Potential Sputtering of Clean SiO$_2$ by Slow Highly Charged Ions

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The recently discovered phenomenon of potential sputtering, i.e., the efficient removal of neutral and ionized target particles from certain insulator surfaces due to the potential rather than the kinetic energy of impinging slow highly charged ions, has now also been observed for stoichiometric SiO$_2$ surfaces. Using a sensitive quartz crystal microbalance technique, total sputter yields induced by Ar^{q+} ($q \leq 14$) and Xe^{q+} ($q \leq 27$) ions have been determined for LiF and SiO$_2$ surfaces. The primary mechanisms for potential sputtering (defect mediated sputtering) and its considerable practical relevance for highly charged ion-induced surface modification of insulators are discussed. [S0031-9007(97)03627-2]

Highly charged ions (HCI) carry a rather large amount of potential energy, which in the case of slow (hyperthermal) collisions with a solid surface can greatly exceed the ion's kinetic energy and therefore dominate the interaction process. Transfer of such a large energy onto a very small surface area (typically about 100 Å^2) within the rather short interaction time of typically ≤ 100 fs corresponds to an immense power flux of $\geq 10^{14}$ W/cm^2, which can give rise to various nonlinear processes and new phenomena ("hollow atoms" etc., see, e.g., [1–5]). The high potential energy of the projectile is eventually released via emission of electrons and photons (x rays), but can also lead to surface modification and sputtering of target particles.

In contrast to the long known kinetically induced sputtering process, the new phenomenon of potential sputtering (i.e., sputtering due to the potential rather than the kinetic energy of the projectile) has only recently been discovered [6]. In first explorative studies an efficient removal of neutral [6] and to a much lesser extent also ionized target particles [7] from clean insulating alkali halide surfaces (LiF, NaCl) when bombarded by rather slow Ar^{q+} ($q \leq 9$) ions has been observed. On the contrary, clean metal (Au) and semiconducting targets (Si, GaAs) showed only normal collisional sputtering [8].

Surface modification of insulators induced by highly charged ion impact can be of considerable practical relevance. First of all, using HCI for sputtering would be attractive due to the possibility of achieving high sputter yields at very low impact energy. This so-called "soft sputtering" would allow removing materials from surfaces without producing radiation defects in deeper layers (avoidance of the kinetically induced collision cascade). Secondly, the preferential removal of insulating layers (no potential sputtering for conducting targets, see above) could be applied for novel cleaning procedures in the semiconductor industry (e.g., soft sputtering of SiO$_2$ oxide layers from Si wafers), for nanostructuring of surfaces (producing nanometer scale structures) and other characteristic surface modifications.

It is therefore of interest how the projectile's potential energy is transferred and deposited in an insulating surface in order to activate particle desorption, and whether other, maybe technologically more relevant, insulators than the so far investigated alkali halides also show potential sputtering.

In this Letter we report on new observations of enhanced sputtering of SiO$_2$ when bombarded by highly charged ions (Ar^{q+}, $q \leq 9$; Xe^{q+}, $q \leq 25$). In addition, our earlier measurements for LiF were extended to much higher projectile charge states (Ar^{q+}, $q \leq 14$; Xe^{q+}, $q \leq 27$). These experiments were performed using the 14.5 GHz ECR source at the Ionenstrahl-Labor of the Hahn-Meitner-Institut in Berlin. The ion source provides projectiles with energies up to $20 \times q$ keV where q is the charge state of the extracted ions. The end of the beam line is equipped with a deceleration lens system to extract ions with energies as low as $5 \times q$ eV. The beam line can be set on high voltage so that the experimental apparatus can be operated on ground potential. For our measurements only ions with total kinetic energies between 100 and 1000 eV have been used. Except for the lowest projectile charge states, the potential energy stored in the projectiles therefore always exceeded their kinetic energy. To study HCI-induced potential sputtering, a quartz crystal microbalance technique has been applied. A detailed description of this technique can be found in [9]. In short, a thin target film is deposited *in situ* onto a quartz crystal microbalance, and the mass loss due to sputtering is determined by measuring the change of the quartz crystal resonance frequency. Our technique is able to detect mass changes of below 10^{-3} monolayers on the quartz crystal microbalance thermally stabilized at a temperature of ≈ 200 °C. Special care has been taken in the preparation and characterization of the target. Polycrystalline SiO$_2$ layers have been produced by *in situ* evaporation of Si at

an oxygen pressure of about 10^{-5} mbar. The target was cleaned by sputtering and heating. To check its cleanliness, quality, and stoichiometry, secondary ion mass spectroscopy and/or Auger electron spectroscopy have been performed *in situ*. All experiments are made in UHV at a residual gas pressure of below 10^{-10} mbar. Charging up of insulating target surfaces under HCI impact has been avoided by (simultaneous) electron flooding (with a built-in electron flood gun) in the case of SiO_2 or by exploiting the conductance of thin films.

In Fig. 1 total sputter yields for Ar^{q+} ($q = 11, 14$) and Xe^{q+} ($q = 14, 19, 27$) on LiF are compared to our earlier results for lower charged Ar^{q+} ($q = 4, 8, 9$) ions [6]. The measured sputter yields continue to increase drastically with increasing ion charge state (i.e., projectile potential energy) and lead to a record-high potential sputtering yield of almost 300 LiF molecules per impinging Xe^{27+} ion (i.e., mass removal of about 8000 amu for a single projectile impact). Figure 2 shows corresponding results for SiO_2 under the impact of Ar^{q+} ($q = 1, 4, 8, 9$) and Xe^{q+} ($q = 15, 20, 25$). While the increase of total SiO_2 sputter yields with projectile potential energy and charge state closely resembles the results obtained for LiF, absolute sputter yields for SiO_2 stay smaller by about one order of magnitude (i.e., factor of 5 in mass removal). In addition, surface decomposition (substoichiometric SiO_x) could be observed when bombarding SiO_2 with very high ion doses of Ar^{4+}, which also led to a gradual decrease in the sputter enhancement.

Sputter enhancement for SiO_2 indicates that in addition to alkali halides also other types of insulating surfaces bear a mechanism allowing one to convert projectile potential energy into kinetic energy of sputtered particles. According to the commonly accepted scenario for HCI-surface interaction (which is largely based on the so-called classi-

cal over-the-barrier model [1]), the potential energy of an HCI is deposited via a series of electronic transitions (resonant electron transitions and Auger processes) between the projectile and the outermost layers of the solid surface ("hollow atom" formation and decay, c.f. [1–4]). These transitions lead to electronic excitation of a small surface region, i.e., 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 it is obvious that such sudden modifications of the electronic structure are rapidly restored and the excitation energy is dissipated within the target material. For insulating targets, however, the electronic excitation might survive long enough to be efficiently converted into kinetic energy of desorbed or sputtered target atoms.

Currently two models for this conversion are competing with each other, i.e., the "Coulomb explosion" and the "defect mediated sputtering" model.

According to the Coulomb explosion model [10], the electron depletion of the near surface region leads to mutual Coulomb repulsion of the remaining target ion cores and in further consequence to the ejection of secondary ions from positively charged microscopic surface domains. The shock wave generated by this Coulomb explosion ablates further target material (emission of neutral target atoms/clusters). Thus this model not only explains an enhanced secondary ion emission yield, but also claims to describe a sputter process which can strongly enhance the overall removal of material from the surface. The Coulomb explosion model is physically quite attractive, but so far not supported by any convincing experimental evidence (see [11] and references therein). Until now sputter enhancement with projectile charge state could not be observed for semiconducting Si, GaAs, and insulating MgO [8]. However, it is questionable whether (delocalized) electron-hole pairs survive long enough (several hundred fs) to initiate such an explosion process.
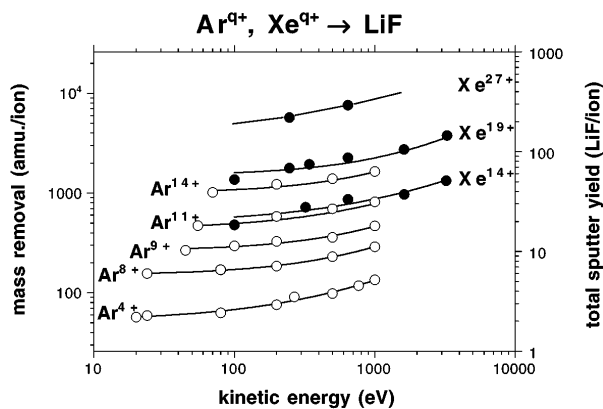

FIG. 1. Mass removal for LiF in atomic mass units (left scale) or number of sputtered LiF molecules (right scale) per incident Ar^{q+} ($q = 4, 8, 9, 11, 14$, open symbols) and Xe^{q+} ($q = 14, 19, 27$, full symbols) is shown in logarithmic scale. Data for impact of Ar^{q+} ($q = 4, 8, 9$) are taken from Neidhart *et al.* [6]. Note that Ar^{11+} and Ar^{14+} carry potential energies comparable to Xe^{14+} and Xe^{19+}, respectively. Solid curves for guidance only.

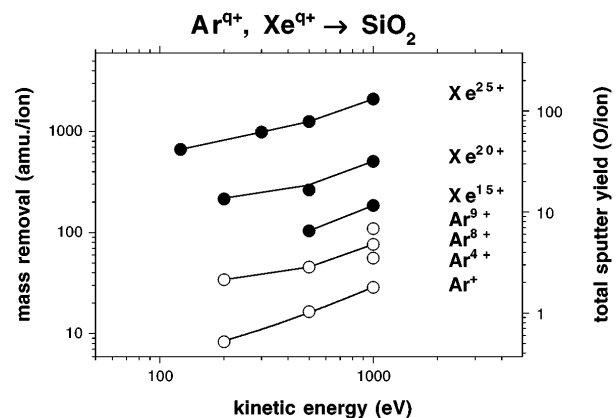
FIG. 2. Mass removal for SiO_2 in amu (left scale) or number of sputtered oxygen atoms (right scale) per incident Ar^{q+} ($q = 1, 4, 8, 9$, open symbols) and Xe^{q+} ($q = 15, 20, 25$, full symbols). Solid curves for guidance only.

In the defect mediated sputtering model, which so far has been proposed for alkali halide target surfaces only [6], the insulating solid reacts to a valence band excitation by self-trapping the latter into a highly excited (localized) electronic defect ("self-trapped excitons" or STE). Above room temperature the STE simultaneously dissociates into a pair of F and H centers [13]. At the given temperature (≈ 200 °C) H and F centers are highly mobile in the bulk. When reaching the surface they release neutral thermal halogen and alkali atoms, respectively [6,12]. Since ion potential energy is deposited in many small steps via Auger deexcitation cascades [2], desorption yields should be proportional to the potential energy related to the ion charge state [6]. The new data on potential sputtering of LiF by impact of Ar^{q+} ($q = 11, 14$) roughly follow this proportionality when compared to the earlier published data for Ar^{q+} ($q \leq 9$) [6]. However, yields for Xe^{q+} ($q = 14, 19$) are generally higher than those for Ar^{q+} ($q = 11, 14$) (Fig. 1) carrying similar potential energies, respectively. Ar^{q+} ions ($q \geq 9$) store a large fraction of their potential energy (400 eV, Ar^{9+}) as inner (L) shell vacancies. Recombination of these inner-shell vacancies by emission of fast (≈ 200 eV) Auger electrons permits a less efficient conversion of ion potential energy to desorption [14,15]. Xe ions at charge states $q = 14$ and 19, on the contrary, have more closely distributed excitation levels, supporting their deexcitation via many small Auger steps. Defect mediated sputtering is therefore more efficient for multiply charged Xe than for Ar ions of similar potential energy.

Strong support for the above defect mediated sputtering model is provided by the fact that formation of STE has also been reported for SiO_2 [13], whereas for Si, GaAs, and MgO no such mechanisms are known. Upon creation of a free exciton in SiO_2 by exciting a valence electron above the bandgap of 9.2 eV [16], a localized defect is formed. Both experiment [17] and theory [18,19] agree on a structure bearing a close resemblance to the alkali halides. The hole localizes in the anionic (i.e., oxygen) sublattice when the oxygen atom moves to an interstitial position. The electron distributes among the Si atoms neighboring the oxygen vacancy (forming an E' center) by relaxing into a configuration of minimum total energy. Another minimum on the adiabatic potential surface of the triplet STE [18] is given for the distorted oxygen atom forming a peroxy bond with a regular oxygen atom, and the electron residing in the oxygen vacancy between two Si atoms. Different from the alkali halides, in SiO_2 trapping of the electron is crucial for energy minimization, a fact that is also correlated with the impossibility of mere hole self-trapping in the same geometry of crystalline quartz. The hole-carrying peroxy bond and the trapped electron (E' center) can be seen as H and F centers as nearest neighbors, as it is well established for alkali halides. Exciton self-trapping in crystalline quartz is an intrinsic property not depending on preexisting defects or impurities [20].

From this additional evidence we conclude that the formation of self-trapped excitons after electronic excitation is probably the basis for "potential sputtering" by HCI. Without the localization of electronic excitation by forming STE, the lifetime of vacancies in the valence band is probably too short even in insulators for permitting "Coulomb explosion" to be a significant contribution in sputtering.

Whereas for alkali halides sputtering by electron bombardment has been reported, no such process has been observed for SiO_2. If SiO_2 is bombarded with electrons, only its decomposition via preferential sputtering of oxygen (emission of the anion only) is observed, which means that for SiO_2 the desorption of Si (i.e., the cation) is not possible by thermal energy only, as in the case of alkali halides. Therefore, for HCI bombardment the observed sputter enhancement on SiO_2 can only be explained by combining different processes. Additional to the desorption of oxygen by defect formation which is strongly related to the potential energy of the projectile, a process removing Si atoms has to be assumed for stoichiometric sputtering. This can be either sputtering of loosely bound Si atoms due to the kinetic ion energy or because of a transient volume increase (of the order of one SiO_2 molecular volume) occurring upon STE formation (see [19] and references therein) in the surroundings of a defect. If, on the other hand, the Si atoms are not removed from the surface, bombardment of SiO_2 with HCI leads to oxygen depletion only and the potential sputtering effect decreases with the ion dose because of the formation of substoichiometric SiO_x at the surface [21].

For LiF at low HCI impact energy, the total sputter yield amounts to typically one emitted LiF molecule per 50 eV potential energy, whereas for SiO_2 a potential energy of about 500 eV is necessary to remove one SiO_2 molecule. It is known that a qualitatively similar difference in efficiency exists for photon-induced STE production between alkali halides and amorphous SiO_2 [13].

In conclusion, significant enhancement of sputtering with increasing projectile charge has now also been observed for stoichiometric SiO_2 surfaces and found consistent with the defect mediated sputtering model, originally proposed for alkali halide target surfaces only. This model also accounts for distinct differences in the sputtering behavior of alkali halides and SiO_2. So far, only target materials with strong electron-phonon coupling, where electronic excitation can be localized by formation of self-trapped excitons, have shown an enhancement of the total sputter yields with increasing charge of the primary ion, i.e., efficient potential sputtering. The preferential removal of SiO_2 layers from Si substrates due to HCI induced potential sputtering could have considerable practical applications as, for example, novel cleaning procedures, for nanostructuring of surfaces, or other characteristic surface modifications.

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