Secondary ion emission from lithium fluoride under impact of slow multicharged ions

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Abstract
Secondary ion emission has been investigated for bombardment of polycrystalline lithium fluoride by slow multicharged Ar ions (charge state \(q \leq 9\), impact energy \(E_k \leq 500\) eV). The \(F^-\) ions originate from collisional energy transfer, almost independent of the primary ion charge, whereas the \(F^+\) yield strongly increases with \(q\). The \(F^+\) ions are produced via interatomic Auger transitions from the \(F^-\) 2p valence band into projectile states, and their desorption from LiF is controlled by Coulomb interaction of \(F^+\) with \(Li^+\) and \(F^-\) surface ions, and LiF lattice relaxation. At high impact energy, emission of \(Li^+\) is also mainly due to collisional energy transfer, but toward lower \(E_k\) the primary ion charge plays an increasingly important role. The present measurements demonstrate that secondary ions account for less than 0.1\% of our earlier measured total sputter yields from LiF.

1. Introduction

Sputtering of insulators has become a topic of much interest and controversies. Sputtering of metals is now reasonably well understood, e.g. from comparison of experimental and simulated data (TRIM [1] or MARLOWE [2]), and no influence of the projectile ion charge (i.e. the projectile potential energy) can be observed [3]. On the other hand, in sputtering of insulators such an influence is definitely present. Its most popular explanation invokes the so called "Coulomb explosion" model introduced by Bitensky et al. [4], who observed secondary ion yields from silicon increasing with the primary ion charge. These authors postulated also a similar behaviour for the total sputter yields for Si, but for impact of 20 keV Ar\(^{q+}\) (\(q \leq 9\)) on Si \(q\)-independent total sputter yields have been found [5]. For impact of slow multicharged ions (MCI) on lithium fluoride, the total sputter yield strongly increases with the projectile charge ("potential sputtering" [3,6]), which suggested as principal sputtering mechanism the creation of electronic defects as "self trapped excitons" and colour centres, rather than Coulomb explosion. For impact of 20 keV Ar\(^{q+}\) (\(q \leq 9\)) on Si, de Zwart et al. [5] found the \(Si^+\) yields to increase with \(q\) for \(q \geq 6\). For alkali halides the influence of the projectile potential energy on the yields of both positive and negative secondary ions is even more pronounced than for Si, as observed, e.g., for Ar\(^{q+}\) (\(q \leq 5\), \(E_k \leq 1\) keV) on sodium chloride [7].

The yield of positive halide ions depends rather critically on the projectile potential energy [8], as was recently shown for LiF bombarded by singly and doubly charged rare gas ions (He, Ne and Ar, \(E_k \leq 500\) eV), where a change of \(q\) from one to two resulted in a jump of the \(F^+\) yield by two orders of magnitude [9]. Emission of \(F^+\) ions is probably dominated by Coulomb repulsion from the surface, but recapture of already ejected ions after surface lattice relaxation [10] causes an impact energy threshold [9]. Below \(E_k = 100\) eV, production of \(F^+\) from LiF can only result from interatomic Auger transitions between the LiF valence band and the impinging ions. For impact of slow \(Ar^+\), potential energy conservation renders such processes impossible, in agreement with observation [11], whereas at higher \(E_k\) the \(F^+\) ions can be produced via electron promotion [12].

In contrast to \(F^+\) emission, no such "potential effects" have been observed for the bulk constituents \(Li^+\) and \(F^-\) (yield ratio \(Y(F^-)/Y(F^+) \approx 10\) at 500 eV [9]). For singly charged projectiles, energy distributions of the secondary ions (\(Li^+\) and \(F^-\)) are typical for pure kinetic sputtering [13], as also seen from the strong \(E_k\)-dependences of secondary ion yields. Below \(E_k = 100\) eV these yields decrease drastically, as reproduced by TRIM [1] and MARLOWE [2] simulations for metal sputtering. Whereas "potential effects" are present for secondary emission of both neutrals and ions, characteristic differences in their yields, energy distributions and impact energy dependences are obvious. For Ar\(^+\) on LiF below \(E_k = 100\) eV, the total sputter yield stays practically constant, but the \(Li^+\) and \(F^-\) secondary ion yields increase with \(E_k\) by...
about two orders of magnitude [9], and no F\(^+\) ions can be
detected. Most notably, total yields of secondary ions are
by three to four orders of magnitude smaller than for
neutral particles [14]. Most neutral alkali atoms are ejected
with thermal energies [14], whereas energy distributions of
positive alkali ions are typical for an origin by collisional
energy transfer. These observations suggest principally
different mechanisms for ejection of secondary neutrals
and ions, respectively. The emission of neutrals is corre-
lated with electron hole production in the target surface,
which results in rather low (i.e. thermal) energies, as
known from electron- and photon stimulated desorption.
On the other hand, the secondary ions may be mainly
released by collisional energy transfer.

In the present paper, for impact of slow MCI on LiF the
influence of projectile ion charge \(q\) on resulting secondary
ion yields will be examined and discussed.

2. Experimental methods

We have performed secondary ion mass spectrometry
(SIMS) with thin (300 nm) poly-crystalline LiF films
evaporated in high vacuum on polycrystalline gold. These
targets were subjected in UHV to impact of slow Ar ions
\((q \leq 9, E_k \leq 500\) eV\) from a 5 GHz ECR ion source [15]
after magnetical charge-to-mass analysis. A 3° kink in the
ion beam-line removed any charge-exchanged neutrals in
front of a deceleration lens which defined the final impact
energy \(E_k\) on the target, with the ions impinging under 45°
on to the surface.

The low impact energy limit was set by the ECR ion
source energy spread of typically 5\(q\) eV. Spatially homo-
genous target irradiation was assured by ion beam scan-
ing. Thin LiF films deposited on amorphous substrates
show polycrystalline structure with favoured orientation of
the LiF [111] axis normal to the substrate surface [16].
During measurements the target was kept at 400°C, to
provide experimental conditions comparable to our earlier
related studies [9] with singly and doubly charged projec-
tiles. Surface stoichiometry was checked in situ by SIMS
mass loss measurements, and by taking into ac-
cept different ejection characteristics for the
different secondary ion species, a conservative estimate led
to total errors of the absolute secondary ion yields of
\(< 50\%\).

3. Results

Secondary ion yields for F\(^-\), F\(^+\) and Li\(^+\) have been
measured in dependence on impact energy \(E_k\) and charge
state \(q\) of the Ar projectiles. Yields of molecular species
like LiF\(^+\), LiF\(^+\), LiF\(^-\), Li\(_2\)F\(^+\), LiF\(_2\) remained by at least
two orders of magnitude below the ones for atomic species,
and are therefore neglected in our further discussion. Fig. 1
gives total yields for sputtered neutrals and ions. "LiF\(_0\)"
designates sputtered neutral yields from our earlier mea-
asurements of target mass losses by means of a quartz
crystal microbalance technique [6].

Our absolute secondary ion yields are in satisfactory
agreement with results of Postawa et al. [14] and stay by
about three to four orders of magnitude below the respec-
tive neutral yields. At 200 \(\leq E_k \leq 20\) eV, the F\(^-\) yield (cf.
Fig. 2) drops by two orders of magnitudes and, within our
experimental accuracy, shows no dependence on the pri-
mary ion charge. In strong contrast, the F\(^+\) yield (cf. Fig.
3) at given \(E_k\) increases steeply with the projectile charge.
Increase of \(q\) from 2 to 9 enhances the F\(^+\) yield by two
orders of magnitudes. For given \(q\) the dependence on \(E_k\)
is much less pronounced than for F\(^-\) emission. For Ar\(^{9+}\),
the yield ratio \(Y(F^-)/Y(F^+)\) is about 6 \(\times 10^3\) at \(E_k = 500\)

![Fig. 1. Sputter yields of neutrals and charged species vs. projectile
kinetic energy, for impact of Ar\(^{2+}\) and Ar\(^{9+}\), respectively. Total
sputter yields (mainly neutrals, given in units of LiF molecule
masses) have been determined from mass loss measurements by
means of a quartz crystal microbalance [6]. The secondary ion
yields have been determined by taking into account the acceptance
solid angle of the quadrupole mass spectrometer (cf. text), and
involve total errors of \(< 50\%\).](image-url)
Fig. 2. Dependence of F\(^-\) secondary ion count rates (for given projectile currents) on projectile kinetic energy, for different projectile charge states \(q = 2, 4, 8\) and 9. Errors as for Fig. 1.

Fig. 3. Dependence of F\(^+\) secondary ion count rates (for given projectile currents) on projectile kinetic energy, for different projectile charge states \(q = 2, 4, 8\) and 9. Errors as for Fig. 1.

Fig. 4. Dependence of Li\(^+\) secondary ion count rates (for given projectile currents) on projectile kinetic energy, for different projectile charge states \(q = 2, 4, 8\) and 9. Errors as for Fig. 1.

4. Discussion

Our present experimental results will be discussed by considering neutralization of the projectile ions during their approach toward the target surface [17]. For a MCI approaching a metal surface, inside a critical distance classically allowed resonance neutralization (RN) to highly excited projectile states can take place and will rapidly convert the multicharged ion into a so called “hollow atom”. Auger deexcitation toward inner shells of the latter are too slow for the available time in front of the surface, which is further shortened by the image-charge self-acceleration of projectiles toward the surface [17]. Resonance ionization and “peeling off” of already captured electrons will gradually reionize again the hollow atom closer to the surface. However, when diving into the first surface layer, the reionized projectile will become quickly neutralized by resonance- and Auger transitions from the target conduction band into now much lower excited projectile states, due to the strong screening inside the solid. This neutralization scenario, which has been adapted for impact of slow MCI on alkali halide surfaces, occurs as the prelude to the production of, respectively, electron holes by RN and electron–hole pairs by Auger transitions, which eventually give rise to the observed large total sputter yields [6].

It has already been shown that Auger transitions between the projectile and the F\(^-\) 2p valence band are primarily responsible for F\(^+\) production at low impact energies \((F_k \leq 100\ \text{eV})\) [9]. At higher \(F_k\), however, F\(^+\) can also be produced by electron promotion in close encounters of the projectiles with target atoms [12]. F\(^+\) production by secondary electrons is improbable because of too low energies of the latter [18] for ionization of free F atoms.

Molecular dynamics calculations [10,19] for a perfect sodium fluoride lattice rule out a direct ejection of F\(^+\) by Coulomb repulsion, which according to Ref. [19] can only take place after four neighbouring halide ions have been neutralized. For LiF, however, the direct F\(^+\) emission may be somewhat more likely because the smaller LiF lattice constant favours Coulomb repulsion between escaping F\(^+\) ions and their nearest Li\(^+\) surface ions [10]. Because of the low projectile current density (typically a few nA/cm\(^2\)), every secondary ion will have collided with one projectile only. For low projectile charge, ionization of four F\(^-\) ions by RN or Auger neutralization (AN) is not possible. For example, Ar\(^{2+}\) can give rise to two RN transitions in front of the surface, and one further RN and one AN after penetration, thus creating at most one F\(^+\) and three F\(^-\), which is not sufficient to initiate a direct F\(^+\) desorption. This is in agreement with our experimental results, which in contrast to Ar\(^+\), where not enough potential energy for AN [9] can be provided, show an increased F\(^+\) emission for Ar\(^{2+}\), but only above a minimum impact energy threshold. From this we conclude that distortion of the
lattice by collisional energy transfer makes desorption of \( F^+ \) possible even if only two or three neutralized next-neighbour F atoms are produced, but the \( F^+ \) yield remains rather low (about \( 10^{-7} \), cf. Fig. 1). For an impact energy below 1 keV, the yield for neutrals, i.e. the probability for production of neutrals at the surface increases roughly with the projectile potential energy \( Y(Ar^+) = 0.5 \rightarrow Y(Ar^{5+}) = 10 \) LiF molecules per ion [6]. A rough estimate shows that for neutralization of \( Ar^{5+} \) about 40 electron holes in the LiF valence band need to be created. Since for \( E_x \leq 100 \) eV the projectile can penetrate at most two monolayers into the target bulk, all these holes can only be produced at the surface, which near the site of impact should create a strongly electron-depleted region. This could enhance direct \( F^- \) emission by Coulomb repulsion [19], which explains that for \( q \geq 2 \) no impact energy threshold is found for \( F^- \) emission (cf. Fig. 3).

A further reason could be the projectile image charge self-acceleration toward the surface [6]. The drastically increasing \( F^+ \) yields with projectile charge can only be understood from the enhanced numbers of AN processes and related sites for \( F^+ \) emission, which possibly give rise to Coulomb repulsion. Although for \( Ar^{2+} \) impact the \( F^+ \) yield becomes comparable to the \( F^- \) yield, the overall emission of charged particles remains far below the total sputter yield, the latter being not caused by Coulomb repulsion but defect production [6].

Emission of \( F^- \) is induced by collisional energy transfer (see introduction). Since within our experimental accuracy the \( F^- \) yield remains independent of the primary ion charge (see Fig. 2), the principal importance of kinetic sputtering throughout our here regarded impact energy range is demonstrated. This is in agreement with calculations [19] showing no potential energy-related emission of \( F^- \) for any conceivable surface configuration. In contrast to \( F^- \) emission, for \( q > 2 \) the emission of \( Li^+ \) is apparently supported by the projectile potential energy (cf. Fig. 4), i.e. by Coulomb repulsion becoming possible after at least four \( F^0 \) atoms have been produced at the LiF surface [19]. Consequently, the \( Li^+ \) yield depends less strongly on \( E_x \) than for singly and doubly charged projectiles.

In conclusion, throughout our here regarded ranges of projectile charge and impact energy, the secondary ion yields from LiF remain by three to four orders of magnitude below the total sputter yields, which have earlier been shown to depend approximately linearly on the projectile potential energy. There is no evidence for "Coulomb explosion" as a primary reason for total sputtering from LiF bombarded by slow multicharged ions.

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