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Slow highly charged ion induced nanopit formation on the KCl(001) surface

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PACS 61.72.J– Point defects and defect clusters

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Abstract –We report on nanostructuring of the KCl(001) surface due to individual impact of slow highly charged ions. Samples were irradiated with Xe ions with charge states of $Q = 15$ to 40 at kinetic energies from 1.7 to 160 keV. The formation of nanopits at the virgin surface is observed and attributed to a defect mediated desorption process involving the removal of up to 2000 surface atoms per incident ion. The depth of the produced pits is shallow, but not limited to the first monolayer. From the variation of the ion parameters (charge state and kinetic energy) we derive a phase diagram for the structuring of the KCl(001) surface with highly charged ions.

1 **Introduction.** – Nanostructuring of surfaces by ion
 2 beam milling is a common method in research and indus-
 3 trial application [1–3]. These methods involve the sput-
 4 tering of surface atoms due to the impacting ion beam.
 5 Typical sputtering yields are in the order of 0.1 to 10 and
 6 thus large ion fluxes need to be applied in order to mill
 7 several surface layers or large structures in a focussed ion
 8 beam setup. The sputtering yield is limited by the amount
 9 of energy which can be deposited close to the surface and
 10 thus by the stopping force of the ion. In order to increase
 11 the sputtering yield one can either increase the stopping
 12 force significantly, which is done in swift heavy ion irra-
 13 diations or one uses another unique feature of heavy ions.
 14 This feature is the potential energy E_{pot} and results from
 15 the charge state of the ion. Swift heavy ion irradiations
 16 yield large sputtering yields (100-10,000) [4, 5], but are
 17 always combined with an elongated damage region in the
 18 bulk. Slow highly charged ions (HCI) instead deposit their
 19 potential energy in the range of a few keV to a few 10 keV
 20 close to the surface, i.e. within the first monolayers. This
 21 energy and the small deposition depth result in a large
 22 energy density giving rise to different kinds of nanostruc-
 23 tures [6, 7]. Among them are nanohillocks due to a local
 24 phase transition at the surface [8, 9], etchable defect
 25 clusters [10], volcano-like structures [11, 12] and epitaxial
 26 nanopits [13, 14]. The latter are features which preserve
 27 the local lattice structure but are associated with a des-
 28 orption process and corresponding desorption (or potential

sputtering) yields of up to a few thousand atoms. 29
 Due to the nature of the interaction only insulating sur- 30
 faces are prone to HCI induced nanostructure formation. 31
 The potential energy is released as a result of the neutral- 32
 ization of the ion leading to a vast amount of electronic 33
 excitations at the surface [7, 15, 16]. These excitations may 34
 either be screened and dissipate rapidly in a metal or they 35
 remain at the impact site and finally couple to the lattice. 36
 The lattice excitation may then lead to local phase trans- 37
 formation, i.e. local melting [9, 17] or sublimation, or the 38
 formation of large defect clusters [10]. 39
 On the KBr(001) surface a defect mediated desorption 40
 process induced by slow HCI could be identified [13]. The 41
 result of a single ion impact with sufficiently high charge 42
 state is a nanopit with a depth of exactly one mono- 43
 layer and a lateral extend of up to 20 nm. Corresponding 44
 desorption yields are in the order of a few 100 to 3,000 45
 atoms/ion. The desorption results from the formation of 46
 a cluster of lattice defects, so called color centers. These 47
 color centers at high special density can lead to a collec- 48
 tive desorption at the flat (001) surface leaving a nanopit. 49
 Here we show that the HCI related defect mediated des- 50
 orption process is not unique to the KBr(001) surface, but 51
 can also be observed on the sister surface KCl(001). Sim- 52
 ilar nanopits are observed, but their depth is not limited 53
 to the first monolayer like on KBr(001). Deeper struc- 54
 tures up to 3 monolayers are observed, whereas the depth 55
 profile depends on the ion’s kinetic energy. Also the po- 56

57 tential energy threshold for the creation of these nanopits
58 is somewhat higher than on the KBr(001) surface.

59 **Experimental Setup.** – KCl single crystals were
60 acquired from KORTH KRISTALLE, Germany and TED
61 PELLA, USA. Samples were cleaved in air with a razor
62 blade parallel to the {001}-plane. Platelets with a size
63 of approx. $10 \times 10 \times 2 \text{ mm}^3$ were produced and im-
64 mediately transferred into an ultra high vacuum chamber,
65 which is maintained at $p < 5 \times 10^{-9}$ mbar during irra-
66 diation. Ion fluencies were kept between 5×10^8 and
67 $1 \times 10^{10} \text{ cm}^{-2}$ to ensure no overlap of ion impacts. Some
68 samples were irradiated at the Rossendorf Two-Source-
69 Facility (2SF) and others at the new highly charged ion fa-
70 cility SNIPER (Surface Nanostructures by Ion’s Potential
71 Energy Release) at the ion beam center of the Helmholtz-
72 Zentrum Dresden-Rossendorf. Samples irradiated at the
73 2SF were transferred in air to an ultra high vacuum
74 atomic force microscope (AFM) from SCIENTAOMICRON
75 (VT UHV-AFM/STM) operated in contact-mode. At
76 SNIPER an AFM (SCIENTAOMICRON room-temperature
77 UHV AFM/STM) is mounted within the target cham-
78 ber enabling us to perform ion irradiation and AFM or
79 STM measurements without breaking the vacuum, which
80 we here refer as *in-vacuo*. Both AFMs use contact-mode
81 cantilevers purchased from NANOSENSORS, USA with a
82 nominal tip radius of 7 nm. Typical loading forces were in
83 the range of -2 to 5 nN, corresponding to attractive and
84 retractive regimes, respectively.

85 Highly charged ions are produced in both facilities in
86 room-temperature electron beam ion traps from DREBIT,
87 Germany. These ion sources provide Xe ions with charge
88 states from $Q = 1$ to 44. Ions with specific charge states
89 are selected by an analyzing magnet or a Wien filter at the
90 2SF or SNIPER, respectively. Ions are decelerated by an
91 electrostatic potential upon entry into the respective tar-
92 get chambers, thus we are able to adjust the ion’s kinetic
93 energy in the range of 100 to $4,500 \text{ V} \times Q$.

94 **Experimental Results.** – At SNIPER samples were
95 analyzed with contact-mode AFM before irradiation to
96 ensure a high quality surface after cleavage. Terraces
97 with several micrometer in length and several hundred
98 nanometer in width were obtained. Terraces are sepa-
99 rated by step edges with single monolayer height. Figure
100 1 shows an AFM image of a KCl(001) surface after irra-
101 diation with 70 keV Xe^{35+} ions with an applied fluence of
102 $1.4 \times 10^9 \text{ cm}^{-2}$. The surface shows large terrace sizes and
103 well aligned step edges. Single ion impacts are visible as
104 nanopits. These pits can be found close to step edges as
105 well as in the middle of a terrace. To evaluate the influence
106 of the ion charge state or it’s potential energy, respectively,
107 a systematic analysis of the pit shape, i.e. it’s depth and
108 width was performed. The depth distributions of nanopits
109 resulting from Xe^{33+} , Xe^{35+} and Xe^{40+} at similar kinetic
110 energies of 66, 70 and 80 keV, respectively, are shown in
111 figure 2(a). For $Q = 33$, i.e. $E_{pot} \approx 21 \text{ keV}$, nanopits show
112 a depth of one monolayer only, similar to the case of KBr

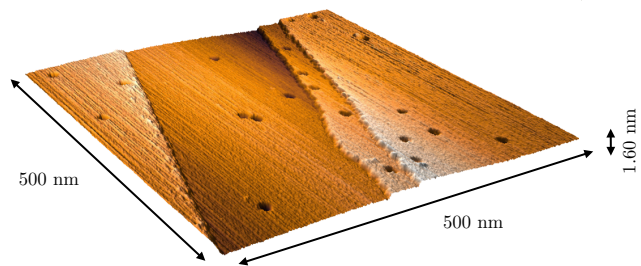


Fig. 1: (color online) $500 \times 500 \text{ nm}$ contact AFM image of a KCl(001) surface irradiated with Xe^{35+} at 70 keV kinetic energy. The applied ion fluence was $1.4 \times 10^9 \text{ cm}^{-2}$.

[13]. Increasing the potential energy to about 25.5 keV
($Q = 35$) results in nanopits with a bimodal depth distri-
bution. Roughly 2/3 of the pits show still a single mono-
layer depth, whereas 1/3 of the pits has a depth of two
monolayers. At even higher potential energy of $\approx 38 \text{ keV}$
($Q = 40$) a bimodal distribution is obtained, which peaks
at 1.5 and 2.3 monolayers.

Similar to the increase in depth pits also grow in lateral
dimension when the ion charge state is increased. This is
shown in figure 2(b) for the same ion parameters as dis-
cussed above. By increasing E_{pot} from 21 to 38 keV the
mean pit diameter increases from about 7 to about 13 nm.
From the AFM images the pit volume can be obtained
directly without the assumption of a specific shape. This
pit volume is shown in figure 3 as function of the poten-
tial energy of ions at different kinetic energies. The kinetic
energies are $2 \text{ keV} \times Q$ (blue squares) and $4.4 \text{ keV} \times Q$ (black
dots). In case of faster ions a threshold for pit formation
was observed between a potential energy of 5 to 8 keV.
Only if the potential energy exceeds the values of 8 keV
nanopits are observed. This threshold effect is consistent
with nanostructure formation on many different materials
[7]. At even higher potential energies the pit volume in-
creases slightly.

Lower kinetic energies lead to steeper increase of the pit
volume with potential energy. Also, by extrapolation, a
threshold in potential energy can be found at about 16-
17 keV, which is significantly higher than in the case above.
In the case of $Q = 35$ the data points are also indicated
with the depth of the nanopits. The volume is larger for
slower ions roughly by a factor 1.75, whereas pits show a
mean depth of more than a single monolayer. The mean
depth differs by a factor of 1.35, i.e. in case of slower ions,
nanopits are not only deeper, but also larger.

The latter effect of the kinetic energy becomes obvi-
ous in figure 4, where nanopit depths for Xe^{35+} ions at
two different kinetic energies are compared. As mentioned
above, slower ions (70 keV) produce pits with 1-2 mono-
layer depth, whereas faster ions (135 keV) produce solely
single monolayer deep pits. This finding can be explained
by the necessary energy density for the desorption process.
In case of faster ions the potential energy is deposited into
deeper layers of the materials and thus the density close

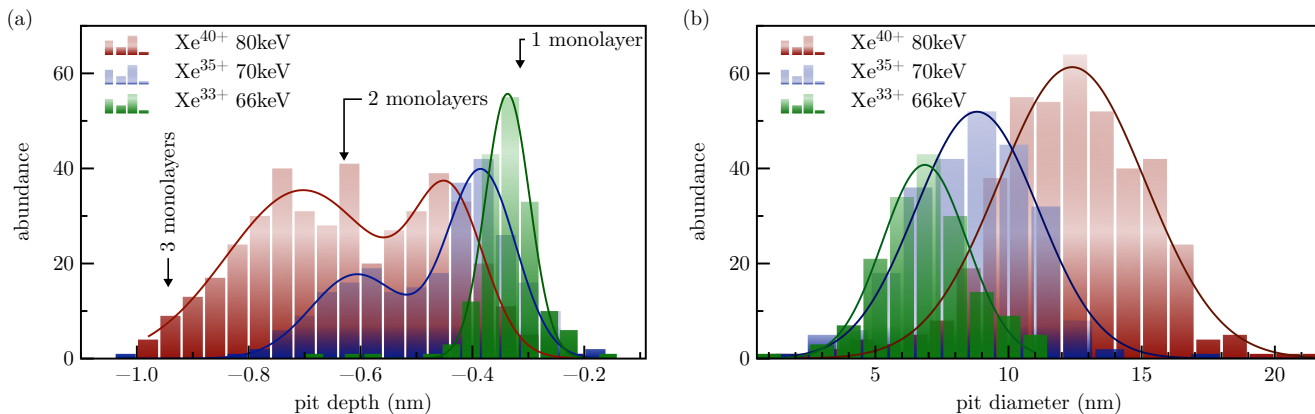


Fig. 2: (color online) (a): Depth distribution of observed nanopits. The distributions were fitted with multi-peak Gaussians. (b): Lateral size distribution of observed nanopits. The distributions were fitted with simple Gaussians.

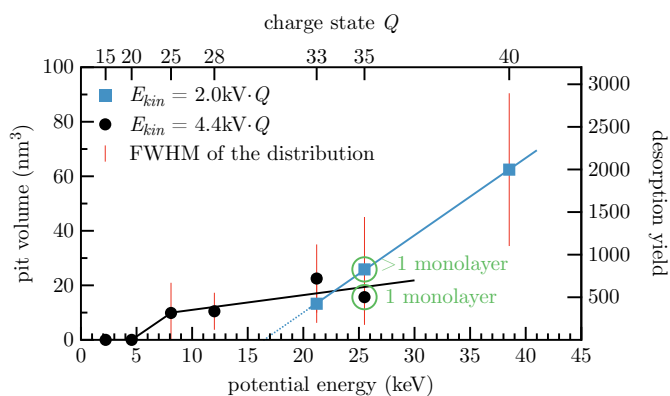


Fig. 3: (color online) Pit volume as function of ion's potential energy. The corresponding desorption yield is given on the right axis and the charge state on the top axis. The two curves correspond to two different kinetic energies. The $2\text{ keV} \times Q$ data is extrapolated to zero volume to determine a threshold. Monolayer and multilayer deep pits are observed for Xe^{35+} ions, depending on the kinetic energy (see fig. 4).

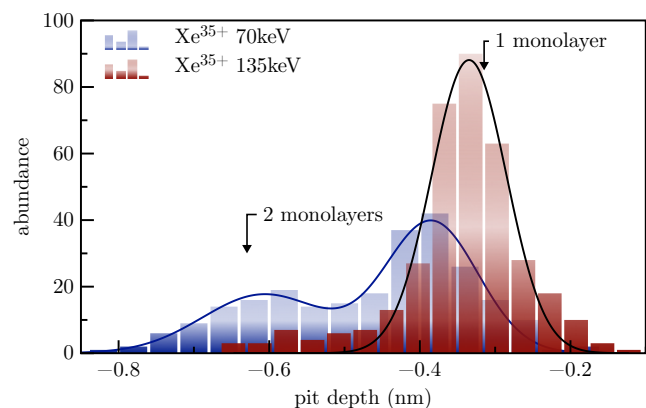


Fig. 4: (color online) Abundance of pit depth for Xe^{35+} ions at two different kinetic energies. At high E_{kin} only monolayer deep pits are observed, while slower ions produce deeper pits.

to the surface is smaller than for slower ions. Produced defects and electronic excitations can lead only to the desorption of atoms at the very surface. At higher energy densities the amount of defects and electronic excitations at the surface becomes sufficient to allow atoms from several monolayers to be removed simultaneously. This effect of the kinetic energy and consequently of the potential energy density was observed and explained by El-Said *et al.* on the $\text{CaF}_2(111)$ surface [9].

Defect Mediated Desorption. – An highly charged ion approaching a solid surface starts to capture electrons from the surface at a large distance of about 10 a.u.. Electrons are bound to the ion in very high Rydberg states with principal quantum numbers of $n = 10 - 20$ [18–20]. The formed object is called a hollow atom or ion. Subsequent de-excitation of the hollow atom results in the emission of Auger electrons and x-rays. Upon impact of the ion electrons still bound at high Rydberg states are stripped off, because their orbitals are much larger than interatomic distances of the surface atoms. The re-charged ion now captures electrons in a multi-electron process rather than a subsequent single electron process. By these complex neutralization processes the surface is locally heavily positively charged and thus structural weakened. The ion above the surface acts as a point source for electrons with energies of 10 to a few 100 eV [21–24]. Within the surface the continuously neutralizing and de-exciting ion still emits electrons. In fact, now deep lying inner shells are filled and thus the electron energies are even higher in the order of keV.

From electron irradiation of alkali halide surfaces a layer-by-layer desorption process was identified [7, 25–28]. Impacting electrons excite bound electrons in the lattice forming an exciton which gets rapidly self-trapped due to the charge background of the ionic crystal. The self-trapped exciton (STE) is a certain form of electronic excitation, which is stable up to picoseconds. Eventually a STE will decay into two color centers, namely a F-center and a H-center. F-centers are lattice defects, where the

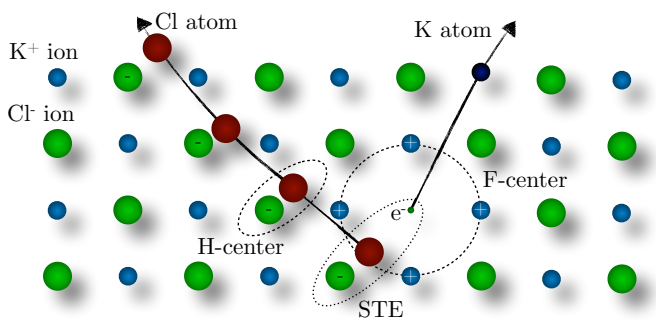


Fig. 5: (color online) The desorption process as a result of a STE decay.

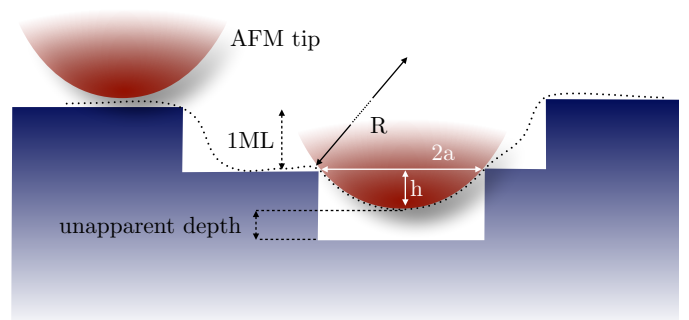


Fig. 6: (color online) Underestimation of pit depth due to the convolution of the tip profile with the pit depth profile.

195 halogen ion is missing and an electron is trapped at the
 196 halogen site. H-centers are quasi-molecular dimers of neu-
 197 tral halogen atoms and negatively charged close halogen
 198 ions (see figure 5).

199 F- and H-centers are mobile in the lattice and can diffuse
 200 by hopping towards the surface. At low coordinated sites
 201 at the surface these lattice defects may recombine with
 202 an alkali ion (F-centers) or simply desorb (H-centers). At
 203 a flat surface, e.g. in the middle of a large terrace, des-
 204 orption may be hindered, because of the enhanced bind-
 205 ing energy compared to a step edge. Since we still find
 206 nanopits far away from step edges and they result from a
 207 single ion impact the authors suggested on the KBr sur-
 208 face the formation of a large F-center cluster [13]. This
 209 cluster, called a X-center, may result in the desorption of
 210 several hundred to thousands of atoms simultaneously.
 211 Since KBr and KCl have the same crystallographic struc-
 212 ture and are very similar in many ways it can be assumed
 213 that a defect mediated desorption process is present here
 214 as well. However, a higher potential energy threshold must
 215 be overcome in case of KCl. Also at even higher poten-
 216 tial energies desorption from deeper layers becomes active.
 217 Since a X-center is a hypothetical object it can also be as-
 218 sumed that it may have different shapes, i.e. oblate or pro-
 219 late. Oblate X-centers may be present if the electron emis-
 220 sion is dominant above the surface and prolate ones if the
 221 electron emission is strongest within the surface. These
 222 details depend heavily on the materials electron supply
 223 under the influence of the ion, i.e. the electron mobility
 224 within an electric field strength of about 10^{12} V/m at a
 225 time scale of about 10 fs. It is difficult to estimate ma-
 226 terial's behaviour under these conditions. The proposed
 227 mechanism works as follows: (i) An ion with charge states
 228 $20 < Q < 35$ at intermediate kinetic energies produces
 229 a monolayer deep pit as described above. (ii) At higher
 230 potential energies the energy density increases and conse-
 231 quently a prolate X-center grows in size. Atoms from
 232 deeper layers can also be emitted. (iii) If now the kin-
 233 etic energy increases, the energy density decreases again.
 234 Thus, the part of a X-center close to the surface will then
 235 only lead to desorption of the first layer. Deeper parts of
 236 the X-center, i.e. F-center clusters will not simultaneously

desorb and just diffuse to the surface, increasing the size
 of the initial pit laterally.

237 Finally it remains open why depths of non-integer num-
 238 bers of monolayers were determined. In order to measure
 239 the true depth of a nanopit one needs to take the convo-
 240 lution of the depth profile with the AFM's tip profile into
 241 account. In the proposed desorption mechanism not all
 242 of the atoms from the second monolayer may be desorbed
 243 (see fig. 6). In this case the AFM tip may not penetrate
 244 the second layer completely and thus an apparent depth
 245 of more than one but less than two monolayers may be
 246 measured. Tips used in this study have a nominal radius
 247 $R = 7$ nm. Assuming the tip being of spherical shape a
 248 cap with diameter $2a$ and a cap height h can be assumed.
 249 The radius a , which a spherical pit must maintain in or-
 250 der for the tip to penetrate completely by the height h
 251 is given by $a = \sqrt{2Rh - h^2}$. For a pit depth h of one mo-
 252 nolayer (0.32 nm), it's lateral dimension must be larger than
 253 4.2 nm to be measured correctly. For a two-monolayer-
 254 deep pit, it's lateral dimension must even exceed 5.9 nm.
 255 Vice versa a shift of the mean depth by 0.5 monolayers
 256 corresponds to a lateral extend of the desorbed region
 257 from the second layer of 2.9 nm. If a two-monolayer-deep
 258 pit is not entirely of cylindrical shape, i.e. only parts of
 259 the second layer are desorbed, it's apparent depth can
 260 adapt values between 1 and 2 monolayers (see fig. 3).
 261 The same holds for even deeper structures. This also means
 262 that the desorption yield of multi-layer-deep pits is
 263 underestimated in the present study.

264 Nanopits of different shapes were observed for certain ion
 265 parameters, i.e. potential and kinetic energy. If the ion
 266 charge state or the kinetic energy is too low no pits are
 267 observed and the surface appears unchanged. Combina-
 268 tions of both ion parameters are shown in green in figure
 269 7 where nanopits were found. A kinetic energy depen-
 270 dent threshold is determined in the range of 0-100 keV
 271 and xenon charge states between 15 and 33. This 'phase
 272 diagram' is similar to the one reported for KBr [14] justifying
 273 once more the adaption of a defect mediated desorption
 274 process.

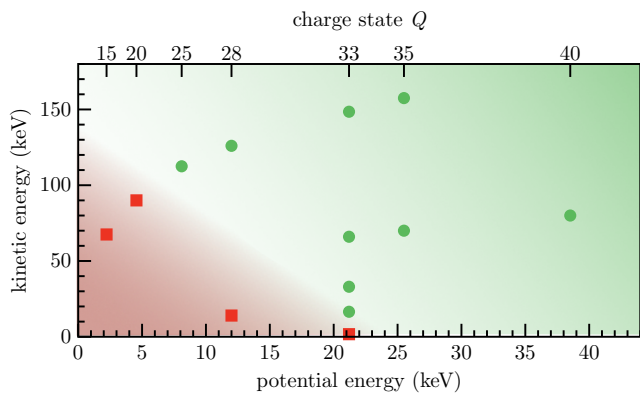


Fig. 7: (color online) Phase diagram for KCl(001) nanostructuring by slow HCl. An estimated area where no pits are expected is colored in red (data points as red squares), an area where pits were observed and expected is colored in green (data points as green dots).

Conclusions. — We showed that individual highly charged ion impact leads to nanopit formation with associated desorption yields of up to 2,000 atoms/ion on KCl(001). Pits are similar to single-monolayer-deep structures observed on KBr(001), but show a depth distribution indicating desorption also from deeper layers. A clear potential energy dependence of the desorption yield is presented. Additionally high kinetic energy alters the depth distribution of ion induced defects and thus reduces the efficiency of the desorption process. A phase diagram for the structuring of the KCl(001) surface with highly charged ions is deduced.

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