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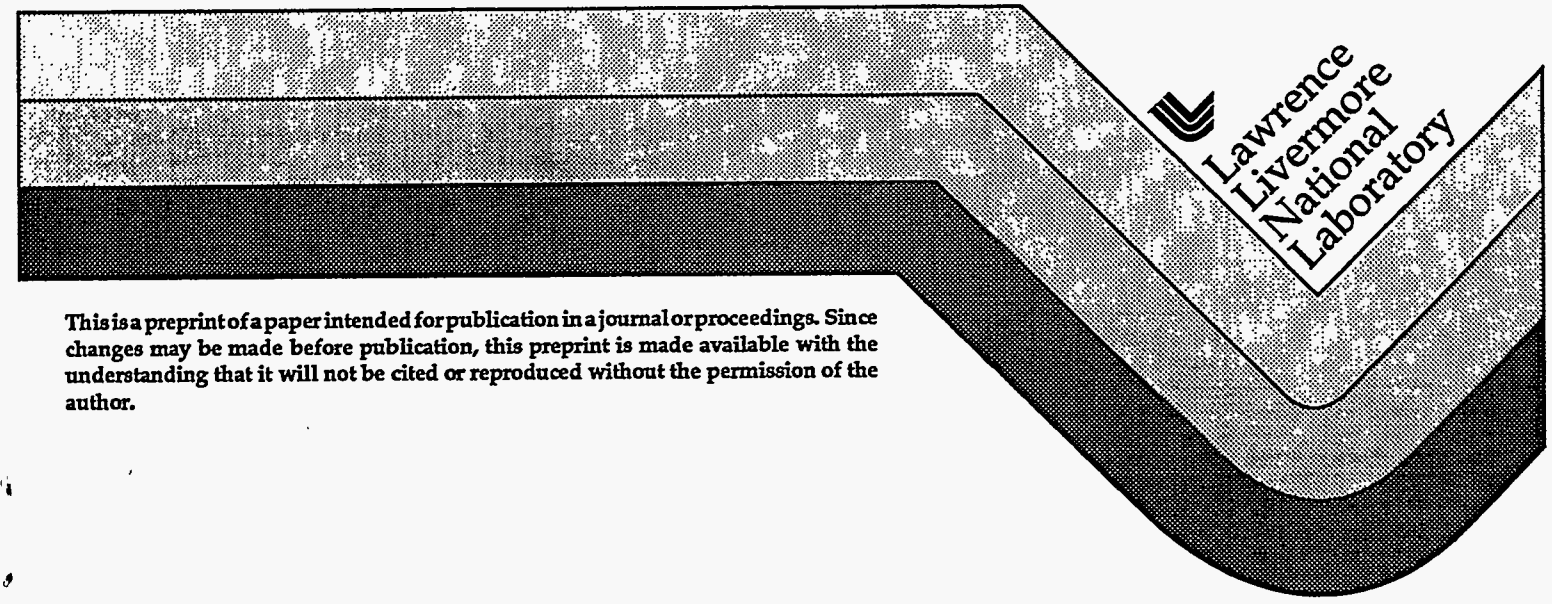

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Electronic Sputtering and Desorption Effects in TOF-SIMS Studies Using Slow Highly Charged Ions like Au^{69+}

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Secondary ion yields from highly oriented pyrolytic graphite (HOPG) and SiO_2 (native oxide on float zone silicon) targets at impact of slow ($v \approx 0.3\ v_{Bohr}$) highly charged ions have been measured by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). A direct comparison of collisional and electronic effects in secondary ion production using a beam of charge state equilibrated 300 keV Xe^{1+} shows a secondary ion yield increase with incident ion charge of ≥100.

1. Introduction

Secondary ion mass spectrometry is among the most widely used surface analysis techniques [1]. In standard SIMS, primary ion beams consist of singly charged, keV ions. Secondary ion production results from momentum transfer along a collision cascaded caused by the incident ion in the target material; a process in which useful yield generation is accompanied by extensive sample damage [2]. Collisional sputter yields scale linearly with the nuclear stopping power, S_n, and amount typically to ~ 2-10 target atoms per incident ion, while secondary ion yields per incident ion are often smaller than 10^{-2}. It is the useful yield, the number of secondary ion counts per unit of sample consumption that primarily determines ultimate sensitivity limits of SIMS [3]. In the case of surface analysis by static SIMS, values for sensitivity limits are mostly in the order of 10^9 atoms/cm^2 e. g. for the detection of transition metal contaminations on silicon wafers [1], a problem crucial for the semiconductor industries. In the following we address this problem of secondary particle generation in static SIMS by use of slow, very highly charged primary ions, like Xe^{44+} or Au^{69+}.

Ions traveling in solids develop an equilibrium charge state distribution according to their velocity, atomic mass number and the Fermi velocity of electrons in the target material ($v_{Fermi} \approx v_{Bohr} = 2.2 \times 10^6$ m/s). Initial charge states of highly charged ions used in this study are much larger than the mean equilibrium charge states that correspond to their low velocities ($v \approx 0.3\ v_{Bohr}$, $E_{kin} \leq 3$ keV/amu). Calling these highly charged ions "slow" sets them apart from "fast" ions of similar high charge states with velocities $v >> v_{Bohr}$, which are produced by charge state equilibration in gaseous or solid targets at relativistic energies (E_{kin} >100 MeV /amu).

Studies of the interaction of slow highly charged ions with surfaces have drawn considerable attention over the last decade [4, 5]. Having reached a critical distance from a metal surface, incoming ions begin to resonantly capture electrons from the target conduction band into highly excited Rydberg states, with binding energies approximately equal to the metal workfunction. Corresponding principal quantum numbers of $n \approx 60$ can be estimated from the "classical-over-the-barrier-model" [4] for the interaction of Au^{69+} with amorphous carbon. While the ion is approaching the surface, highly excited states decay predominantly by autoionization, giving rise to

electron emission into the vacuum [6]. Typical transition times for Auger- and radiative transitions are by far too long for the ion to de-excite completely above the surface. With most of it's electrons populating high n Rydberg states, a highly excited, but neutral "hollow atom" finally hits the surface. Now electrons in Rydberg states with radii in excess of a characteristic surface screening length are peeled off. De-excitation continues below the surface via rapid side-feeding processes of target electrons into energetically favorable ion vacancies, accompanied by a multitude of radiative and Auger transitions. Total neutralization times are in the order of tens of femtoseconds (see below). During this time highly charged ion potential energies of several hundreds of keV are dissipated. The quantitative differentiation of the various energy dissipation channels (target lattice excitations, secondary photons, x-rays, Auger-electrons, secondary ions and neutrals) is currently a matter of intense research [5]. Secondary electron yields amount to ~180 electrons per incident ion for Th^{75+} impact at $v = 6\times10^5$ m/s on gold surfaces and to ~90 electrons/ion from thin SiO_2 films (50 nm on Si) [7]. In a model for electronic sputtering, Parilis et al. have suggested a "Coulomb explosion" mechanism for the description of high secondary particle yields form insulators at highly charged ion impact [8]. The model assumes that electron emission leads to the formation of a charge depleted region on insulator surfaces. Coulomb repulsion between ionized target atoms results in an explosive lattice relaxation before charge neutrality can be reestablished.

2. Experimental

Beams of multiply and highly charged ions were extracted from the electron beam ion trap (EBIT) at Lawrence Livermore National Laboratory [9]. Ions were analyzed according to their mass to charge ratios with a 90° bending magnet. Residual gas pressures in the beam transport system and the target chamber were 10^{-8} torr and 2×10^{-10} torr, respectively. For the neutralization and TOF-SIMS measurements, a highly charged ion flux of ~ 1000 ions/s was used. The beam spot size was 1 mm^2. A schematic representation of the experimental setup is shown in Fig. 1. A position sensitive detector was used for measurements of ion charge states after transmission through a 10 nm thick carbon foil. Electrostatic charge state analysis of transmitted ions was accomplished by a pair of parallel plates. A TOF coincidence between secondary electrons (start) and transmitted ions (stop) was used for energy loss measurements [10]. Each TOF-SIMS-cycle is triggered by secondary particles that are emitted from the target at ion impact. High yields of secondary electrons and protons were used in TOF-SIMS of negative and positive secondary ions. Start efficiencies were 100% for electron- and 10-80% proton starts. Start signals and secondary ion stop signals were both detected by an annular micro channelplate detector. Secondary ion acceleration is accomplished by biasing the target to + or - 3000 V. Typical secondary ion flight times are ~ 0.1 - 5 μs, while the electronic setup of detectors and amplifiers had a time resolution of ~ 2 ns. TOF-SIMS spectra where recorded by a high resolution (≤ 1 ns) one-start-one-stop TAC-ADC system and a multi-stop multichannel scaler (time resolution: 5 ns). For preparation of a 300 keV Xe-ion beam in charge state equilibrium, a 10 nm thick carbon foil was placed into the beam line in front of the annular micro channelplate detector. TOF-SIMS targets consisted of as received highly oriented pyrolytic graphite (HOPG) and float zone silicon (native oxide).

3. Results

Fig. 2 shows charge state distributions Th^{65+} ions after transmission through a 10 nm thick carbon foil. The incident ion velocity was 6.4×10^5 m/s. The potential energy that corresponds to the initial charge state is 113 keV. The thorium ions have developed a mean final charge state of 1.6+ in the foil, a result that agrees well with values for mean equilibrium charge states of

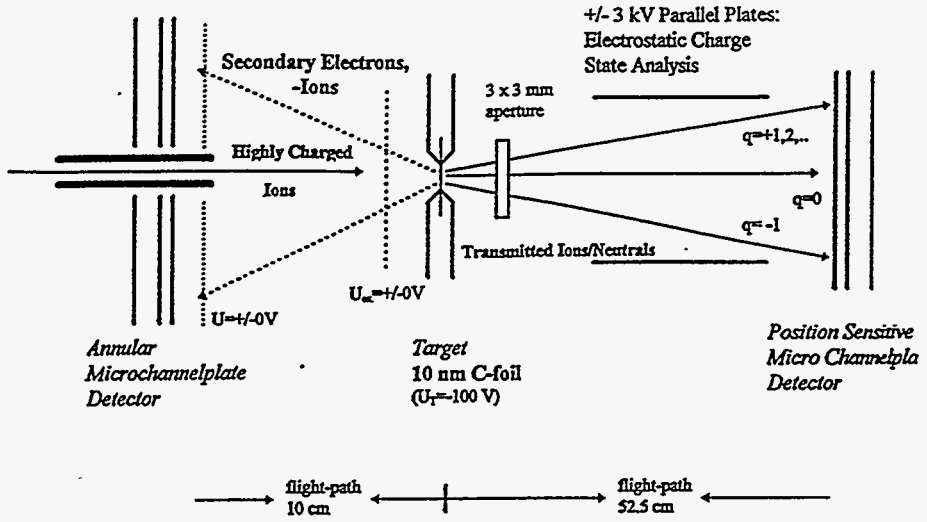
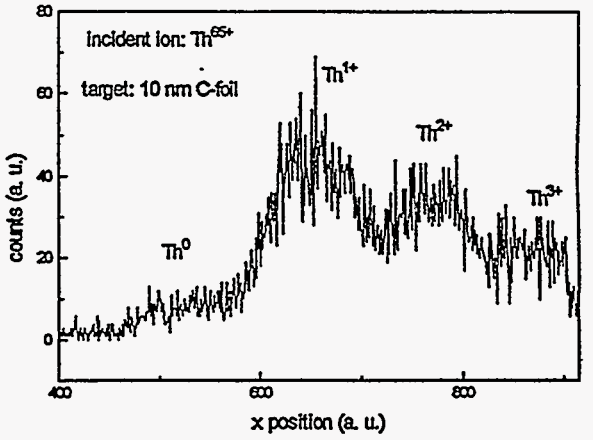
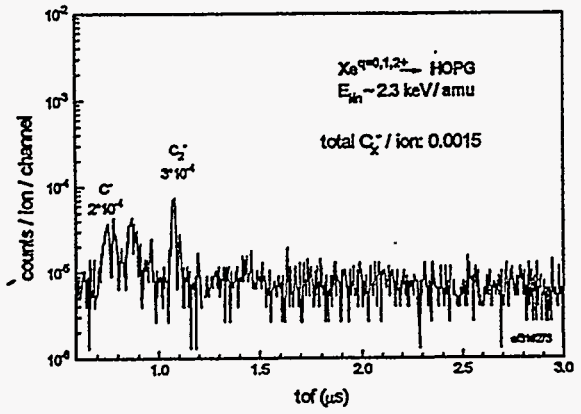


Fig. 1: Schematic of the experimental setup for studies of highly charged ion neutralization in 10 nm thick carbon films, and highly charged ion based TOF-SIMS.

Fig. 2: Charge state distribution of highly charged thorium ions after transmission through a 10 nm thick carbon foil. Data represent projections of two dimensional position distributions on the axis perpendicular to the direction of electrostatic charge state separation.





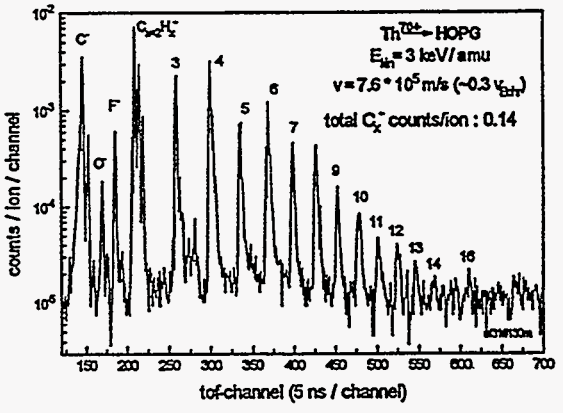
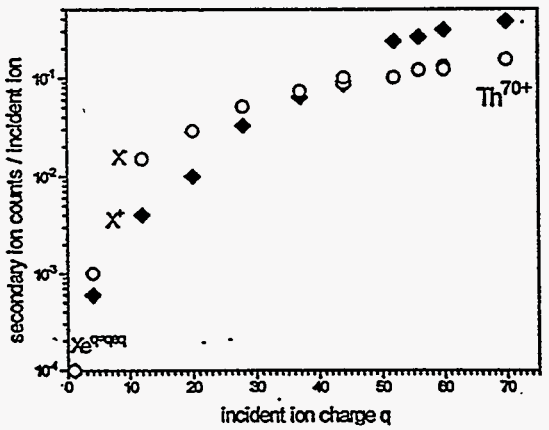


Fig. 3: Negative secondary ion production from graphite (HOPG) at impact of Xe^{1+} (left) and Th^{70+} (right) ions at kinetic energies of 2.3 and 3 keV/amu.

Fig. 4: Positive and negative secondary ion production from a FZ-Si native oxide target as a function of incident ion charge state. Ion energies are 4 (positive) and 10 keV×q (negative).



corresponding low charge state ions as determined by beam foil experiments [11]. We conclude that highly charged thorium ions reach charge state equilibrium in the 10 nm thick target, within a time of ≤ 17 fs (Th^{65+}).

In order to be able to directly compare contributions to secondary ion yields from collisional and electronic, i. e. ion charge state dependent, processes, we used the 10 nm thick carbon foil as a highly charged ion neutralizer. Incident ions loose approximately 10% of their initial energy in the foil [10]. A beam of ions exiting the foil in charge state equilibrium was used as a reference beam for in situ assessment of collisional contributions to observed secondary ion yields. Fig. 3 shows TOF-SIMS negative secondary ion spectra from a HOPG target at impact of $Xe^{q=q_{eq}}$ and Th^{70+} at 2.3 and 3 keV/amu. The energy density in highly charged ion neutralization is much higher than the corresponding near surface nuclear energy loss of singly charged ions at similar kinetic energies ($S_n \leq 5$ keV/nm). The ion charge (ion potential energy) based yield increase amounts to a factor of ~100. Significant is the observation of high yields of carbon clusters up to C_{16}^- at highly charged ion impact. Fig. 4 shows the incident ion charge state dependency of positive and negative secondary ion production from a float zone silicon native oxide target. The sum of positive and negative secondary ion counts per incident Th^{70+} -ion amounts to 0.6, an increase of over three order of magnitude as compared to collisional secondary ion production from low charge state, 300 keV Xe ions. The detection efficiency of the setup of ~ 10% is not included. Corresponding total ablation rates in collisional sputtering (i. e. secondary ions and neutrals) are ~ 5 atoms/ion. The observed yield increase is a convolution of an increased total ablation rate and higher ionization probabilities. Measurements of total sputtering yields are being performed.

4. Conclusion

Secondary ion production rates in highly charged ion solid interactions show substantial increases over corresponding rates in collisional sputtering. The very efficient electronic sputtering and desorption processes can be utilized for the development of highly charged ion based static SIMS. Given the compactness and availability of the basic ion source, EBIT, slow highly charged ions are promising candidates for the development of versatile surface analysis techniques with sensitivity limits $<< 10^9$ atoms/cm^2.

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