Nanostructures induced by highly charged ions on CaF₂ and KBr

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Abstract. Impact of a highly charged ion upon a solid surface can induce dramatic changes in the morphology only by the release of its potential energy. Hillocks and mono-atomic deep pits have been observed on the surfaces of CaF₂ and KBr, respectively. For both processes a threshold in the potential energy exists for the creation of these nanostructures. Above this threshold the structure size increases linearly with potential energy. The mechanisms for the formation of hillocks and pits are discussed and a first attempt to present a unified microscopic picture is made.

1. Introduction
The potential energy of a highly charged ion (HCI), which is the sum of all binding energies of the missing electrons, can reach values up to several tens to hundreds of keV. This energy is released during the relaxation of the HCI at the surface and is deposited to a major part into a small surface volume [1]. Therefore, it has been expected that materials modifications close to the surface can be induced by the potential energy alone. Early investigations indeed showed that structures with nanometer size are created by the impact of HCIs on MICA and HOPG and that their size correlates with the charge state [2, 3, 4]. These studies have been extended in the last years to more systematic investigations of the structure size as a function of the potential energy [5, 6, 7]. Major findings of these studies are that a threshold in the potential energy exists for the formation of the nanostructures and that above this threshold their size increases linearly with the potential energy. The observed structures on different materials and the mechanisms for their creation have been reviewed recently [8, 9]. In the following we present recent results on nano-size structures created by the impact of single highly charged Xe ions on atomically flat CaF₂ and KBr surfaces and the mechanisms for their formation are discussed briefly.

2. Nanostructures on CaF₂
CaF₂ is an ionic crystal, which can be cleaved easily along the (111) surface producing large defect free terraces separated by mono-atomic steps. Figure 1(a) shows a contact atomic force

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Figure 1. (a) c-AFM image of a CaF$_2$ surface freshly cleaved in air and measured in UHV. The visible step edge has a height of $\sim 0.5$ nm. (b) CaF$_2$ surface irradiated with Xe$^{33+}$ with a kinetic energy of $2 \text{ keV} \times q$. The visible hillocks have a height of $\sim 0.7$ nm. The scan sizes of both images are $1 \mu\text{m} \times 1 \mu\text{m}$.

Figure 2. (a) Line profile of a single hillock in Fig. 1. (b) Diameter distribution and (c) height distribution of hillocks as obtained from a series of AFM images with irradiation parameters like Fig. 1.
Figure 3. "Phase Diagram" of hillock appearance on CaF$_2$. For different pairs of potential and kinetic energy, the appearance (full symbols) or absence (open symbols) of hillocks after irradiation by highly charged Xe (circles) and Ar (triangles) ions is shown. The diagram uses data from [5, 6].

In Fig. 2(b) and (c) the distribution of the diameter and of the height are represented, respectively. For Xe$^{33+}$ with a potential energy of 21 keV the mean hillock diameter is 21 nm and the mean height is 0.7 nm. Compared to swift heavy ion irradiation of the same material, the height of the hillocks, but not necessarily their diameter seems to be smaller.

In this way the volume of the hillocks has been determined as a function of the potential energy for different kinetic energies. For a given kinetic energy, the hillock volume depends strongly on the projectile’s potential energy and shows a distinct threshold around 12-14 keV [5, 6]. Below this potential energy, no hillocks can be found regardless of the projectile ion species (Xe$q^+$ or Ar$q^+$). Above the threshold the hillock volume increases with the charge state [5, 6]. The hillock size, however, does not depend significantly on the kinetic energy for a given charge state [6]. The potential energy is thus clearly the responsible parameter for the formation of nanostructures after slow HCI bombardment of CaF$_2$ surfaces. In Fig. 3 the appearance or absence of hillocks is shown for various pairs of potential and kinetic energy of the projectile. The threshold for hillock formation runs almost vertically through the plot, underlining the importance of the potential energy. This boundary is slightly tilted to the right at higher kinetic energies which means that faster ions require higher potential energy to induce nanostructures. This counter-intuitive behavior suggests that any additional energy carried into the collision by the velocity of the projectile does not contribute significantly to hillock formation and is cancelled out or even dominated by negative effects of the different distribution of the available potential energy due to the faster ion impact.

Numerical calculations based on the inelastic thermal spike model [12] developed for swift
heavy ion irradiation of insulators and using an extended classical-over-the-barrier model [13] showed that the emission of electrons and secondary electron production leads to population of slow electrons in the target material. These electrons efficiently heat up the target atoms locally to above the melting temperature of the crystal (0.55 eV/atom). The imperfect recrystallization of this molten material is the principal cause of the permanent slow HCI induced nanostructures on CaF$_2$ [6, 13]. The threshold line running through the "Phase Diagram" (Fig. 3) is therefore indeed linked to a real phase transition. The recrystallization dynamics are yet to be fully understood on the atomic level by means of a currently ongoing molecular dynamics simulation. However, it is clear that the elongated high temperature core resulting from faster HCI is more efficiently cooled due to its larger surface-to-volume ration compared with a hemispherical core as induced by very slow HCI.

3. Nanostructures on KBr

Recently, also the interaction of highly charged Xe ions with the ionic crystal KBr has been studied in detail [7]. Prior to irradiation the surfaces have been cleaved in air and transferred immediately into the transfer chamber. The KBr crystal is naturally cleaved along the (100) surface. Figure 4 shows c-AFM images recorded in an VT-AFM/STM from Omicron operated under ultra high vacuum conditions. In Fig. 4(a) a freshly cleaved KBr(100) surface is shown exhibiting large defect-free terraces separated by a mono-atomic step. In Fig. 4(b) the KBr surface is imaged after irradiation with Xe$^{25+}$ at 40 keV kinetic energy. In contrast to the irradiated CaF$_2$, where hillocks are created on the surface by the impact of HCIs, pit like structures are observed on the KBr surface. These pits, depressions of one atomic layer depth only, result from sputtering a huge amount of material from the surface. Also in this case the sputtering is induced by the potential energy of the highly charged ions [7]. This effect is well known and has been termed "potential sputtering" [14].

The diameter and the depth of the pit structures have also been analyzed for a series of AFM images. In Fig. 5(a) a line profile of a single structure is depicted. The diameter of the pit is given by the outer edges of the depression. By this means the error resulting from the convolution with the AFM tip (nominal radius of 7 nm) is minimized. Figure 5(b) and (c) represent the diameter and the depth distribution, respectively, of several pit structures. Comparing the number of structures on a 1$\mu$m × 1$\mu$m image of 70-80 with the applied fluence of $8 \times 10^9$ cm$^{-2}$ demonstrates that every HCI creates a structure at these conditions. Noticeably, the depth of the pits is 0.4 nm only corresponding to one atomic distance in the (100) direction. No single pit structure was found in this case with more than one monolayer depth. The average
The diameter of the pits is determined to 17 nm giving a pit volume of around 90 nm³. To produce such a structure a sputter yield of 1800 atoms/ion has to be assumed. The sputter yield resulting from the kinetic energy of the ions is expected to be only 5 atoms/ion [15].

Irradiations were repeated for different charge states of the Xe ions, thus varying the potential energy from 31 eV (Xe²⁺) to 23 keV (Xe³⁺), and for different kinetic energies. The result of this systematic investigation can again be represented as a “phase diagram” for the formation of pit structures on the KBr surface shown in Fig. 6. Irradiations where pit structures were found are represented by green circles whereas irradiations without structures are represented by red squares. As in the case of CaF₂ a threshold in the potential energy exists also for the formation of pit structures on the KBr surface. However, as obvious from Fig. 6 this threshold much more strongly depends on kinetic energy. With increasing kinetic energy the threshold shifts to lower...

Figure 6. Phase diagram for the formation of pit structures on KBr (100) surfaces by the impact of highly charged Xe ions. The kinetic as well as the potential energy of the ions must be higher than a specific threshold to create the structures. The diagram uses data from [7].
Figure 7. Defect creation and diffusion by fast electron (a) and by electrons resulting from the relaxation of HCl at the KBr surface (b) and (c). In the case of HCl many electrons create simultaneously defects in the surface region leading to desorption of K.

potential energy. Above the threshold the size of the pits increases linearly with the potential energy [7].

The high sputtering yield and the formation of the pit structure on the KBr surface can be understood in the framework of defect induced desorption by electronic transitions [7]. In the case of ionic crystals the electron-phonon coupling is strong leading to the localization of the excitation into so called "self-trapped holes" and "self-trapped excitons" [16]. The decay of these excitation leads to the creation of defects in the bulk or to particle emission from the surface. In addition, defects can diffuse from the bulk to the surface and induce also desorption, however, only at step edges were the surface atoms are weakly bond (see Fig. 7(a)). This mechanism has been identified to be responsible for the layer by layer erosion induced by electron bombardment [17] and light ion irradiation [18]. During the relaxation of HCl a large number of electrons is emitted leading to a high density of defects close to the surface as sketched in Fig. 7(b). As the defects diffuse to the surface they combine to complex defect centers from which desorption is possible without step edges [7]. Above the potential energy threshold the density of defects is high enough to initiate this process.

4. Summary and Discussion
The results presented in chapters 2 and 3 demonstrate that the impact of individual slow HCl is able to produce nanostructures on surfaces like CaF$_2$ or KBr. The size of the generated nanostructures strongly depends on the charge state and therefore on the potential energy deposited by the HCl into the surface. In both cases nanostructures are only found above certain thresholds. For KBr an increase of the kinetic energy of the impinging HCl lowers the necessary potential energy for nano-pit formation (Fig. 6), while for nano-hillock generation in CaF$_2$ the kinetic energy of the projectile has an opposite effect (increasing the potential energy threshold, see Fig. 3), which is however much smaller. The decisive role of the potential energy for the formation of nanostructures can be explained taking into account the fact that damage creation in ion-surface collisions is strongly correlated to the form of energy deposition in the solid. For slow singly charged or neutral atoms, nuclear stopping dominates the energy loss. This energy transfer to target cores leads to atomic displacements and lattice vibrations in the target (phonons). On the other hand, slow highly charged ions transfer their potential energy via a series of Auger processes to the electronic subsystem of the target [19]. As a consequence
Figure 8. Scenario for nanostructure formation by slow HCI (c.f. text).

a) a large number of electrons is not only emitted into vacuum [20] but also into a shallow region close to the HCI impact zone [13].

b) inelastic interaction of these electrons with target atoms leads to a strong electronic excitation of a nanometer size region around the impact site [14], i.e. generation of defects like excitons, color centers, holes, etc. and production of further (secondary) electrons.

c) elastic collisions of these electrons with target atoms (electron-phonon coupling) heat the lattice in the surrounding of the impact site [13].

Our experimental findings can be combined into the following joint scenario for nanostructure formation by slow HCI depicted in Fig. 8. For singly charged ions or ions in low charge state (scenario A in Fig. 8) individual defects are created at or below the surface due to the projectiles potential or kinetic energy. Depending on the type of material, these defects remain below the surface, anneal again, or are too small (single vacancies) to show up in typical AFM investigations. They might however be seen as electronic defects in high resolution STM [21] or as frictional forces in lateral force AFM [22]. With increasing charge state (scenario B in Fig. 8) the potential sputtering yield strongly increases [23], sometimes assisted by the kinetic energy of the projectiles (kinetically assisted potential sputtering [24]. The density of defects (excitons, color centers, etc.) increases until large clusters of defects are formed, which (depending on defect mobility) diffuse to the surface and lead to the formation of (monatomic) pits as observed in the case of KBr (see Figs. 7(b) and 7(c)). Kinetically induced defects created in the collision cascade amplify the trapping of the electron-hole pairs created by the potential energy [7] and therefore aid to the defect formation. The boundary region between "pits" and "no-pits" in Fig. 6 therefore has a negative slope.

At still higher projectile charges (scenario C in Fig. 8) heating of the lattice atoms by primary and secondary electrons from the de-excitation of the HCI surpasses the melting threshold of
the solid. Heat and pressure deforms the surface and after cooling down a hillock or caldera like structure remains at the surface as observed e.g. for CaF$_2$ [6] or TiO$_2$ [25]. With increasing projectile kinetic energy the region where the potential energy of the HCI is deposited only slightly shifts away from the surface [13]. The dependence of the boundary region between "hillock" and "no-hillock" in Fig. 3 on kinetic energy is therefore rather weak and the slope slightly positive.

Of course, the exact boundaries between scenario A, B and C are strongly dependent on material parameters. In some materials other phase transitions will have to be considered, like crystalline to amorphous, etc. Figure 8 should therefore just be considered as a first attempt to sketch a unified picture. More systematic investigations for other materials of course will be needed to identify the exact mechanisms at work.

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