Slow Highly Charged Ions - A New Tool For Surface Nanostructuring? -

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The large potential energy stored in highly charged ions is liberated when these ions recombine during impact on a solid surface. For certain target species this can cause enhanced sputtering and nanodefect formation. We summarize the properties of slow highly charged ions which are relevant for surface interaction and propose their use as a new and very selective tool for nanostructuring of surfaces. [DOI: 10.1380/ejssnt.2003.171]

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I. INTRODUCTION

One important way to produce nanostructured surfaces involves kinetic sputtering with and implantation of fast ions. However, fast ions unavoidably cause some unwanted radiation damage. As opposed to this, potential energy (PS), i.e. desorption induced by potential energy of slow highly charged ions (HCI), holds great promise as a much more selective nanostructuring tool [1, 2]. It may cause large surface sputter yields even at such low ion impact energy where kinetic sputtering and defect creation in deeper layers is not possible. While the physical mechanisms of PS have been the subject of extensive investigation [3-7], practical applications of slow multiply-charged ions have so far remained largely unexplored, although slow HCI provide unique opportunities for etching, ultra-thin film growth and nanostructure fabrication.

In this contribution we first summarize the mechanisms of slow highly charged ion interaction with surfaces (Section 2) and then describe new opportunities of using slow highly charged ions for nanostructuring of surfaces and related applications.

II. HIGHLY CHARGED IONS AND THEIR INTERACTION WITH SURFACES

In kinetic sputtering the projectile ions transfer kinetic energy and momentum to the target atoms, displacing them from their original position and eventually causing their ejection into vacuum [8]. Singly charged ions with kinetic energies of typically some keV interact mainly via direct collisions with the target atoms (nuclear stopping) [9]. For faster ions and especially swift heavy ions (typically MeV/amu) the electronic energy loss (electronic stopping) dominates [10, 11], leading to electronic excitation and ionization in tracks of a few nm diameter.

In addition to their kinetic energy, ions can also carry internal (i.e. potential) energy, particularly if these ions carry a high charge. For highly charged ions (HCI) the potential energy corresponds to their production where q electrons (q: ion charge state) have to be removed from an originally neutral atom. This potential energy becomes rather large for higher values of q as shown in Fig. 1. Upon surface impact the potential energy is available for inducing various inelastic processes while the HCI regains its q missing electrons to become again fully neutralized [1, 12-14]. If the HCI is slow (i.e. when it carries more potential than kinetic energy upon surface impact) it interacts rather selectively with the outermost layers of the solid only. It deposits its potential energy in a short time (typically about hundred femtoseconds) within a small area (typically less than one nm²), with the following consequences.

(a) Image charge acceleration: As long as the projectile is charged it will be accelerated toward the surface by its mirror charge which provides an additional “vertical kinetic energy” [12, 15] and thus sets a lower limit to the impact energy [16-18].

(b) Hollow atom formation and electron emission: The projectile will be rapidly neutralized in front of the surface by resonant capture of electrons into highly excited states, resulting in the transient formation of so-called “hollow atoms” [1, 12, 13, 19-21]. These multiply excited atoms decay via auto-ionization and other Auger-type processes, accompanied by the emission of a large number of slow (< 10 eV) electrons. For example, for impact of one Th⁸⁺ ion (v ~ 10⁴ m/s) on a Au surface, on the average close to 300 electrons are emitted [16]. Electron emission and re-neutralization continue until the hollow atom collapses upon close surface contact.

FIG. 1: Total potential energy W_{pot}(q) of multiply charged Ar⁺⁺, Xe⁹⁺ and Th⁸⁺ ions vs. charge state q.
(c) Potential energy deposition and sputtering: Only a fraction of the potential energy originally stored in the projectile is released above the surface, because the image charge attraction limits the available interaction time. The larger part of this potential energy will be liberated close to the topmost layer, where potential energy of the projectile is converted into electronic excitation of a small surface region. This electronic excitation corresponds to creation of electron-hole pairs, of "hot holes" in the conduction and or valence band of the target, and of inner-shell holes of target atoms. For metal surfaces such sudden perturbation of the electronic structure can be rapidly accommodated and the excitation energy will dissipate within the target material without inducing structural surface modification. Therefore no charge state dependence of sputtering has been observed for Au, Si and GaAs [22, 23]. In materials with reduced electron mobility (e.g. insulator targets), a sudden modification of the near-surface electronic structure cannot be restored immediately and may therefore induce structural surface modifications (defect formation, desorption, sputtering etc.), giving rise to sputtering induced by the projectile’s potential energy, i.e. potential sputtering. This potential sputtering process is characterized by a strong dependence of the observed sputtering yields on the charge state of the impinging ion (cf. Fig. 2). It can already take place at ion impact energies well below the kinetic sputtering threshold. For a more detailed discussion of the mechanisms for potential sputtering the reader is referred to recent reviews [4, 5, 24].

III. POSSIBLE APPLICATIONS FOR SLOW HIGHLY CHARGED IONS

While kinetic sputtering and implantation of fast ions are always accompanied by unwanted radiation damage, potential sputtering by slow HCI promises a much gentler nanostructuring tool because of the following reasons.

(a) Their kinetic energy is small, so they will only interact with the first few surface layers without penetrating deeper 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 HCI with surfaces is highly material-selective, i.e., large differences between (semi-) conducting and insulating target materials are observed.

(e) The recently observed kinetically assisted potential sputtering mechanism [7] considerably expands the opportunities to modify surfaces by slow highly charged ions.

Considering these advantages and specific properties of HCI (as compared to singly charged ions) we might use slow HCI for the following applications.

(a) Surface cleaning ("soft sputtering") : Beams of slow HCI could be used to gently (no radiation defects in deeper layer) remove insulating layers (e.g. oxides, adsorbates) from a conducting substrate. If the kinetic projectile energy is below the kinetic sputtering threshold, the process would be self-terminating after removal of the adsorbate layer.

(b) Gentle tool for surface modifications: Production of nano-defects (e.g., vacancy and interstitial defects, blisters, craters) and structural changes (amorphisation, ...) due to HCI impact onatomically clean single crystal surfaces has been demonstrated by means of atomic force- and scanning tunneling microscopy [25-29]. In some cases the defect size was dependent on the charge state of the HCI projectile (cf. Figs. 3 and 4). One big advantage of using slow HCI instead of fast singly charged ions would be
that all structural changes are limited to the topmost layers only. Due to the large electron emission yield the impact of a single HCI can be detected with 100% efficiency, which allows to implant single ions in shallow depths as e.g. desirable for quantum manipulation/computing [30].

(c) HCI ion lithography and surface patterning: HCI lithography with better than 100 nm edge resolution (limited only by the quality of the mask) has recently been demonstrated by irradiating self-assembled monolayers (SAMs) of dodecanethiolate on gold covered by a mask (10 m squares) with Xe$^{44+}$ ions [31]. The HCI were found to be 20 times more efficient in etching the surface than metastable He atoms. For a mask-less imprint of regular patterns, insulator surfaces covered with "self-organized" metal clusters in variable size may be bombarded with HCI. Such metal cluster-on-insulator layers are presently investigated primarily in view to the development of surface-catalyzers. They can be produced either via electron impact-induced formation of metal colloids from the target bulk (as for alkali- or earth alkaline-halides), or by metal vapor deposition on appropriate insulator surfaces (e.g. alumina). We expect that potential sputtering will not take place at the insulator area covered by self-assembled metal clusters. Therefore, these clusters provide "masks" for producing regular rather than randomly distributed defects on the insulator surfaces of interest.

(d) SiO$_2$ nanodot formation on Si substrates: Nanometer sized surface modifications on silicon substrates can be produced by bombarding hydrogen-terminated silicon monocrystals in UHV with low fluxes of slow HCI. At a HCI impact site (with a nanometer size radius) we expect the hydrogen atoms to be removed (bond-breaking, c.f. Fig. 5). By introducing oxygen gas of a sufficient partial pressure, the now open silicon bonds will react with the O$_2$ molecules, in this way producing ultra-shallow silicon oxide nanodots [32]. We are presently studying the formation of such nanodots and will optimize the conditions by using (non-contact) atomic force- (AFM) and scanning tunneling microscopy (STM) as well as high resolution scanning Auger spectroscopy. We expect that on such produced SiO$_2$ nanodots large molecules (e.g. carbon nanotubes [33]) can be selectively grown.

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FIG. 5: Mechanism for HCI-induced SiO$_2$ nanodot formation on Si (see text and Ref. [32]).

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