Sputtering of Insulator Surfaces by Slow Highly Charged Ions: "Coulomb Explosion" or Defect-Mediated Desorption ?

In recent studies on the impact of slow highly charged ions on insulator surfaces, a dramatic increase of the yields for sputtering and secondary ion emission with projectile charge state has been observed for certain target species. We critically discuss the currently available experimental evidence in view of two competing models for the "potential sputtering" process. The so-called "Coulomb explosion" model predicts potential sputtering for any insulator surface, whereas a model involving defect-mediated desorption explains why strong projectile charge state dependence of sputtering is exclusively found for insulators with strong electron-phonon coupling.

Keywords: *multicharged-ion surface interaction, hollow atoms, potential sputtering, Coulomb explosion, electronic sputtering*

1. INTRODUCTION

Highly charged ions (HCI) carry a considerable amount of potential energy (e.g., 14 keV for bare Ar^{18+}, 51 keV for Ne-like Xe^{44+}, 250 keV for Ne-like Th^{80+}), which can greatly exceed the projectile kinetic energy in slow (hyperthermal) collisions with solid surfaces. Transfer of such large potential energies to a very small surface area of, typically, about 100 $Å^2$ within a time of less than 100 fs corresponds to a power

flux of $\geq 10^{14}$ W/cm^2, which may give rise to strong nonlinear processes and other exotic phenomena such as, e.g., "hollow atom" formation.[1-5] The projectile potential energy may be released via electronic excitation of the target or ejection of electrons and X-rays, but also by removing atoms and ions from the target surface. While the process of kinetically induced sputtering is well established, ejection of target atoms and ions due to potential sputtering of insulators (henceforth to be abbreviated PSI) is still almost unexplored. Since PSI involves high sputter yields at low impact energy and is not accompanied by strong radiation defects in deeper target layers as is kinetically induced sputtering, it could become of considerable technological relevance: Preferential removal of insulating layers (no PSI occurs for conductor surfaces, see Section 2) could be the basis for novel cleaning procedures in the semiconductor industry (e.g., soft sputtering of SiO$_2$ from Si-wafers). Other applications for nanostructuring and characteristic surface modifications of insulators are also conceivable. A more detailed understanding of mechanisms responsible for the conversion of projectile potential energy in PSI processes is therefore highly desirable.

In Section 2, the relevant experimental evidence will be summarised; in Section 3 two competing models for PSI ("Coulomb explosion – CE" vs. "defect-mediated sputtering – DS") will be presented; and in Section 4 the available experimental evidence will be discussed with respect to the two models. This comparison favours the DS model. A list of abbreviations used in this article is given in the Appendix.

2. EXPERIMENTAL EVIDENCE FOR POTENTIAL SPUTTERING OF INSULATOR SURFACES

Recent experimental studies of the impact of slow HCI on atomically clean solid surfaces involved electron emission (total yields, energy spectra, number statistics), projectile-characteristic soft X-ray spectra and grazing projectile scattering (image-charge attraction, neutralisation). A fairly complete account of these methods and results is given in Refs. 1 and 3–7.

When pursuing a critical comparison between theory and experiment for HCI interaction with insulator surfaces, it is important to recall specific experimental difficulties encountered in the interaction with insulating targets. These difficulties may often complicate the data

202

interpretation as well as the comparison with other experiments and theory. In general, influence of the charge state of the projectile (i.e., its potential energy represented by the total ionization energy of the respective neutral atom) becomes most effective at the lowest impact velocity where processes due to the kinetic projectile energy will be drastically reduced or absent altogether. A basic requirement for reproducible results which can be compared with theory is clean and well-characterised surfaces. Also, in the case of polycrystalline targets, structural properties cannot be neglected. For semiconductor as well as insulator surfaces, sputtering and annealing as commonly applied to metal targets are less effective or even destructive. The extreme sensitivity of oxides to ion bombardment may cause preferential sputtering of oxygen in the near surface region, which severely modifies the surface properties. Another difficulty in such ion beam experiments is the possible charging-up of the target surface. Both primary ions and ejected electrons give rise to a positively charged surface layer which not only can influence the effective ion impact energy and ion-beam geometry, but also the energy distribution of emitted charged particles. Since secondary ions as well as ejected electrons involve kinetic energies peaking at a few eV only, a target charge-up by only a fraction of one volt can already strongly influence the total yields. Special precautions are needed to overcome such difficulties (e.g., electron flooding, deposition of insulator target material as ultra-thin films on metal substrates, heating of samples up to a temperature where ion conduction becomes sufficiently large, as in the case of alkali halides). Not all experimental results discussed below have been obtained under conditions where all the parameters mentioned above were well controlled, a fact to be kept in mind when sometimes highly contradictory experimental data are compared.

First experimental work on charge-state-dependent sputtering of insulators by HCI has been carried out in Tashkent/Uzhbekistan, [8, 9] from which it was concluded that for impact of Ar^{q+} ions ($q \leq 5$) on silicon and alkali halide surfaces, secondary ion yields increased rapidly with both the incident ion charge and the decreasing impact energy. Etching patterns on a KCl surface previously bombarded with equal fluxes of slow Ar^{q+} and Kr^{q+} ions were larger for higher q.[10] In Ref. 11 it was claimed that for bombardment of Si with singly charged ions, sputter yields are larger by more than a factor of two than for neutral projectiles of equal mass and energy. However, for 20 keV Ar^{q+}($q \leq 9$) impact on a

Si surface, only the secondary ion yield increased noticeably with q, whereas the respective total sputter yields (dominated by ejection of neutral Si atoms) did not change with q.[12] This apparent contradiction to Ref. 11 was explained with a different conductance of the Si samples.

AFM (atomic force microscopy) for mica samples irradiated with low fluences of very highly charged ions (e.g., Xe^{44+} and U^{70+}) revealed single-ion-induced blister-like defects, the size of which increased with the incident ion charge beyond a certain charge state "threshold" at around $q = 30$.[13] These measurements have been performed at comparably high impact energies (several hundred keV). For bombardment of SiO_2 with Xe^{q+} ($q \leq 44$) and Th^{q+} ($q \leq 70$) at similar kinetic energy as in Ref. 13, TOF spectra of ejected positive and negative secondary ions were dominated by single-atomic species, but also molecular clusters have been observed.[14] Again, the yields increased in proportion to the incident ion charge above a "threshold" of about $q = 25$. Secondary ion yields were made absolute by taking into account the acceptance solid angle and efficiency of the applied TOF system, resulting in, e.g., total yields of 25 ± 12 for positive and 5 ± 2.5 for negative secondary ions from impact of Th^{70+}, respectively. These remarkably high values suggested that the total sputtering yields (i.e., including neutrals) must be significantly larger than the known kinetic sputtering yield of about 2.5 target particles for impact of 500 keV singly charged Th ions.[14]

A different set of results stems from HCI-induced proton sputtering from "dirty" (i.e., untreated, hydrocarbon-covered) surfaces. The proton sputtering yields show a remarkably strong dependence on ion charge q, ranging from $\sim q^3$ in the kinetic sputtering regime[15,16] to $\sim q^5 - q^6$ in the pure potential sputtering regime.[17,18] In addition, a relatively high yield of about one proton per incident highly charged ion ($q = 20$) was measured. An enhancement in secondary ion emission yield with primary ion charge state has recently also been claimed for thin "conducting" carbon foils.[19] However, the fact that in these experiments almost exclusively hydrocarbon ions, protons and H^- were detected points to sputtering from an insulating hydrocarbon overlayer rather than from the conducting amorphous carbon foil.

No firm conclusion can be drawn on the total sputter yield from such secondary ion emission measurements. On the other hand, accurate determination of the total sputter yields (including both neutral and ionized secondary particles) has been achieved by means of a sensitive quartz crystal micro-balance technique developed at TU Wien.[20–25]
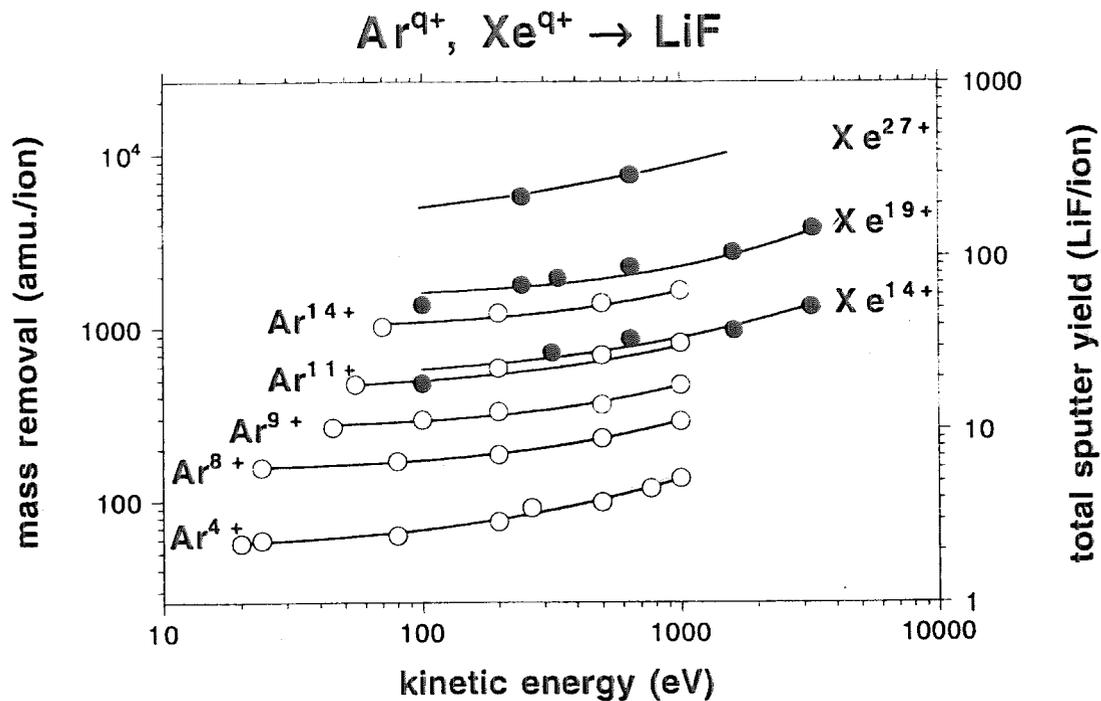
FIGURE 1 Mass removal for LiF in atomic mass units (left scale), and number of sputtered LiF molecules (right scale) per incident Ar^{q+} (open symbols) and Xe^{q+} (full symbols) as a function of ion impact energy. Data from Ref. 25

With this method, measurements have been carried out for impact of Ar^{q+} ions up to $q = 9$ on various surfaces as Au (a metal), alkali halides (LiF, NaCl), oxides (SiO_2, MgO) and semiconductors (Si, GaAs). As expected, for Au targets no q-dependent total sputter yield was observed (only kinetic sputtering[23]), but for alkali halide surfaces a considerable sputtering yield could be observed down to very low impact energies ($\geq 5xq$ eV), which increases nearly linearly with the potential energy carried by the projectile.[21] Accompanying secondary ion yield measurements showed that the sputter yield is dominated by neutrals which are at least two orders of magnitude more abundant than secondary ions.[22] It is important to note that this potential sputtering of insulators (PSI) was only found for alkali halides (LiF, NaCl)[21] and, to a lesser extent, for SiO_2, whereas no PSI was observed for any other target surface (Au, Si, GaAs, MgO), for which only kinetically induced sputtering has been found.[23,24] For impact of slow Ar^{q+} ($q \leq 9$) on SiO_2 the potential sputtering decreases with increasing ion dose, indicating preferential sputtering of oxygen. By contrast, for alkali halide surfaces stoichiometric sputtering was found. Measurements with the quartz crystal micro-bal-

ance technique have recently been continued for LiF and SiO_2 up to Xe^{27+} (kinetic energies from a few eV up to 1 keV), and yielded record-high neutral sputtering yields of about 300 LiF molecules (Ref. 25, cf. Fig. 1). Table I summarises the dependence of PSI on the surface material.

TABLE I Potential sputtering for HCI (enhancement relative to kinetic sputtering). PSI effect for different surface materials (cf. text)

Au	metal	No
Si	semiconductor	No
GaAs	semiconductor	No
MgO	insulator (oxyd)	No
SiO_2	insulator (oxyd)	Yes
LiF	insulator (alkalihalide)	Yes
NaCl	insulator (alkalihalide)	Yes

3. "COULOMB EXPLOSION" VS. "DEFECT-MEDIATED SPUTTERING"

Our current understanding of the interaction of slow HCI with **metal** surfaces is based on the so-called "classical over-the-barrier" model (COB-model),[2,3,26] the main features of which include acceleration of the HCI towards the metal surface by its own image charge, and resonant transfer of conduction band electrons into highly excited electronic states of the projectile. This results in the transient formation of very short lived "hollow atoms", for which outer Rydberg orbitals are transiently populated while the inner shells stay empty. Although the projectiles become already completely neutralised in front of the surface, and excited states decay rapidly by autoionisation via emission of many low energy electrons,[27] 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. A larger part of this potential energy can thus only be liberated in the vicinity of or below the surface, when Rydberg electrons have become "peeled off"

206

and more tightly bound shells (e.g., M, L, K) have become filled by Auger neutralisation from the conduction band or in close collisions with target atoms.[28–32] In this way, the potential energy of the projectile is converted into kinetic energy of emitted electrons and electronic excitation of a small surface region (creation of electron–hole pairs, "hot holes" in the conduction/valence band of the target, and inner shell holes of target atoms). For metal surfaces these sudden perturbations of the electronic structure can be rapidly accommodated. The excitation energy dissipates within the target material without being able to induce structural surface modification.

For *insulator* targets, however, such a strong electronic excitation might survive long enough to also be efficiently converted into kinetic energy of desorbed or sputtered target atoms and/or ions. This is the origin of sputtering induced by the projectile's potential energy, i.e. PSI. Currently two competing models for such conversion processes are being considered, named "Coulomb Explosion – CE" and "Defect-mediated Sputtering – DS." Both models agree in so far that for well-conducting (i.e. metal) targets there should be no influence of the projectile ion charge on the sputtering yield, i.e. only kinetic sputtering is possible.

In the CE model proposed by Parilis and co-workers,[33–35] the neutralisation of a HCI impinging on an insulator surface is assumed to result in a strong electron depletion of the near surface region. Consequently, the mutual Coulomb repulsion of target ion cores gives rise to ejection of secondary ions from positively charged microscopic surface domains. Shock waves generated by this CE then ablate further target material (emission of neutral target atoms/clusters). In this way the CE model not only explains an enhanced secondary ion emission yield but also accounts for sputtering of neutrals which can strongly enhance the removal of surface material.

Recently, molecular dynamics (MD) simulations for CE processes in pure Si have been performed.[36] In these calculations the following CE scenario was *assumed*.

a. The HCI-Si interaction leaves a half-sphere containing 265 or more positively charged silicon ions on a Si (111) surface.

b. The replenishment of electrons from the surrounding solid does not proceed rapidly enough, such that the repulsive electrostatic energy

stored in the charged region leads to a Coulomb-driven shock wave that eventually leaves a crater-like feature in the surface.

These MD calculations showed that the shock wave needs about 100 fs to fully develop, and the resulting crater formation time is about 1 ps. Moreover, the energy distribution of the emitted ions is rather broad, with a mean energy of about 100 eV.

In a different approach, PSI has been explained by a "Defect-Mediated Sputtering – DS" model. In certain insulator materials (alkali halides, SiO_2), electronic defects are induced by bombardment with energetic electrons (electron-stimulated desorption – ESD) as well as UV photons (photon-stimulated desorption – PSD).[37–41] As described above, the strong interaction of HCI with any target surface causes formation of electron-hole pairs and "hot holes" (i.e., holes in the "lower" part of the valence band). Due to the strong electron–phonon coupling (i.e. efficient energy transfer from the electronic to the phononic system of the solid) in alkali halides and SiO_2, such an electronic excitation of the valence band becomes localised by formation of "self-trapped excitons" (STE) and/or "self-trapped holes" (STH), i.e. excitons or holes trapped in a self-produced lattice deformation,[42,43] respectively (c.f. the more detailed description for LiF targets below). As in the case of ESD/PSD, decay of such STH and/or STE into different "colour centers" (H and F centers in the case of alkali halides and E' in the case of SiO_2) leads to the desorption of neutralized anions (halide atoms, oxygen). In LiF, e.g, a H-center is a F_2^- molecular ion at one anion lattice site, while a F-center is an electron localised at the next or second-next anion site.[42,43] The created neutral cations are either evaporated (as in the case of heated alkali halide samples) or can be removed by small momentum transfer from the impinging projectiles.

As an example, in Fig. 2 the PSI process for a LiF target surface is schematically depicted. If the HCI approaches the LiF surface, holes in the F(2p) valence band will be created by resonance neutralisation (RN). "Cold holes" (i.e., holes localised at the Fermi edge) in the first surface layer will form V_k-centers (F_2^- molecular ions adjacent to two anion sites),[42,43] while the resulting highly excited projectiles become de-excited by Auger and autoionization processes, leading to electron emission. When the projectile penetrates the surface layer while still in an ionised or highly excited state, inter-atomic Auger neutralisation (AN) and RN will take place and further neutralise and/or de-excite the
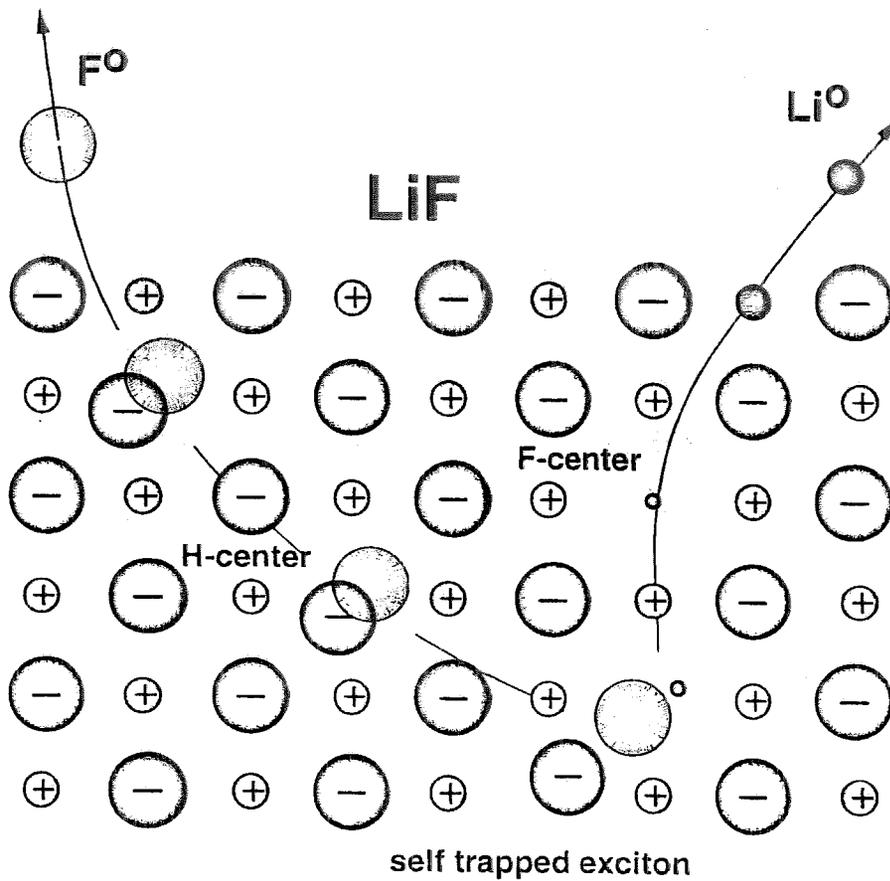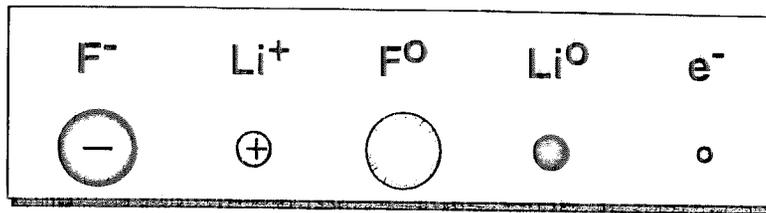
208

FIGURE 2 The potential sputtering process explained according to the "Defect-mediated sputtering" model (cf. text). Negatively charged F⁻ and positively charged Li⁺ ions of the ionic LiF crystal are shown as open circles. An electronic excitation (electron-hole pair) becomes localized as a self-trapped exciton (lower right) which subsequently decays into color (H⁻ and F⁻) centers. These color centers diffuse to the surface and lead to the emission of neutral atoms (full circles)

projectile, producing further electron-hole pairs. "Hot holes" will be formed with higher probability because of the larger electron density in

the center of the valence band. Resulting V_k-centers can trap available electrons, thus forming STEs, which at room temperature will immediately decay into two colour centers, i.e. a H-center (F_2^- molecular ion at one anion lattice site) and a F-center (electron localised at the next or second-next anion site).[42,43] H-centers and F-centers created in the bulk can diffuse to the surface, where the H-center decays by emitting a F^0 atom and the F-center can neutralise a Li^+ cation. For electron bombardment, Li atoms created at the surface will form a metallic overlayer which will stop further progress of ESD or PSD at room temperature, but can be evaporated at surface temperatures above 150°C. In contrast to ESD, even at rather low impact energy, the heavy HCI projectiles provide sufficient momentum transfer for removing single, weakly (van der Waals) bound Li atoms from the LiF surface, leading to stoichiometric desorption at low surface temperatures.

Within the DS model of PSI it is not sufficient for a target surface to be an insulator. An enhancement of the absolute total sputter yields with increasing charge state of the primary ion is predicted only for targets with strong electron-phonon coupling, where electronic excitation can be localised by formation of STE and/or STH.

4. DISCUSSION

The experimental results reviewed in Section 2 have in common that they report marked (sometimes even strong) effects of the primary ion charge state on emission of secondary target particles (ions or neutrals). These effects have so far almost exclusively been found for insulating or semiconducting targets. The only exception is the reported potential sputtering from conducting carbon foils.[19] Since the latter was strongly contaminated by deposition of hydrocarbons, the microscopic conducting properties of this target surface are, in the opinion of the present authors, not convincingly established.

The majority of these experiments focused on the emission of secondary *ions* (positive and/or negative). The reported high secondary ion yields are a clear indication that the total sputtering yields (i.e., including neutrals) must be significantly larger than the well-known kinetic sputtering yield. The measured q-dependencies, in particular in the cases of proton sputtering from "dirty" (hydrocarbonated) surfaces[17,18] or of F^+ emission from HCI-bombarded LiF surfaces,[22] can be taken as

210

indication for a CE-type mechanism. By means of a quantitative model calculation[44] based on the classical over-the-barrier model, it has recently been shown that sputtering of protons can be explained by a localised CE process after breaking the covalent C-H bond in hydrocarbons at the surface. This model indicates that conditions for CE are favourable only for light ions such as protons, which can escape relatively rapidly to distances from the surface where re-neutralization becomes unlikely.

It should be noted that secondary ion measurements do not allow us to draw firm conclusions on the dominant sputtering mechanism, since neutral sputter yields have been found which are two orders of magnitude larger than secondary ion emission yields.[22]

While experimental evidence which allows us to infer the dominant sputtering mechanism is therefore still rather scarce, a closer look at the experimental data[21,23,25] favours the "defect-mediated sputtering" over the "Coulomb explosion" model.

i. Only for alkali halides (LiF, NaCl)[21], and to a weaker extent for SiO_2, [23,25] has PSI been observed so far. Both SiO_2 and alkali halides are materials which are known to exhibit strong electron-phonon coupling and STH or STE formation.

ii. All other target species investigated by the quartz crystal micro-balance technique (Au, Si, GaAs and MgO) show only kinetically induced sputtering up to the highest available Ar^{q+} charge state of $q = 9$.[23,24] According to the CE model insulators like MgO and semiconductors like Si and GaAs should also show a charge state dependence of the sputtering yield. However, no STH or STE formation is known for these materials. Without that ability, even in insulators the lifetime of valence band holes seems to be too short for developing enough repulsive energy by Coulomb forces.

iii. The electronic defects in the surface (e.g., number of electron-hole pairs and holes created) should be roughly proportional to the potential energy carried by the projectile into the surface. In the case of defect-mediated sputtering, the number of STH's and STE's and, in further consequence, the number of sputtered particles should therefore also increase nearly linearly with the potential energy, as has been observed in experiment[21]. However, for the CE mechanism a strong increase with the potential energy is also to be expected.

211

iv. A CE process should favour the production of positively charged secondary ions while hampering the emission of negatively charged ions and electrons. At least for alkali-halide targets, predominantly neutrals and less than 1% ions have been observed.[22] In secondary ion emission experiments with very highly charged ions (up to $q = 78$) on SiO_2,[13] negatively charged ions have been found to be as abundant as positively charged ones, which is difficult to reconcile with the notion of CE.

v. At very low impact energy of Ar^{q+} ($q \leq 9$) on SiO_2, the effect of potential sputtering was found to decrease with increasing ion dose. According to the defect-mediated sputtering model, the cations are removed by evaporation (alkali halides) or by momentum transfer from the impinging projectile to the now weakly bound (because neutralized) cation. In SiO_2 the removal of the cations is only possible by the latter mechanism (the main difference between alkali halides and SiO_2). Therefore, at very low impact energy, only oxygen is being sputtered and the surface becomes enriched in Si. Consequently, the potential sputtering effect decreases with increasing ion dose. The same effect leads to the formation of a metallic Li overlayer in the case of ESD from LiF at low target temperatures.[37] An alternative explanation in terms of the CE model is not obvious.

vi. Additional evidence in favour of the DS model comes from the energy distribution of sputtered particles. The recent molecular dynamics simulation, which uses the CE mechanism as input for the initial conditions,[36] predicts the ejection of energetic sputtered particles. In the numerical example of Ref. 36, the average energy was $\approx$ 4 a.u. (ca. 100 eV). This is in striking contrast to experimental findings of sputtered neutrals and ions whose overwhelming majority have low energies ($\approx$ eV).

The importance of a transient trapping mechanism as a precursor for potential sputtering can also be shown by simple, yet semi-quantitative theoretical arguments. For an insulator with a narrow, fully occupied valence band, taken to be LiF in the following, the energy spectrum can be approximated by a tight-binding dispersion relation of the form

$$E(k) = E_0 - \beta \cos(ka\sqrt{2}). \tag{1}$$

where β is the half-width of the band ($\beta = 2.5$ eV for LiF[45]), E_0 is the center position of the band and a is the lattice constant ($a = 3.9$ a.u. for

LiF[46]). The group velocity with which holes travel in the absence of strong lattice distortions is

$$v(k) = \beta a \sqrt{2} \sin(ka\sqrt{2}). \tag{2}$$

Accordingly, the maximum hot hole velocity near the center of the band $(k = \pi/(2\sqrt{2}a))$ is $v_h^{hot} \approx 0.5$ a.u., i.e. comparable to metallic Fermi velocities. For cold holes produced in resonant electron transfer from the top of the valence band to the projectile, assuming a spectral width of the captured electrons of ≈ 1 eV, we find an average value of $v_h^{cold} \approx 0.2$ a.u. This estimate results from the fact that v_h^{cold} at the Fermi edge is zero, while at an energy of 1 eV below the Fermi edge it is about $v_h^{cold} \approx 0.4$ a.u.. These characteristic speeds for hot and cold holes govern the time scale for hole diffusion. The average hopping time to the nearest F-site is of the order of

$$t_{hop} = \frac{a\sqrt{2}}{\nu_h}. \tag{3}$$

The number of jumps during the neutralisation sequence is of the order of

$$N = \frac{t_N}{t_{hop}}, \tag{4}$$

where t_N is the characteristic time for neutralisation of a highly charged ion. Within the classical over-barrier (COB) model, $t_N = 2\sqrt{q}/(W \cdot v_{p\perp})$ with q the charge of the projectile, W the work function of the surface and $v_{p\perp}$ the perpendicular component of the projectile velocity with which the slow highly charged ion approaches the surface. Inserting numerical values for cold holes in LiF and assuming a perpendicular velocity of $v_{p\perp} \approx 5 \times 10^{-3}$a.u., we find

$$N \approx 40\sqrt{q}. \tag{5}$$

The value for the perpendicular velocity used is estimated from the lower velocity limit given by the image charge acceleration. The radius within which q holes will be distributed in a random walk is $R = a\sqrt{2N} \approx 9aq^{1/4}$. The mean distance between two adjacent holes follows as

$$\langle d \rangle \approx \left(\frac{2\pi}{3}\right)^{1/3} 9aq^{-1/12}. \tag{6}$$

213

This distance is very weakly dependent of the incident charge and quite large since the speed of hole diffusion is to within of factor of 2 or 3 comparable to that of metals. Consequently, the repulsive Coulomb interaction V_c between two adjacent holes in LiF is quite weak,

$$\langle V_c \rangle \approx \frac{1}{\varepsilon \langle d \rangle} \approx 3 \times 10^{-3}. \tag{7}$$

(ε = static dielectric constant[47]), and unlikely to induce Coulomb explosion. For hot holes, the Coulomb repulsion will be even weaker. Note that this estimate depends linearly on the neutralization time t_N. Therefore, even when one would assume the effective neutralization time to be much shorter (say, 5×10^{-15} s), $<V_c> \approx 3 \times 10^{-2}$ would still be very small.

Alternatively to the neutralisation time t_N used above, another time scale can be utilized to estimate the characteristic time within which sputtering and atomic motion take place. Using for the latter the characteristic period for an optical phonon $t_{ph} = 2\pi/\omega_{ph} \approx 5 \times 10^{-14}$ s, we find similar but somewhat larger values of N and $\langle d \rangle$ and, accordingly, an even weaker Coulomb repulsion. Note that the validity of the latter estimate does not require the validity of the COB model as a prerequisite. These simple considerations clearly indicate that trapping of electronic defects due to strong electron-phonon coupling is essential in mediating potential sputtering.

Conventional wisdom in electron- and photon-stimulated desorption considers primarily the formation of self-trapped excitons (STE), their subsequent decay into an F and H pair, and diffusion to the surface as the mechanism for stoichiometric sputtering. Such a mechanism will also be operative for potential sputtering induced by slow highly charged ions when charge transfer proceeds by Auger capture. Due to the limited number of Auger capture events, only a limited number of STEs can be produced. However, resonant capture, which is more probable than Auger capture, creates only holes (the number of holes being roughly proportional to the charge state of the incoming projectile[1,27]). Unlike for photon- or electron-stimulated desorption, it is quite plausible that self-trapped holes are equally important in potential sputtering by highly charged ions. While a self-trapped hole at the surface can result in the sputtering of the neutral halide, the presence of a large number of electrons in the impact zone of a highly charged ion due to resonant re-ionization ("recycled electrons"), secondary electron emis-

214

sion and Auger deexcitation processes may account for the concomitant emission of the neutral alkalis. The latter process is less likely for photon- or electron-stimulated desorption because of the lack of a comparable source of electrons. Self-trapped holes as a new agent specific for potential sputtering by ions could also account for the fact that sputtering yields for Ar^+ are about 1/3 to 1/2 of that of Ar^{2+}. Within the STE mechanism, a much smaller ratio would be predicted, since Ar^{2+} permits Auger capture and formation of excitons, while Ar^+ lies energetically below the threshold for STE formation. On the other hand, Ar^{2+} will create about twice the number of holes of Ar^+, and the observed ratio is consistent with an STH-induced sputtering process.

SUMMARY AND CONCLUSIONS

In the present Comment we have critically reviewed the available experimental evidence for potential sputtering of insulators (PSI), i.e., the ejection of neutral and ionized target particles from insulator targets bombarded by highly charged ions at impact energies too low for the common kinetic sputtering process to take place. A number of groups have investigated the dependence of secondary ion yields on the projectile charge state and velocity, but only recently has a quantitative measurement of the related total sputter yields become feasible.

The so-called Coulomb explosion (CE) model assumes such PSI effects arise as a consequence of the rapid electron depletion in the surface region from where the impinging MCI is being neutralised, with a subsequent ejection of positively charged target particles left behind. This CE mechanism should work for any insulator material, which is in contrast to experimental evidence: As discussed in this Comment, PSI has only been observed for some classes of insulators, for which MCI neutralisation can initiate self-trapped holes and/or self-trapped excitons in the near surface region. Theoretical arguments suggest that trapping of electronic defects is crucial for the conversion of potential energy of the projectile into kinetic energy of the target atoms or ions. The decay of these MCI-induced defects into colour centers gives rise to desorption of (primarily neutral) target particles. It is shown that this defect-induced desorption requires a strong electron-phonon coupling of the target material, and it should thus only be observed for particular classes of insulators, such as alkali halides, and to a lesser extent SiO_2.

Despite this evidence, at our present state of knowledge the CE mechanism should not completely be ruled out as a minor contributor to PSI,

especially for higher projectile charge states than applied so far in quantitative measurements of the total sputtering yield. It is therefore highly desirable to carry out similar PSI studies for projectile charge states $q \geq 30$.

Appendix: List of Abbreviations

AFM	atomic force microscopy
AI	auto-ionization
AN	Auger neutralisation
CE	Coulomb explosion
COB	classical over-the-barrier (model)
DS	defect-mediated sputtering
ESD	electron stimulated desorption
HCI	highly charged ion
MCI	multi-charged ion
MD	molecular dynamics
PE	potential electron emission
PSD	photon stimulated desorption
PSI	potential sputtering of insulators
RN	resonant neutralisation
S-DOS	surface density-of-states
STE	self-trapped excitons
STH	self-trapped holes
TOF	time of flight

Acknowledgments

F. AUMAYR

Institut für Allgemeine Physik, TU Wien, Wiedner Haupstr. 8–10, A-1040 Wien, Austria

and J. BURGDÖRFER

Institut für Theoretische Physik, TU Wien, Wiedner Haupstr. 8–10, A-1040 Wien, Austria

P. VARGA and HP. WINTER*

Institut für Allgemeine Physik, TU Wien, Wiedner Haupstr. 8–10, A-1040 Wien, Austria

References

1. A. Arnau, F. Aumayr, P. M. Echenique, M. Grether, W. Heiland, J. Limburg, R. Morgenstern, P. Roncin, S. Schippers, R. Schuch, N. Stolterfoht, P. Varga, T. J. M. Zouros and HP. Winter, Surf. Sci. Reports **229**, 1(1997).
2. J. Burgdörfer, P. Lerner and F. W. Meyer, Phys. Rev. A **44**, 5647 (1991).
3. J. Burgdörfer, in *Fundamental Processes and Applications of Atoms and Ions*, C. D. Lin, Ed. (World Scientific, 1993).
4. F. Aumayr and HP. Winter, Comments At. Mol. Phys. **29**, 275 (1994).
5. F. Aumayr, in *The Physics of Electronic and Atomic Collisions*, L. J. Dubé, J. B. A. Mitchell, J. W. McConkey and C. E. Brion, Ed. (American Institute of Physics (AIP Press), New York, 1995), Vol. 360, p. 631.
6. J. Das and R. Morgenstern, Comments At. Mol. Phys. **29**, 205 (1993).
7. H. Winter, J. Phys.: Condens. Matter **8**, 10149 (1996).
8. S. S. Radzhabov, R. R. Rakhimov and P. Abdusalumav, Izv. Akad. Nauk SSSR Ser. Fiz. **40**, 2543 (1976).
9. S. N. Morozov, D. D. Gurich and T. U. Arifov, Izv. Akad. Nauk SSSR Ser. Fiz. **43**, 137 (1979).
10. S. S. Radzhabov and R. R. Rakhimov, Izv. Akad. Nauk SSSR Ser. Fiz. **49**, 1812 (1985).
11. A. J. Eccles, J. A. van den Berg, A. Brown and C. Vickerman, Appl. Phys. Lett. **49**, 188 (1986).
12. S. T. de Zwart, T. Fried, D. O. Boerma, R. Hoekstra, A. G. Drentje and A. L. Boers, Surf. Sci. **177**, L939 (1986).
13. D. H. Schneider, M. A. Briere, J. McDonald and J. Biersack, Rad. Eff. Def. Solids **127**, 113 (1993).
14. D. H. Schneider and M. A. Briere, Physica Scripta **53**, 228 (1996).
15. S. Della-Negra, J. Depauw, H. Joret, Y. LeBeyec and E. Schweikert, Phys. Rev. Lett. **60**, 948 (1988).
16. I. Bitenskii, E. Parilis, S. Della-Negra and Y. LeBeyec, Nucl. Instrum. Meth. Phys. Res. B **72**, 380 (1992).

* Corresponding Author: e-mail address: winter@iap.tuwien.ac.at.

17. N. Kakutani, T. Azuma, Y. Yamazaki, K. Komaki and K. Kuroki, Jap. J. Appl. Phys. **34**, 580 (1995).
18. K. Mochiji, N. Itabashi, S. Yamamoto, I. Ichiai and K. Okuno, Jap. J. Appl. Phys. **33**, 7108 (1994).
19. T. Schenkel, M. A. Briere, H. Schmidt-Böcking, K. Bethge and D. H. Schneider, Phys. Rev. Lett. **78**, 2481 (1997).
20. T. Neidhart, Z. Toth, M. Hochhold, M. Schmid and P. Varga, Nucl. Instrum. Meth. Phys. Res. B **90**, 496 (1994).
21. T. Neidhart, F. Pichler, F. Aumayr, HP. Winter, M. Schmid and P. Varga, Phys. Rev. Lett. **74**, 5280 (1995).
22. T. Neidhart, F. Pichler, F. Aumayr, HP. Winter, M. Schmid and P. Varga, Nucl. Instrum. Meth. Phys. Res. B **98**, 465 (1995).
23. P. Varga, T. Neidhart, M. Sporn, G. Libiseller, M. Schmid, F. Aumayr and HP. Winter, Physica Scripta **T73**, 307 (1997).
24. T. Neidhart, F. Pichler, F. Aumayr, HP. Winter, M. Schmid and P. Varga, 3S'95 Symposium on Surface Science, P. Varga and F. Aumayr, Eds., Kitzsteinhorn, Salzburg, Austria, (1995), p. 74.
25. M. Sporn, G. Libiseller, T. Neidhart, M. Schmid, F. Aumayr, HP. Winter, P. Varga, M. Grether and N. Stolterfoht, Phys. Rev. Lett. **79**, 945 (1997).
26. C. Lemell, HP. Winter, F. Aumayr, J. Burgdörfer and F. W. Meyer, Phys. Rev. A **53**, 880 (1996).
27. F. Aumayr, H. Kurz, D. Schneider, M. A. Briere, J. W. McDonald, C. E. Cunningham, and HP. Winter, Phys. Rev. Lett **71**, 1943 (1993).
28. S. Schippers, S. Hustedt, W. Heiland, R. Köhrbrück, J. Kemmler, D. Lecler and M. Stolterfoht, in *Ionization of Solids by Heavy Particles*, R. Baragiola, Ed. (Plenum, New York, 1993), Vol. 306, p. 117.
29. N. Stolterfoht, A. Arnau, M. Grether, R. Köhrbrück, A. Spieler, R. Page, A. Saal, J. Thomaschewski and J. Bleck-Neuhaus, Phys. Rev. A **52**, 445 (1995).
30. A. Arnau, P. A. Zeijlmans van Emmichoven, J. I. Juaristi and E. Zaremba, Nucl. Instrum. Meth. Phys. Res. B **100**, 279 (1995).
31. A. Arnau, R. Köhrbrück, M. Grether, A. Spieler and N. Stolterfoht, Phys. Rev. A **51**, R3399 (1995).
32. J. Burgdörfer, C. Reinhold and F. Meyer, Nucl. Instrum. Meth. Phys. Res. B **98**, 415 (1995).
33. E. Parilis, Proc. Int. Conf. Phenomena in Ionized Gases, Editura Academia Repulicii Soc. Romania, 1969), p. 24.
34. I. S. Bitenskii, M. N. Murakhmetov and E. S. Parilis, Sov. Phys. Tech. Phys. **24**, 618 (1979).
35. I. S. Bitensky and E. S. Parilis, J. de Physique (Paris) C2, 227 (1989).
36. HP. Cheng, and J. D. Gillaspy, Phys. Rev. B **55**, 2628 (1997).
37. M. Szymonski, A. Poradzisz, P. Czuba, J. Kolodziej, P. Piatkowski, J. Fine, L. Tanovic and N. Tanovic, Surf. Sci. **260**, 295 (1992).
38. M. Szymonski, in *Fundamental Processes in Sputtering of Atoms and Molecules*, P. Sigmund, Ed. (Royal Danish Academy of Sciences, Copenhagen, 1993), p. 495.
39. N. Seifert, D. Liu, A. Bernes, R. Albridge, Q. Yan, N. Tolk, W. Husinsky and G. Betz, Phys. Rev. B **47**, 7653 (1993).
40. R. E. Walkup, P. Avouris and A. Ghosh, Phys. Rev. B **36**, 4577 (1987).
41. T. Green, Phys. Rev. B **35**, 781 (1987).
42. R. Williams, Phys. Rev. B **33**, 7232 (1986).
43. R. Williams and K. Song, J. Phys. Chem. **51**, 679 (1990).
44. J. Burgdörfer and Y. Yamazaki, Phys. Rev. A **54**, 4140 (1996).
45. W. Gudat, C. Kunz and H. Petersen, Phys. Rev. Lett. **32**, 1370 (1974).

46. H. Bilz and W. Kress, *Phonon Dispersion Relations in Insulators* (Springer-Verlag, Berlin, 1979).
47. E. D. Palik and W. R. Hunter, in *Handbook of Optical Constants,* E. D. Palik, Ed. (Academic Press, New York, 1985), p. 675.