An Investigation of Enhanced Secondary Ion Emission Under Au_n^+ (n = 1–7) 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)

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. Kiloelectronvolt 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], $(CsI)_nCs^+$ [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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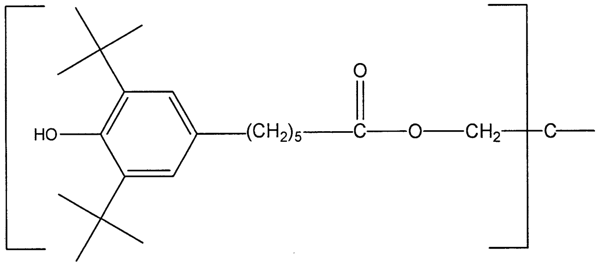
guerba et al. [3] who observed that enhanced ion yields were independent of the melting points of various inorganic solids. These authors also concluded that the yield enhancements observed were dependent on the energy density deposited (energy deposited/area) into the surface by the polyatomic projectile 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 investgated 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 ($[M + H]^-$ *m/z* = 164), Irganox 1010 ($[M - H]^-$ *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 = 1–5) 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/Å^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 $(CsI)_nI^+$ 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