PRODUCTION OF MICROSTRUCTURES BY HEAVY IONS

B.E. Fischer and R. Spohr
GSI Darmstadt

Abstract

To most people the only known application of etched nuclear tracks is the production of filters with very uniform filter pores. But besides that, nuclear track etching is a much more versatile microtool. Its basic properties are: lateral resolution down to 10 nm, well controlled depth up to some 100μm, and an unusually wide range of materials to which this tool can be applied. In contrast to other microtools (light, x-rays, electrons) a single heavy ion can produce a useful microstructure or a defect, if the ion is scattered into the wrong position. This is the basis for unique applications and at the same time the most severe limitation of the method.

To illustrate the method, basic geometries of etched nuclear tracks are described and how they can be influenced by the etch process and by the choice of the base material.

Examples of applications are given in order of growing sophistication starting from single hole membranes and ending with the direct writing of microstructures by precisely aimed single ions in a scanning heavy ion microprobe.

PROLOG

When you hear about applications of nuclear tracks you probably can't avoid remembering phantastic things like

free quarks
magnetic monopoles
superheavy elements or
anomalons

appearing and disappearing in nuclear track detectors. Therefore you may find it hard to believe that nuclear tracks can be useful at all.

But some of you may also remember that filters can be made by etching nuclear tracks. And these filters are real (see fig. 1) of unmatched quality, easy to produce and highly profitable. Therefore filters have also been the motivation for this talk at first. But over the many years we have thought and worked on the application of etched nuclear tracks we became convinced that a lot more interesting things can be done by that tool, as the following examples are going to tell you.

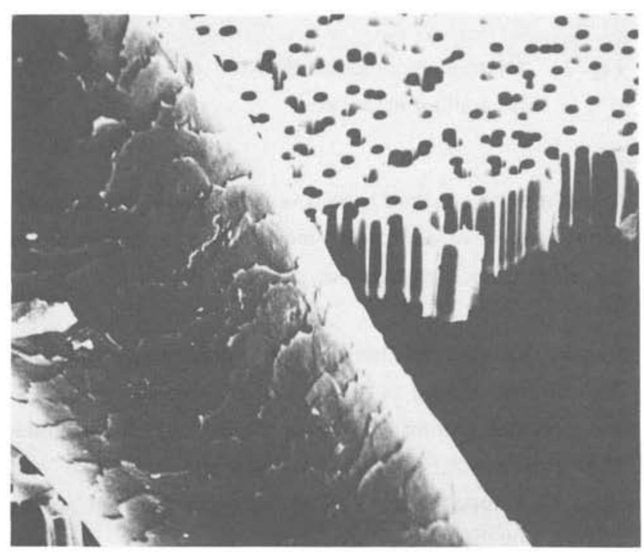

Fig. 1 Nuclear track filter and human hair. Scanning electron micrograph.

How are heavy ions drilling such small holes?

They start by producing a "latent" track and there are different ways it happens in crystalline solids and glasses or in plastics.

When a heavy ion is passing through a crystal at MeV-energies (fig. 2) lots of electrons are swept out of the track core in the electromagnetic "bow wave" of the ion leaving a highly charged region behind. In insulators this region "explodes" under the influence of electrostatic repulsion and ends up as a zone of slightly decreased density (about 5-10 %)[1] - the latent track - which can be more easily attacked by an etching solution.

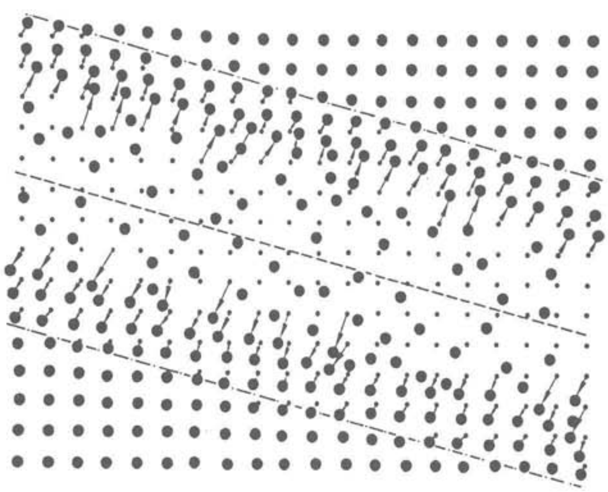

Fig. 2 Microscopic model of latent track production in crystalline material[2].

In metals the charged region is neutralized so fast that the ions don't have sufficient time to move appreciably, and no latent track is generated.

In plastics (fig. 3) there is an additional effect: The δ-electrons emitted in the ions bow wave can directly cut the polymer chains to smaller pieces which also eases chemical attack. In some plastics there is also some electron-induced cross-linking between different polymer chains, which reduces solubility in an etchant. Generally both effects happen simultaneously and it depends on the local electron dose, which of both effects is dominant.

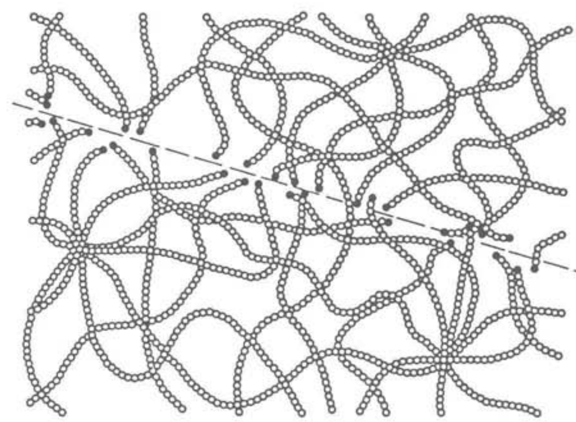

Fig. 3 Latent track production in polymers[2].

Fig. 4 shows latent tracks of fission-fragment-ions in mica which have been made visible in a transmission-electron-microscope[2]. Important for the production of microstructures is the diameter of the latent tracks, which can be estimated from the scale bar below to be around 10 nm. Therefore the smallest structure that can be produced by track etching will be slightly larger than 10 nm.

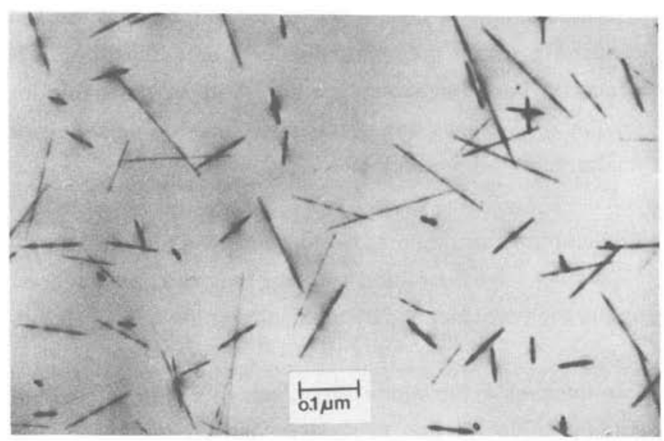

Fig. 4 Transmission-electron-micrograph of fission fragment ions in mica. Courtesy of P.B. Price[2].

When an irradiated material is exposed to an etching solution, etching proceeds much faster along the less dense, and maybe chemicly activated, latent track than it proceeds in the bulk of the material. The result is a chemical "Mach cone" indicated for $t = t_1$ in fig. 5. When the etchant reaches the end of the latent track, there is no longer a preferred direction of etching. The etch cone gets a rounded tip ($t = t_2$) and some time later ($t = t_3$) the straight portion of the original cone is etched away completely. A perfect spherical depression results, the radius of which is increasing with prolonged etching time until it can no longer be detected against the surrounding flat background.

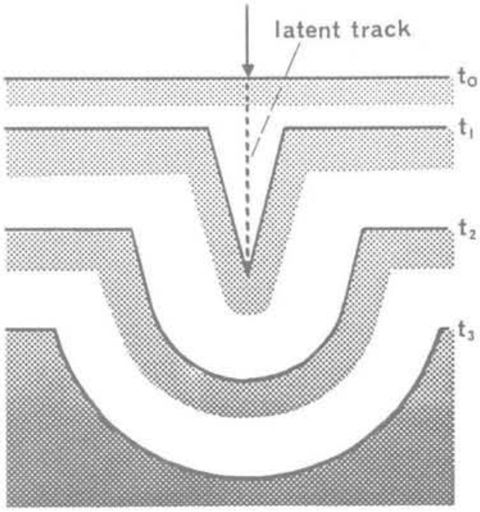

Fig. 5 Several developmental stages during track etching.

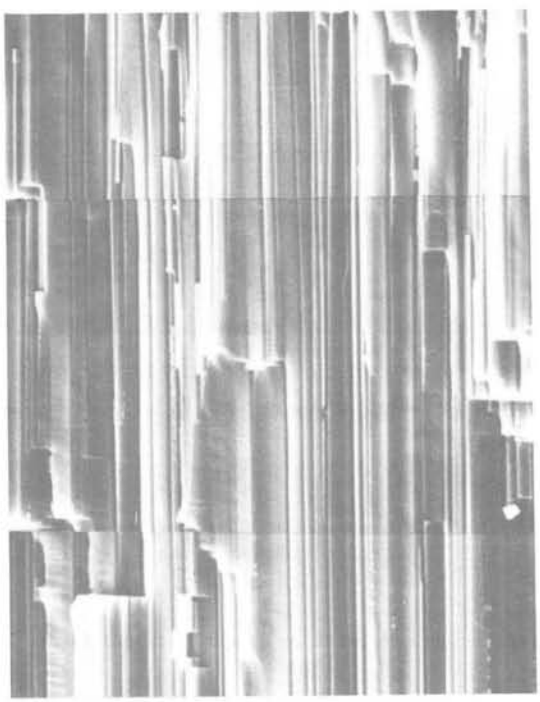

Fig. 6 Etched tracks of 7.5 MeV/u Xe-ions in mica. In order to reveal the full length of the tracks, the mica sample has been broken along the tracks. Diameter of the etched tracks about 0.2μm . Scanning electron micrograph.

If there is a large increase in etching speed along the latent track one can etch very deep track-channels with almost no indication of a cone angle as demonstrated in fig. 6 for the case of mica irradiated by 7.5 MeV/u Xe-ions. Please note also that the ions penetrate into the material essentially undeflected, a property which demonstrates the usefulness of heavy ions for the production of very deep microstructures.

In other materials the increase in etching speed is less pronounced. In plastics it is still high, as can be seen in fig. 1. In glasses one usually gets only a slight increase in etching speed - no wonder, it is already amorphous - and one can etch tracks with very different cone angles in glasses (figs. 7 and 8).

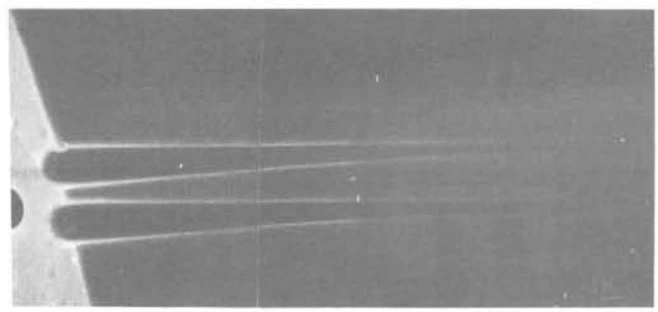

Fig. 7 Example of a slender etch cone in phosphate-glass.

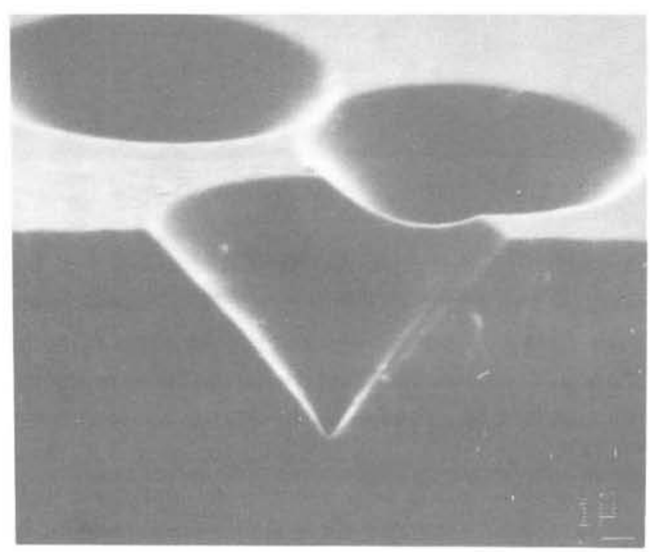

Fig. 8 Example of a widely opened etch cone in soda lime glass.

Using double-layer-materials with different bulk etching speeds you may even etch microscopic cavities (fig. 9) here demonstrated in an ion-implanted magneto-optic film.

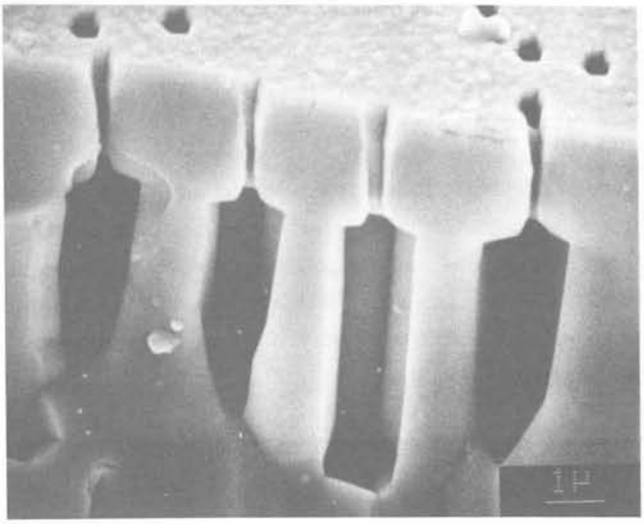

Fig. 9 Micro-cavities in a magneto-optic film[9].

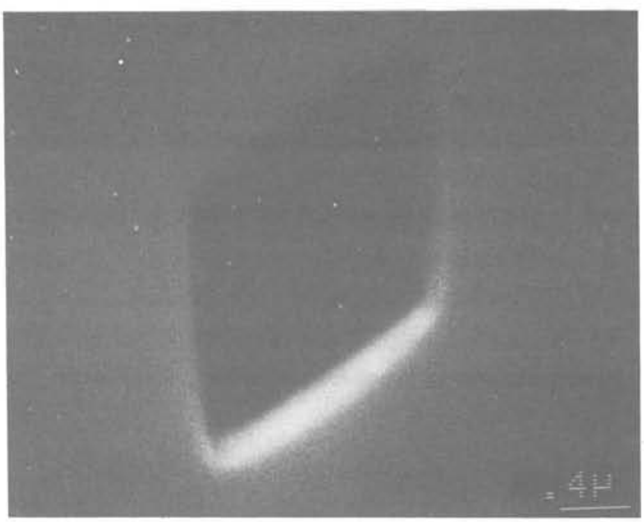

Fig. 10 Cross-section of an etched track in mica.

Depending on the nature of the irradiated material the cross section of the etched track can also take different shapes. In an isotropic material it is necessarily round as shown in fig. 1. In crystalline material the speed of etching will generally be influenced by the crystal orientation and the resulting cross-section of the etched track will reflect the crystal-symmetry of a material, as demonstrated in figs. 10 and 11. That does not mean however, that you always get the same track structure in the same crystal. There is also a strong influence of the etchant itself, as a comparison of fig. 10 and fig. 12 shows. Here mica has been etched in boiling NaOH to produce track channels with a funnel-shaped entrance section.

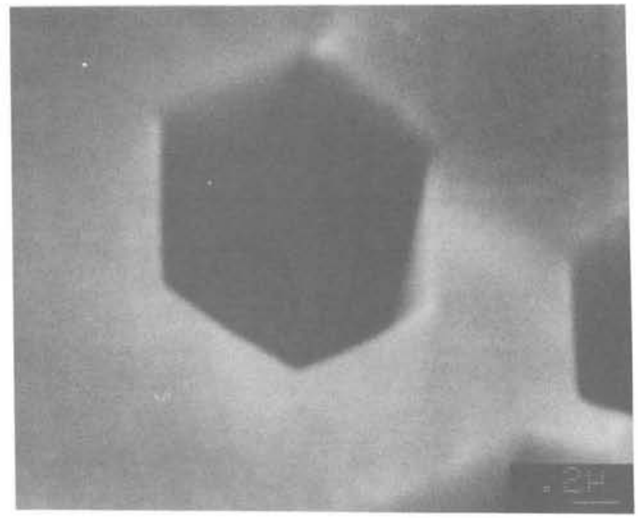

Fig. 11 Cross-section of an etched track in a magneto-optic film[9].

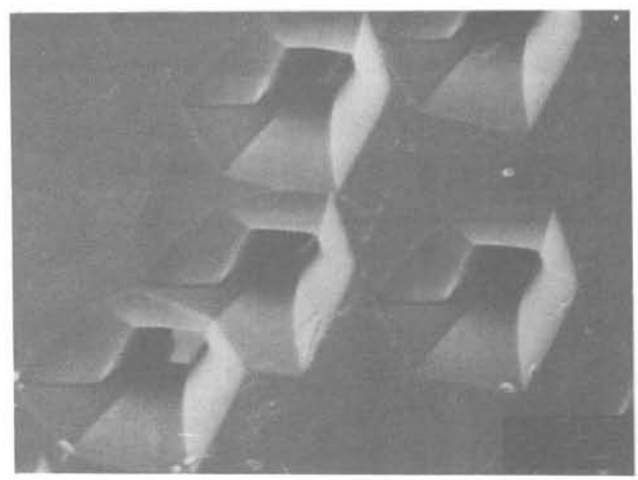

Fig. 12 Funnel-shaped cross-section of etched tracks in mica, which develop by etching in boiling NaOH[3].

Which materials can be structured by nuclear tracks ?

The proper choice of materials is determined by 2 criteria

* it must be possible to generate latent tracks in that material
* a chemical process must exist that attacks the latent tracks and the bulk of that material with different speed.

Only insulating materials meet the first criterion. It has been suggested in ref. 2 that also semiconductors with a specific resistance of more than 2000Ωcm should store latent tracks. But until now we have not been able to etch tracks in p or n-type silicon of more than 5000Ωcm even when we irradiated the silicon samples by Uranium-ions (It is, however, possible to etch tracks in the SiO_2 layer which is used as an insulator in semiconductor technology.)

The effort needed to produce a latent track can differ considerably in different materials as indicated in fig. 13. A track can be etched if the amount of damage is above the dashed line belonging to a certain material. What should be remembered from fig. 13 is, that

* ever more materials can be structured by track etching when heavier ions are used. Unfortunately (fortunately for nuclear waste materials) there exist also very hard materials that don't store nuclear tracks. One known example is sapphire.
* for a given material and projectile-ion, the track is etchable only within certain energy-limits of the ion. (The nuclear charge number Z of relativistic ions, which produced fossile tracks in meteorites, can be identified on that basis.)

Generally it is easier to generate latent tracks in softer materials and the etching speed along latent tracks in crystals is usually more strongly enhanced than in amorphous materials.

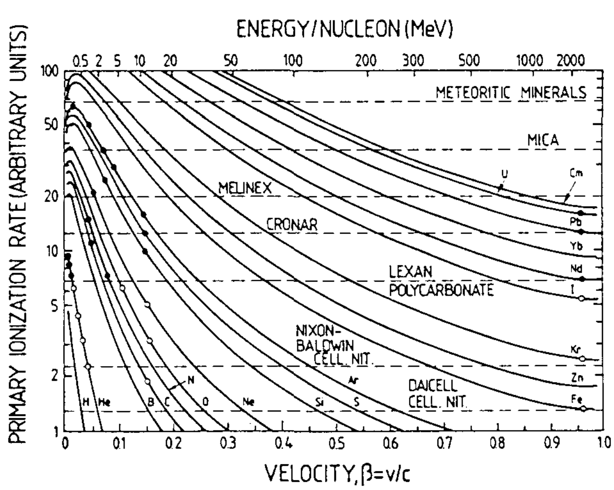

Fig. 13 Etch-thresholds for various materials in comparison to the "damaging power" of some ions [2].

There are also important constraints on the choice of materials from the side of chemistry. The molecules of an etchant must be small enough to slip easily into a latent track. It may therefore happen that etch-recipes from standard semiconductor technology don't reveal nuclear tracks [4]. Moreover chemistry must work at "normal" temperatures. Etching that is effective only at very high temperatures may anneal latent tracks before they can be revealed by the etch process (example diamond).

Chemistry also requires that materials for track etching are homogeneous. In polycrystalline materials etching is also enhanced along the grain boundaries. Therefore polycrystalline materials may simply be converted into mud by etching.

For all these reasons the chemical treatment of latent tracks is still some sort of an black art and only a few basic recipes really work. But in spite of all these restraints on the choice of materials it should be kept in mind that much more materials can be structured by heavy ions than by any other type of radiation.

What can etched nuclear tracks do for you ?

1. Single hole membrane

Even the simplest microstructure one can imagine - a membrane with just one single hole of defined diameter and length - can have useful applications. For example to form the poor man's ion-microbeam to

* look for single event upsets in integrated circuits fig. 14
* investigate the radiation sensitivity of single biological cells[5]

One micropore of several 10 nm diameter can be used to build an optical near-field-microscope which can surpass the diffraction limited resolution of the classical light microscope [6]

A single pore of about 5μm diameter and 50μm length can be used to simulate the capillaries in the human circulatory system and test the deformability of red blood cells when they enter and pass such a pore [7] (fig. 15). Relaxed red blood cells are much larger than the diameter of the finest blood vessels. They must therefore be easily deformable in order to sustain a sufficient flow of blood.

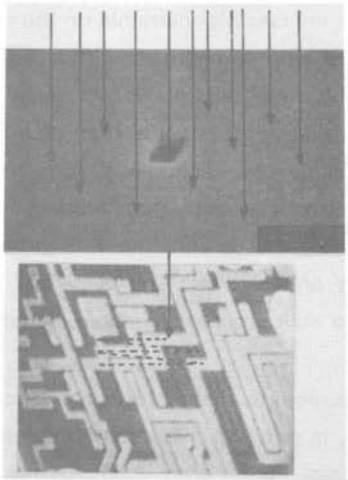

Fig. 14 Simple concept to measure single event upsets: The circuit to be tested is moved along a zigzag pattern under the microbeam formed by a single-hole-membrane.

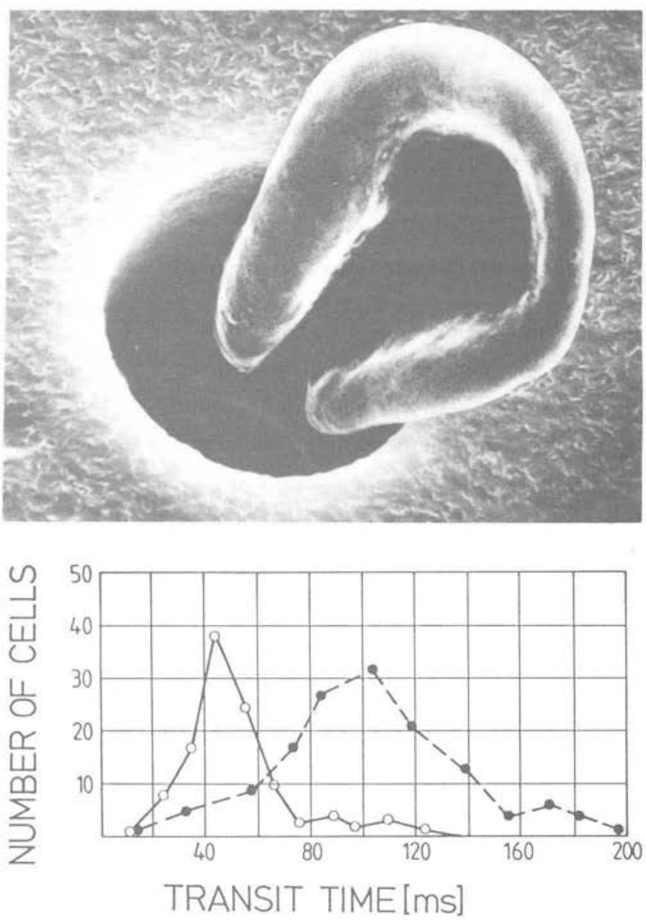

Fig. 15 Red blood cell entering a model capillary (top) and transit time (bottom) through model capillary for normal (solid line) and diseased blood (dashed curve).

And last not least there are attempts to build a quantum-interference-device working with superfluid helium using two micropores near to each other. [8)]

The production of single- or oligo-pores is very simple in principle and represents one of the most economical uses of an ion beam. Fig. 16 describes how the irradiation takes place. The ion beam coming from the accelerator is diluted as much as to deliver no more than 100 ions per second through a 0.1 mm diameter aperture. When the surface-barrier-detector behind the plastic foil detects one hit, the beam is switched off, the foil is advanced some centimeters and the next ion is allowed to hit the foil.

2. More complicated microstructures

From a commerical point of view filters are still the most interesting application of etched tracks. They are of unmatched quality, and they can be produced relatively easy. And still more important: They promise high profits as everybody can convince himself looking at the retail-prices in a filter catalogue.

A real filter does not look like the one shown in fig. 1. Parallel filter pores, which can be easily produced by an accelerated ion beam, lead to problems with overlapping tracks, which allow larger particles to pass the filter. If the irradiation takes place at random angles, track channels do not overlap over the whole thickness of the film. Therefore we have adopted a strategy analogous to that used in Dubna and randomized the irradiation angle in one direction by moving the filter foil over a pulley (Fig. 17). In order to use the beam most effectively and to average over the macro-pulse-structure of the Unilac-beam several layers of film are irradiated at once. Fig. 17b shows a light microscopic image of the resulting filter foil.

Sometimes drilling microscopic holes can have other than mechanical consequences: It can influence magnetic properties of a material, for example in the magneto-optic film [9)] shown in fig. 18 which has been irradiated and etched in the round central region. As a result much smaller magnetic domains (the black and white patches are oppositely magnetized domains) can exist in that region with the consequence that more information can be stored in a smaller area.

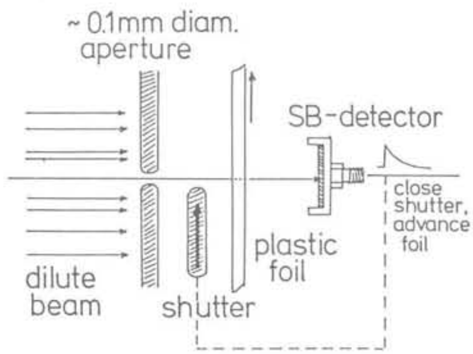

Fig. 16 Schematic drawing of an irradiation setup for the production of single hole membranes.

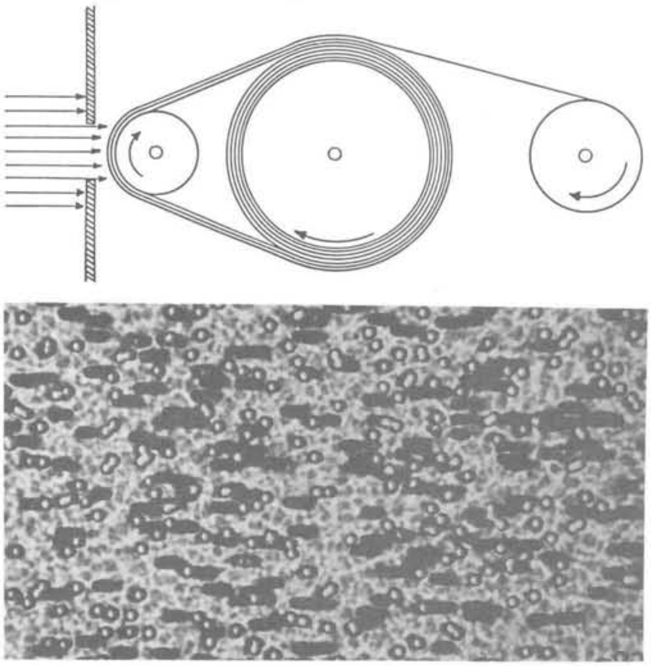

Fig. 17 Apparatus to irradiate filter foils under random angles and filter irradiated with the above apparatus. Etched tracks traversing the polycarbonate foil under different angles appear as black streaks of different length in this light-optical micrograph.

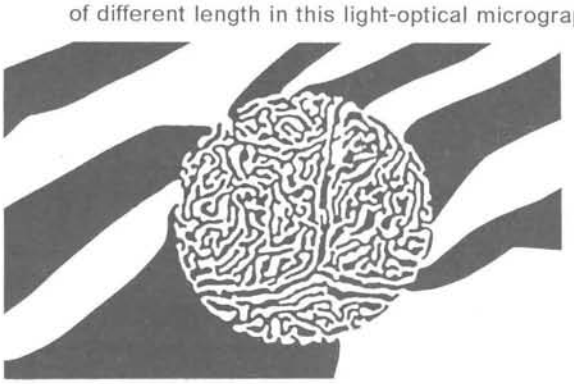

Fig. 18 Effect of etched tracks on the storage density of a magneto-optic film[9)]The etched tracks are in the round central region.

If we look at the magnetic domains at higher magnification (fig. 19) we see that the domain walls run preferentially through etched tracks (the dark spots). The domain walls are immobilized by etched tracks because it costs energy to cross them: The part of the domain wall crossing the track is first annihilated, and its energy content dissipated as heat, and then it must be recreated by an energy input from an external driving field.

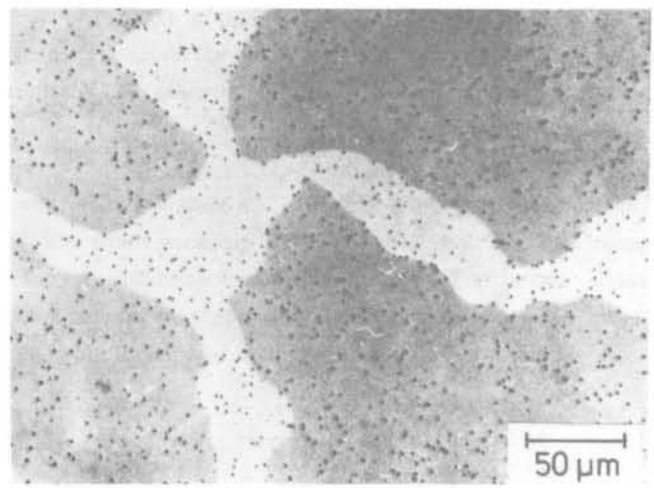

Fig. 19 Magneto-optic film [9)] at higher magnification. The domain walls run preferentially through the etched tracks (black dots).

If the magneto-optic film is not irradiated perpendicularly but, say, under 45° you can also introduce some anisotropy like the one shown in fig. 20. And in both cases the etched tracks don't have to be as large as the ones in fig. 19. If the track density is higher, extremely small tracks and even latent tracks can have the same effect.

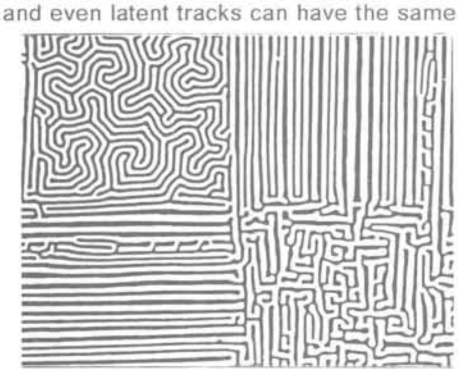

Fig. 20 Production of a magnetic anisotropy in a magneto-optic film [9)] by irradiating the film under 45° vertically (upper right quadrant) or 45° horizontally (lower left quadrant). In the lower right quadrant the film has been irradiated in both directions.

You can also create surprising optical effects by track etching. Imagine you irradiate a piece of glass with about 10^{11}ions/cm² and etch it gently (fig. 21). Then you get a submicroscopic carpet of etch cones so small that they don't scatter light. That means, the micro-rough surface still behaves like a perfectly flat one whith a smooth transition of the refractive index. The result is an excellent wide band antireflecting surface.

Fig. 22 shows a theoretical calculation for a realistic refractive index profile and the resulting reflectivity which could also be confirmed experimentally (fig. 23) for the sample shown in fig. 24.

Unfortunately the transmission of the sample did not improve quite so dramatically (fig. 25) because there is still some scattering. But as transmission losses due to scattering decrease with increasing wavelength, they should be negligible in infrared-optics treated by track etching.

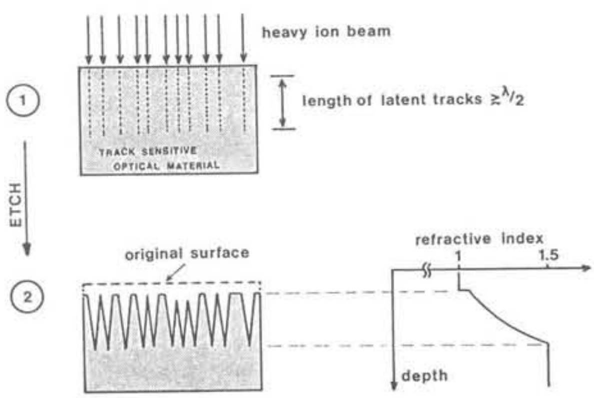

Fig. 21 Microscopic model of antireflection treatment by etched tracks.

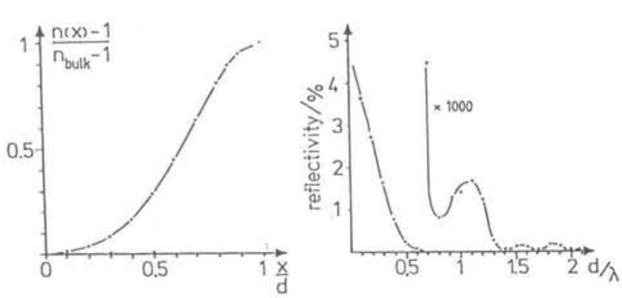

Fig. 22 Calculated shape of refractive index profile (left) and reflectivity corresponding to that profile (right).

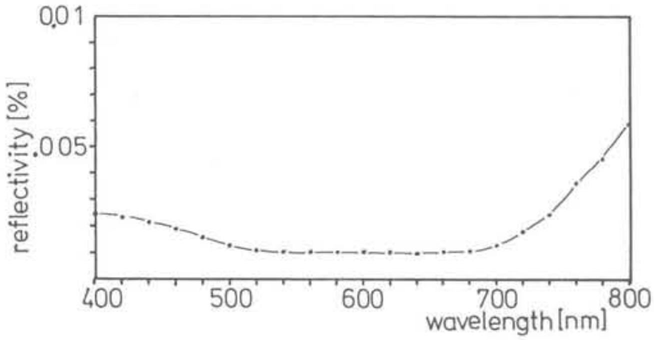

Fig. 23 Measured reflectivity of a treated surface.

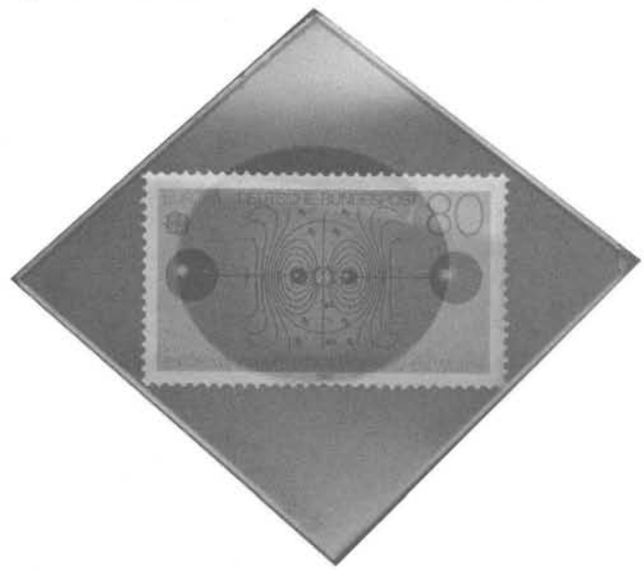

Fig. 24 Photograph of a phosphate glass with antireflecting surfaces in the central round area.

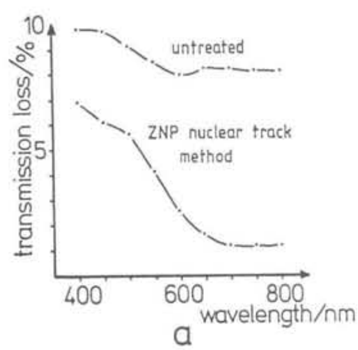

Fig. 25 Measured transmission through the phosphate glass sample shown in fig. 24

3. Still more complicated microstructures

Up to now we have only considered processes using a normal wide ion beam "raining" down onto the target. What happens if we want to produce more complicated microstructures by using irradiation masks which modulate the energy of the ion beam spatially as shown schematically in fig. 26 ?

Then the mass distribution of the mask is stored in the track-sensitive material in the form of latent tracks of different length. Etching enlarges these tracks until the individual tracks overlap and a relief-like replica of the mask appears. For a proof of principle experiment one can use a small insect as a mask. The result of such an experiment is shown in fig. 27. It clearly demonstrates the capability of heavy ions to produce very deep microstructures with very small lateral dimensions.

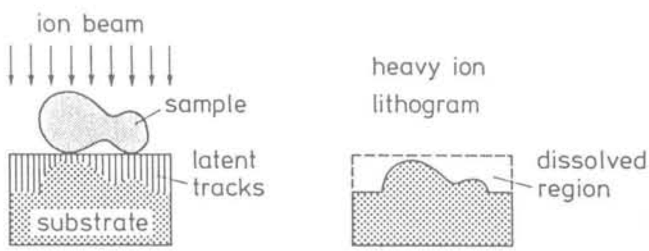

Fig. 26 Production of microstructures by using an irradiation mask.

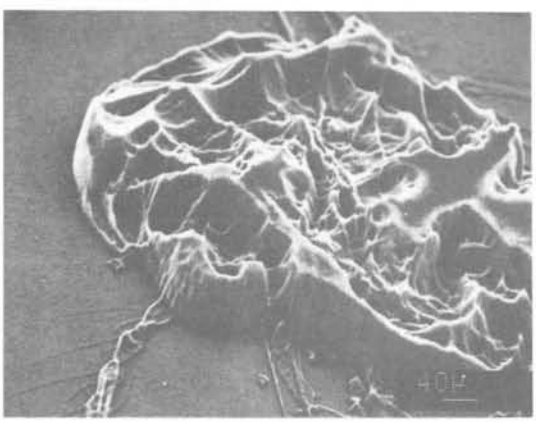

Fig. 27 Microlithography of a small insect, produced by the method described in fig. 26.

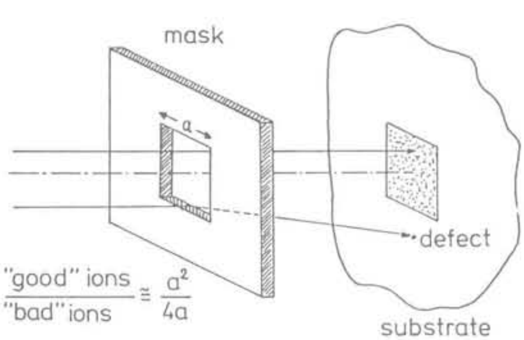

Fig. 28 Scattering of ions at the irradiation mask.

But if you want to produce technically interesting structures, you need a mask nearly as thick as the desired depth of the structure. Presently, only x-ray-lithography is capable to produce masks of that thickness. And still worse, x-ray-lithography in turn needs light or electrons for mask production.

Even if a mask could be produced easily, there remains still the problem of ions scattered by the mask, as every misguided ion can produce a defect. And the relative influence of scattered ions becomes ever more severe when you want to produce ever smaller micro-structures. (see fig. 28) So ion-lithography does not look very reasonable at first sight.

But one should not give up so quickly. There are games you can only play with heavy ions. It is for example possible to produce, positive as well as negative copies of a mask-structure by a suitable choice of the ion-energy. (fig. 29) And one may even speculate about the possibility to produce buried microstructures in an analogous way if the etchant can be somehow delivered to the damaged zone below the surface.

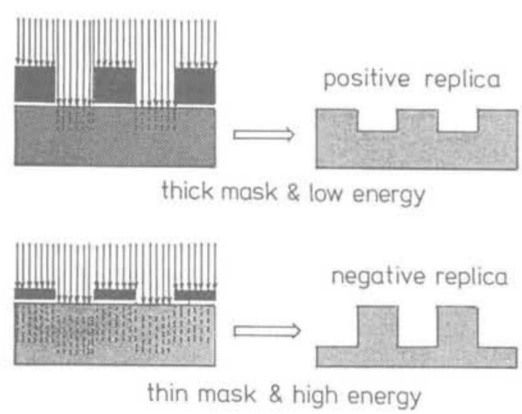

Fig. 29 The effect of varying energy on the shape of a heavy-ion-microlithography.

There exist also strategies to alleviate the problem of ions scattered by the mask. One is, to marry light and ions to get microstructures with the characteristic lateral dimensions of light-lithography and the great depth characteristic for ion-lithography. (fig. 30).

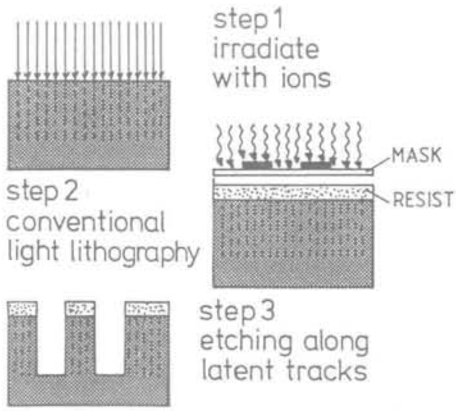

Fig. 30 The combination of heavy ion irradiation and light-lithography to produce defectfree microstructures of high aspect ratio.

Another strategy is, to use a demagnifying projection system (fig. 31). Then, for a given size of the intended microstructure, you can use a mask with a larger window. Such a mask is easier to produce, it scatters relatively fewer ions and in addition the scattered ions can be prevented from reaching the target by suitable slits. Fig. 32 shows a demagnified image of a simple mask etched into a CR-39 target as example, and fig. 33 shows the heavy-ion-microprobe at GSI [10], where this work has been done.

Having a microprobe at hand, it is natural to consider direct-beam-writing by heavy ions and - perhaps less obviously - create patterns by single precisely aimed ions. These patterns can only be produced by heavy ions and there is therefore no competition with other faster direct-beam-writing systems.

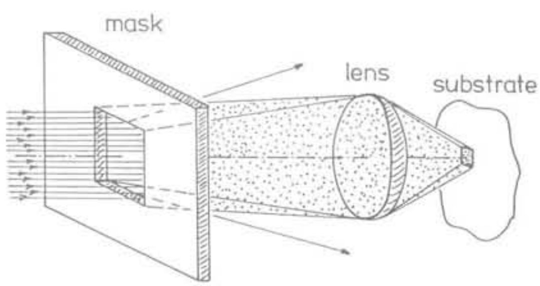

Fig. 31 Principle of a demagnifying ion projection system.

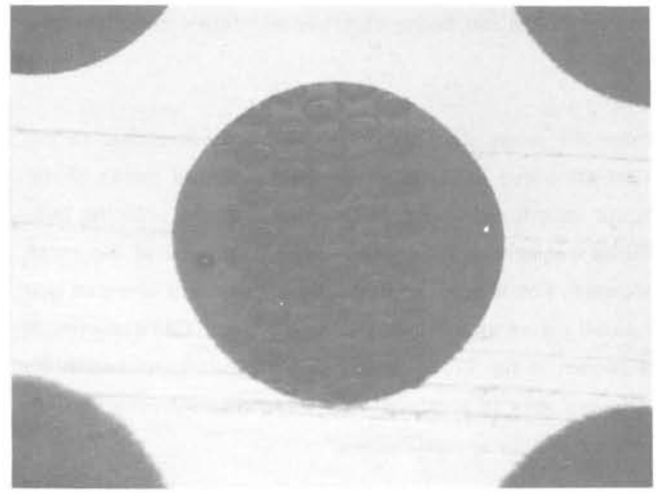

Fig. 32 Light-optical micrograph of an irradiation mask with round windows of 150μm diameter. Insert: Demagnified replica of that mask in a CR-39 plastic target. (The round windows are elliptically distorted because the magnetic triplett used as projection lens has different demagnification factors along horizontal and vertical directions.)

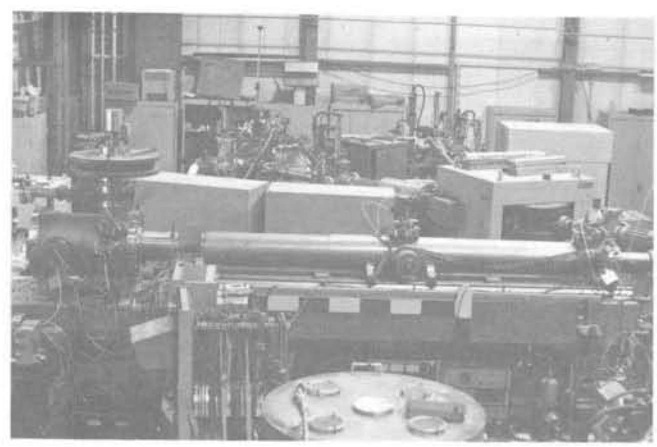

Fig. 33 The heavy ion microprobe at GSI [11].

One particular microstructure became technically interesting with the advent of the scanning accoustical microscope: A microscopic spherical concave mirror, which is used to focus ultrasonic waves onto the specimen. It usually has a diameter of about 50μm and is still ground and polished mechanically.

Such a micro-optical element can be produced much cheaper and more accurately by track etching. The deviation from an ideal spherical shape is less than 30 nm in the sample shown in fig. 34 and no surface roughness could be detected under the scanning electron microscope even at the highest magnification. If necessary, these microoptical elements can be made still much smaller by track etching and even aspheric corrections can be introduced into their outer rim.

Arrays of these microoptical elements could one day be used to replace the mechanical scanning movement in present-day scanning accoustical microscopes by some sort of electrical scanning. A first succesful result on the way to that goal is shown in fig. 35 - a part of a 20 x 20 array of etched tracks produced with the GSI heavy-ion-microprobe[11].

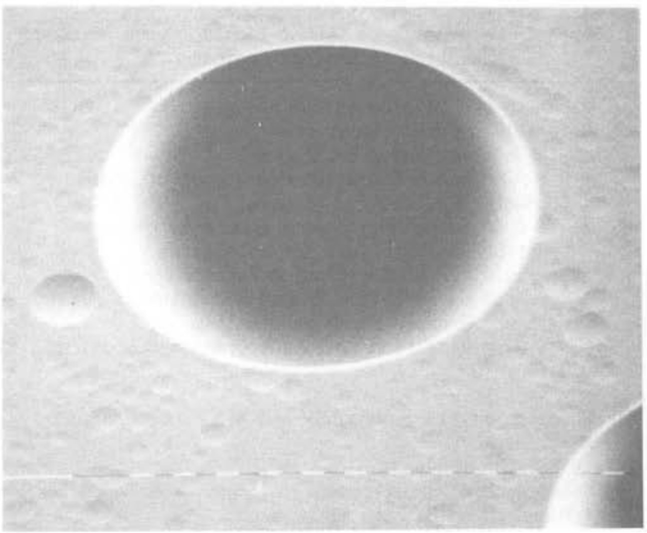

Fig. 34 Microscopic spherical depressions produced by track etching in fused silica.

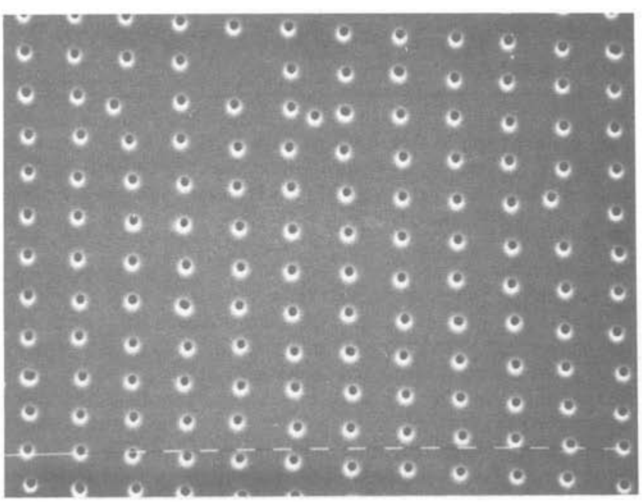

Fig. 35 Regular array of single track structures produced by irradiation with the microprobe shown in fig. 33 and subsequent etching.

References:

1. Albrecht, D., P. Armbruster, M. Roth, R. Spohr, "Small Angle Neutron Scattering Observations from Oriented Latent Nuclear Tracks", Radiation Effects, Vol 65, 145-148 (1982)
2. Fleischer, R.L., P.B. Price, and R.M. Walker, Nuclear Tracks in Solids: Principles and Applications, (University of California Press, Berkeley, 1975)
3. Khan, H.A., N.A. Khan, and R. Spohr, "Scanning Electron Microscope Analysis of Etch Pits Obtained in a Muscovite Mica Track Detector by Etching in Hydro-Fluoric Acid and Aqueous Solutions of NaOH and KOH", Nucl. Instrum. Methods, Vol. 189, 577 (1981)
4. Fischer, B.E., "Miscellaneous Applications of Nuclear Track Techniques", GSI Scientific Report, p. 269 (1985)
5. Weisbrod, U., "Exposure of Individual Spores with Single Heavy Ions", GSI Scientific Report, p. 216 (1986)
6. Lewis, A., and M.S. Isaacson, "Light Transmission Through Submicron Apertures", Engineering Cornell Quarterly, Vol. 18, No. 1/2, p. 36-40 (1983)
7. Roggenkamp, H.G., H. Kiesewetter, R. Spohr, U. Dauer, and L.G. Busch, "Production of Single Pore Membranes for the Measurement of Red Blood Cell Deformability", Biomedizinische Technik, Vol. 26, 167-169 (1981)
8. Avenel, O., and E. Varoquaux, "Josephson-Effect and Phase Slippage in Superfluids", Japanese Journal of Applied Physics Vol. 26, 1798-1803 (1987), Supplement 26-3
9. Heitmann, H., C. Fritsche, P. Hansen, J.P. Krumme, R. Spohr, K. Witter, "Influence of Irradiation with High Energy Ions on Storage Properties of Magneto-optic $(Gd,Bi)_3(Fe,Ga)_5O_{12}$ Epitaxial Films", J. Magn.Magn. Materials, Vol. 7, 40-43 (1978)
10. Fischer, B.E., "The Scanning Heavy Ion Microscope at GSI", Nucl. Instr. Meth. Vol. B10/11, 693-696 (1985)
11. Fischer, B.E., "The Heavy Ion Microprobe at GSI - Used for Single Ion Micromechanics", Nucl. Instr. Meth. Vol. B30, 284-288 (1988)