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Prospects for imaging with TOF-SIMS using gold liquid metal ion sources

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Abstract

Gold liquid metal ion sources produce high quality TOF-SIMS spectra with excellent prospects for imaging using either Au^{++}, Au^{+} or Au_2^{+} primary ions. The beam is stable and exhibits a long lifetime when employing eutectic alloys of Si or Ge. In general, the yields are found to be considerably higher than when using Ga beams, but the increased yield associated with using dimer ions is also associated with an increase in surface damage. Finally, it appears that Au^{++} ion bombardment may yield improved spectra for certain types of compounds.
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1. Introduction

Molecule-specific imaging experiments with TOF-SIMS reveal chemical information about small spatial domains with unprecedented chemical specificity. These experiments are made possible in part by the use of liquid metal ion sources that provide a short pulse of ions focused into a sub-micron spot on the target. A time-of-flight mass analyzer detects the desorbed ions in parallel fashion. Modern instrumentation is very impressive, exhibiting mass resolution in excess of one part in 10 000, transmission efficiencies of up to 10%, and spatial resolution of better than 100 nm. To achieve meaningful chemical information, it is generally believed that it is necessary to keep the incident ion dose to within the static limit—about 1% of the number of surface molecules. Since there are only about 10^4 mol/100 nm^2/monolayer, achieving the necessary sensitivity is critical to attaining an adequate count rate.

During the last decade, it has become clear that the ion yield of molecules can be increased dramatically by using cluster ion beams as projectiles [1]. In some cases, more than an order of magnitude improvement in the high mass component of various biomolecules and polymers were reported. These ions include such species as SF_5^{+}, coronene, and C_{60}^{+} [2,3] as well as other carbon-containing species [4]. The improved yield often occurs with increased efficiency. For these cases, the increased desorption yield is not accompanied by a corresponding increase in the damage cross-section. Although this discovery is important for many TOF-SIMS applications, it is more difficult to use it to improve molecule-specific imaging experiments. Although cluster ion sources can be focused to a limited degree, the focusing process occurs at great cost to the ion beam flux. Only the brightness associated with the liquid metal ion source has so far provided adequate flux for sub-micron imaging.

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Most imaging TOF-SIMS studies have been performed using Ga^+ ions as a projectile. This ion is not very effective, when compared to ions like Cs^+, at desorbing high mass species because of its relatively light mass of 69 Da. Recently, several groups have reported that In^+ ion sources produce yields of high mass ions with about four times the yield of Ga^+, along with excellent image quality [5]. But perhaps the most interesting is the gold liquid metal ion source. This projectile not only has a higher mass than In or Ga but also exhibits a propensity to form dimer and trimer ions of Au_2^+ and Au_3^+ [2]. If these sources could be used as imaging sources in TOF-SIMS experiments, they might provide the enhancement observed in other cluster ion sources as well as achieve the desired spatial resolution. There have been a number of earlier examples where Au sources have been employed in SIMS experiments, but details remain sketchy [6]. In this work, we report on a newly developed gold liquid metal ion source and present a preliminary assessment of its applicability to TOF-SIMS imaging experiments. In general, the results show that these sources can be operated with a long lifetime, good imaging quality and can provide modest improvement in the yield of high mass ions.

2. Experimental

Experiments were performed using the IOG-25 liquid metal ion source from Ionoptika. The source was modified to allow for mass selection of the primary ions by incorporating a set of chopping plates that selects the appropriate ion by time-of-flight. The mass resolution of this setup is about 50 Da for mass selection at m/z 197 at 25 keV and 25 ns pulse width. A Wein filter could be employed for mass selection, but this device is not very effective above a mass of about 200 Da. Two different gold emission tips were examined as obtained directly from FEI. The first tip consisted of a pure gold source. This tip produces a stable beam of Au^{++}, Au^+ and Au_2^+ ions, and yields images similar to that found for Ga^+ ions. To achieve this stability, however, the tip must be heated to a high temperature (a heater current of 3.5 A, a value sufficient to melt gold, melting point 1337 K), resulting in rapid evaporation of gold residing in the source. In our hands, the lifetime never exceeded 50 A h. The second tip consists of a AuSiBe eutectic alloy. This source produces 63% Au^+, 13% Au^{++} and 5% Au_2^+ at a heater current of 1.2 A, a value sufficient to melt the AuSiBe alloy, melting point ~693 K. As noted below, the image quality is degraded somewhat from that found for Ga^+, but still provides sub-micron spatial resolution. The lifetime of this tip is on the order of 1600 A h.

A AuGe eutectic source is now available from Ionoptika [7]. Initial testing of this tip indicates that it exhibits similar behavior to the FEI tip mentioned above, although initial reports indicate that the lifetime is nearly 2000 A h. The beam composition of the ions emitted from this tip are similar to that found for the AuSi source.

3. Results and discussion

Total ion images using the two tips are shown in Fig. 1. Although we have not yet attempted a detailed measurement of the probe size, it is apparent that the spatial resolution is well below 1 μm.

Since the lifetime of the pure gold source is so short, we have only tested the eutectic as a potential source for TOF-SIMS experiments.

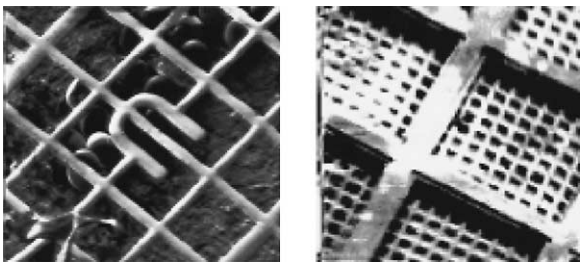

Fig. 1. Total ion image of a copper grid bombarded with an unfiltered gold beam produced from a pure gold source (left) and a gold/silicon alloy source (right). The field of view is 150 μm.

Table 1
Phenylalanine yield at M + H and M − H bombarded by 10 keV per Au ion

Ion	Yield, −ve ions	Yield, +ve ions	Yield from Ref. [8]
Au^+	1.2×10^{-5}	3.4×10^{-5}	<0.002
Au_2^+	3.4×10^{-4}	9.3×10^{-4}	0.03
Ratio	29	27	>15

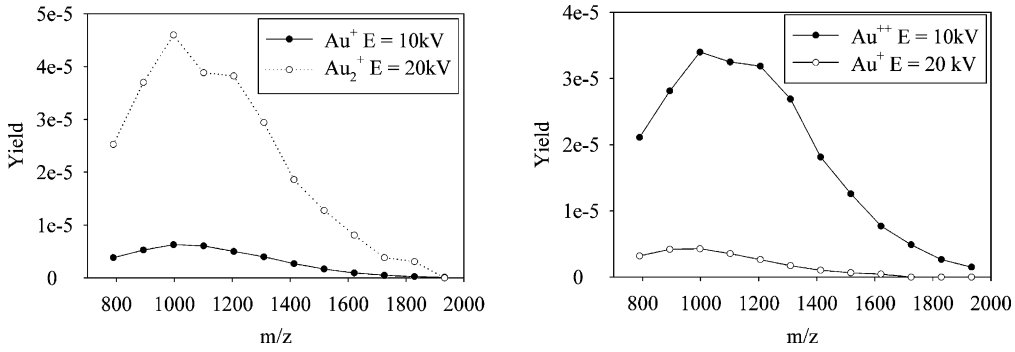

Fig. 2. TOF-SIMS spectra of oligomers emitted from a thin film of polystyrene on Ag. The yield measurements in the two plots are not directly comparable since the spectra were taken from different regions of the film.

This AuSi source produces TOF-SIMS spectra that exhibit yield enhancements that are similar to those reported earlier by LeBeyec and coworkers [8]. As shown in Table 1, using a phenylalanine thin film as a test case, the yield from bombarded dimers relative to monomers is generally enhanced by a factor of 10 or more. Enhancements are also observed for a thin polystyrene film on a silver substrate, although the degree of enhancement is less than a factor of 10. Although the yield of high mass ions is increased, we also find that the yield of low-mass fragment ions is also increased, so it is not clear that dimer bombardment increases the efficiency of molecular ion formation. Perhaps more interestingly, however, we find that bombardment with Au^{++} results in the same degree of enhancement relative to gold than does gold dimer ion. These effects are illustrated in Fig. 2. Low-mass fragment ions are increased in this case as well. These results are a bit surprising since the kinetic energy of the projectiles is identical. Other workers have observed enhancements with very highly charged ions [9], although to our knowledge, such reports have not been made for doubly charged species. Apparently, the combination of the insulating properties of the polymer film, the 20 eV or so of potential energy associated with the two charges, and the propensity for gold to deposit its energy nearer the surface lead to this effect. More work will be required to sort out the details.

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