Collisions of ions with insulator surfaces: charging and discharging dynamics

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Abstract. The guiding of ions in keV to MeV energy range by insulator microcapillaries opens interesting perspectives such as direct injection of ions inside a living cell, formation of surface nano-structures, etc. We have studied the dynamic behaviour of charge deposition and beam deflection on insulators having well defined planar geometry when the exact number of charges implanted into the surface, as well as the time evolution of the beam deflection, can be monitored. The used materials, borosilicate, fused silica and quartz, are of interest for production of tapered microcapillaries. Depending on the temperature of the sample, surface composition and structure, charging and discharging dynamics varies by orders of magnitude, giving rise to different guiding effects in insulator microcapillaries. The charging process is compared to simple simulations in order to explain the observed behaviour.

1. Introduction

Interaction of slow highly charged ions (HCI) with different materials have interesting perspective in several fields. The physical reason is mainly in their high potential energy, relative to their kinetic energy: during the interaction process the potential energy is locally deposited onto a material. This results in different effects such as potential sputtering, formation of different structures on a nano-scale (nano- dots, hillocks), applications in surface analysis etc. [1]. The potential of slow highly charged ions as tools in nano-fabrication is essentially related to providing intense micro- and nano-beams. The conventional techniques (employing electrical and magnetic fields) are not convenient in this case since they are strongly influenced by the divergence and the energy spread of the initial ion beam. Hence, the discovery of HCI transmission through PET nanocapillaries [2] drew a lot of attention. The main point was that the charge state was kept, meaning that ion transmit without touching the inner walls. By tilting PET foils above 10° some ions were still transmitted which is a clear proof of HCI guiding through nanocapillaries. The observed behaviour was explained by the self-organizing process of inner wall charge up [2], which was confirmed by computer simulations of this process [3].

More recently discovery that a single tapered-glass micro-capillary has been used for guiding and maybe even focusing of HCI beams [4-6] which would have higher technological impact. Since the
ion trajectories are parallel to the inner walls (as in PET nanocapillaires), ions are focused due to the
taper angle: the observed focusing factor has been estimated close to 10.

In the experiments dedicated to propagation of HCIs through micro-capillaries the macroscopic
values observed are mainly time evolution of the intensity of the transmitted beam, its angular
distribution, and the charge state analysis [5]. Although important information is gained in these
experiments, closer insight into the guiding/focusing effects is hard to achieve without knowing the
charge distribution along the capillary including its time evolution. This can be partly overcome
using modelling, for which information on the charging/discharging parameters of a given material are
essential. Grazing incidence of ions onto a surface is a good model system for the experimental
investigation of charging, discharging and secondary electron emission dynamics of corresponding
materials. This experiment would also exclude some ‘geometric effects’ that influence ion
transmission through micro-capillaries.

We report here experimental investigation of the charging/discharging dynamics in the case of
grazing incidence highly charged ions onto materials of interest for production of taper-glass micro-
capillaries. The influence of the surface temperature, composition and structure, as well as the sample
history, is investigated. A simple Monte Carlo simulation of the surface charging evolution by grazing
incidence ion beam is also developed. Comparisons between the simulation and the experiments
explain some of the observed effects and suggest hints concerning those which are less understood.

2. Experimental
The experimental setup is described in detail elsewhere [7]. A primary beam of highly charged ions is
extracted from an ECR ion source. The beam is analyzed using sector magnetic field and collimated
before impinging the insulator surface at grazing incidence. The incident angle $\psi$ is in the range 0.5°-
1.5°, and the extraction voltages are 1-2.5 kV. A position sensitive detector (PSD) facing the primary
ion beam is placed behind the target. When the target is introduced into the beam by translation
perpendicular to the primary beam direction, part of the beam hits and charges the target while the rest
of the ions fly above the previously deposited charges towards PSD (figure 1). The later are therefore
repelled by the charges already deposited at the surface, so their deflection corresponds to surface
charging. The charging dynamics is determined by the time evolution of the direct beam deflection.
For discharging measurement the beam is left free to discharge with the beam turned off most of the
time. It is turned on just for a few seconds in regular time intervals to monitor time evolution of the
beam deflection. This method cannot be applied if the discharging is too fast. However, the
temperature dependence of the time constant can be determined using the procedure proposed in [8]. It
consists of measuring the primary beam rate needed to reach, in equilibrium, a specified direct beam
deflection.

![Figure 1](image1.png)

Figure 1. Scheme of the experimental setup; PSD is the position sensitive
detector, $\phi$ and $\theta$ are azimuthal and polar angles respectively

The charging rate is directly proportional to the ion flux hitting the sample surface. This flux can be
determined from measuring the intensity of scattered particles if the total reflection coefficient is
known. In the case of grazing incidence, the angular distribution of scattered particles is narrow
enough to be recorded on the PSD. The number of scattered particles per second is enough to
determine the reflection coefficient provided the incident beam intensity is stable. The additional
contribution to the surface charging is secondary electron emission which can be also measured by a
system of 16 microchannel plates positioned on a hemisphere surrounding the target.

3. Computer simulation
A simple algorithm is adopted to model the surface charging dynamics. The coordinate at which
particle hits the surface is the position of a point charge equal to \( q + \gamma \), where \( q \) is the charge of an ion
and \( \gamma \) is the secondary electron yield, both being input parameters. For a specified beam profile, a
sequence of ions with appropriate starting conditions is defined using the Monte Carlo procedure. The
trajectory calculations are performed by 4th order Runge-Kutta method with adaptive time step.
Incident angle and the target distance from the beam axis are input parameters. Whenever an ion hits
the target the field distribution is recalculated. Surface discharging is described by exponential time
decay (linear model [3]), which corresponds to bulk diffusion of holes. Before proceeding with the
calculation of the next ion trajectory, the field is decreased by appropriate exponential factor.

Besides this simulation there is also an additional program used to calculate the distribution of
deflected projectiles for a defined charge distribution on the surface. Its execution time is short, and it
can give some useful hints for further detailed analysis. This simulation is denoted here as static, while
the former is referred to as dynamic simulation. The simulation results will be presented in section 5,
in order to support the interpretation of the experimental results.

4. Results
Charging and discharging has been studied on the example of three materials based on \( \text{SiO}_2 \): fused
silica, quartz and borosilicate. Concerning the employed primary beams, no dependence on the ion
species was observed. Consequently, we focus to the influence of temperature and material properties
on the charging and discharging processes.

4.1. Surface charging
The typical angular distributions obtained by the 50 s data accumulation at the beginning of charging,
and for the equilibrium are given in Figure 2. The charging beam is 10 keV \( \text{Ar}^{4+} \) and the target is fused
silica. Before the target is introduced into the beam, there is a single spot on PSD, corresponding to
undisturbed direct beam (Fig. 2a). At the beginning of the charging, scattering signal can be observed
in the upper half of the PSD and at the same time the direct beam is deflected, magnified and
deformed (Fig. 2b).

![Figure 2. Fused silica charging by 10 keV \( \text{Ar}^{4+} \) ions, direct beam rate is 1000 ions/s, \( T = 550 \) K. The distributions are obtained for a) beginning of the experiment and b) equilibrium beam deflection](image-url)

The time evolution of the beam deflection and of the number of scattered particles for the same
experiment is presented in Figure 3. In general, the beam deflection increases with time and reaches
saturation, while the scattering intensity decreases. The time coincidence between the minima of the
one and maxima of the other function is a consequence of using the same beam for both surface
charging and monitoring the surface charge: whenever the beam is deflected, smaller number of
particles hit the surface and vice versa. This is most probably the same negative feedback which provides stability of the transmittance of HCIs through capillaries.

![Figure 3](image3.png)

**Figure 3.** Time evolution of the 10 keV Ar$^{4+}$ direct beam deflection and the intensity of the scattered particles. The surface temperature is $T = 550$ K. Solid line is the scattering intensity and dashed line is averaged beam deflection.

The secondary electron yield depends on the ion type but it disappears quickly after the charge up begins, since the electrons are suppressed by the electrical field of surface charges. Hence, the influence of $\gamma$ to surface charging is important only at the very beginning of the charging process. This behaviour was observed for all samples. The charging was measured in the temperature range from 440 K to 550 K. Below 400 K the discharging was extremely slow. A strong temperature influence on surface charging is observed. Additionally, the total fluence of ions implanted into the sample also plays a role. Both influences are probably related to the discharging process. Corresponding results will be thus presented in the section 4.2 devoted to discharging, and discussed later.

In the case of single crystal quartz, which has the same composition as the fused silica, the initial charging behavior was quite different: it was not possible to considerably charge up the surface even at room temperature in spite of more than 10 times greater fluxes as compared to those used for fused silica at elevated surfaces temperature. But the real surprise was that the discharge was also very slow, which is going to be discussed later. However, when the target was annealed to about 750 K for about 20 hours, the surface could be charged even with moderate beam flux.

Borosilicate glass, which is of particular interest for production of tapered-glass microcapillaries, shows significantly different behavior in terms of charging as compared to other samples. The typical rates needed for charging was 10-100 times higher as compared to those used for fused silica, at temperatures of 350 K and below. The reason is in extremely efficient discharging of this material. Besides, a number of peculiarities during the charging of this material was observed such as separation of the deflected direct beam into two or more beamlets, sudden appearance of beamlets above the major spot of the direct beam, fast rearranging of beamlet intensities while keeping the same overall intensity of the deflected beam, oscillatory deflection of the directed beam, etc. The time evolution typical angular distribution of the 22.5 keV Kr$^{9+}$ deflected beam(s) is presented on Figure 4. The distributions are obtained by the 50 s data accumulation at three different moments. Two discrete banana-shaped spots clearly appear in fig. 4b. Multiple beams were not observed with other materials.

![Figure 4](image4.png)

**Figure 4.** Borosilicate charging by 22.5 keV Kr$^{9+}$ ions, direct beam rate is 16000 ions/s, $T = 300$ K. The angular distributions are recorded at a) $t = 175$ s, b) $t = 225$ s and c) $t = 275$ s.
4.2. Surface discharging

The time dependence of the direct beam deflection during the discharging of fused silica is presented in Figure 5 and shows a single (5a) or multiple (5b) exponential decay. On the other hand, there are two slopes on figure 5b. The experimental parameters for these two measurements were exactly the same with the exception of the incident angle. The increased incident angle (figure 5a) corresponds to an increase of the surface charge density as the same beam is deposited on a smaller area. The results presented in figure 5 are obtained on the surface which was not previously bombarded. In the discharging measurement for similar experimental parameters as in figure 5a, but on the surface previously bombarded by a fluence of about $5 \times 10^{12}$ cm$^{-2}$, only one slope was observed but the discharge time constant was $\tau = 629$ s which is 2.4 times greater than for a fresh surface.

![Figure 5](image-url)

**Figure 5.** Logarithm of the beam deflection during the fused silica discharging. Primary ion beam is 4 keV Ar$^{4+}$ and $T = 550$ K. The incidence angles are a) $\psi = 1.1^\circ$ and b) $\psi = 0.7^\circ$.

![Figure 6](image-url)

**Figure 6.** Temperature dependence of the discharge time constant of fused silica; Incident angles and surface condition are denoted in the figure. When two values are reported, they correspond to a two slope discharging dynamics. For identical conditions, a fresh surface (full circles) discharges faster than a previously bombarded (hollow circles). Besides, for identical conditions, discharging is faster as the incident angle increases.

The results of the discharge time constants vs. temperature for fused silica are given in figure 6. The primary beam flux was kept roughly constant. The incident angles and the surface quality (hollow circle for previously bombarded and full circle for fresh surface) are denoted. The observation of two slopes in some cases, influence of the incident angle (decrease of $\tau$ with $\psi$) and of the surface history (increase of $\tau$ due to the surface bombardment) makes determining the temperature dependence of $\tau$ very hard. Still, it can be concluded that the temperature difference of 100 K produces change of the discharge time constant by two orders of magnitude.

The influence of the surface structure to the discharge dynamics can be clearly seen on the example of quartz which is a single crystal with the same composition as fused silica. Its discharge time constant at room temperature is around 50000 s, while for this temperature discharging of fused silica is too slow to be measured. The strong influence of the composition can be observed on the example
of borosilicate which consists mainly of SiO$_2$ (80.9 %), B$_2$O$_3$ (12.7 %) Al$_2$O$_3$ (2.3 %) and Na$_2$O/K$_2$O (4.1 %). The discharge dynamics could not be measured directly for this material since it discharges too fast. However, using the dynamic equilibrium method explained in [8] where flux is adjusted to reproduce the same deflection, it was possible to observed an Arrhenius behavior suggesting that $\tau \sim \exp(E_a/kT)$, where $E_a$ is activation energy for discharging and $k$ is Boltzmann constant. The measured value of $E_a$ is 0.48 ± 0.04 eV.

5. Discussion
The general physical picture of the surface charging process of glasses is the following. When an ion hits the surface it is efficiently neutralized, so it introduces a charge equal to $(q+\gamma)e$ in a small area (few nm$^2$) around the impact point. The impact points are spread along the charging area which is approximately the beam projection to the surface plane. These charges are actually electronic holes initially localized in the nonbonding 2p orbitals of oxygen [9]. They form a field distribution above the surface which deflects the subsequent ions away from the charging area, resulting in beam deflection and in some cases its deformation into a banana (figure 4b) or helmet (figures 2b and 4c) shape, but also in widening of the charged track. The same field is responsible for suppression of the secondary electron yield, which decreases and finally disappears relatively quickly. At the same time the charges migrate along the surface, which further changes their surface distribution, and into the bulk, which is actually discharging. Increase of the surface charge contributes to decreasing the fraction of the primary beam hitting the surface and at some point there is an equilibrium in which charging and discharging are compensated. While the charging is interplay between the surface charge up by ions hitting the surface and the migration of charges, the discharging is solely influenced by the later effect, which makes it simpler to understand. Hence, we shall begin the discussion with the surface discharging.

5.1. Surface discharging
The clear difference between the discharging behavior of fused silica and quartz can be understood in terms of two mechanisms of hole migration. Initially, the discharging takes place by hole hopping between nonbonding 2p orbitals, which is common to both glass and crystal since it depends only on the short range ordering. This migration mechanism, known as intrinsic, should be dominant in the case of quartz. On the other hand, amorphous materials have high concentration of defects which can act as hole traps. Sooner or later, hole gets trapped and its further migration becomes slowed since the potential barrier is much higher than the one corresponding to the intrinsic migration. Above 200 K the transport is thermally activated and the residence time in the hole trap can be described by the Arrhenius behavior [9].

The fact that quartz could not be charged up enough to measure discharging before the annealing seem to be related to small concentration of hole traps: the holes efficiently diffuse by the intrinsic mechanism. Nevertheless, the small concentration of hole traps did not allow fast discharging. The sample annealing probably triggered segregation of hole traps i.e. defects towards the surface (which is thermodynamically favorable), and the surface charging became much more efficient.

In the case of fused silica, the thermal dependence of the discharge time constant qualitatively follows the Arrhenius behavior, although we cannot say much on the nature of this dependence. The influence of the surface bombardment on the discharge time constant measurement is rather surprising knowing that the corresponding ion fluence hitting the surface is very small. Nevertheless, since the surface bombardment increases the time constant, the only explanation would be that additional defects are introduced that way. The observation of two slopes in some cases suggests the existence of two discharge mechanisms.

Two different mechanisms of nanocapillary discharging have been proposed in [3]. The first is the linear model in which the discharge time constant has a constant value. It corresponds to pure diffusion process. The other is a non-linear model in which discharge time constant exponentially decays with the square root of the local electric field. It is convenient for high surface charge
concentrations when the local electric field is strong enough to provide electron tunneling by traps. The discharging rate then increases exponentially with the square root of the surface charge density, which was indeed observed in ref. [10]. This physical picture also corresponds qualitatively to here-observed decrease of the $\tau$ with $\psi$. It is hard to say if the existence of two discharge time constants (Fig.3a) could also be explained by this model without the information on the surface charge distribution introduced in every experiment.

The discharging behavior of borosilicate implies that another mechanism takes place besides those proposed above. The temperature dependence of the discharge time constant of borosilicate follows the Arrhenius law. The corresponding activation energy is very close to that for migration of Na$^+$ ions binded to non-bridging oxygen atoms (NBO) in a borosilicate glass (0.55 eV) [11]. According to this scenario, not the holes but Na$^+$ ions migrate in order to provide surface discharging. Apparently, weak point of this suggestion is that sodium is preferably binded to BO$_2^-$ defect which has higher activation energy. Hence, Na$^+$ can be binded to NBO only if the concentration of Na$_2$O exceeds half of the concentration of B$_2$O$_3$ [11] which is not the case unless there is a surface segregation of Na. Indeed, strong surface segregation of Na in borosilicate glass has been measured in ref. [12].

5.2. Surface charging

The basic problem with the mentioned details is that they are not reproducible: not all relevant experimental parameters are well controlled and/or small deviations of some of them yield in significantly different behavior. This particularly stands for the borosilicate sample. We shall concentrate here to possible qualitative explanations of some of the features. Let us emphasize before that the two clear differences in the borosilicate experiment with respect to other samples: a) the employed beam intensity is at least for one order of magnitude higher and b) the discharge time constant is much shorter.

The time evolution of the direct beam deflection is strongly correlated not only to the amount of surface charges but also with its surface distribution. The static simulations show that propagation of the primary beam above the charged surface yields in magnification of the primary beam, and its deformation, as observed in experiment. These simulations reproduce curved shape of comparable radius as the one observed in experiments for the same beam fluence. Depending on the surface charge distribution, the magnification can be either positive (Gaussian charge distribution) or negative (uniform charge distribution). The later can explain sudden appearance of beam spots above the averaged direct beam image on PSD, which is sometimes observed in the borosilicate charging experiments (fig. 4c).

Figure 7. Dynamic simulation of insulator surface charging by 10 keV Ar$^{4+}$ ions, the direct beam rate is 10000 ions/s, $\gamma = 10$, and a discharge time constant $\tau = 1000$ s. The angular distributions correspond to snapshots taken at a time a) 0.07 s b) 0.75 s and c) 1.5 s.

One example of the dynamic simulation result is given in Figure 7. The primary ion beam is 10 keV Ar$^{4+}$, overall number of ions is 156250 (corresponding to overall charge of $1 \cdot 10^{-14}$ C carried by ions), and the discharge time constant is $\tau = 1000$ s, which should correspond to experiments with fused silica at 550 K. Indeed, the magnitude of the direct beam deflection, the spot magnification, including the spot deformation into a helmet shape is comparable to the fused silica experiment and
even to that of borosilicate (figures 2b and 4c). Additional feature that usually appears, a sharp well
defined spot superimposed to the blurred helmet (figure 2b), the simulation did not succeed to
reproduce.

While the simulations have some success in reproducing results on fused silica, it seems to be
much less efficient in the case of charging dynamics of borosilicate. Decrease of the discharge time
constant down to $\tau = 10$ s, did not yield in observation of multiple bananas. Two bananas were
observed in simulation when the surface charge distribution has two maxima. However, it is not easy
to imagine physical situation in which this would appear. The oscillations of the beam deflection are
observed in the dynamic simulations. The analysis of the surface charge distribution shows that they
are correlated with local surface discharging which lowers the beam deflection but at the same time
increases the surface charging rate, contributing again to the beam repelling. However, the amplitude
of these oscillations are much smaller than those observed experimentally. The possible explanation of
the strange behavior of borosilicate could be the interplay between the beam instability and fast
discharging. The first results of dynamic simulations with randomly introduced beam shifts give some
promising results (fast shifts along the azimuthal direction), but more work is necessary to see if this
interpretation is correct.

6. Summary
Discharge time constants of fused silica and quartz were experimentally determined for different
physical conditions. Influence of the temperature and previous surface bombardment was observed in
the case of fused silica. Charging properties of quartz were modulated by sample annealing, which
was explained as a consequence of defect segregation towards the surface. Observation of very fast
discharging of borosilicate is of particular interest since taper-glass microcapillaries are made of this
material. The determined activation energy of the borosilicate discharge time constant suggests that
migration of sodium ions is responsible for discharging rather than that of hole as for other two
materials. Influence of the ion species to the studied processes is not observed. Simple simulations of
surface charging are introduced, which reproduce in a first approximation, the experimental findings.
Still, several effects, particularly in the case of borosilicate, are left unclear. Further work on more
refined simulations is in progress.

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References
[1] Schenkel T, Hamza A V, Barnes A V and Schneider D H 1999 Progr. Surf. Sci 61 23
[2] Stolterfoht N et al. 2002 Phys. Rev. Lett. 88 133201
[3] Schiessl K et al. 2005 Phys. Rev. A 72 062902
[4] Ikeda T et al. 2006 Appl. Phys. Lett. 89 163502
[5] Ikeda T et al. 2007 J. Phys:Conf. Ser. 58 68
[6] Cassimi A et al. 2008 J. Nanotechnology 5 809
[7] Morozov V A, Kalinin A, Szilagyi Z, Barat M and Roncin P 1996 Rev. Sci. Instr. 67 2163
[8] Bundaleski N et al. submitted
[9] Hughes R C 1976 Phys. Rev. B 15 2012
[10] Stolterfoht N et al. 2007 Phys. Rev. A 76 022712
[11] Grandjean A, Malki M and Simmonnet C 2006 J. Non-Crystal. Solids 352 2731
[12] Sumner A L et al. 2004 Phys. Chem. Chem. Phys. 6 604