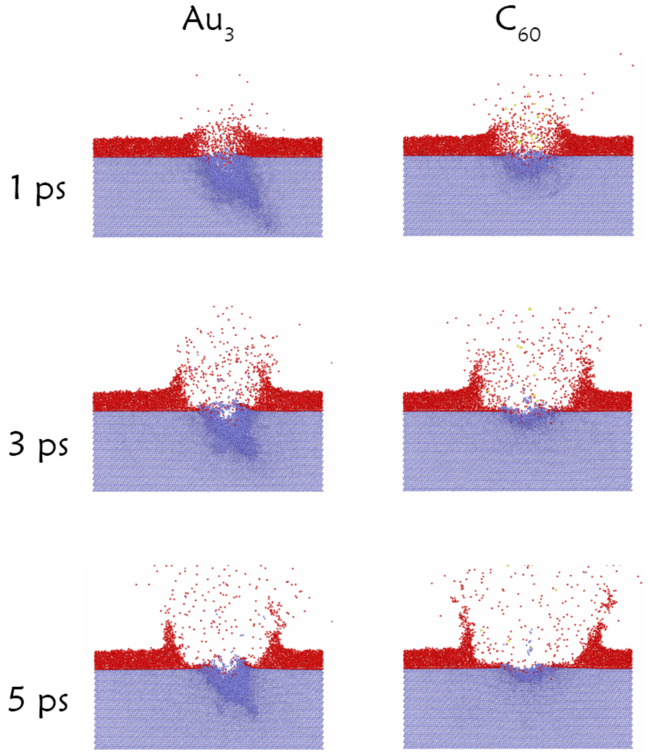

FIG. 2 (color online). Snapshots of the atom positions for $Au_3{}^+$ and C_{60} bombardment of a 25 Å film of ice (dark gray) on Ag (light gray). The incident particle impinges from the left with 15 keV at an angle of 40° with respect to the surface normal. The time snapshots are at 1, 3, and 5 ps for the frames from top to bottom, respectively.

bombardment, a crater is not generally formed for target materials with higher binding energies like Ag, thereby restricting the depth of origin of sputtered atoms essentially to the first layer.

In summary, we have shown from a combined experimental and theoretical study that when cluster projectiles are employed for surface analysis, particularly when studying weakly bound overlayers, the characteristic depths of projectile energy loss are smaller than for their atomic counterparts, resulting in higher yields of the overlayer material and a higher surface sensitivity. Specifically, C_{60} exhibits the highest yields and lowest characteristic depth of primary projectile energy loss, making it most effective for maintaining adequate depth resolution during depth profiling of multilayer systems. Moreover, we find that substrate particles eject from a previously unreported mechanism whereby the overlayer is swept away, providing an easy escape route for the substrate particles. This mechanism is in sharp contrast to a mechanism in which the ejected substrate particles would have to travel through the overlayer through a series of collisions that ultimately lead to desorption.

The authors gratefully acknowledge support from the Chemistry Division of the National Science Foundation and the National Institute of Health. C. S. acknowledges joint support from the Analytical Chemistry Division of the American Chemical Society and the Society for Analytical Chemists of Pittsburgh. The authors thank Professor Andreas Wucher for insightful discussions of this manuscript.

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