Slow multicharged ions hitting a solid surface: From hollow atoms to novel applications

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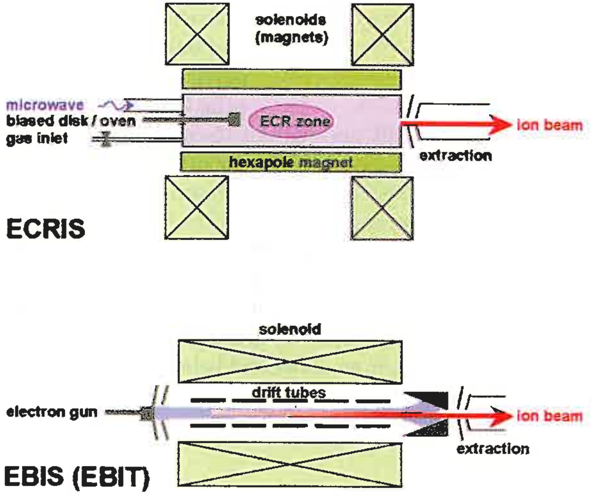


▲ **Fig. 1:** Sources for producing slow multiply charged ion beams. (top): ECRIS (electron cyclotron resonance ion source). Microwave radiation (2.45–28 GHz) fed into a magnetical plasma trap causes resonant heating of the plasma electrons while the also confined ions remain comparably cold. Fairly high ion charge states can be produced via step-by-step ionization, and relatively large ion currents may be extracted. (bottom): EBIS (electron beam ion source). Ions are confined in the space charge potential of a magnetically compressed electron beam (energy from keV up to 100 keV). Step-by-step ionization proceeds until the axial electric field barrier on the right hand side is lowered for ion extraction. In pulsed operation, up to fully stripped ions of any species can be produced but extractable ion currents are lower than for ECRIS. A closely related version (EBIT – electron beam ion trap) has been developed for studying highly charged ion spectra but can also be modified for MCI extraction.

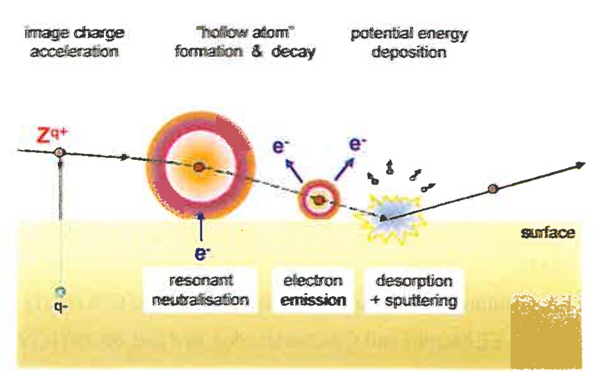
Impact of slow heavy particles (atoms, molecules, ions; impact velocity ≤ 1 a.u. = 25 keV/amu) on solid surfaces is of genuine interest in plasma- and surface physics and related applications (plasma technology, gaseous electronics, micro-electronics, surface analytics and -spectroscopy). Nature and intensity of the resulting interactions depend both on the kinetic and the potential energy which is carried by the projectile toward the surface. This can result in, e.g., sputtering, electron- and secondary ion emission, and elastic and inelastic projectile scattering (for details see [1, 2]).

In the last two decades a new branch of particle-surface interaction has evolved, comprising the surface-impact of slow multicharged ions (MCI) [3]. This branch was strongly promoted by the successful development of efficient, affordable MCI sources (cf. figs. 1a, b).

Basic processes

Fig. 2 illustrates various phenomena, which occur during the approach of a slow MCI in initial charge state q towards a clean metal surface with work function W. A classical over-the-barrier model developed by J. Burgdörfer [4] predicts for $q \gg 1$ first quasi-resonant electronic transitions from the surface to arise at a

Article available at http://www.europhysicsnews.org or http://dx.doi.org/10.1051/epn:2002610



▲ **Fig. 2:** MCI – surface interaction scenario (cf. text)

"critical distance" $d_c \approx (2q)^{1/2}/W$ into excited projectile states with hydrogenic principal quantum numbers $n_c \approx q^{3/4}/W^{1/2}$ (atomic units). E.g., for fully stripped argon ($Z = q = 18$; Z: projectile nuclear charge) on Al(111) ($W = 0.16$ au) the classical over-the-barrier model predicts $d_c \approx 2$ nm and $n_c \approx 22$.

The particle becomes rapidly neutralized and eventually a so-called "hollow atom" is formed. This hollow atom, an exotic creation during atomic collisions, is a short-lived multiply excited neutral atom which carries the larger part of its Z electrons in high-n levels while some inner shells remain transiently empty. This extreme population inversion can last for typically hundred femtoseconds during the approach of a slow MCI toward the surface.

Despite its short lifetime the formation and decay of hollow atoms may be conveniently studied through their ejected electrons and characteristic soft X-rays (see below), and the trajectories, energy loss and final charge state distribution of surface-scattered projectiles [3]. Hollow atoms decay primarily via autoionisation by ejection of slow (≤ 10 eV) electrons. Subsequent re-neutralisation and electron emission continues until the hollow atom collapses upon close surface contact. Until its first full neutralisation the projectile will be accelerated toward the surface by its rapidly decreasing mirror charge, which provides an additional "vertical kinetic energy" $\Delta E_{q,im} \approx 1/4.q^{3/2}.W$ [3, 4]. For our above example, $\Delta E_{q,im}$ amounts to more than 80 eV.

This image charge acceleration could be experimentally demonstrated in different ways (cf. fig. 3), in excellent agreement with classical over-the-barrier model predictions. On the one hand, the slow electron emission proceeds until close surface impact and the corresponding electron yield increases with decreasing perpendicular impact energy, for which $DE_{q,im}$ is setting the lower limit [6]. On the other hand, for grazing incident MCI on a very flat (monocrystalline) target surface the outgoing trajectory of the neutralized projectile becomes steeper than its incoming one due to image charge acceleration which acts until the close surface contact and subsequent specular reflection [7].

Above-surface electron emission and projectile image charge acceleration have also been observed for insulator surfaces and can be explained by the classical over-the-barrier model in a similar way as for metals, if the different electronic structure and time-dependent response of the target surface is properly taken into account.

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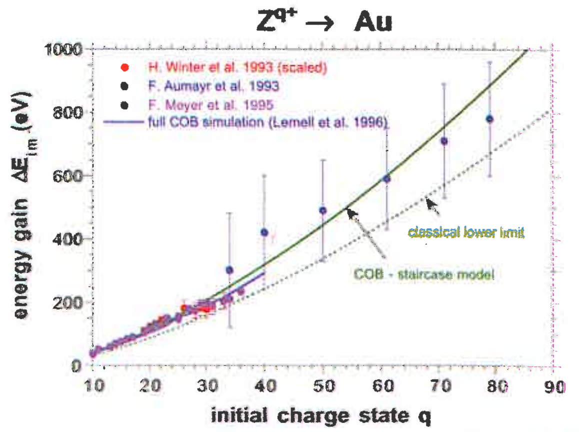
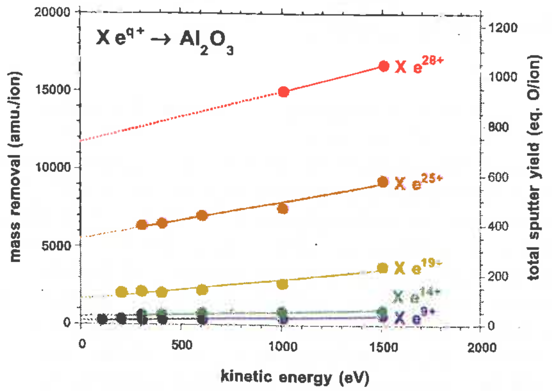
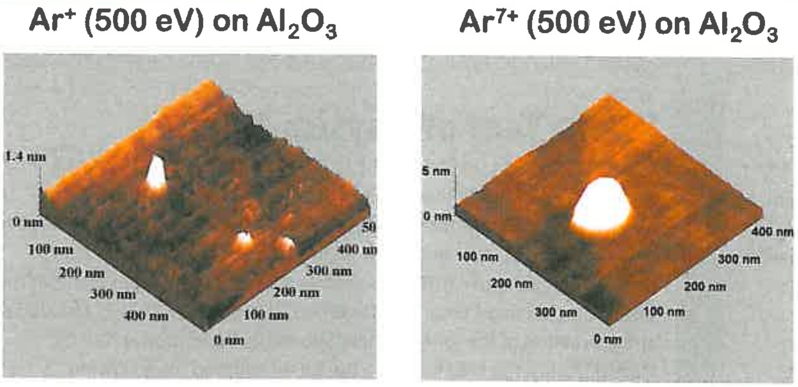
Fig. 2 indicates that upon and after close surface contact a considerable excitation energy remains stored in the hollow atom which can give rise to further electron emission at and below the surface. In particular, fast Auger electrons can result from filling of projectile inner shells, alternatively to emission of projectile-characteristic soft X-rays [3]. On the other hand, the rapid electron capture by a MCI during its approach to and contact with the surface causes a strong excitation of the latter, which in case of metal- and semiconductor targets can be effectively dissipated among the target quasi-free electron gas, but for an insulator surface may cause desorption of target constituents ("potential sputtering – PS", see below). With grazing incident MCI on flat surfaces contributions from above and below the surface can be



▲ **Fig. 3:** Test for MCI neutralization scenario: Comparison of measured image-charge energy gains (symbols) with predictions from the classical over-the-barrier model, for impact of MCI on clean gold surfaces [5].



▲ **Fig. 4:** Absolute mass (in atomic mass units) and number of oxygen atoms sputtered per primary ion vs. impact energy, for bombardment of clean polycrystalline Al_2O_3 by slow Xe^{q+} ions [12].



◄ **Fig. 5:** Al$_2$O$_3$ (0001) single crystal surface bombarded with 500 eV Ar$^+$ (left) and Ar^{7+} ions (right) as seen in UHV AFM contact mode. The observed defect size (both height and lateral dimension) increases with projectile charge state (from [13]).

separated [8]. Moreover, such a collision geometry is useful for elucidation of effects caused by the kinetic projectile energy [9].

Potential sputtering and its possible applications

To what extent the electronic relaxation of hollow atoms takes place above or below the surface is closely related to the way how this hollow atom dissipates its large potential energy. Emission of electrons and X-ray photons carries away only a fraction of the total potential energy originally stored in the MCI. The remaining part will be dumped into the solid and cause electronic excitation of a very small surface region. For metal surfaces even rather sudden perturbations of the electronic structure can be accommodated by the excitation energy being rapidly dissipated in the target material without inducing any structural modification. However, in recent studies on slow MCI impact on certain insulator surfaces a quite dramatic increase of the yields for total sputtering and secondary ion emission with increasing q has been observed (c.f. fig. 4).

... potential sputtering by MCI promises a much more gentle nanostructuring tool

This effect has been termed potential sputtering [10, 11], as compared to the more conventional kinetic sputtering by momentum transfer between impinging ion and recoiling target atoms in a collision cascade.

The possibility of exploiting the huge amount of potential energy stored in MCI for nano-fabrication, e.g. "writing" on a surface, has for some time captured the imagination of researchers. Applications have been envisioned for a broad spectrum ranging from information storage via materials processing to biotechnology.

While nanostructures produced by kinetic sputtering with and implantation of *fast* ions are subject to unwanted radiation damage, potential sputtering (PS) by MCI promises a much more gentle nanostructuring tool since,

a. their kinetic energy is small, so they only interact with the first few surface layers without penetrating into the target bulk;
b. they interact with the surface mainly through their potential energy, which can be tuned by varying the ion charge;
c. the potential energy causes primarily electronic excitation which leads to bond breaking and lattice defect production via electron-phonon coupling rather than violent momentum transfer in kinetic collision cascades;
d. the interaction of slow MCI with surfaces is highly material-selective, i.e. large differences between (semi-) conducting and insulating target materials are observed.

Beams of slow multicharged ions have so far been used to produce nanometer sized surface modifications [11, 13] on various substrates (fig. 5) as well as to form ultra-thin silicon oxyd layers or SiO$_2$ nanodots on Si surfaces [14].

Such nano-defects can be more conveniently studied by using (non-contact) atomic force- and scanning tunneling microscopy. They have already shown unusual excitonic features in their photoluminescence spectra [15].

The field of MCI–surface interaction has started out as a playground for exotic albeit fundamental atomic phenomena. First promising applications of multicharged ions are now emerging which make use of the unique opportunities provided by slow MCIs for engineering the topmost layers of insulating surfaces.

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