

Electronic Sputtering of Thin Conductors by Neutralization of Slow Highly Charged Ions

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Charge states of slow ($v \approx 0.3v_{\text{Bohr}}$) highly charged ions (O^{7+} , $\text{Ar}^{16,18+}$, Kr^{33+} , Th^{65+}) have been determined after transmission through 10 nm thick amorphous carbon foils. Up to the highest charge states, ions reach charge state equilibrium in the foils within less than 21 fs. High yields of secondary ions are emitted from the foils as a result of the dissipation of tens to hundreds of keV of potential energy during ion neutralization. Positive secondary carbon ion yields increase strongly for $q > 25+$. Our results demonstrate, for the first time, the occurrence of electronic sputtering in the interaction of slow ions with thin conductors. [S0031-9007(97)02753-1]

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Secondary particle production in the interaction of energetic ion beams with solid surfaces is an active area of basic and applied research. Linear collision cascade theories have been utilized most successfully for the description of sputtering processes in the interaction of singly charged, keV ions with metal surfaces [1]. Secondary particle production results from direct momentum transfer from incident ions to target atoms and sputter yields scale linearly with the nuclear stopping power of incident ions in a given target material. Total ablation rates typically amount to 2–20 atoms/ion [2]. Secondary ion production probabilities depend strongly on surface conditions, target, and incident ion species and range commonly from 10^{-2} to 10^{-5} of the total ablation rate [3,4].

Electronic energy loss processes have been found to be important for sputtering of insulators and poor conductors [5]. The effect of incident ion charge in electronic sputtering has drawn considerable attention following reports on strong charge state dependent secondary particle yield increases from LiF and Si at impact of slow ions (<1 keV/u) with incident charge states $q \leq 8+$ [6,7]. Parilis *et al.* suggested a “Coulomb explosion” model [6,8] for electronic sputtering of nonmetals by slow highly charged ions, in which charge state dependent electronic sputtering was related to electrostatic repulsion of target ions in a charge depleted region at the surface. No evidence for the occurrence of electronic sputtering effects was found in studies of total sputter yields from clean silicon targets using Ar^{q+} with charge states up to $9+$ [4], and in observations of secondary ion yields from SiO_2 and CsI at impact of slow Ar^{q+} with $q \leq 11+$ [9]. Charge dependent increases of total ablation rates at impact of slow Ar^{q+} ($5 \leq q \leq 9$) on GaAs have been attributed to Coulomb explosion sputtering [10]. Strong electronic sputtering effects have been observed in studies of secondary ion production in the interaction of slow (≤ 3 keV/u), very highly charged ions, like Au^{69+} and Th^{75+} , with insulators (e.g., SiO_2) [11]. Positive and negative secondary ion

yields were found to increase strongly with incident ion charge to values comparable to total ablation rates in collisional sputtering. Electronic sputtering effects have not been observed in the interaction of slow (~ 1 keV/u) ions with conductors; neither has such an effect been predicted by theory.

The production of secondary hydrogen ions is a special case of electronic sputtering. Yields of secondary protons ejected from insulators and conductors at impact of slow (0.5 keV/u) [9] and fast (~ 1 MeV/u) [12] heavy ions were found to increase with the incident ion charge state q^3 ($5 \leq q \leq 29$) [13]. The q^3 scaling was valid while incident ion velocities were changed over 2 orders of magnitude, indicating the minute influence of collisional contributions in the electronic sputtering regime. In studies of potential sputtering of C_{60} targets by slow (12.5–120 eV/u) Ar^{q+} ions with $4 \leq q \leq 16$, secondary H^+ and H_2^+ yields were found to increase with incident ion charge like q^{4-5} [14,15]. No strong charge state dependent increases of secondary carbon- or C_{60} -ion yields was reported.

The time scale for neutralization and charge equilibration of slow ($v < v_{\text{Bohr}}$) highly charged ions (HCI) in their interaction with solids is one of the key questions in investigations of charge state dependent, electronic sputtering phenomena, since it is the neutralization time that determines the density of electronic excitation energy that can be deposited into a surface near volume at highly charged ion impact. Charge relaxation of slow highly charged ions incident on surfaces has been studied for over a decade [11,16], leading to a model of hollow atom formation above metal surfaces followed by rapid deexcitation inside the target through Auger cascades and “side-feeding” mechanisms. Neutralization of slow, highly charged ions is being investigated, e.g., in small angle scattering experiments in conjunction with ion trajectory simulations. It was found that ions up to Th^{70+} (at ~ 2.2 keV/u) are dominantly neutral or single positively charged after an

interaction time of less than 100 fs with metal (Au) and nonmetal surfaces (e.g., mica) [11]. An upper limit of 30 fs was determined for complete charge equilibration of 3.75 keV/u O^{q+} ($3 \leq q \leq 8$) during specular scattering from an Au surface [17]. In a recently presented side-feeding model, a time of ~ 20 fs was predicted for neutralization of 1.275 keV/u Ar^{17+} at normal incidence in graphite [18].

We have measured charge states of slow ($v < v_{Bohr}$) highly charged ions after transmission through a 10 nm thick carbon foil, and determined the production of positive and negative secondary ions emitted from the carbon foil at highly charged ion neutralization. The experimental setup has been described in detail elsewhere [11,19]. Ions were extracted from the electron beam ion trap (EBIT) at Lawrence Livermore National Laboratory [11]. The pressure in the target chamber was kept below 2.7×10^{-8} Pa. Targets consisted of ~ 10 nm thick ($\sim 2 \pm 0.5 \mu\text{g}/\text{cm}^2$) amorphous carbon foils with diameters of 3 and 12.5 mm, mounted on high transmission TEM grids. Impurity concentrations in the foils were precharacterized to be 1 and 3.5 at. % of oxygen and hydrogen, respectively [20]. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis of the amorphous carbon foil surfaces showed oxygen contributions to secondary ion yields of 1% (O^+) and 2.3% (O^-), indicating low degrees of surface coverage from water and organic contaminants. Distortions of TOF-SIMS spectra due to charging of foil targets was not observed. Typical values for the resistivities of the foils are $< 10^{-2} \Omega \text{ cm}$ [20,21]. Transmitted projectiles were detected by a position sensitive microchannel plate detector after a flight path of 52.5 cm, and provided the start signals for TOF-SIMS measurements. A pair of parallel plates was positioned along the flight path between the target foil and the start detector for electrostatic analysis of charge state distributions of transmitted projectiles. Charge state fractions were obtained by normalization to transmission yields recorded at zero deflection plate bias. This normalization showed that typically more than 90% of transmitted species were included in the charge state analysis. The error in the values for the charge state fractions is $\pm 10\%$. It results from the accuracy of the fits utilized to determine contributions to individual charge states from measured contributions and from the statistical uncertainty in the data used for normalization. The incident ion flux was $\leq 10^3$ ions/s, and the total dose of ions used in this study $< 10^8$. Positive and negative secondary ions, emitted at impact of highly charged ions at normal incidence from the carbon foil, were accelerated from the target foils ($U_t = \pm 2$ kV) to a grounded extraction grid and were detected by an annular microchannel plate detector after a flight path of 10 cm. Secondary ion signals were used as stop signals in the TOF-SIMS measurements. TOF-SIMS spectra were recorded with a multichannel scaler allowing for the detection of many stop signals for each start

trigger. The detection efficiency of the TOF-SIMS system is $\sim 10\%$.

Charge state fractions of ions after transmission through a 10 nm thick carbon foil are shown in Fig. 1. Incident ions were O^{7+} ($v = 8.0 \times 10^5$ m/s), Ar^{16+} ($v = 7.6 \times 10^5$ m/s), Ar^{18+} ($v = 8.1 \times 10^5$ m/s), Kr^{33+} ($v = 7.5 \times 10^5$ m/s), and Th^{65+} ($v = 6.4 \times 10^5$ m/s); initial kinetic energies were $7.5 \text{ keV} \times q$. Resulting average transmitted ion charge states range from 0 for O^{7+} to 1+ for Ar^{18+} and 1.6+ for Th^{70+} ions. These values agree with measurements and calculations of mean equilibrium charge states of ions at similar velocities [22]. We observed a reduction in average charge states after passage through two stacked 10 nm thick carbon foils from 1.1+ to 0.7+ for Kr^{33+} and from 1.6+ to 1.1+ for Th^{65+} and attribute this to the continuous slowdown of ions in the foils, and to the decay of any excited states left after transmission of the first foil. The total time available for charge equilibration of highly charged ions incident on thin film targets, τ_{eq} , is the sum of the above surface neutralization time [16] and the time ions travel in the target. Depending on incident charge states, highly charged ions at $v \approx 0.3v_{Bohr}$ lose 10%–15% of their initial kinetic energy in a 10 nm thick carbon foil [19]. Resulting values for τ_{eq} are 14 fs for O^{7+} , 17 fs for Kr^{33+} , and 21 fs for Th^{65+} . We show for the first time that up to the highest charge state of $q = 65+$ for Th ions, slow highly charged ions reach charge state equilibrium in 10 nm thick carbon foils and within $\tau_{eq} \leq 21$ fs.

As a result of the massive disturbance of the local charge equilibrium at highly charged ion neutralization, the dissipation of tens to hundreds of keV of neutralization energy into a small target volume, a large number of secondary particles are emitted from the target.

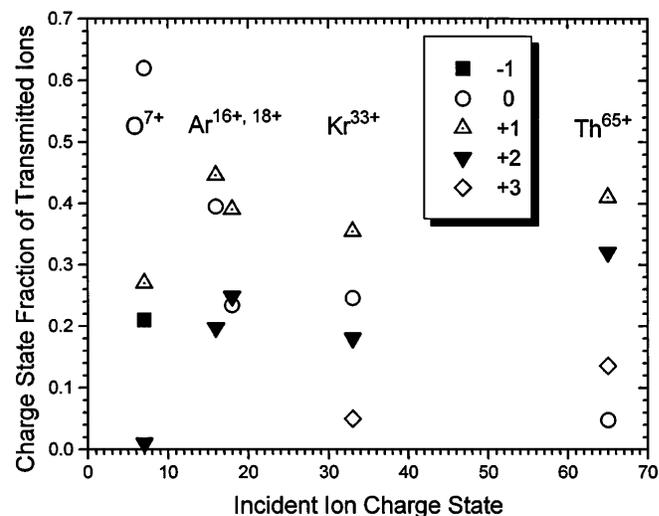


FIG. 1. Charge fractions of ions transmitted through a 10 nm thick carbon foil vs incident ion species. Errors in the charge fractions amount to $\pm 10\%$. Incident ion energies were $7.5 \text{ keV} \times q$.

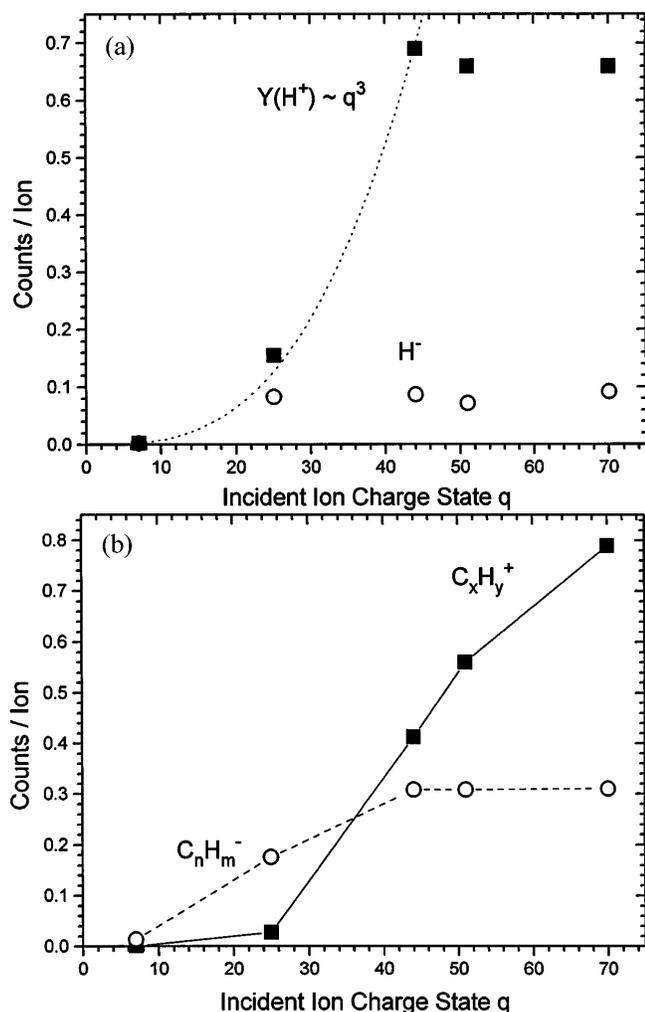


FIG. 2. (a) Production of positive and negative secondary hydrogen ions from a 10 nm thick carbon foil as a function of incident ion charge. Incident ions are O^{7+} , $Xe^{25,44,51+}$, and Th^{70+} . The dotted line is a fit to a cubic charge dependency for $7 \leq q \leq 44$. (b) Production of carbon ions $C_xH_y^+$ and $C_nH_m^-$. Lines are shown to guide the eye. The statistical error in the count rates is $\leq 5\%$.

Figure 2(a) shows positive and negative secondary hydrogen ion production rates from a 10 nm thick carbon foil at highly charged ion neutralization as a function of incident ion charge q . The TOF-SIMS detection efficiency is not included in Figs. 2(a) and 2(b). Incident ions were O^{7+} , Xe^{25+} , Xe^{44+} , Xe^{51+} , and Th^{70+} , with kinetic energies of $5 \text{ keV} \times q$ for detection of positive and $9 \text{ keV} \times q$ for detection of negative secondary ions. Small variations in initial ion velocities in the regime from $(4-9) \times 10^5 \text{ m/s}$ have been shown to have negligible effects on charge dependent secondary particle emission [11,13]. In order to allow for a qualitative comparison with the previously observed cubic dependency of secondary proton yields on incident ion charge [8,9,13,23], we included a q^3 fit to the three data points for O^{7+} , Xe^{21+} , and Xe^{44+} in Fig. 2(a).

For incident ion charge states $q \geq 44+$, both positive and negative secondary hydrogen ion yields are found to saturate. The hydrogen coverage of a fully terminated amorphous carbon surface is in the order of $2 \times 10^{15} \text{ atoms/cm}^2$ [24]. The surface area from which electron capture to an incoming highly charged ion takes place, A_q , can be estimated from the classical over-the-barrier model [15,16] to be $0.2 \leq A_q \leq 0.8 \text{ nm}^2$ for the ion charges used in this study. Accordingly, the number of hydrogen atoms in the impact area can be estimated to be 4–16. Secondary proton count rates saturate at a value of $\sim 0.7 H^+$ counts per incident highly charged ion. Ionization probabilities for formation of secondary ions at highly charged ion impact are not known. With the given detection efficiency of our TOF-SIMS system, we conclude that secondary hydrogen ion production saturates, because all hydrogen atoms are removed from the interaction area at impact of individual ions with charges $q \geq 44+$.

Charge state dependencies of the positive and negative secondary carbon ion production from a thin carbon foil are shown in Fig. 2(b). Positive secondary ion spectra are dominated by C_2^+ . Integrated contributions from C_2^+ , C^+ and $C_xH_y^+$ ($x = 2, 3, 4$; $y = 1, 2$) amount typically to less than half of all positive secondary ion counts. Negative secondary ion spectra are dominated by $C_2H_m^-$ ($m \leq 2$). The relative abundance of hydrocarbon ions is higher in negative than in positive secondary ion spectra. Like secondary hydrogen ion yields, negative carbon ion yields ($C_nH_m^-$, $n \leq 8$, $m \leq 2$) saturate for incident ion charge states $q \geq 44+$. Yields of positive carbon ions show no saturation and increase with ion charge to a value of $0.79 C_xH_y^+$ counts/ion. Integration of molecular contributions and inclusion of the detection efficiency yields a carbon ion production rate of $\sim 16 C^+$ /ion. In comparison, the total ablation rate (secondary neutrals and ions), in collisional sputtering of carbon by Xe^{1+} (at 2.2 keV/u) amounts to ~ 4.5 atoms/ion [2]. The charge dependent increase of positive secondary ion production from an amorphous carbon target is the first observation of electronic sputtering of a conductor by slow ions.

The potential energy of highly charged ions, dissipated in a thin target, in a neutralization time of a few tens of femtoseconds, produces a high density of target excitations. Electronic energy loss effects, like amorphization and track production, have been observed in the interaction of GeV heavy ions [25] and MeV fullerenes [26] with metal targets above an electronic stopping power threshold of $\sim 30-40 \text{ keV/nm}$. The total amount of energy dissipated during neutralization of slow Th^{70+} in a 10 nm thick carbon foil, i.e., the sum of ion potential energy ($E_{\text{pot}} = 152.6 \text{ keV}$) and integrated kinetic energy loss in the foil ($\sim 55 \text{ keV}$ at $E_0 = 350 \text{ keV}$) [19], yield values of $E_{\text{total}} \approx 205 \text{ keV}$ for Th^{70+} . The corresponding average stopping power of 20.5 keV/nm (5 keV/nm for Xe^{35+}) is lower than the electronic stopping power threshold as found for the onset of electronic damage pro-

duction in metals by swift heavy ions. This is likely to result from a higher density of target excitations at the much lower incident ion velocities during highly charged ion neutralization.

The Coulomb explosion model [6,8] predicts electronic processes in the interaction of highly charged ions with poor conductors to result in the surface equivalent of an ion explosion spike [27], i.e., the Coulomb explosion of a charge depleted, surface near target volume. We conclude that for slow, very highly charged ions, like Xe^{51+} or Th^{70+} , neutralizing in thin conducting targets, the density of electronic excitations of target atoms becomes so high that it cannot be dissipated efficiently before ionized target atoms respond to electrostatic Coulomb stress in electronic sputtering events. We note that the Coulomb explosion model [8] reproduces the q^3 dependency of H^+ yields on incident ion charge correctly, but does not predict the observed near linear increase in C^+ yields for $q > 25$. The continuing increase of positive secondary ion yields reflects both an increase in target volume with high ionization density and a likely increase in secondary particle ionization probability. Negative ion yields saturate when most of the target atoms in the interaction region are positively charged at secondary ion emission, and fractions of negatives can be formed by electron capture from neutrals or emitted from the fringe of the interaction region where the ionization density of target atoms is lower. A threshold charge for the onset of electronic sputtering at neutralization of slow highly charged ions in a 10 nm thick amorphous carbon foil can be estimated from the crossover of positive and negative secondary carbon ion production rates to be $q \approx 35+$ for slow Xe^{q+} ions.

In summary, we have shown that slow highly charged ions with incident charge states up to $65+$ reach charge state equilibrium in 10 nm thick amorphous carbon foils, within $\tau_{\text{eq}} \leq 21$ fs. Analogous to the induction of electronic energy loss effects in metals by swift heavy ions, the deposition of high amounts of electronic excitation energy during neutralization of slow highly charged ions results in strong electronic sputtering of surface adsorbates and target material. Our results demonstrate, for the first time, the occurrence of electronic sputtering in the interaction of slow ions with thin conductors.

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- [1] P. Sigmund, in *Inelastic Ion-Surface Collisions*, edited by N.H. Tolk *et al.*, (Academic Press, New York, 1977), p. 121.
- [2] N. Matsunami *et al.*, *At. Data Nucl. Data Tables* **31**, 1 (1984).
- [3] A. Benninghoven, *Angew. Chem. Int. Ed. Engl.* **33**, 1023 (1994).
- [4] S. T. de Zwart *et al.*, *Surf. Sci.* **177**, L939 (1986).
- [5] K. Wien, *Radiat. Eff. Defects Solids* **109**, 137 (1989), and references therein.
- [6] E. S. Parilis, *Z. Phys. D* **21**, S127 (1991), and references therein.
- [7] T. Neidhart *et al.*, *Phys. Rev. Lett.* **74**, 5280 (1995).
- [8] I. S. Bitensky *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. B* **72**, 380 (1992).
- [9] S. Della-Negra *et al.*, *Phys. Rev. Lett.* **60**, 948 (1988).
- [10] N. Itabashi *et al.*, *Jpn. J. Appl. Phys. I* **34**, 6861 (1995).
- [11] D.H. Schneider *et al.*, *Phys. Scr.* **53**, 228 (1996), and references therein.
- [12] S. Della-Negra *et al.*, *Phys. Rev. Lett.* **58**, 17 (1987).
- [13] M. Benguerba *et al.*, *Int. J. Mass Spectrom. Ion Phys.* **107**, R11 (1991).
- [14] N. Kakutani *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. B* **96**, 541 (1995).
- [15] J. Burgdörfer *et al.*, *Phys. Rev. A* **54**, 4140 (1996).
- [16] J. Burgdörfer *et al.*, *Phys. Rev. A* **44**, 5674 (1991); **47**, R20 (1993).
- [17] L. Folkerts *et al.*, *Phys. Rev. Lett.* **74**, 2204 (1995).
- [18] S. Winecki *et al.*, *Phys. Rev. A* **53**, 4228 (1996).
- [19] T. Schenkel *et al.*, (to be published).
- [20] Foils were made and characterized by The Arizona Carbon Foil Co., Tucson, AZ.
- [21] G. A. Porkolab *et al.*, *Appl. Phys. Lett.* **61**, 2045 (1992).
- [22] K. Shima *et al.*, *Phys. Rev. A* **40**, 3557 (1989).
- [23] E. F. da Sivera *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. B* **99**, 107 (1995).
- [24] A. V. Hamza *et al.*, *Surf. Sci.* **237**, 35 (1990).
- [25] A. Audouard *et al.*, *Phys. Rev. Lett.* **65**, 875 (1990).
- [26] H. Dammak *et al.*, *Phys. Rev. Lett.* **74**, 1135 (1995).
- [27] L. Fleischer, P.B. Price, and R.M. Walker, *Nuclear Tracks in Solids* (UC Press, Berkeley, 1975).