Nanostructuring CaF₂ surfaces with slow highly charged ions

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Abstract. In recent years the potential of slow highly charged ions (HCI) as tools for nanostructuring purposes has received considerable attention and a wide range of material classes, from insulating ionic crystals, polymers and ultrathin films, to semiconducting and conducting substrates have been investigated regarding their response to individual HCI impact. For the majority of investigated materials, however, consistent theoretical modeling to supplement with experimental evidence and to satisfactorily explain the complete physical process from ion approach and impact to the formation of an individual nanostructure is still lacking. CaF₂, from both an experimental and theoretical point of view, might be considered the most thoroughly investigated material. Combining results from numerous studies has allowed for the generation of a "phase diagram" for nanostructuring of CaF₂ in dependence of ion beam parameters. This paves the way for a first unified picture, as implications from this phase diagram should be applicable to similar materials as well.

1. Introduction

The potential energy, i.e., the sum of binding energies of all missing electrons, of a slow highly charged ion (HCI) is released as it is neutralized at a solid surface. This process, according to the currently accepted scenario [1-5], can be divided into the following stages (see Figure 1). As the slow HCI approaches the surface, it will be accelerated towards it by its own image charge, which naturally sets a lower limit for the final impact energy.

The neutralization of the HCI sets in as a transient, multiply excited particle with mostly empty inner shells, a so-called "hollow atom" (HA, [4,6]) is formed via resonant neutralization (RN) processes. The HA will also experience auto-ionization, but it remains dynamically neutral through continuous RN. For metallic targets this part of the interaction scenario is well described within the so-
called "classical over-the-barrier model" (COB model, [5]). In close contact with the surface, decay of the HA sets in as screening by the metal electron gas leads to a "peel-off" of the remaining outer shell electrons. Finally, inside the solid, remaining inner shell vacancies will be filled, resulting in the emission of fast Auger electrons and/or soft X-rays. Although neither of the involved processes can be precisely distinguished nor separated in time, for metal targets they could largely be identified in experimental and theoretical studies [1,3,7].

Although the description above refers to metal surfaces, the main aspects of the neutralization sequence remain applicable to insulator targets as well [8], albeit some huge discrepancies have to be considered due to the drastic changes in valence and conductance band structure. Especially the lack of electron mobility at the surface will transiently result in a significantly different response regarding, e.g., image charge acceleration and hole mobility. Electron transfer will transiently result in local charge-up of an insulating surface and the wide electronic bandgap will generally alter electronic processes as compared to conducting surfaces.

A strong excitation of the electronic system of the solid is induced by the high and very localized potential energy deposition. Consequently, many effects related to the potential energy of HCI have been observed in the past, e.g., potential electron emission [3,9-11] and potential sputtering [2]. The interesting aspect of the potential energy release is the high electronic excitation comparable to the excitation with high power laser pulses or particles with much higher kinetic energy, e.g., swift heavy ions (SHI), with the essential difference that in the case of a slow HCI the excitation is strongly localized at the surface in a volume of only a few nm$^3$. Therefore, local phase transformations may occur, which can be identified as permanent surface modifications [12]. From the point of view of applications the advantages of HCI for surface modifications are the high local excitation not accessible with conventional beams and the high surface selectivity when using ions with low kinetic energy. This combination makes HCI promising for surface analysis [13] and as a gentle tool for surfaces modifications [14].

Figure 1. Schematic depiction of the neutralization and de-excitation processes taking place as a highly charged ion approaches and impacts a solid surface. For a detailed description cf. text.

One of the most intriguing aspects of slow HCI-surface interaction, especially in the light of possible technological applications, is the creation of surface nanostructures. The neutralization sequence as a HCI approaches and impacts on a surface, as described above, takes place in a very localized area of only a few nm$^2$. Consequently, nanostructures of a similar size are expected from experiments. The final shape and size of produced features strongly depend on specific material properties and the involved interaction processes, which in turn are determined and influenced by the ion beam parameters, i.e., potential and kinetic energy.
Nanostructuring with SHI with kinetic energies in the MeV–GeV range has been studied extensively for a long time. Despite of fundamental differences in the initiation of electron dynamics, the final appearance of nanostructures due to SHI irradiation can be remarkably similar to those produced by slow HCl irradiation (for a recent review, which compares experimental and theoretical results of studies in the high and low kinetic energy regime, the reader is referred to [12]).

In the field of slow (eV–keV) HCl-surface interaction (for recent reviews, the reader is referred to [12] and [15]), a spectrum of surface nanostructures as diverse as the investigated materials, ranging from purely insulating ionic crystals to semi-conducting and conducting materials, has been discovered: From hillocks on CaF$_2$ [16] and SrTiO$_3$ [17], pits or craters on KBr [18], PMMA [19,20] and Si [21], caldera-type structures on TiO$_2$ [22], to nanopores in carbon membranes [23] and regions of enhanced friction on HOPG [24,25] and mica [26-33]. We would like to stress that in our studies on CaF$_2$ and the numerous examples cited above, the projectile ions have no K-shell vacancies. If such vacancies were present, a large fraction of the potential energy would be lost either via energetic Auger electron emission or via X-ray emission and the appearance of ion-induced features may be altered.

Under the typical experimental conditions most of the studies find a well-defined dependence of feature size on potential energy, while the effect of varying kinetic energy remains weak. Consistent theoretical modeling, which can satisfactorily describe the complete process from the beginning of neutralization to the production of an individual nanostructure, however, is limited to very few cases.

CaF$_2$ in this regard is perhaps the most thoroughly investigated material. In this contribution we therefore intend to give the full scope on related experimental and theoretical work conducted from 2007 to the present day, parts of which have been separately published in [16,34-37].

2. Experimental Setup and Sample Preparation

Calcium fluoride (CaF$_2$) is an ionic compound of calcium and fluorine. The crystal unit cell is cubic (see Figure 2(a)): Calcium is coordinated to eight fluorine anions (shown in red), each of which is surrounded by four Ca$^{2+}$ ions. (shown in blue).

Experiments presented were performed on thin platelets of CaF$_2$ air-cleaved from a single-crystal block along the (111) plane. Cleavage produces a stable, fluorine-terminated surface, which is atomically flat and therefore ideal for observing topographic modifications down to the nanoscale. A typical contact mode AFM image of a freshly cleaved and otherwise untreated CaF$_2$(111) surface is displayed in 3D in Fig. 2(b). Step edges of different height are a characteristic result of the cleaving process. The root mean square (RMS) roughness on the flat terraces is ~0.1 nm.

![Figure 2](image)

Figure 2. (a) Schematic crystal structure of CaF$_2$ with Ca$^{2+}$ ions (blue) and F$^{-}$ ions (red). Image created with [38]. (b) Typical topographic contact mode AFM image in 3D of an unirradiated and freshly cleaved CaF$_2$(111) surface, showing step edges of increasing height from left to right.

For irradiation of the samples, highly charged Ar$q^+$ and Xe$q^+ \ (q = 11–48)$ were extracted from two different electron beam ion traps (EBITs): The Heidelberg EBIT [39] at the Max-Planck-Institute for
Nuclear Physics Heidelberg and the Dresden EBIT [40] at the Two-Source-Facility of Helmholtz-Zentrum Dresden-Rossendorf (HZDR). Ions were brought onto the samples under normal incidence and at typical fluences of $10^8–10^{10}$ ions/cm$^2$.

After exposure to the ion beam, and in some instances an additional step of chemical etching (see section 6), samples were investigated with contact mode atomic force microscopy (AFM) with a constant loading force of less than 5 nN with a UHV AFM (Omicron), a Multimode AFM (Veeco) or a MFP-3D AFM (Asylum Research), the latter two operating under ambient atmosphere. Nonconductive Si$_3$N$_4$ sensors (Veeco) with cantilevers of force constants $\sim 0.1$ Nm were employed. The image processing was performed using the WSXM software [41].

3. First Results on Hillock Formation

First results on the generation of surface nanostructures induced by slow HCI on cleaved CaF$_2$ (111) surfaces [35], were reported after irradiation with Xe$^{44+}$ ions from the Heidelberg EBIT with impact energies of 2.2 and 3.3 keV/amu. Topographic AFM images, in both cases, revealed the generation of nanoscopic protrusions, so-called hillocks, from the surface, this observation was made despite the fact that the electronic energy loss of the projectiles was well below the kinetic threshold for hillock production of 5 keV/nm known from SHI irradiation [42], a first indication of the importance of the high potential energy carried into the collision by a slow HCI. The number of hillocks per unit area corresponded well with the applied ion fluence, indicating that basically each ion produces a hillock at the surface. Evaluation with respect to hillock height and width yielded no significant differences for the two employed impact energies. This independence on impact energy further supported the notion that the potential energy and not the kinetic energy is responsible for the hillock production.

![Figure 3. Hillocks on CaF$_2$(111) surfaces induced by Xe$^{44+}$ ions with a kinetic energy of 2.2 keV/amu (left) and 3.3 keV/amu (right), respectively. Reprinted from [34], with permission from ELSEVIER.](image-url)
4. Potential Energy Threshold

After these first results, systematic studies on the influence of projectile charge states (potential energies) and kinetic energies were conducted with slow Ar$^q$ and Xe$^q$ HCI in charge states between $q = 11$ and 48. Analysis of the irradiated CaF$_2$ crystals revealed a surprisingly sharp and well-defined threshold of potential energy necessary for hillock formation. First estimations of the deposited energy density suggested that the threshold is linked to a solid-liquid phase transition on the nanoscale. With increasing potential energy, both the basal diameter and the height of the hillocks were shown to increase [35]. This first indication of a potential energy threshold on the basis of material "melting" on the nanoscale was further elaborated in a collaboration with HZDR where experiments could be performed with ultra-slow HCI, i.e., close to the image charge acceleration limited impact energy [16].

Irradiation of CaF$_2$ samples (freshly cleaved before their transfer into a vacuum chamber of pressure in the $10^{-10}$ mbar range) took place at the ion-beam center of HZDR. Isotopically pure $^{129}$Xe$^q$ ions ($q = 24–36$) were extracted from a Dresden EBIT ([43]) and decelerated by a two-stage deceleration system to the desired final impact energy before impinging onto the single crystal CaF$_2$ surface under a normal angle of incidence. Deceleration to a final potential difference between source and target down to 150 V resulted in the lowest impact energies of 150 eV/q, i.e., an impact energy of only 28–42 eV/amu. After exposure to fluences of about $10^{10}$ ions/cm$^2$, the crystals were inspected by contact mode AFM.

![Figure 4](image)

**Figure 4.** Topographic contact mode AFM image of a CaF$_2$(111) surface irradiated with 2 keV/q Xe$^{33+}$ ions showing hillocks protruding from the surface. Reprinted from [16]. Copyright (2008) by the American Physical Society.

A typical AFM topographic image of a CaF$_2$(111) surface (see Figure 4) after irradiation with 2 keV/q Xe$^{33+}$ ions (~500 eV/amu) displays hillocks protruding from the surface. The AFM images were evaluated in terms of their areal density, height, and width distributions of the hillocks. The hillocks in Fig. 4 are typically 20 nm in diameter and 0.8 nm in height. Because of the finite radius of curvature of the AFM tip (nominally 7–10 nm), the diameter of the hillocks is subject to a systematic error [42]. Measurements of heights of structures, however, are known to be reasonably accurate. From the number of hillocks per unit area and the applied ion fluence, it is determined that a vast majority of projectiles (about 80% ± 10%) produce one hillock each.

To demonstrate that the hillocks are solely due to the deposition of potential rather than kinetic energy (in the form of nuclear or electronic stopping) of the projectiles, the kinetic energy of the Xe$^{33+}$ ions was varied by more than a factor of 10. In Figure 5, the measured mean volume of the hillock-like nanostructures on CaF$_2$ produced by the impact of Xe$^{33+}$ projectile ions as a function of their kinetic energy is shown together with previous results for much more energetic (10 keV/q) Xe$^{33+}$ ions [35]. Despite the reduction of the kinetic energy by almost 2 orders of magnitude, the measured hillock volume is essentially unaffected and stays almost constant. The data might even indicate a slight
increase with decreasing kinetic energy, a trend that was also found for other charge states (see Figure 6).

![Image: Figure 5. Mean volume of hillocks on CaF$_2$ produced by the impact of Xe$^{33+}$ projectile ions as a function of their kinetic energy. Full symbols: results from the Dresden EBIT [16], open symbol: results from the Heidelberg EBIT [35]. Reprinted from [16]. Copyright (2008) by the American Physical Society.]

In order to explore the dependence on the potential energy of the projectiles, Xe$^{q+}$ ions with charge states ranging from $q = 24$ to $q = 36$ were employed while leaving the potential difference between the ion source and target surface at a constant value of 150 V. The hillock volume was found to be strongly dependent on the potential energy of the projectiles (see Fig. 6).

A remarkably well-defined sharp threshold in potential energy (between 10.4 keV for Xe$^{27+}$ and 12.0 keV for Xe$^{28+}$) for hillock formation emerges. Above this threshold, an increase of the potential energy leads to a strong increase of hillock volume. The hillock volume seems to increase slightly for decreasing kinetic energy, and the threshold shifts by about 2 keV. Repeated measurements confirmed that hillocks are produced by slow (150 eV/q) Xe$^{28+}$ but not for fast (10 keV/q) Xe$^{28+}$ projectiles. While above the threshold the hillock volume increases linearly with potential energy, the shape of the hillocks does not depend on beam parameters; also the base diameter shows only a small dependence on the potential energy of the projectile.
5. Theoretical Model - Melting on the Nanoscale

Surprisingly, the hillocks observed resemble the surface structures generated by SHI. For the latter, hillock formation was observed above an energy loss of 5 keV/nm [42], which results from 500 eV/nm nuclear stopping $S_n$ and 4.5 keV/nm electronic stopping $S_e$ [44]. While $S_n$ corresponds to direct transfer of kinetic energy into lattice heating, i.e., excitation of phonons along the projectile trajectory, $S_e$ is a measure for the excitation of the electronic subsystem of the target. It acts as a precursor for lattice excitation via electron-phonon coupling [45,46]. By contrast, for very slow HCI (kinetic energy of about 5 keV for 150 eV/q Xe$^{33+}$), the total stopping power amounts to only 1.3 keV/nm with a less than 5% contribution from $S_e$. Deposition of the potential energy ($E_{pot}$) of the highly charged projectile, 75% of which is stored in the target material [47], must therefore play a decisive role for slow HCI. However, as the potential energy threshold was found around 12 keV, it is obvious that only part of $E_{pot}$ is effectively converted into lattice excitations.

Simulations of the energy transfer from the HCI to the lattice of the CaF$_2$ target were carried out combining above and below surface electron emission processes along the projectile trajectory [8] with electron transport within the target material including the generation of secondary electrons and heating of the crystal lattice [36]. This sequence involves a twofold conversion of energy: First, potential energy is converted into kinetic energy of emitted primary electrons. In turn, electrons deposit their energy in the crystal as heat, eventually leading to melting of the material.
As pointed out in section 1, HCI approaching solid surfaces undergo a large number of neutralization and de-excitation processes, which are well described within the COB model developed for metal surfaces [5] and its extension for insulator targets [8]. Electrons from the target are transferred into highly excited states of the projectile, which may decay by collisional, radiative, and Auger processes. Transfer of electrons to the projectile leaves unbalanced holes (F_0 atoms) in the surface, which store part of the potential energy carried into the collision. Upon impact of the projectile, the target is structurally weakened.

Projectiles reach the surface far from ground state, as the time spent in front of the surface is not sufficient for a complete relaxation. At this stage, electrons are captured into moderately excited states by either resonant charge transfer from the valence band or Auger neutralization processes followed by an Auger de-excitation sequence. Along this sequence, electrons with low to intermediate energies up to a few hundred eV are emitted. If inner-shell holes are to be filled (e.g., in the cases of Ar^{17+} and Ar^{18+} [35]), electrons with keV kinetic energies are released. The potential energy stored in the incoming HCI will be deposited along the first few nm of its trajectory below the target surface. The kinetic energy of the projectile determines the depth within which the neutralization is completed (–1 nm for 150 eV/q and –4 nm for 10 keV/q projectiles [36]; see Figure 7). It is much smaller than the total range of the ion in the solid (–6 nm for 150 eV/q and –90 nm for 10 keV/q projectiles [44]).

For an HCI with q = 40, the creation of about 250 unbalanced holes [48] is estimated in the course of the interaction of a single ion affecting the crystal structure of the target. In the electron-transport simulation, elastic and inelastic scattering processes are taken into account, leading to the creation of secondary electrons (whose trajectories are followed as well) and to excitations of phonons in the interaction with the crystal atoms. Energy transfer to the lattice will eventually lead to heating and melting of the crystal. As a consequence of the high-energy density required for melting of a CaF_2 crystal (~0.55 eV/atom), low-energy electrons contribute more efficiently to the melting process than high-energy electrons, which distribute their energy over a much larger volume because of their larger inelastic and elastic mean free paths [36], see Figure 8. Contrary to naive expectations and quite surprisingly, the decisive difference between below and above threshold charge states is not the
additional fast Auger electron but the many additional slow electrons emitted along the de-excitation sequence resulting from the filling of the additional inner-shell hole.

**Figure 8.** Electrons travelling through a CaF$_2$ crystal are scattered elastically and inelastically. a) Inelastic, elastic, and total mean free paths calculated from optical data [36]. b) Average energy deposition to the CaF$_2$ crystal of electrons with 10, 250, and 5000 eV kinetic energy above the vacuum level as a function of distance from the point of emission. Note that slower electrons lead to a higher energy density in the immediate vicinity of their origin. Reprinted from [36], with permission from ELSEVIER.

The average energy density deposited in the target along the trajectory as a function of the distance from the projectile track features a ‘‘hot’’ core (bright yellow region in Fig. 7), in which the critical energy density required for melting is reached [16]. The shape of this volume strongly depends on the velocity of the projectile. While for slow projectiles the volume is almost hemispherical, fast projectiles create an elongated volume resembling the shape of a candle flame [16]. If either the velocity is increased or the potential energy is reduced (smaller initial charge states), the diameter of the heated volume shrinks. While the electron-transport simulation assuming a structureless medium cannot account for effects of the crystalline structure, important information on the spatial distribution of energy deposition into the electronic degrees of freedom preceding structure modification and melting can be inferred: A minimum volume heated above the threshold energy density of 0.55 eV/atom is needed for restructuring and hillock formation. The core volume in Fig. 7(a) is found to be about 2.5 nm$^3$ or, equivalently, about 15 unit cells of CaF$_2$ (lattice constant of 5.462 Å) containing about $10^2$ atoms. Equally important is the (smallest) linear dimension of the hot core. Only if the diameter of the core exceeds the size of the unit cell can the above-critical energy density be retained for a sufficiently long time such that the relatively slow processes of restructuring and melting occur before cooling sets in. Hillock formation was experimentally observed for all cases displayed in Fig. 7 except for Fig. 7(c) (Xe$^{28+}$, 10 keV/q) in which the diameter of the core region is reduced to about the lattice constant. In this case, the deposited energy is apparently dissipated too quickly, and the melting process is suppressed.

**6. Phase Diagram for Nanostructuring**

Surprisingly, even for very similar prototypical wide-band-gap insulators, ionic crystals of alkali halides and alkaline earth halides, vastly different and seemingly contradictory results have been found regarding their response to slow HCl bombardment. Irradiation of KBr single crystals by individual highly charged Xe ions leads to the formation of pits of one atomic layer depth [18] while irradiation
of CaF$_2$ single crystals produces nanometer high hillocks protruding from the surface [16]. In both cases the surface nanostructures were shown to be the result of individual ion impacts; i.e., every structure is caused by the impact of a single ion and a threshold value for the potential energy of the projectile has to be surpassed before the nanostructure can be observed. However, while for KBr this threshold potential energy for pit formation strongly decreases with increasing kinetic energy of the HCl [18], for hillock formation on CaF$_2$ only a slight yet noticeable increase with increasing kinetic energy is observed [16].

The key, which supplies the missing pieces to this puzzle, is the search for previously unobserved “hidden” surface structures after irradiation by ions with potential energies below the threshold for nanohillock formation. By etching the samples a second threshold at lower potential energy is discovered, above which CaF$_2$ undergoes a nanoscale structural transformation even though it is not evident as a topographic change. It becomes, however, visible in the form of triangular pits after chemical etching. This threshold depends on both the potential and the kinetic energies of the HCl, closely resembling the threshold behavior found for pit formation on KBr. Accompanying molecular dynamics simulations suggest this second threshold to be associated with lattice defect aggregation in CaF$_2$ following electronic excitations caused by the HCl-surface interaction.

Thin platelets of CaF$_2$ were irradiated with $^{129}$Xe$^{49+}$ ions extracted from the EBIT at the Two-Source-Facility of HZDR using an electrostatic potential of 4.5 kV. By using a two stage deceleration system and adjusting the potential difference between source and target from 4.5 kV down to 0.18 kV, highly charged Xe$^{49+}$ projectiles over a wide range of charge states ($10 \leq q \leq 33$, corresponding to potential energies of $0.8 \text{ keV} \leq E_{\text{pot}} \leq 21.2 \text{ keV}$) and kinetic impact energies ($6 \text{ keV} \leq E_{\text{kin}} \leq 150 \text{ keV}$) could be produced. The applied ion fluences were chosen between 0.5 and $5 \times 10^8 \text{ ions/cm}^2$, small enough to avoid overlapping of impact sites and high enough to obtain reasonable statistics. Ion irradiated CaF$_2$ samples were chemically etched using a HNO$_3$ solution (10% vol.) at room temperature without agitation [49]. Each platelet was immersed once in the etchant, subsequently in deionized water, and was finally dried in a stream of dry nitrogen. It should be emphasized that much shorter etching times $t_e$ than applied in standard etching techniques were used. For the latter, typically $t_e \geq 1 \text{ minute}$ yields etch pits even starting from randomly occurring atomic-scale dislocations and much of the sensitivity to hidden defect aggregates would be lost. Due to the dramatically enhanced etching speed in regions with a high defect density caused by the HCl (~20 nm/s compared to a regular lateral etching speed of less than 3 nm/s [49]), $t_e = 10 \text{ s}$ turned out to be the optimum etching time combining good visibility of etch pits in AFM while selecting only defect clusters created by HCl impact. The presented structures with dimensions in the range of a few 100 nm in lateral and vertical direction are by far larger than the topographic resolution of the ambient AFM in contact mode.

The observation of a pattern of well-defined irradiated and masked areas (see Figure 9) for 150 keV Xe$^{33+}$ ion impact on CaF$_2$ (111) is direct evidence of HCl induced surface defects, which can be clearly distinguished from randomly occurring dislocations and surface damage. In irradiated areas, etch pits of regularly structured 3-faced symmetric triangular depressions appear, which are similar to those observed after irradiation and etching of BaF$_2$ [50]. This particular geometrical shape originates from the (111) crystal lattice orientation of the CaF$_2$ sample [49]. The number of pits is in good agreement with the applied ion fluence; i.e., each etch pit is created by a single ion impact. The pits are presumed to be localized at the sites where HCl impact created hillocks were situated prior to etching. The charge state ($q = 33$) of the incident ion corresponds to a potential energy well above the threshold for nanohillock formation.
Figure 9. AFM topographic image (50 x 50 μm²) of a CaF₂ surface showing etch pits after exposure to 150 keV Xe³³⁺ ions. The sample was irradiated through a mask (indicated by dotted lines) and subsequently chemically etched using HNO₃. The inset in the upper left corner shows a magnification of the etch pits (1.5 x 1.5 μm²). Reprinted from [37]. Copyright (2012) by the American Physical Society.

Figure 10. (a) 3D topographic AFM image of pits on CaF₂ irradiated with Bi⁶²⁺ (Eₖᵢₙ = 36 keV) ions, which are found after etching in HNO₃ solution (10% vol.) for 3 s. (b) Zoom-in from (a) showing 10 typical etch pits. (c) Depth profile along 3 etch pits indicated by dashed arrow in (b).
Lowering the charge state to values below the potential energy threshold for hillock formation ($q_{th} \approx 28$ for Xe; $E_{pot} = 12$ keV) reveals the appearance of similar pits in the absence of preceding hillocks (see Figure 11). At the same kinetic energy of $E_{kin} = 40$ keV for ‘‘low’’ charge states ($q \leq 18$) no damage of the etched surface is visible, whereas at a higher charge state ($q = 25$, $E_{pot} = 8.1$ keV) etch pits appear.

|     | $Xe^{18+}$ | $Xe^{25+}$ | $Xe^{33+}$ |
|-----|------------|------------|------------|
| un- |            |            |            |
| etch | (a) | (b) | (c) |
| etch | (d) | (e) | (f) |

Figure 11. Topographic contact-mode AFM images of CaF$_2$(111) samples irradiated by 40 keV Xe ions in different charge states (columns): (a), (d) $Xe^{18+}$, (b), (e) $Xe^{25+}$, and (c), (f) $Xe^{33+}$. In each frame an area of 1 $\mu$m x 1 $\mu$m is displayed. Upper row: resulting images without etching (a), (b), (c). Lower row: images after etching by HNO$_3$ (d), (e), (f). Ion fluences were $2 \times 10^9$ ions/cm$^2$ for (e), (f) and $1–2 \times 10^9$ ions/cm$^2$ for (a), (b), (c), (d). Reprinted from [37]. Copyright (2012) by the American Physical Society.

In order to investigate the influence of both potential and kinetic energies on etch pit formation, systematic irradiations were performed with $^{129}$Xe$^{q+}$ projectiles of different charge states ($q = 10$ to 33) and with varying kinetic energies. The resulting thermodynamically stable damage structures and modifications can be summarized by a ‘‘phase diagram’’ with potential and kinetic energies as state variables (see Figure 12). Three different phases pertaining to surface restructuring can be distinguished: the stability region A without detectable surface modification after HCI impact [see Figs. 12(a) and 12(d)], region B in which defect clusters become visible as regularly shaped pits only upon etching [see Figs. 12(b) and 12(e)], and the nanohillock region C [see Figs. 12(c) and 12(f)] in which hillocks resulting from nanomelting can be observed after irradiation. The nanomelting arises from the transfer of high local energy density during HCI impact and is followed by a rapid quenching resulting in the formation of a hillock (see section 5 and [16]). Pits appear in phase C only after etching presumably at the positions of the hillocks, which could not be found on the etched surface.

While the threshold for hillock formation strongly depends on potential energy but only weakly on kinetic energy [12,16] implying an almost vertical boundary of region C in, the border separating the stability region A and the defect agglomeration region B (etch pits) is strongly dependent on both kinetic and potential energies. Ions with lower kinetic energy require more potential energy to create etchable damage than faster ones. Such synergistic effects of kinetic and potential energies have
previously been observed for pit formation in KBr [18], however, with the difference that no chemical etching was required for the pits to be observed. This may be related to the much higher defect mobility in KBr than in CaF$_2$ leading to a more efficient transport of defects to the surface immediately followed by material desorption.

![Figure 12](image-url)

**Figure 12.** Hillock and etch pit formation on CaF$_2$(111) induced by irradiation with highly charged Xe ions. Full (open) green circles show pairs of potential and kinetic energies where hillocks are produced (absent) after irradiation, full (open) red triangles indicate pairs where pits are present (missing) after etching the irradiated samples. Reprinted from [37]. Copyright (2012) by the American Physical Society.

7. **The Bigger Picture**

These experimental findings suggest a scenario for nanostructure formation on alkaline earth halides and alkali halides involving initial heating of electrons by multiple electron transfer and Auger relaxation, hot electron transport and dissipation with accompanying lattice heating by electron-optical phonon coupling, and finally atomic motion in the heated crystal, which results in dislocations, defects, and structural weakening of the cooled lattice. The early stages of defect formation can be simulated within a three-step model exploiting disparate time scales of the underlying processes: the initial electronic energy deposition of the HCI occurring on the (sub) femtosecond time scale can be described by the COB model [5], the hot electron transport and lattice heating occurring on a sub-picosecond time scale by classical electron-transport simulations [51], and finally the atomic motion by a molecular-dynamics (MD) simulation, which is followed for up to 15 ps [52], see Figure 13.

It should be noted that accurate potential surfaces for ionic crystals, in particular in the presence of excitations and charge transfer entering the MD simulation, are not available. Following the system on longer time scales and reaching the regime of formation of thermodynamically stable phases is, thus, not possible. Simulation results can therefore provide only qualitative, yet important, insights into the early stages of defect formation and aggregation. The following qualitative trends can be readily extracted. For HCI in “low” charge states (see Figure 14, left) only a few (i.e., low density) individual
defects (point defects, single vacancies) are created at or below the surface, where the distance individual fluorine atoms travel during −15 ps is taken as a measure for the eventual defect formation probability. These defects remain below the surface, easily anneal or are too small to be detected by means of AFM. Since the etchability of CaF\textsubscript{2} is strongly coupled to the creation of large-defect aggregates [53] rather than to point defects, no pits are observed after etching. MD simulations do not yield any significant number of lattice displacements for low \( q \) (well below −1%).

\[ \approx 5 \text{ fs} \quad \text{de-excitation of the projectile & primary excitation of the electronic system} \]
\[ \leq 100 \text{ fs} \quad \text{electron cascade & energy deposition to lattice} \]
\[ > 1 \text{ ps} \quad \text{atomic motion & restructuring} \]

**Figure 13.** Schematic of involved processes and corresponding time scales de-excitation of the HCI to eventual nanostructure formation.

For larger \( q \) and, correspondingly, larger potential energy, the sputtering yield [2] as well as the density of defects (excitons, color centers, Ca enriched regions due to F\textsubscript{2} formation) strongly increase. The latter is now large enough to lead to defect clusters and aggregates (see Fig. 14, center column). Depending on their mobility, defects may diffuse to the surface, leading to defect-mediated desorption [54] and thus form (monoatomic) pits as observed in the case of the alkali halide KBr [18]. The defect-mediated desorption mechanism is less probable in CaF\textsubscript{2} since color-center recombination below the surface is much more likely [55] due to the small energy gain of color-center pair formation as well as the formation of more complex (and therefore immobile) defect agglomerates [56,57]. The material in the vicinity of the impact region is not ablated but structurally weakened and forms the nucleus of an etchable defect subsequently removed by a suitable etchant similar as in the case of a BaF\textsubscript{2} target [50]. The synergistic effect induced by the accompanying kinetic energy originates from kinetically induced defects created in the collision cascade, which enhance the trapping of the color centers created by potential energy [58] and therefore increases defect agglomeration.

 Conversely, the border between the regions A (stable) and B (etchable surface defects) has a negative slope in the phase diagram (see Fig. 12). While MD simulations presently cannot directly account for the defect cluster formation (due to the lack of realistic binary potentials for color centers and charge-exchanged constituents), it shows in the regime of phase B atomic displacements of the order of a few percent of the impact region, the overwhelming majority of which are fluorine atoms (see Fig. 14, center). This is believed to be a necessary precursor for defect aggregation [59].

At still higher potential energies (see Fig. 14, right column), heating of the lattice atoms by primary and secondary electrons from the de-excitation of the HCI surpasses the melting threshold of the solid [16,59]. Heat and pressure deform the surface and after rapid quenching a hillock remains at the surface. With increasing kinetic energy, the region where the potential energy of the HCI is deposited, extends slightly deeper into the target [16]. Therefore, the kinetic energy dependence of the border between the region of nanohillock formation (region C) and defect clustering without protrusion (region B) is only weak with a slightly positive slope. The overall surface damage (lattice distortion, defect aggregations) extends well beyond the molten core. While the latter determines the size of the hillock, the former determines the size of the nucleus of the etch pit. Within the MD simulations a much larger number of displacements (−25%) is observed in region C, a significant fraction of which are calcium atoms.
Figure 14. Schematic scenario for surface modification as a function of charge \( q \) or, equivalently, potential energy of the HCI. Upper row: the charge state controls the created surface modification from non-etchable single defects (low \( q \)) to defect aggregates (medium \( q \)) and to locally molten zones (high \( q \)). Lower row: AFM images. Center row: typical results of molecular dynamics simulations showing that the initial electronic excitation of the surface and energy transfer to the lattice leads to a considerable number of displacements (center column) even before melting of the surface sets in (right column); center figures created using AtomEye [60]. Reprinted from [37]. Copyright (2012) by the American Physical Society.

8. Conclusions and Outlook

Much experimental and theoretical work has been done on the interaction of slow HCI with CaF\(_2\), and piece by piece this "puzzle" has been brought closer to completion: From the first observation of stable topographic hillocks induced by slow HCI [34] and the indication of a potential energy threshold [35] to definite and unambiguous experimental evidence that the potential energy of the HCI alone is the driving force in hillock formation, while the kinetic energy in the investigated regime has practically no influence [16]. Through modeling calculations the observed threshold could be linked to a solid-liquid phase transition [16] and recent experiments [37] have shown that latent defect clusters created in the sub-threshold charge state regime can be revealed as triangular pits after chemical etching. Combining the results from these studies, a phase diagram for nanostructuring of CaF\(_2\) in dependence of ion beam parameters could be derived, which should, in principle, be applicable to other alkaline earth and alkaline halide surfaces as well.

Even though the present scenario is demonstrated specifically for CaF\(_2\), we surmise that it should hold for other halide crystals as well. While borders between different regions A, B, and C will, of course, depend on the specific target material, we expect the phase diagram (see Fig. 12) to remain qualitatively valid. For BaF\(_2\) (111) and KBr (001), for example, we have previously observed the A and B phases [50,61]. The phase diagram predicts that by further increasing the potential energy of the HCI we should be able to reach region C, i.e., hillock formation (or melting) in line with first indications for hillock formation on BaF\(_2\) [62]. Further investigations will have to be carried out in the future in order to check the validity of our generalized model.
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