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## Super TOF Secondary Ion Mass Spectroscopy Using Very Highly Charged Primary Ions up to Th<sup>70+</sup>

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# Super TOF Secondary Ion Mass Spectroscopy using Very Highly Charged Primary Ions up to $\text{Th}^{70+}$

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## 1. Introduction

For the purposes of quantitative and sensitive analysis of deep sub-micron scale materials ( e.g. 100 nm ), it is desirable to develop a method for the production of very high, matrix independent, ionization probabilities for as-emitted secondary particles, as well as large molecular ion yields. One approach is to change the nature of the secondary ion generation itself. It has long been known that high energy heavy ion impact can cause the efficient production of secondary ions, as well as enhanced molecular ion yields [1]. This is due to the response of the solid to extreme high density ionization, from ion nuclear-target electron scattering, which includes a "Coulomb explosion" [1] in the immediate vicinity of the incident particle track and an associated shock-wave or pressure pulse expanding to the target surface [2]. The resulting phenomenon is often referred to as "electronic" sputtering [1], in contrast to the kinetic binary collisional cascade mechanism responsible for low energy primary ion induced sputtering. Unfortunately, due to the nature of the sources used to produce such primary ion species, insufficient flux is available for sub-micron scale lateral spatial analysis. Another technique for the production of secondary ions through electronic processes is laser induced desorption [1]. This technique has been especially successful in secondary molecular ion analysis. However, this method also has some disadvantages: It often requires a volatile matrix into which the material of interest is suspended. Further, the high intensity laser power required cannot be localized into the sub-micron regime. Laser induced fragmentation provides an additional limitation of this technique. Some time ago, it was proposed that an effective mechanism for secondary ion generation would be available with the use of slow highly charged ions [3], such as keV/u  $\text{Th}^{70+}$ . Until now, however, it was not feasible to pursue this idea, due to the lack of appropriate ion sources. The advent of new ion source technologies, such as the LLNL EBIT (Electron Beam Ion Trap), has recently made low emittance (  $< 0.2 \pi$  mm mrad ) beams of slow (  $\leq 3$  keV /amu ) very highly charged ions ( in principle up to  $\text{U}^{92+}$  ) available for use in ion-solid interaction studies [4]. The prominent features of such interactions, compared to that for singly to moderately charged ions, is the dominance of electronic over collisional effects. While such an incident ion approaches a solid surface, up to several hundred electrons are emitted, from an area of only a few square nanometers. This potential electron emission yield has been found to increase linearly with incident charge for

Figure 1: Mass spectrum of positive secondary ions for 5.5 keV \* q Th<sup>70+</sup> incident on (500 eV Ar<sup>+</sup> sputter) cleaned 100 nm thick SiO<sub>2</sub> film on Si, obtained through integration of peaks of the blocking-corrected TOF spectrum.

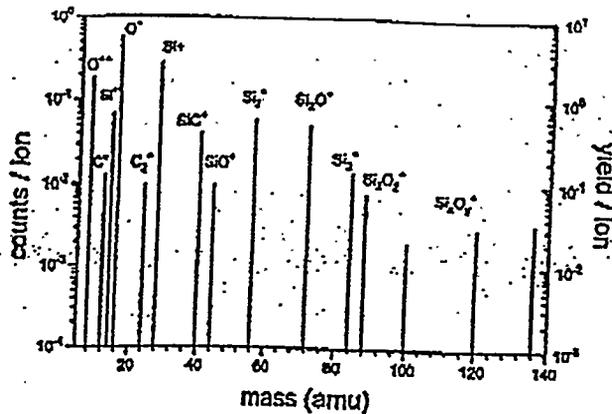


Figure 2: Integrated secondary positive and negative ion yields vs. incident charge state of the primary ion for a 100 nm thick SiO<sub>2</sub> film on Si. A sample bias of +/- 1.5 kV was used. The yield is determined using an effective detection efficiency of 10%.

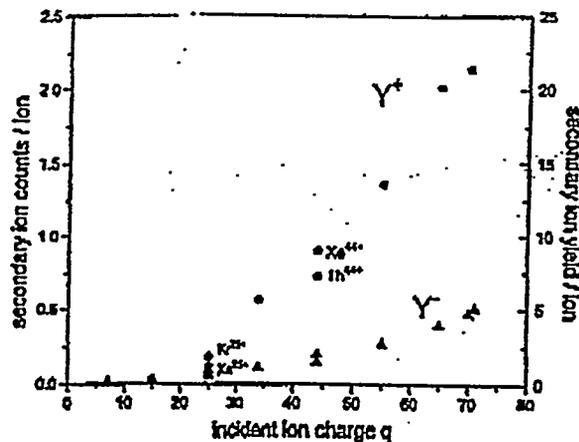


Figure 3: Mass spectrum of negative secondary ions for 9 keV \* q Th<sup>70+</sup> incident on (500 eV Ar<sup>+</sup> sputter) cleaned 100 nm thick SiO<sub>2</sub> film on Si, obtained through integration of peaks of the blocking-corrected TOF spectrum.

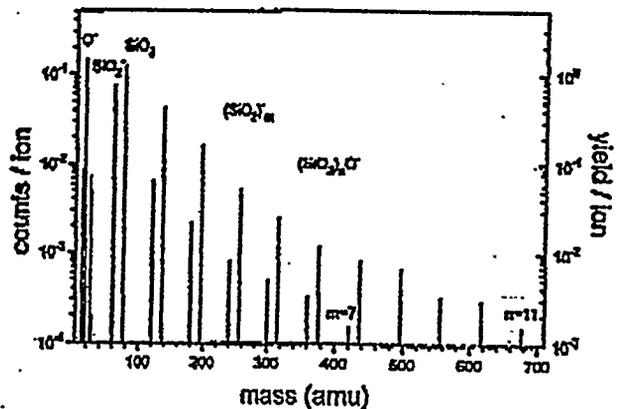
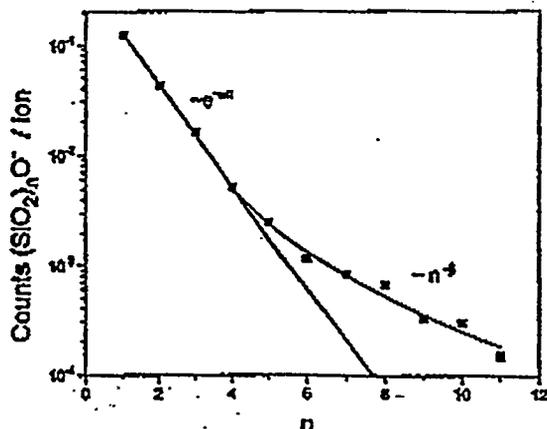


Figure 4: Measured relative yield for negative ion clusters in the series (SiO<sub>2</sub>)<sub>n</sub> O<sup>-</sup> for 9 keV \* q Th<sup>70+</sup> incident on 100 nm thick SiO<sub>2</sub> on Si as a function of the cluster order n. The detection efficiency of 10 % has not been included.



clean conductors and insulators (e.g.  $\text{SiO}_2$  on Si) at least up to  $\text{Th}^{70+}$ . In insulators, the resulting local disturbance of the charge equilibrium cannot be compensated before the lattice relaxes in a "Coulomb explosion". Some of the ionized target atoms in the near surface and central region of the resulting space charge are ejected from the solid through mutual repulsion, while remaining ionized target atoms are correspondingly compressed and initiate a shock wave. The shock wave is capable of causing the desorption of large numbers of large molecular species from the surface [2]. Such phenomena exhibit a threshold behavior, occurring when the energy density stored in ionization just exceeds the binding energy density in that volume. The present work represents the first systematic study of the sputtering process due the incidence of slow very highly charged ions.

## 2. Experimental Arrangement

The measurements were performed under UHV conditions ( $<10^{-10}$  Torr) and the sample surfaces were in-situ sputter cleaned using 500 eV to 2 keV Ar ions to insure reproducible surface composition. The secondary ions were identified using a single microchannel plate detector based time-of-flight (TOF) arrangement developed at LLNL for this purpose [4]. The technique relies on the bimodal pulse height distribution for single particle (e.g. secondary ions) and multiple particle events (e.g. electrons/photons), for the production of stop and start pulses, respectively. This arrangement is very efficient for the detection of the incidence of each ion (start), due to the high electron and photon (vuv) / proton yields associated with the incidence of HCl's. Absolute yields for secondary ion emission are obtained by normalization to the start signal count. A grounded grid before the detector housing was parallel to the sample surface at a nominal distance of ca. 7 cm. The sample was typically biased at  $\pm 1.5$  kV, for measurements of positive and negative secondary ion yield, respectively. The sample bias was systematically varied between 0.25 to 2.5 kV, to calibrate the TOF to mass conversion. The primary highly charged ion beam was incident at an angle of  $30^\circ$  with a diameter of ca. 1 mm and a flux of 500 to 1000 ions/s. The achieved mass resolution of only ca 1.5% was sufficient for these initial investigations. An effective detection efficiency for the secondary ions of 10% was determined for this setup. The measured TOF spectra were corrected for the blocking effects inherent to the one-stop-per-start electronics used here.

## 3. Results and Discussion

Results for  $\text{Th}^{70+}$  ions, extracted from the EBIT source at an energy of  $7 \text{ keV} \cdot q$ , incident on thin  $\text{SiO}_2$  films on Si are presented here. Note that no significant influence was found on the secondary ion emission for incident primary ion energies ranging from 2.5 to  $15 \text{ keV} \cdot q$ . Figure 1 shows the resultant integrated mass spectrum of secondary positive ions. It can be seen that the secondary ion yield is significantly enhanced over that for singly or moderately charged ions. The integrated secondary ion yield is shown in Figure 2 as a function of incident ion charge. Together with a detection efficiency of 10 %, these results suggests secondary ion yields of up to 25 per incident ion, for  $\text{Th}^{70+}$ . It is found that the ratio of positive oxygen to silicon ion yields is constant above threshold (27+), at the stoichiometric value of  $1.98 \pm 0.05$ ,

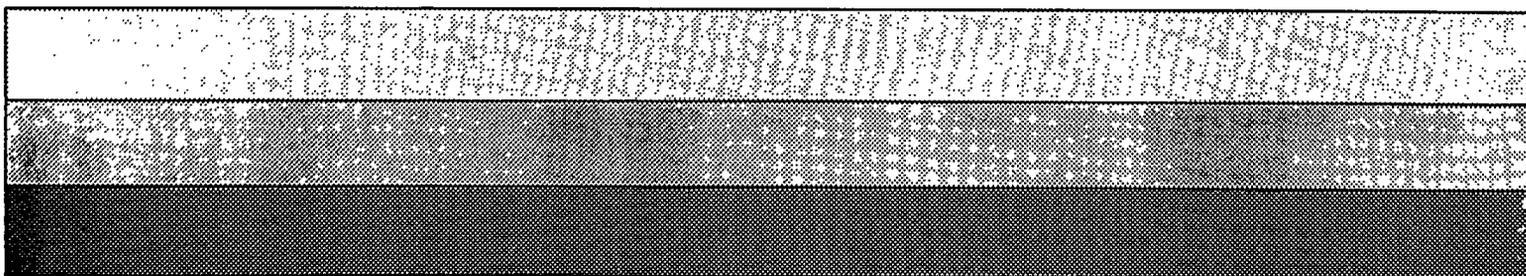
increasing rapidly below threshold (already 20:1 for  $\text{Kr}^{2+}$ ). These data strongly suggest that the ionization probability for the secondary particles changes rapidly at, and is constant above, threshold. It can be argued that, together with its stoichiometric value, this behavior is a strong indication that the ions are produced in a very hot plasma and that the ionization probability in this case approaches unity. Therefore, the linear increase in the ion yield of Figure 2 is concluded to be due entirely to increasing total ablation yield, corresponding to larger volumes of the target surface region involved in the "Coulomb explosion". Furthermore, the mass spectrum of negative secondary ions, exhibit a rich series of molecular cluster ions, as shown in Figure 3. In the case of  $\text{SiO}_2$ , the clusters can be described the series  $(\text{SiO}_2)_n^-$  and  $(\text{SiO}_2)_n\text{O}^-$ , where  $n$  is the order of the cluster. As shown in Figure 4, the yield of such clusters is found to decrease exponentially for relatively small clusters (to  $n=4$ ), consistent with emission as clusters of order  $n$ , and combinatorially for larger cluster orders ( $n>4$ ), consistent with the formation of clusters through coalescence of smaller clusters upon emission. This behavior is in very good agreement with that found for shock-wave induced desorption by high energy (MeV/u) heavy ions [2] and suggests the use of HCI SIMS for enhanced molecular analysis of sub-micron materials. Such large cluster yields are also found for other targets. It is found that the negative ion yield, dominated by  $\text{O}^-$ ,  $(\text{SiO}_2)^-$  and  $(\text{SiO}_2)\text{O}^-$ , is directly proportional to the positive ion yield above threshold (ca. 27+), decreasing rapidly for lower incident charge states. This strongly suggests a correlation between the mechanisms involved in the two emission processes, as provided by the "Coulomb explosion"-shock wave mechanism. The cluster ion yield (e.g.  $(\text{SiO}_2)\text{O}^-$ ) are found to increase as the cube of the charge of the incident ion, in excellent agreement with the results for swift heavy ions [2]. It should be noted that a linear correlation has been determined for the results of HCI SIMS and that of in-situ Auger electron spectroscopy. Together with the fact that EBIT produced ions can be focused to beam diameters of  $< 0.1\mu\text{m}$ , the enhanced atomic and molecular ion yields results have very important implications for the application of highly charged ion induced sputtering for enhanced sensitivity and quantitative (absolute) SIMS analysis of deep sub-micron scale surface layers and polymeric and bio-molecular material analysis.

## References

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- [2] *Atomic Collisions on Solid Surfaces*, E.S. Parilis et.al. (North Holland, Amsterdam) (1993) 539- and references therein.
- [3] E.S. Parilis, *Proc.ICACS I*, Amsterdam, 1970 p.324.
- [4] For a recent review of HCI-solid interactions see D.H.G. Schneider and M.A. Briere, *Physica Scripta*, in press, and references therein.

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