An Investigation of Enhanced Secondary Ion Emission Under Au_n^+ ($n = 1\text{--}7$) Bombardment

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We investigate the mechanism of the nonlinear secondary ion yield enhancement using Au_n^+ ($n = 1, 2, 3, 5, 7$) primary ions bombarding thin films of Irganox 1010, *DL*-phenylalanine and polystyrene on Si, Al, and Ag substrates. The largest differences in secondary ion yields are found using Au^+ , Au_2^+ , and Au_3^+ primary ion beams. A smaller increase in secondary ion yield is observed using Au_5^+ and Au_7^+ primary ions. The yield enhancement is found to be larger on Si than on Al, while the ion yield is smaller using an Au^+ beam on Si than on Al. Using Au_n^+ ion structures obtained from Density Functional Theory, we demonstrate that the secondary yield enhancement is not simply due to an increase in energy per area deposited into the surface (energy deposition density). Instead, based on simple mechanical arguments and molecular dynamics results from Medvedeva et al, we suggest a mechanism for nonlinear secondary ion yield enhancement wherein the action of multiple concerted Au impacts leads to efficient energy transfer to substrate atoms in the near surface region and an increase in the number of secondary ions ejected from the surface. Such concerted impacts involve one, two, or three Au atoms, which explains well the large nonlinear yield enhancements observed going from Au^+ to Au_2^+ to Au_3^+ primary ions. This model is also able to explain the observed substrate effect. For an Au^+ ion passing through the more open Si surface, it contacts fewer substrate atoms than in the more dense Al surface. Less energy is deposited in the Si surface region by the Au^+ primary ion and the secondary ion yield will be lower for adsorbates on Si than on Al. In the case of Au_n^+ the greater density of Al leads to earlier break-up of the primary ion and a consequent reduction in energy transfer to the near-surface region when compared with Si. This results in higher secondary ion yields and yield enhancements on silicon than aluminum substrates. (J Am Soc Mass Spectrom 2005, 16, 733–742) © 2005 American Society for Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is widely used to study the chemical composition of surfaces in areas from biological systems to materials chemistry [1, 2]. One of the problems with the SIMS analysis of surfaces is that low secondary molecular ion yields are often observed for atomic primary ion impacts. Kilo-electronvolt polyatomic projectiles greatly enhance observed secondary molecular ion yields when compared to monoatomic ions such as Ar^+ , Ga^+ , Xe^+ , and Cs^+ . Examples of polyatomic ions that exhibit this behavior include Au_n^+ [3–8], $(\text{CsI})_n\text{Cs}^+$ [3, 9, 10], C_{60}^+ [8, 9, 11–15], SF_5^+ [16–21], and Au_n^- [22, 23]. Thus, using polyatomic projectiles can potentially improve secondary ion yields, which may lead to an increase in the maximum useful spatial resolution that can be achieved, currently ~ 200 nm [1]. To improve spatial resolution, we require both high secondary ion yields and primary ion beams with a small beam diameter. Gold cluster ion beams, Au_n^+ , can have beam diameters of <50 nm and are therefore suitable for this purpose [6, 24].

The use of polyatomic projectiles for sputtering surfaces and as SIMS primary ions has been investigated for several decades ([25] and references therein). At low primary ion beam kinetic energies (≤ 100 keV), such as those used in our experiments, the predominant energy loss mechanism is nuclear stopping. In the 1960s and 1970s, there were several reports that using polyatomic ions greatly improved sputter yields (for example see [26, 27]). In 1979, Johar and Thompson investigated the sputter yields from Ag, Au, and Pt targets using monoatomic and polyatomic ions of P, As, Sb, and Bi with kinetic energies from 10 to 250 keV [28, 29]. Greatly increased sputter yields were observed for diatomic and triatomic projectiles and the yield enhancement was strongly nonlinear with the number of atoms in the primary ion (a “nonlinear” yield enhancement). One important conclusion from this work was that the high sputtering yields were due to the polyatomic projectiles creating a “collisional” spike in the sample surface, rather than a “thermal” spike. That is, the high sputter yields were generated by inducing a region of high atomic motion and mass transport rather than by creating a localized region of high temperature which causes molecules to “evaporate” from the surface as suggested by Sigmund and Clausen [30]. A “collisional” spike mechanism was further supported by Ben-

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guerba et al. [3] who observed that enhanced ion yields were independent of the melting points of various inorganic solids. These authors also concluded that the yield enhancements observed were dependent on the energy density deposited (energy deposited/area) into the surface by the polyatomic projectile and not on the linear energy loss of the projectile, dE/dx , where x is the penetration depth of the primary ion. This supports a “collisional” spike mechanism since energy density is dependent on the size and mass of the projectile; as the number of constituent atoms in the projectile increases there is an overlap of collision cascades within the material causing a “collisional” spike.

Molecular dynamics (MD) simulations have also been employed to examine the mechanism of nonlinear yield enhancement [31–37]. These simulations suggest that multiple collision cascades are required to cause the ejection of a molecule into the gas phase. For a polyatomic projectile there is a higher probability that multiple collision cascades will be generated simultaneously from the collision of the constituent atoms of the projectile with the substrate atoms/molecules. Thus there is an enhancement in the sputter yield observed due to the “nonadditive” effects of the collision cascades. Krantzman and coworkers have investigated the role of the substrate in the sputtering process by modeling Xe^+ and SF_5^+ striking Cu and Si surfaces covered with a biphenyl adlayer [36, 37]. They observed that the substrate significantly influenced the observed yield enhancement, with larger yield enhancements observed for less dense substrates such as Si.

In this paper we investigate the secondary ion yield enhancement observed using Au_n^+ ($n = 1, 2, 3, 5, 7$) primary ions. We survey three different organic samples employed in a number of technologically and medically important applications. Samples used were thin films of *DL*-phenylalanine ($[\text{M} + \text{H}]^+ m/z = 164$), Irganox 1010 ($[\text{M} - \text{H}]^- m/z = 1175$) and polystyrene adsorbed on different substrates. *DL*-phenylalanine is an amino acid and was chosen because it has been previously used in experiments examining yield enhancements from Au_n^+ ($n = 1\text{--}5$) primary ions [3, 5, 6]. Irganox 1010 is a polymer additive and its SIMS mass spectrum is well known [38]. Irganox 1010 is composed of four monomer units and so also allows us to investigate fragmentation (see Structure 1). Finally, polystyrene thin films were employed since they are often characterized by TOF SIMS.

Structure 1. Irganox 1010

We first examined the secondary yields from these samples using Au_n^+ primary ions with different energies. We observe, in agreement with previous work, that there is a significant secondary ion yield enhancement using Au_n^+ ($n > 1$) primary ions and that the ion yield increase is linear with v^2 (and therefore kinetic energy), where v is the velocity of the projectile. We then test whether the observed yield enhancement is explained by the energy deposition density into the surface (energy/ $\text{\AA}^2$). To calculate the energy deposition density, we determined the structures and cross-sectional areas of the primary ions using density functional theory (DFT). We have also investigated the yields of the fragment ions from these films to try to elucidate the fragmentation mechanisms. It has been observed that the yield of fragment ions increases faster than the molecular ion yield when Au_n^+ and $(\text{CsI})_n^+$ primary ions are used, suggesting that there is an increase in prompt fragmentation [25]. Finally, we examine secondary ion yield enhancements from Si and Al in order to test whether the use of more open substrates leads to an increase in the yield enhancement as suggested by Krantzman and coworkers. Si and Al have similar atomic masses but very different structures: Si has an open diamond crystal lattice whereas Al has a face-centered cubic structure, and so any differences in yield enhancement observed will be due to the substrate structure.

In this paper, we demonstrate that the secondary ion yield enhancement is not simply due to an increase in the energy deposition density into the surface by Au_n^+ ($n > 1$) primary ions. Based on simple mechanical arguments and the MD results of Garrison and coworkers [34, 36, 37], we suggest a simple mechanism for nonlinear secondary ion yield enhancement involving multiple concerted Au impacts on substrate atoms which leads to efficient energy transfer to the near-surface region. This model explains well the large changes in nonlinear yield enhancement observed going from Au^+ to Au_2^+ to Au_3^+ primary ions.

Experimental

Time-of-Flight Secondary Ion Mass Spectrometry

Time-of-flight secondary ion mass spectra were obtained using a TOF SIMS IV (ION TOF Inc.) The instrument consists of a loadlock, a preparation chamber, and an analysis chamber, each separated by a gate valve. The preparation and analysis chambers are kept under ultra high vacuum (10^{-9} mbar). The primary ion beam was generated using an AuGe liquid metal ion gun capable of producing Au^+ , Au_2^+ , Au_3^+ , Au_5^+ , and Au_7^+ ions. The primary ions were mass selected using their flight time, and their energy was varied from 8.3 keV to 25 keV. The primary ion beam current was measured using a Faraday cup.

The secondary ions generated were extracted into a

time-of-flight mass spectrometer. Before reaching the detector the secondary ions were reaccelerated to 10 keV energy.

Analyzed sample areas were ($200 \times 200 \mu\text{m}^2$) for Irganox 1010 and *DL*-phenylalanine on Ag foil and ($250 \times 250 \mu\text{m}^2$) for all the other samples. Positive and negative secondary ion mass spectra were collected for each sample. The primary ion dose during data acquisition was less than 10^9 ions cm^{-2} . The secondary ion peak intensities were reproducible within $\pm 5\%$ from scan-to-scan.

Sample Preparation

Irganox 1010 was obtained from Ciba Specialty Chemicals (Tarrytown, NY), *DL*-phenylalanine from Sigma-Aldrich (St. Louis, MO) and narrow-distribution polystyrene from Scientific Polymer Products, Inc. (Ontario, NY).

Irganox 1010 and polystyrene were dissolved in chloroform as 1.00 mg/ml solutions. A 10^{-2} M solution of *DL*-phenylalanine was prepared using a 1:1 2-propanol:water mixture as the solvent. Chloroform (EMD Chemical, Gibbstown, NJ) and 2-propanol (obtained from Fisher Scientific, Pittsburgh, PA) solvents were high purity and HPLC grade, respectively.

The substrates used were silver foil (99.9% purity, 0.05 mm thick, Alfa Aesar, Ward Hill, MA), aluminum foil (99.99% purity, 0.1 mm thick, Alfa Aesar) and single crystal silicon wafer ($\langle 111 \rangle$ orientation, Addison Engineering, San Jose, CA). The Ag and Al foils were prepared by etching in nitric acid, rinsing several times in water, and drying using N_2 gas. The Si wafers were prepared using Piranha etch (1:3 H_2O_2 : H_2SO_4), followed by rinsing with copious amounts of water and 2-propanol, and drying with N_2 gas.

Thin film samples of Irganox 1010 and polystyrene* were prepared by spin-coating in the following way: ~ 1 ml of the appropriate solution was dropped onto a 2.25 cm^2 ($1.5 \times 1.5 \text{ cm}$) substrate (silver foil, aluminum foil or silicon wafer) and the sample spun at 2000 rpm for one minute using a KW-4A spin-coater (Chemat Technology, Inc., Northridge, CA). The thin samples of *DL*-phenylalanine* were made by allowing a drop of solution (< 0.1 ml) to evaporate on the substrate.

Quantum Mechanical Calculations

In order to determine the cross-sectional area of the primary ion used, density functional theory (DFT) geometry optimization calculations were performed to determine the lowest energy structures of gold clusters with the formula Au_n and Au_n^+ ($n = 1-7$). The calculations were carried out using the NWChem 4.5 program

package [39]. The LANL2DZ basis set [40–42], which includes an effective core potential, was employed in the calculations. Our calculations utilized the generalized gradient approximation (GGA) with the exchange-correlation potential parameterized by Perdew et al. [43].

The accuracy of the computational method was checked by benchmark calculations on the gold atom and Au_2 cluster. From our calculations, the ionization potential and electron affinity obtained for the gold atom are 9.58 eV and 2.31 eV, respectively, in good agreement with the experimental values of 9.23 eV [44, 45] and 2.31 eV [45]. For the gold dimer, the calculated ionization potential, binding energy, bond length, and frequency were 9.59 eV, 2.12 eV, 2.55 Å, and 170 cm^{-1} , respectively. This compares well with the experimentally determined values of 9.50 eV [44], 2.35 eV [45], 2.47 Å [45], and 191 cm^{-1} [45].

A more detailed discussion of the calculation method and results is given in a reference [46].

Calculation of Average Cross-Sectional Area of the Au Clusters

The geometry-optimized (lowest energy) Au_n^+ clusters were employed to calculate the minimum, maximum and orientationally-averaged cross-sectional areas of the primary ions used in this work.

The calculation was performed in the following way. Using the Cartesian coordinates of the gold atoms in the cluster and a Van der Waals radius of 1.66 Å for Au [47], a space-filling model of the Au_n^+ cluster was constructed. From this structure, the cross-sectional area was evaluated by projection onto a planar surface. To obtain the orientationally-averaged cross-sectional area, this area was recalculated for each possible Eulerian orientation of the cluster, $\phi = 0-360^\circ$, $\theta = 0-180^\circ$, and $\psi = 0-360^\circ$, and the mean of these areas determined [48].

Figure 1. The secondary ion yields of the molecular ion of Irganox 1010 spin-coated on a Si substrate. The dotted lines are drawn as a guide to the eye.

* We estimate that these films are 100–300 Angstroms thick. In all SIMS spectra taken we clearly observe ions from the substrate indicating that the Au_n^+ ions penetrate through the organic layer to the substrate.

Table 1. Molecular ion yields and yield enhancement for thin films of Irganox 1010, *DL*-phenylalanine, and polystyrene upon Au^+ , Au_2^+ , and Au_3^+ primary ion bombardment

Sample	Molecular ion; mass (Da)	Y_{Au^+}	$Y_{\text{Au}_2^+}$	$Y_{\text{Au}_3^+}$	Yield enhancement Au_2^+	Yield enhancement Au_3^+
Irganox 1010 on a Si substrate	(M-H) ⁺ ; 1175 Da	2.86×10^{-5}	1.25×10^{-3}	2.72×10^{-3}	21.8	31.6
<i>DL</i> -phenylalanine on a Si substrate	(M-H) ⁺ ; 164 Da	7.38×10^{-5}	1.13×10^{-3}	2.79×10^{-3}	7.66	12.6
polystyrene, PS 771, on a Ag substrate	[(monomer)+ Ag] ⁺ ; 1621 Da	1.19×10^{-4}	2.48×10^{-4}	4.98×10^{-4}	1.08	1.4

Results and Discussion

Effect of Au_n^+ ($n = 1, 2, 3, 5, 7$) Projectile Velocities on Secondary Ion Yields

From the mass spectra of Irganox 1010, polystyrene and *DL*-phenylalanine, secondary ion yields, Y , were calculated.† **Figure A1** displays the secondary ion yield of the Irganox 1010 molecular ion (M-H)⁺, $m/z = 1175$, from a film on a Si substrate bombarded with Au_n^+ ($n = 1, 2, 3, 5, 7$). Au_4^+ and Au_6^+ primary ion beams were not included in this study because in our AuGe liquid metal ion gun they are generated with extremely low ion currents. Presenting the secondary ion yields as a function of the kinetic energy per atom of the primary ion beam (proportional to v^2 , where v is the primary ion velocity) permits us to compare the yields obtained with different gold cluster projectiles at the same impact velocity. For a given Au_n^+ primary ion the secondary ion yield increases linearly with the incident energy per atom (the square of the incident ion velocity) in agreement with previous work [3]. The greatest increase in yield when changing from an Au_n^+ to Au_{n+1}^+ primary ion beam occurs at $n = 1$ when the atomic ions are replaced with dimer ions. Secondary ion yields for bombardment of Irganox 1010, *DL*-phenylalanine and polystyrene films with Au_n^+ ($n = 1, 2, 3$) and the ratios of the secondary ion yields for Au_2^+ and Au_3^+ with respect to Au^+ projectiles, at constant velocity, are given in **Table A1**. A useful parameter is the yield enhancement factor defined as

$$\text{Yield Enhancement} = \frac{Y_n(E)}{nY_1\left(\frac{E}{n}\right)} \quad (1)$$

where $Y_n(E)$ is the secondary ion yield for Au_n primary ions at energy E and $Y_1(E/n)$ is the secondary ion yield observed using Au^+ primary ions at the same velocity. If this ratio is greater than one, the yield enhancement is said to be nonlinear, i.e., many more secondary ions are generated than would be expected if the secondary ion yield was proportional to primary ion size, $Y_n(E) = nY_1(E/n)$. We observe nonlinear yield enhancements for

all systems studied. Nonlinear yield enhancements are also observed for Au_5^+ and Au_7^+ primary ion bombardment. For Irganox 1010 [(M-H)⁺ of $m/z = 1175$, negative ion mode), the ratios of the secondary ion yields are 1:43.5:94.9:66.2:111.7 for $\text{Au}^+:\text{Au}_2^+:\text{Au}_3^+:\text{Au}_5^+:\text{Au}_7^+$ primary ion bombardment. For *DL*-phenylalanine ($m/z = 164$, negative ion mode) the secondary ion yield ratios are 1:15.3:37.8:19.5:25.4, and for polystyrene ($m/z = 1517$, positive ion mode) the ratios are 1:2.2:4.2:6.5:17.3. We note that the ion currents for the Au_5^+ and Au_7^+ ion beams are very low, typically 0.015 pA for Au_5^+ and 0.010 pA for Au_7^+ . The yield enhancements for these ions may therefore be underestimated, and we estimate that the error may be as large as 20%.‡

We also examined the yield of secondary fragment ions versus E/n for $m/z = 175, 607$, and 915 from an Irganox 1010 film on a Si substrate (**Figure A2**). The fragment secondary ion yields increase both with increasing E/n of the primary ion beam and with the mass of the primary ion, in a similar manner to that observed for the molecular ions. We also observe this phenomenon for *DL*-phenylalanine and polystyrene (data not shown).

The secondary ion yield of a given species is dependent not only on its ionization probability and the primary ion flux but also upon the sputter rate of material from the surface. To ensure that the observed yield increases are not due simply to an increased sputter rate, the damage cross-sections, σ , were determined. For polystyrene at a primary beam energy of 25 keV, $\sigma(\text{Au}_3^+) \sim 2.5\sigma(\text{Au}^+)$ and $\sigma(\text{Au}_2^+) \sim 1.5\sigma(\text{Au}^+)$. The damage cross-sections for Au_5^+ and Au_7^+ primary ion bombardment were not measured because of relatively high uncertainties in the primary ion currents. The secondary ion yields increase far faster than these measured damage cross-sections. There is therefore a substantial increase in the efficiency of secondary ion formation (efficiency = secondary ion yield/damage cross-section) even at low primary ion velocities.

For each primary ion Au_n^+ , the secondary ion yields are approximately proportional to the square of the primary ion velocity (and therefore the primary ion beam kinetic energy = $1/2 mv^2$). However, if yield was determined

† $Y = (\text{number of secondary ions detected})/(\text{number of primary ions that struck the target})$.

‡ This is due to uncertainties in measuring the primary ion beam current. The current may be lower than reported since we are near the limit of detection for primary ion current in our instrument.

only by the primary ion kinetic energy we would expect that the yield enhancement would be linear, i.e., $Y_n(E) = nY_1(E/n)$, in all cases. The source of nonlinear secondary ion yield enhancements remains an open question. A possible correlation for the observed nonlinear yield enhancement is that yield is proportional to the energy

Figure 2. Secondary ion yields of fragment ions of Irganox 1010 from negative ion mode mass spectra. (a) $m/z = 175$, (b) $m/z = 607$, and (c) $m/z = 915$. Secondary ion yields from Au^+ primary ions are shown as filled circles, Au_2^+ open circles, Au_3^+ filled triangles, Au_5^+ open triangles, and Au_7^+ filled squares. The dotted lines are drawn as a guide to the eye.

Table 2. The calculated lowest energy structures of gold cationic clusters, Au_n^+ ($n = 1 - 7$). Also shown is the orientationally-averaged cross-sectional area of the Au_n^+ cluster calculated using an atomic radius of 1.66 Å

Number of Au atoms in the cluster	Structure of the lowest energy Au_n^+ cluster	Area of the lowest energy Au_n^+ cluster (Å ²)
1		8.64
2		14.93
3		19.65
4		24.66
5		30.36
6		34.18
7		37.74

deposition density (energy/projectile area, $\text{keV}/\text{Å}^2$) at the surface. This might seem reasonable since the secondary ion yields are linearly dependent on the kinetic energy of the primary ion and the cross-sectional area of Au_n^+ will vary nonlinearly with the number of constituent atoms, n , in the cluster. To investigate this possibility we employed DFT calculations to determine the structures of Au_n^+ ions, $n = 1 - 7$. Table 2 displays the results of these calculations and the orientationally-averaged cross-sectional areas of the gold clusters. It can easily be seen that the lowest energy structures of the gold cations are planar for $n = 1 - 7$.⁵ From the cross-sectional area we calculated the energy density, in $\text{keV}/\text{Å}^2$, deposited into the surface upon impact of an Au_n^+ ion, assuming that the cluster remains intact (Figure 3). We note that recent Molecular Dynamics (MD) simulations indicate that Au dimers maintain their identity for at least 50 fs after striking a $\text{Si}(100)(2 \times 1)$ surface.³⁴ As can be seen in Figure 3, the energy density deposited into the surface is larger for Au_n^+ ($n > 1$) than for Au^+ , and the slope increases with the number of Au atoms present in the cluster, in agreement

⁵ We note that these structures have also been calculated in reference [49].

Figure 3. The energy density, $\text{keV}/\text{\AA}^2$, versus the energy per particle in the cluster, $1/2 m_{\text{Au}} v^2$, for the calculated lowest-energy Au cationic clusters.

with the experimental observations. However, these changes in slope are not large enough to account for the experimental observation; the ratios of the slopes (n/A where n = number of atoms in the primary ion and A is the area of the projectile) are 1:1.12:1.37 for $\text{Au}^+:\text{Au}_2^+:\text{Au}_3^+$. Further, there is not a large difference in the calculated energy deposition density for Au_2^+ and Au^+ projectiles. Thus, the nonlinear yield enhancement is much larger for polyatomic gold ions than this simple correlation predicts and hence there must be other factors at work.

When an ion strikes a substrate it transfers energy into the substrate by colliding with surface atoms. We consider a simple classical model of a single collision. The percentage of energy transferred by a projectile of mass M and velocity v striking an atom of mass m at rest is

$$\left(\frac{2M}{M+m} \right)^2 \left(\frac{m}{M} \right) \times 100\% \quad (2)$$

The kinetic energy transferred to the substrate atom is

$$\left(\frac{2M}{M+m} \right)^2 \left(\frac{m}{M} \right) \times \text{Kinetic Energy of the Primary Ion} \quad (3)$$

For Au^+ and Au_2^+ ions striking a Si substrate atom, the energy transferred upon collision is 42.4 and 24.0 % of the kinetic energy of the primary ion. The most efficient energy transfer—when all the energy is transferred to the atom from the projectile—occurs when $M = m$. For $M \gg m$, the percentage of energy transferred is $\sim 4m/M \times 100\%$. If we assume that near the surface, the constituent atoms of Au_n^+ act like a single projectile, then at a given kinetic energy the percentage of energy transferred *per collision* will be decreased compared to

the atomic projectile, Au^+ .** An Au_n^+ projectile should therefore decelerate more slowly than an Au^+ primary ion, as observed in recent MD simulations which indicated that more Au_2 projectiles retained their initial energy for 50 fs after collision with a $\text{Si}(100)(2 \times 1)$ surface than did monoatomic Au projectiles [34]. At first glance, this would suggest that using an Au_n^+ projectile would not greatly enhance the secondary ion yield. However, the kinetic energy of a typical primary ion beam is 2–25 keV, while the binding energy of an Au_n^+ ion is only a few tens of eV. Thus, even though the primary ions maintain their coherence [34] for some time as they penetrate into the substrate, after a single collision the primary ion should be thought of as collection of individual atoms moving in the same direction with similar velocities. In the near surface region a substrate atom can be struck near-simultaneously by many Au atoms from the primary ion and the amount energy of transferred to individual substrate atoms in the surface region can therefore be much larger for the Au_n^+ projectile than for an Au^+ primary ion. That is, in the surface region although the efficiency of energy transfer is lower, the *absolute* energy transfer to the substrate atoms is still greater for polyatomic primary ions than for monoatomic ones. As the Au_n^+ primary ion penetrates into the substrate its constituent atoms will move further apart and will cease to act in concert: further collisions, therefore, will lead to energy transfer at the rate characteristic of monoatomic primary ions. Thus, individual impacted substrate atoms closer to the surface will have a higher energy than those deeper in the substrate. The increased energy (and velocity) of these surface atoms will lead to the ejection of more secondary species and an increased secondary ion yield. As the primary ion cluster size increases, it will create more high-velocity substrate atoms as it passes through the topmost substrate layer. We note that from geometrical considerations it is unlikely that a single substrate atom will be struck simultaneously by more than three Au atoms. Hence, the largest increases in secondary ion yield are expected in going from Au^+ to Au_2^+ to Au_3^+ ion beams, in agreement with our experimental observations.

Fragment Ion Formation

Although it is now clear that polyatomic primary ions increase the molecular secondary ion yield, there is contradictory evidence about the dependence of the yield of fragment ions on projectile size [3,4]. For example, Benguerba et al. [3] observed that for an DL-phenylalanine film the yield of light ions such as H^+ increased linearly with the number of atoms in Au_n^+ , where $n = 1$ –5. In contrast, Davies et al. [4] observed that for a gramicidin A ($m/z \sim 1880$) film adsorbed on

** We note here that the Au–Au bond strength is much smaller than the projectile kinetic energy. Therefore the Au_n^+ projectile will break up upon striking the surface.

an aluminum substrate the yield enhancement for ions below $m/z = 100$ is of the same order of magnitude as for the quasi-molecular ion ($m/z = 193$), while the yield enhancement increases significantly above $m/z = 200$. In our experiments, we observe that the yield enhancement of fragment ions depends on the analyte. In the case of Irganox 1010, the yield enhancement initially decreases to a minimum at $m/z \sim 500$ and then increases to the mass of the molecular ion, $[\text{M} - \text{H}]^+$ of $m/z = 1175$ (Figure 4a and Table 3). For DL-phenylalanine, the ratio of the secondary ion yields increases from a mass-to-charge-ratio of 90 to 166 (the mass-to-charge ratio of the molecular ion $[\text{M} - \text{H}]^+$) (Figure 4b and Table 4). In the m/z region of the positive ion mass spectrum of polystyrene adsorbed on silver, the yield enhancement is approximately constant between $m/z = 600$ and 700 (Figure 4c).

MD simulations [49, 50] have demonstrated that there are three mechanisms for molecular and fragment ion ejection from a substrate: (1) molecules very close to the impact point receive the largest amount of energy and fragment; (2) molecules slightly further away from the impact point desorb intact but are sufficiently excited to fragment before reaching the detector; and (3) stable, whole molecules are gently ejected by the action of upward moving substrate atoms. As the number of Au atoms in the primary ion increases, the energy deposited into the surface region increases, leading to an increase in the amount of surface damage; the increase is approximately proportional to the increase in the cluster ion area (and therefore to the number of atoms in the cluster). Hence, there will be an increase in analyte fragmentation close to the primary ion impact point, and an approximately linear increase in the yield of very light fragment ions.

In the case of the Irganox 1010 samples, we observe that the yield enhancement decreases to a minimum at $m/z \sim 500$. For fragment of m/z less than 500, the ions formed derive from the Irganox 1010 monomer (Structure 1). As argued above, as the number of Au atoms increases in the polyatomic primary ion there is an increase in the energy deposited into the surface region. Energetic (fast-moving) substrate atoms strike analyte molecules from underneath leading to their ejection from the surface. The energy transferred to the analyte molecules by the substrate atoms will be larger after Au_n^+ primary ion bombardment than for Au^+ bombardment, because the substrate is more efficiently “energized” by the polyatomic primary ion. Thus there will be more monomer and fragment ions (mass range: $m/z = 200$ –500) ejected with sufficient energy to fragment into lighter mass ions before reaching the detector. This fragmentation will lead to an increase in the number of lower mass ions that are detected ($m/z \leq 200$). Hence, for Au_n^+ primary ions the observed yield enhancement of fragment ions with mass-to-charge ratios less than 200 is larger than the yield of fragment ions with mass-to-charge ratios between 200 and 500, and the

Figure 4. Yield Enhancement $[Y(\text{Au}_n^+)/nY(\text{Au}^+)]$ at constant primary ion velocity versus m/z for thin films of (a) Irganox 1010 on a Si substrate, (b) DL-phenylalanine on a Si substrate, and (c) polystyrene on a Ag substrate. The total energy of the Au_n^+ ($n = 2, 3, 5, 7$) primary ion was 25 keV except on the Irganox substrate where the yield enhancement was also determined for an Au_2^+ primary ions with an energy of 20 keV.

observed yield enhancement is higher for these lighter mass ions than for heavier ones.

Heavier fragments and ions ($m/z \geq 500$) will be formed via the “lift-off” mechanism. As the number of

Table 3. A comparison of the secondary ion yields and ratios of ion yields using Au₃⁺ and Au⁺ primary ion bombardment of thin films of Irganox 1010 adsorbed on Si and Al substrates

<i>m/z</i> (Da)	Yield on Si substrate			Yield on Al substrate			
	<i>Y</i> _{Au⁺}	<i>Y</i> _{Au₃⁺}	<i>E</i> _{Si} = $\frac{Y_{Au_3^+}}{Y_{Au^+}}$	<i>Y</i> _{Au⁺}	<i>Y</i> _{Au₃⁺}	<i>E</i> _{Al} = $\frac{Y_{Au_3^+}}{Y_{Au^+}}$	$\frac{E_{Si}}{E_{Al}}$
41	2.64 × 10 ^{−4}	0.0214	80.87	3.08 × 10 ^{−4}	0.0202	65.67	1.23
59	2.11 × 10 ^{−4}	0.0168	79.35	2.21 × 10 ^{−4}	0.0139	62.70	1.27
71	3.68 × 10 ^{−5}	3.30 × 10 ^{−3}	89.76	4.57 × 10 ^{−5}	1.08 × 10 ^{−3}	23.63	3.80
175	3.02 × 10 ^{−5}	1.87 × 10 ^{−3}	62.01	3.54 × 10 ^{−5}	1.69 × 10 ^{−3}	47.62	1.30
205	3.36 × 10 ^{−5}	1.75 × 10 ^{−3}	52.09	4.05 × 10 ^{−5}	1.75 × 10 ^{−3}	43.25	1.20
231	3.76 × 10 ^{−4}	0.0164	43.50	4.63 × 10 ^{−4}	0.0180	38.80	1.12
277	1.29 × 10 ^{−4}	4.77 × 10 ^{−3}	36.83	1.92 × 10 ^{−4}	6.25 × 10 ^{−3}	32.48	1.13
607	1.56 × 10 ^{−6}	4.89 × 10 ^{−5}	31.44	3.10 × 10 ^{−6}	1.04 × 10 ^{−4}	33.55	0.94
915	2.21 × 10 ^{−6}	1.73 × 10 ^{−4}	77.94	5.48 × 10 ^{−6}	3.79 × 10 ^{−4}	69.09	1.13
1175	2.86 × 10 ^{−5}	2.72 × 10 ^{−3}	94.91	1.03 × 10 ^{−4}	8.46 × 10 ^{−3}	82.13	1.16

Au atoms in the primary ion increases, more energy is deposited near the surface, and this process becomes more likely. For Irganox 1010, the secondary ion yields increase above *m/z* = 500, with the largest yield enhancements observed for the molecular ion, [M − H][−] of *m/z* = 1175. For polystyrene adsorbed on silver, the yield enhancements remain approximately constant between *m/z* = 600 and 1700. In this case, the secondary ions ejected are of the form [Ag + M]_n⁺ (*n* = 5–15), where M is the styrene monomer unit.

Substrate Structure

Secondary ion yield enhancements are dependent on a wide range of experimental variables including the substrate composition and structure [36]. Silicon and aluminum have similar atomic weights but very different molecular structures and bonding. Al is a face-centered cubic metal [45] with a density of 2.70 g cm^{−3} [51] whereas silicon has a more open diamond structure [45] with a density of 2.33 g cm^{−3} [51] and is covalently bonded. Using these two substrates we can, therefore, directly evaluate the effect of substrate structure on secondary ion yields and yield enhancements. Figure 5 displays the secondary ion yield of the molecular ion of Irganox 1010 (M − H)[−], *m/z* = 1175, on an Al substrate bombarded with Au_n⁺ (*n* = 1, 2, 3, 5, 7). It can be seen

that the secondary ion yields behave in a similar manner as those observed for an Irganox 1010 thin film on a Si substrate. (This is also observed for *DL*-phenylalanine films on Al and Si substrates, for which data is not shown.) For Irganox 1010 and *DL*-phenylalanine, the observed yield enhancement is larger on the silicon substrate than on the aluminum (Tables 3 and 4). For Irganox 1010 the yield enhancement on silicon is ~1 to 2 times that observed on Al for both Au₂⁺ and Au₃⁺. In the case of *DL*-phenylalanine the yield enhancements on Si for Au₂⁺ and Au₃⁺ primary ions in the negative ion spectrum are 1 to 2 times that observed on Al. In the positive ion mode, the yield enhancement on Si is 1 to 2.5 times and 4.5 to 18 times that observed on Al for Au₂⁺ and Au₃⁺ primary ions, respectively. Interestingly, in all cases the measured secondary ion yields for Au⁺ primary ion bombardment are smaller on Si than on Al. For polyatomic projectiles the secondary ion yields are larger on the Si substrate above *m/z* ~ 200 and *m/z* ~ 100 for Irganox 1010 and *DL*-phenylalanine, respectively. Thus, polyatomic Au ions more efficiently produce secondary ions on Si than on Al, while the reverse is true for atomic Au⁺ ions.

When an Au⁺ ion passes through the more open Si surface, it will contact fewer substrate atoms than in the more dense Al surface. Therefore, less energy will be deposited in the Si surface region by the Au⁺ primary

Table 4. A comparison of the secondary ion yields and ratios of ion yields using Au⁺, Au₂⁺, and Au₃⁺ primary ion bombardment of thin films of *DL*-phenylalanine adsorbed on Si and Al substrates

Substrate	<i>m/z</i> (Da)	<i>Y</i> _{Au⁺} /10 ^{−5}	<i>Y</i> _{Au₂⁺} /10 ^{−4}	<i>Y</i> _{Au₃⁺} /10 ^{−3}	<i>E</i> _{Si} = $\frac{Y_{Au_2^+}}{Y_{Au^+}}$	<i>E</i> _{Al} = $\frac{Y_{Au_3^+}}{Y_{Au^+}}$	$\frac{E_{Si}(Au_2^+)}{E_{Al}}$	$\frac{E_{Si}(Au_3^+)}{E_{Al}}$
Negative ions								
Si	164	7.38	11.3	2.79	15.26	37.80	1.52	1.98
Al	164	8.78	8.82	1.68	19.07	10.04		
Positive ions								
Si	91	26.3	8.13	8.15	3.09	30.99	1.12	4.69
Al	91	32.6	8.98	2.16	2.75	6.61		
Si	120	29.1	11.1	12.2	3.81	41.91	1.52	7.63
Al	120	46.4	11.7	2.55	2.52	5.49		
Si	166	4.73	3.90	6.15	8.26	130.17	2.43	18.06
Al	166	9.19	3.12	0.662	3.40	7.21

Figure 5. The variation of secondary ion yields of the molecular ion of Irganox 1010 spin-coated on a Al substrate. The dotted lines are drawn as a guide to the eye.

ion, and the secondary ion yield will be lower for adsorbates on Si than on Al. For Au_n^+ ions, the projectile will undergo a larger number of collisions on the Al substrate in the near-surface region than on Si, and the constituent atoms will move apart faster than in Si. We therefore expect that the energy deposited near the surface of Si would be greater than for Al, leading to a larger increase in secondary ion yield using Si substrates. Thus, the yield enhancement observed on the Si substrate will be larger than on the Al substrate.

Conclusions

Using Au_n^+ ($n = 2, 3, 5, 7$) primary ions significantly enhances the secondary ion yield of both molecular and fragment ions when compared to Au^+ bombardment. Further, the yield enhancements of molecular and pseudomolecular ions are larger than for fragment ions. The observed yield enhancement is also larger on more open surfaces, such as Si, than on more dense surfaces, such as Al.

The mechanism of yield enhancement is complex and depends on a number of different experimental factors including the deposited energy density at the surface, the rate of energy transfer from the primary ion to the substrate atoms, and the identities of the analyte and substrate. As an Au_n^+ ion strikes the substrate, its constituent atoms likely remain close together and so a substrate atom can be struck simultaneously by a number of them. Deeper in the substrate the primary ion fragments, and a substrate atom is unlikely to be struck by multiple Au atoms. Thus, more energy is deposited into individual substrate atoms at the surface of the substrate than deeper in the sample. This leads to the ejection of a larger number of secondary ions. Since it is unlikely that a substrate atom will be struck by more than three constituent atoms of the primary ion in this region, the largest differences in secondary yields are observed for Au_2^+ and Au_3^+ primary ion bombardment.

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