

Guiding of highly charged ions through insulating nanocapillaries¹

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Abstract: The guiding of highly charged ions through nanocapillaries in different insulating materials, such as polyethylene terephthalate, SiO₂, and Al₂O₃ has been investigated by our group, using 7 keV Ne⁷⁺ ions. We find transmission of ions incident at angles larger than the angle given by the capillary aspect ratio in all these materials. The measured angular distributions, however, vary with the membrane material. In this report we compare the experimental findings with the different membranes.

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Résumé : Notre groupe a utilisé des ions Ne⁷⁺ de 7 keV pour étudier le guidage d'ions hautement chargés dans les nanocapillaires de différents matériaux isolants, comme le terephthalate de polyéthylène (PET), le SiO₂ et le Al₂O₃. Nous observons la transmission d'ions incidents à des angles plus grands que les angles formés par l'aspect du capillaire dans tous ces milieux. Les distributions angulaires mesurées varient cependant avec le matériau de la membrane. Nous comparons ici les résultats expérimentaux obtenus avec différentes membranes.

[Traduit par la Rédaction]

Introduction

Highly charged ions (HCI) from an EBIT can be very effectively used for studying their interaction with solid surfaces [1–3]. The phenomenon of the creation of hollow atoms has attracted considerable attention [3, 4]. There is a unique possibility for studying hollow atoms of the first generation using metallic microcapillaries as a target for a beam of slow HCIs [5]. After penetration through the capillaries, it is possible to observe the decay of hollow atoms in the vacuum by X-ray or electron spectroscopy [5, 6]. The HCI pass through the metallic capillaries only when their axes are parallel to the beam direction and the angular distribution of the transmitted beam is very narrow (with a width given by the capillaries' aspect ratio).

When using nanocapillaries in insulating materials as a membrane there is transmission of ions even when the capillary membrane is tilted with angles very much larger than that given by the aspect ratio. Furthermore, the majority of the transmitted ions are still in their initial charge state. This astounding feature in the interaction of slow HCIs with insulating nanocapillaries, was first reported by Stolterfoht et al. for nanocapillaries in

polyethylene terephthalate (PET) [7]. The significant difference in the phenomena involved in the interaction of HCI with metallic and insulating nanocapillaries must be due to the different electrical properties of the walls of the capillaries.

As is known, the surface of an insulator can accumulate charge through impact of an ion beam. It is proposed that a process of charging-up of the internal capillary walls facilitates the transmission of ions incident at angles much larger than the angle corresponding to the capillary aspect ratio ($\approx 0.6^\circ$) [7]. This phenomenon gives us the opportunity to study HCI interaction with solid surfaces in nanometre scale. The HCIs are used to charge up the capillary and the transmitted HCIs are used as probes of the electrical properties of the capillary walls.

The first experiments with 3 keV Ne⁷⁺ ions that were transmitted through capillaries in the insulating material PET reported transmission of ions for tilt angles up to 25°, with an angular width of 5°, full width at half maximum (FWHM) [7]. Our group performed experiments with nanocapillaries in PET of 100 nm in diameter and 10 μ m length with a beam of 7 keV Ne⁷⁺-ions [8]. At this higher kinetic energy, the angular width of the transmitted ions is somewhat narrower; approximately 3.2° and ion transmission can be discerned for capillary tilt angles up to 4°.

The guiding of highly charged ions through insulating nanocapillaries has been attributed to the forming of charge patches on the inner walls of the capillaries, the main patch being located close to the entrance. For a fully discharged capillary membrane, oriented in a way that the capillary axes are tilted at some angle, with respect to the direction of the ion beam, there is no transmission of ions at the beginning. When ions collide with the capillary walls they deposit positive charge, which diffuse into the bulk and on the surface of the walls, through the hopping of charges. Charge patches are formed at locations where most of the ion-wall collisions occur, which then deflect ions entering the capillaries at a later instant. Full transmission is achieved when the equilibrium point between deposition of

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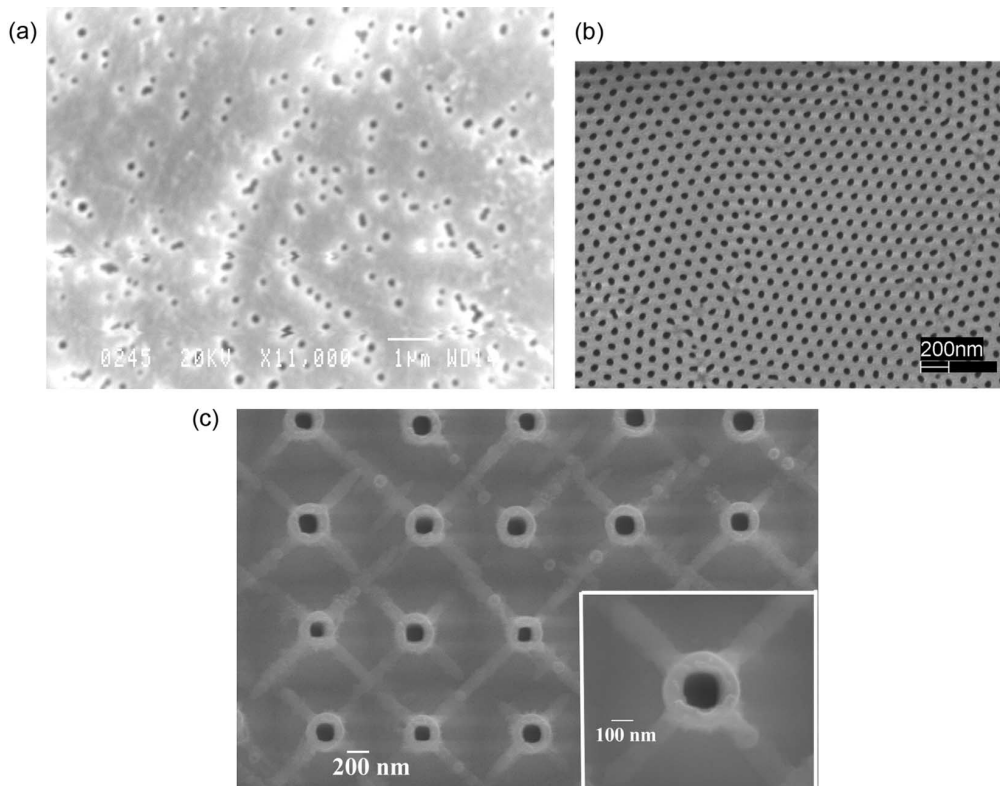
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Fig. 1. (a) PET-capillaries, (b) Al_2O_3 nanocapillaries, and (c) SiO_2 nanocapillaries [12].



charges on the walls — through ion–wall collisions — and diffusion of charges — through diffusion into the bulk and the hopping of charges on the surface [9] is reached. The electric properties of the capillary wall and membrane material should thus influence the charge-up and transport features. To investigate the guiding characteristics of nanocapillaries in different materials, we studied the guiding of slow highly charged Ne ions through PET, SiO_2 , and Al_2O_3 nanocapillaries. The distribution of charge states of the transmitted ions has been measured as well. It is found in all cases that the majority of the transmitted ions are still in their initial charge state [7, 10].

Experiments

The experiments were performed using a beam of 7 keV Ne^{7+} ions from the 14 GHz ECR ion source at the Manne Siegbahn Laboratory (MSL) in Stockholm. The beam was analyzed with a bending magnet, focused by two electrostatic quadrupole doublets and an Einzel lens and then collimated by a pair of four-jaw slits set 1.55 m apart, the last double-pair being set to $\leq 2 \times 2$ mm. The size of the beam was ≤ 2 mm in diameter and the intensity was on the order of 0.1 nA/mm^2 at the target position. The angular divergence of the primary beam was measured to be approximately 0.36° for all experiments with the three different capillary membranes. Given that the acceptance angle of the spectrometer is $\approx 0.3^\circ$, we deduce that the actual beam divergence is negligible. The primary beam charge-state distribution shows a $\leq 0.03\%$ content of other charge states than Ne^{7+} . The base pressure in the beam line was approximately 1.5×10^{-8} mbar and the experimental chamber was evacuated down to 10^{-9} mbar. A 127° electrostatic analyzer is on a rotatable table (to vary the observation angle θ) and an additional

channeltron can detect neutrals or ions when the analyzer is off. The registered number of ions is normalized to the current measured on the target surface. The capillary membrane is mounted in a holder on a goniometer, which allows independent adjustment of the target position in three axial dimensions and around two rotational axes. At the beginning of each experiment the capillary membrane is oriented perpendicularly to the incoming beam direction, i.e., to find the capillary alignment for both the azimuthal and elevation angle. After aligning the capillary to the beam direction, the azimuthal angle is set to zero and the elevation angle was changed in the measurements by tilting the capillary membrane relative to the beam direction, which is normally called tilt angle ψ .

In the following we describe briefly the capillary fabrication procedures.

PET capillaries

The PET membranes were first bombarded by GeV energy HCl's. The ion tracks were chemically etched to a diameter around 100 nm used in the measurements. Front and back side of the membrane was then gold plated to avoid charging up [7]. The ion tracks from heavy ion bombardment are randomly distributed (see Fig. 1a), and have an angular spread of 2° of the capillary axes. Further properties of the PET-capillaries are given elsewhere [7, 8].

Al_2O_3 capillaries

The Al_2O_3 capillaries were manufactured using the method of anodic oxidation of aluminium foils described in ref. 11, resulting in a hexagonal pattern of highly parallel Al_2O_3 nanocapillaries. The capillaries have diameters of 60 nm, and they are $10 \mu\text{m}$ long, giving an aspect ratio angle of 0.34° . The capillary

membrane was covered with gold layers, approximately 20 nm, on both surfaces to prevent charging up of the surfaces. The geometrical transparency of the membrane is approximately 20%, which corresponds to a capillary density of approximately 10^8 capillaries/mm². Figure 1b shows the regular distribution of the highly ordered, parallel nanocapillaries over the surface.

SiO₂ capillaries

The SiO₂ nanocapillaries were fabricated from a moderately (0.1–1 Ω cm) n-doped <100> Silicon wafer by making use of optical lithography and photo-assisted electrochemical etching [12]. To get insulating electric properties, the capillary membrane is thermally oxidized to yield a 100 nm thick layer of silicon dioxide on the capillary walls. Finally, the capillary membrane permeated by a silicon dioxide nanocapillary array containing regularly distributed, 1.4 μm apart, nanocapillaries of 100 nm diameter and 25 μm length (see Fig. 1c) was obtained. Both front and back surfaces of the membrane used in the experiments were plated with 30 nm of gold to prevent the surfaces from charging-up during ion-beam exposure.

The nanocapillaries besides being very highly ordered are also strictly parallel as the electrochemical-etching proceeds along the crystal axis. But the thin membrane is not perfectly flat; it has a slight overall curvature due to the strain induced by the differing lattice constants of the SiO₂ capillary walls and the Si bulk. However, the curvature is estimated to be much less than 1° over the area exposed to the ion beam in the experiments.

Results and discussion

The angular distributions as a function of the observation angle θ for different capillary tilt angles ψ are shown in Fig. 2, for the different membrane materials.

The integrated angular distributions of each capillary tilt angle reveal that the number of transmitted ions at 4° tilt angle is only 10% of that at 0° tilt angle. The transmission at the centre position decreases to approximately 6% at 4° compared to 0° due to the larger angular spread of the transmitted ions at larger tilt angles. The peak positions of the transmitted distributions as a function of tilt angle shows a linear relation, as can be seen in Fig. 3.

From the measurement of the charge-state distribution of the transmitted ions it was found that the initial charge state is dominated and only a small fraction (<2%) of the ions passing through the capillaries have picked up one or more electrons, thus justifying the use of the 0° detector for the measurements of the angular distributions in all cases [7, 10].

The ions transmitted through the SiO₂ capillaries have the narrowest width of 0.8° (FWHM) at 0° tilt angle, increasing to 1.1° at 4° tilt angle [10]. Taking the small geometrical transparency into account, we see that approximately 20% of the ions entering the capillaries are transmitted through them.

From Fig. 2 and Table 1, we see that the angular distributions of the transmitted ions through SiO₂ capillaries are somewhat narrower than those measured for Al₂O₃ capillaries and much narrower compared to PET capillaries (Fig. 2b). For instance, an angular distribution of FWHM 0.8° is observed for 7 keV Ne⁷⁺ ions through SiO₂ capillaries whereas we measure 3.2° FWHM for 7 keV Ne⁷⁺ ions transmitted through PET capillaries of 100 nm diameter and aspect ratio of 100 [8].

Fig. 2. (a) Angular distribution measured with 7 keV Ne⁷⁺ ions through SiO₂ capillaries [10]; (b) angular distribution measured with 7 keV Ne⁷⁺ ions through PET capillaries [8]; (c) angular distribution measured with 7 keV Ne⁷⁺ ions through Al₂O₃ capillaries.

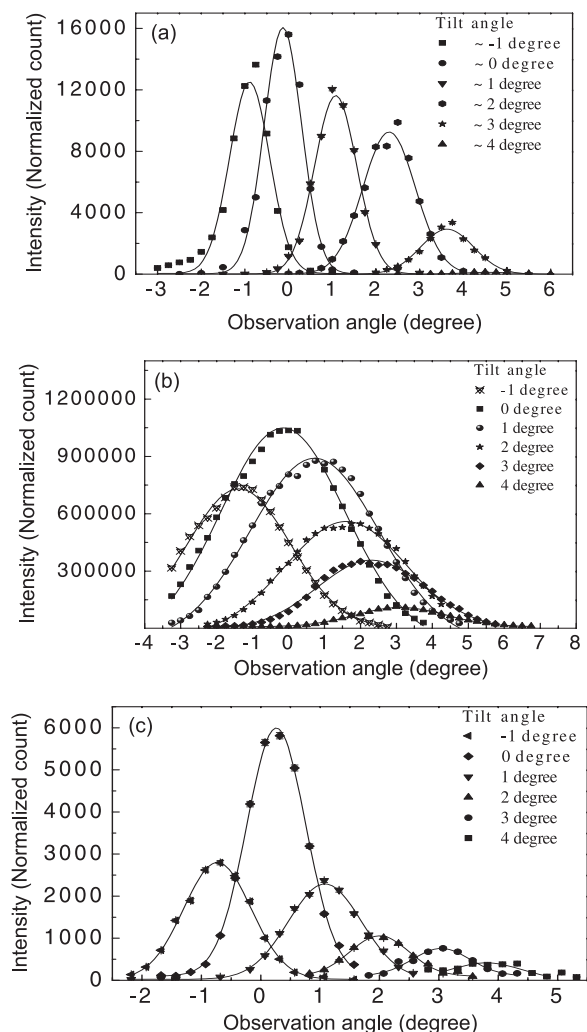
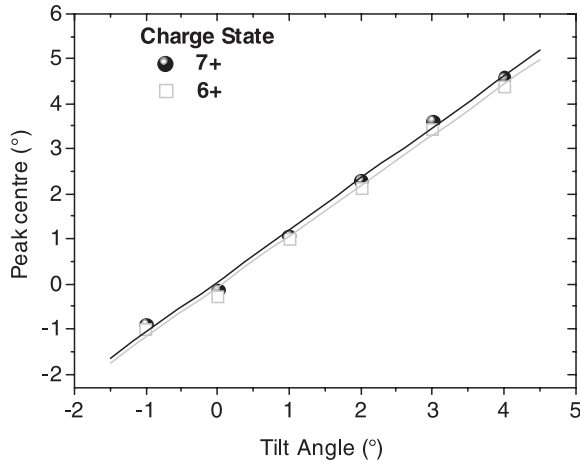


Table 1. Parameters of the different capillaries and membranes.

	SiO ₂ on Si	Al ₂ O ₃	PET
Dimensions			
Diameter	100 nm	60 nm	100 nm
Length	25 μm	10 μm	10 μm
Geometrical transparency	0.4%	20%	3.5%
Capillary density	10 ⁶ /mm ²	10 ⁶ /mm ²	10 ⁸ /mm ²
Angular spread of the capillary orientation	<0.3°	<1°	<2°
Measured FWHM	0.8°	1.2°	3.2°

The centroids of the angular distribution as functions of capillary tilt angle ψ are shown in Fig. 3 for two different transmitted ion charge states. It can be seen that when the capillary membrane is tilted with respect to the incident beam, the peak positions of the transmitted ions shift accordingly in a linear dependence.

Fig. 3. The centroid of the angular distributions as a function of capillary tilt angle ψ is shown for two different transmitted ion charge states.



The angular distributions, current density, integrated counts, charge-state distributions of the primary beam, and the centre positions, as functions of capillary tilt angle for Al_2O_3 capillaries are all comparable with the results of SiO_2 capillaries, except that the transmission is very much smaller for Al_2O_3 capillaries than for SiO_2 capillaries, $\leq 1\%$ compared to $\approx 20\%$ [10]. This could be due to the different surface properties and the smaller diameter of Al_2O_3 capillaries used in the measurement. Note that the dielectric constant for Al_2O_3 is 9.5 which is different from the 3.9 of SiO_2 . The dielectric strength of Al_2O_3 is 10^4 V/mm which is lower by one order of magnitude than that of SiO_2 (10^5 V/mm). The electrical resistivity of Al_2O_3 is $\sim 10^{14}\Omega$ cm which is lower by 2 orders of magnitude than that of SiO_2 ($\sim 10^{16}\Omega$ cm). The smaller resistivity will reduce the ability to store charge on the capillary wall. Hence, the electric fields due to the charge patches would be reduced. The potential distributions by the charge patches will be changed inside the capillaries due to the smaller diameter, which can affect the transmission of ions.

The angular width of the ions transmitted through Al_2O_3 capillaries is also much smaller compared to the results of Mátéfi-Tempfli et al. [13]. They report angular widths of 5.5° for 3 keV Ne^{6+} ions transmitted through Al_2O_3 nanocapillaries of 280 nm in diameter and $15\ \mu\text{m}$ in length. The width is expected to be narrower in our experiment, as the kinetic energy of the ions is larger. This should be similar to the reported angular width of 5° and 3.2° for PET capillaries, using 3 keV and 7 keV ions, respectively [7, 8]. Another difference in the Mátéfi-Tempfli's et al. results and our experiments is the ion charge state. We refrain here from a complete quantitative comparison of the results, since other parameters of the two experiments differ as well: membrane fabrication, capillary diameters, capillary lengths, geometrical transparency, and divergence of the primary beam. However, the most obvious and remarkable difference between PET capillaries and Mátéfi-Tempfli's et al. results [13] and our results with Al_2O_3 and SiO_2 capillaries is clearly the different

width that is not explained presently. It could be due to a field that developed at the capillary exit. Such a field at the capillary exit must cause a deflection and divergence of the transmitted ions and be very much different for different capillary materials and capillary dimensions [9].

In conclusion, the transmission of HCl through insulating capillaries has been considered as a self-organizing charge-deposition process depending on electrical properties, aspect ratio, and geometrical transparency of capillaries. The FWHM of transmitted ions vary with different capillary materials used in experiments. More work is needed to clarify by what amount and how the electrical properties, aspect ratio, and geometrical transparency of capillaries affect the transmitted distributions and guiding ability.

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