Ion tracks – a new route to nanotechnology

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Ion tracks are created when high-energetic heavy ions with energy of about 1 MeV/nucleon (e.g. 140 MeV Xe ions) pass through matter. The extremely high local energy deposition along the path leads to a material transformation within a narrow cylinder of about 10 nm width. Unlike in the more conventional lithographic techniques based on ion or electron beam irradiation, a single heavy ion suffices to transform the material. Thus, problems like straggling or diffusively broadened features do not occur. Ion beams with the required properties are available e.g. at the national accelerator centres HMI Berlin, GSI Darmstadt and GANIL Caen. Some recent developments of this field are described in Ref. 1 and 2.

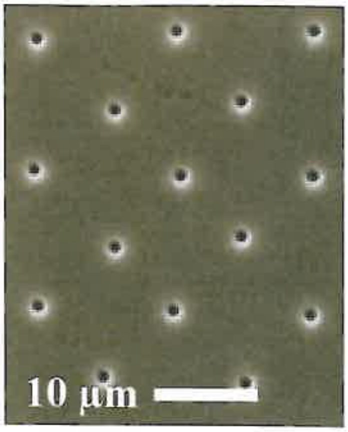
Ion tracks have a long tradition in science and technology. They play a role, e.g., in geology where the dating of geological formations is based in some cases on fission fragment tracks. Industrially, ion tracks are used for the production of porous media, e.g. for particle filters. Here, polymer foils are irradiated with heavy ions and subsequently etched to remove the material from the track region. A unique variant of this ion beam method is the single-hole filter which reaches an extremely high selectivity for particle filtering [3]. With modern microbeam facilities, the tracks can be placed in an ordered array [4] (see Fig.1). This is important for electronic applications since it facilitates the addressing, which is problematic for statistically distributed tracks.

Recently it became clear that heavy ion beams can also be used in nanotechnology [5,6] since ion tracks have just the right size for nanostructuring: the track diameter is of the order of 10 nm and the track length can be varied from a few nanometers up to several micrometers by choosing the appropriate sample thickness. In this way, quasi zero-dimensional nanodots or quasi one-dimensional nanowires can be created.

There are essentially two ways to use ion tracks for nanostructuring. The first is based on track etching as used in the filter production, i.e. one irradiates a polymer foil and etches the tracks to create thin pores in the foil. These pores are subsequently filled with an appropriate material to make nanostructures. In this process, the polymer foil serves as a template and can be removed (dissolved) if required.

The second method uses the ion tracks directly without additional etching and refilling steps. This method is simpler than the template technique since no filling of the pores is required but it is of course strongly limited in the choice of materials and structures. The often occurring material transformation in the track from crystalline to amorphous is mostly not very useful for applications. Recently however, a dramatic increase of the electrical conductivity in ion irradiated diamond-like carbon (DLC) was found [6], the material changing from insulating (diamond-like) to conducting (graphite-like) carbon in the track. In this way, thin conducting wires in an insulating matrix are created.

Another material with a potentially useful ion irradiation effect is zinc-ferrite ($ZnFe_2O_4$) which is paramagnetic in its original state but converted to ferrimagnetic by ion irradiation [7]. A similar conversion can be induced in YCo_2 [8]. The number of such examples is certainly limited but two good ones, one for electronic and one for magnetic (spintronic) devices is in principle sufficient to further pursue this field.



▲ **Fig. 1:** Regularly spaced (10 µm apart) single ion tracks in a polymer matrix [4]. The picture (from GSI Darmstadt) shows the pores which are produced by etching the polymer foil after irradiation. The close and regular spacing is achieved by using a focused ion beam (microbeam) and single ion detection. After the detection of an ion impact, the beam is switched to the next position.

In the following, some examples of already realized nanostructures will be presented and some proposed devices implementing ion track-induced structures will be discussed showing the great potential of this technique in nanotechnology.

Template-grown nanostructures

The method of etching thin long pores along ion tracks in polymer foils is well developed [2] and, as mentioned above, is used in the production of filters for various applications. To give an idea of possible pore sizes and pore densities, table 1 of Ref. 2 is reproduced here. Other combinations of pore diameter, foil thickness and pore density are of course also possible.

These hollow channels in the solid material can be used as templates to grow nanostructures in them. The material deposition into the channels is usually performed by chemical or electrochemical methods from solutions. The track etched polymer foils have in some cases advantages over other template structures (e.g. porous alumina or lithographically prepared membranes) since they are more variable in the choice of parameters (radius, distance and length of the pores and the material to be used) and, compared to lithography, they reach a much larger aspect ratio (length to diameter) of the pores. Aspect ratios of 100 to 1000 are possible.

A large variety of nanostructures has been grown in polymer pores [5] in the form of compact cylinders of single or multi-layered material but it is also possible to create tubules [2], i.e. hollow cylinders, if the material deposition starts from the walls of the pores. In the following, two examples of compact structures will be discussed in more detail.

Magnetic multilayered nanowires

Magnetic multilayered materials are of great interest because of the so-called giant magnetoresistance (GMR) effect which occurs in some materials if magnetic and non-magnetic layers are stacked. The current through these layers depends on the relative orientation of the magnetisation. If this orientation is anti-parallel in zero external field – this can be achieved by choosing the appropriate spacing – it can be switched to parallel orientation by applying a magnetic field, thereby lowering the resistance by some per cent. This effect can be used in reading devices for magnetic recording media.

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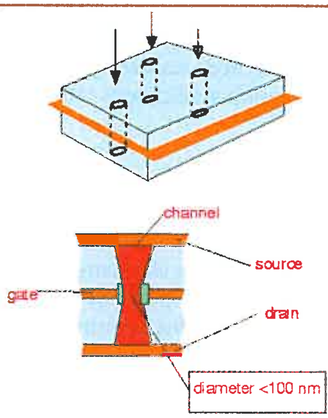
Pore diameter (nm)	Pore density (cm^{-2})	Thickness (µm)
20	4.0×10^{9}	10
50	2.0×10^{9}	10
80	2.0×10^{9}	10
100	6.0×10^{8}	10
200	5.0×10^{8}	20
220	5.0×10^{8}	10
600	4.0×10^{7}	19
1000	2.2×10^{7}	19

▲ **Table 1:** Typical parameters of ion track-etched polymer templates [2]. The pore diameter is determined by the etching time, the pore density corresponds to the fluence of the ions (number of ions per cm^2) and the thickness of the foil determines the pore length.

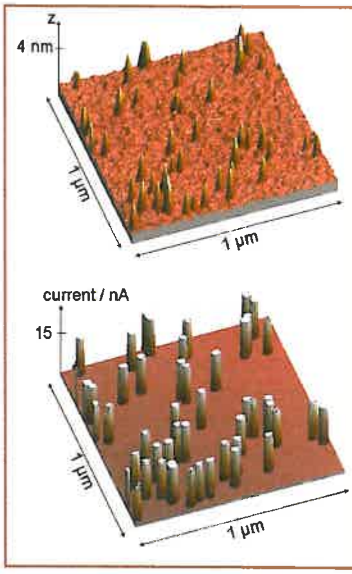
An ideal arrangement of these devices is a thin nanometric wire with the current perpendicular to the plane. Such a structure was grown in an ion track template and the magnetoresistance was measured [5]. The arrangement of the layers, i.e. their spacing and thickness, can be adjusted to obtain the optimum effect (high GMR and reasonable switching field and switching time).

Nanotransistor
Because of its central role in electronic devices, the realisation of a transistor is usually the primary goal of a new research field in this area. The progressing miniaturisation in electronics requires structure dimensions in the nanometer range. Here the perpendicular-to-plane orientation is advantageous for close packing. In some cases a flexible transistor which does not break upon bending is desirable. A device with these specifications, a vertical nanotransistor in a flexible polymer matrix, was recently realised [9]. The principal concept is shown in Fig.2.

A two-terminal device, i.e. a semiconductor structure with source and drain contacts, is usually easy to fabricate, the problem is the third contact, the gate. Here the ion track method allows an elegant solution: A polymer foil is metallized on one side and glued to a second foil to form a polymer stack with a central metallic layer. After ion irradiation, the material in the track, first in the polymer sheets and afterwards the exposed part of the metal are etched away. Then the metal adjacent to the channel has to be insulated either by oxidation or by under-etching, before finally the semiconductor material is introduced and contacts are deposited. The principal operation of such a device has been demonstrated [9].



► **Fig. 2:** Schematics of the production process of a nanotransistor in a track-etched membrane (picture by courtesy of R. Könenkamp [9]): Two polymer foils, one with a metal bottom layer, are glued together and irradiated with heavy ions (upper part). After etching, the ion track pores are filled with a semiconductor material and contacted with electrodes. The important part is the gate electrode which is formed by the middle metal sheet. The metal must be oxidized or otherwise insulated after pore opening in order to avoid the direct contact to the semiconductor. Such a device, a vertical nanotransistor in a flexible polymer matrix, was recently realized [9].



◄ **Fig. 3:** Scanning probe microscopy images of topography and current of a diamond-like carbon (DLC) film [6]. The 50 nm thick DLC film was irradiated with 1-GeV Uranium ions. Each ion impact is characterised by a surface hillock (top) and an increased electrical conductivity (bottom). The measurements were performed with an atomic force microscope (AFM) in contact mode. The current is measured between the substrate and conducting AFM tip.

Direct use of ion tracks

Conducting ion tracks in diamond-like carbon
Diamond-like carbon (DLC) is a well developed material and, e.g., used in industry for protective coating. The structure of DLC is amorphous and the bonding is primarily sp^3 (tetrahedral)-like as in crystalline diamond and therefore the material is insulating. Hydrogen-free DLC, as necessary for the present application, is produced in thin sheets on substrates (e.g. Si) by plasma deposition. The energy of the deposited particles has to be about 100 eV in order to form the compact tetrahedral (sp^3) structure.

High energy heavy ions, e.g. 1 GeV uranium ions, convert the material along their path from insulating diamond-like to conducting graphite-like carbon [6]. The large change in the conductivity is easily seen with a scanning probe microscope. Fig. 4 shows the topography and current image of an irradiated film. Each ion track is characterized by a small hillock at the impact site of a single ion and by a huge increase of the current through the film.

The electrical resistivity of the tracks is on the order of 1-10 S/cm and is approximately four orders of magnitude larger than outside of the tracks, depending on the properties of the original DLC layer. Transmission electron microscopy (TEM) measurements have shown that the diameter of this converted region is approximately 8 nm [6]. Thus, by this ion irradiation, a thin straight wire in an inert matrix has been created. It can be used as a building block in nanoelectronics, as is discussed below.

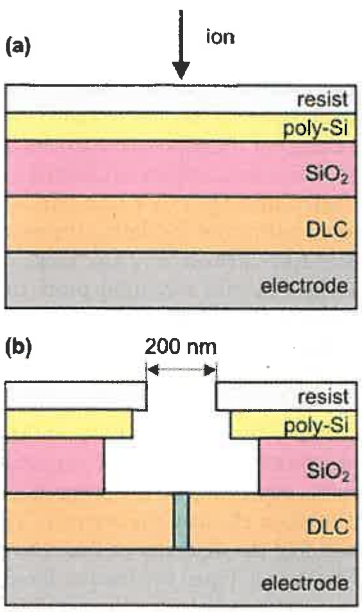
Ferrimagnetic filaments in a paramagnetic matrix
It was found [7] that $ZnFe_2O_4$ converts along the ion track from a paramagnetic to a ferrimagnetically ordered material. This effect is due to a randomization of the Fe atoms on the Zn and Fe sites. Thus the effective magnetic interaction becomes stronger and leads to magnetic ordering up to temperatures well above room temperature (about 500 K). The nm-sized converted region can be used in spintronic applications.

A similar magnetic conversion of $ZnFe_2O_4$ is known for nanostructured material obtained by mechanochemical milling. That this conversion can be induced also by ion tracks was clearly demonstrated by Mössbauer measurements that exhibit the well known six line splitting after irradiation [7]. Since this effect is present also for widely separated tracks (low dose irradiation), it is demonstrated that the conversion takes place in the individual tracks. Thus magnetic filaments in a non-magnetic environment are produced by ion irradiation.

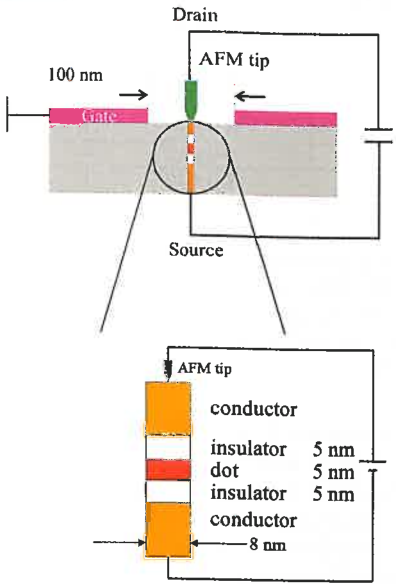
Self-aligned contacts

Contacting nanostructures is usually a considerable problem since the contacts must be small (nm sized) themselves and must be aligned with the structures for which the contacts are made. The situation is even worse for statistically distributed ion tracks since a safe distance between the structures has to be maintained in order to avoid overlapping. A partial solution, which regulates at least the immediate environment of the track, is a lithographic process initiated by the track itself. In this procedure, one applies a resist (polymer) on top of the sample. After passage of the ion, the resist is developed giving access to the track in a well aligned manner. Through this open space, the contact can be applied, e.g. by metal deposition. The continuation of the contact to the outside can be achieved with less precise but well-established methods like electron-beam lithography.

A further development of this technique would be to align complete electronic circuits to the tracks. This can be achieved by using multilayer systems and multiple etching and deposition processes as in conventional device fabrication. A proposed simple example is shown in Fig.4. Here, a multilayer stack with a resist on top is irradiated with heavy ions. After etching with different solutions, the final structure of an aligned gate electrode (heavily doped poly-Si) is obtained. A similar structure as shown in Fig. 4 has been realized by the Livermore-Candescent group for field emission applications [10].



▲ Fig. 4: Production scheme for a close-spaced gate electrode (highly doped poly-Si) aligned with the conducting ion track in DLC: A stack of layers of different materials with a resist (polymer) as the last layer is irradiated with heavy ions. After developing the resist at the ion impacts, the lower lying layers are etched in the freely accessible region to create the structure shown in the figure. Because of its compact design, it is expected that such a structure could be useful in field emission devices. A similar device, but without the conducting track in DLC, was realized in Ref. 10.



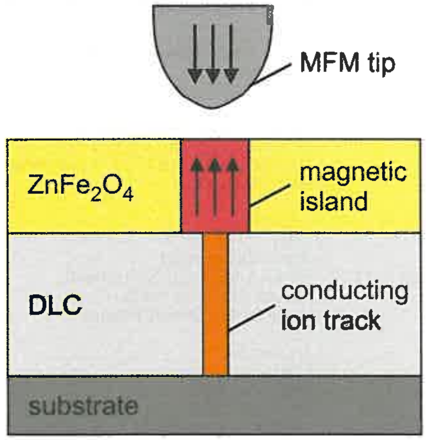
► Fig. 5: Scheme of a quantum dot and a nanotransistor structure. The upper part shows the ion track in an insulating DLC multilayer stack. The track is electrically connected via the conducting substrate and the conducting AFM tip. The gate electrode is placed on the surface close to the track structure. The lower part shows an enlarged view of the track region. The approximately 8 nm wide cylinder corresponds to the ion track embedded in the insulating DLC matrix. The interruptions of the conducting track may consist e.g. of SiO_2. They serve as tunneling junctions to the quantum dot. The length of the conductors, insulators and dot are determined by the respective film thickness and can be adjusted to meet the requirements for Coulomb-blockade. The values for the thickness are just first guesses; they have to be optimized by experiment. The contact to the nano-wire is made by an atomic force microscope (AFM) tip and can be ultimateely replaced by a self-aligned metal contact.

Outlook

Presently, there exist research collaborations on a European level to realize some of the basic structures with this new technique. The national research centres, GANIL in France, GSI Darmstadt and HMI Berlin in Germany are involved in this research. In the following, three proposed devices will be discussed, one from electronics, one from magnetism and one from field emission.

i) Quantum dot and Coulomb blockade

The basic concept for making a small dot is to interrupt the conducting track at two points by insulating intersects. This can be achieved by inserting insulating layers which do not convert to conductors by the ion passage. In this way, one obtains pieces of nano-wires connected by tunnel junctions. The multilayer samples, consisting of DLC layers and insulating layers (e. g. SiO_2), are prepared by conventional deposition techniques and irradiated after preparation.



▲ **Fig. 6:** Scheme of a nano spin filter device consisting of a magnetic island in Zn ferrite ($ZnFe_2O_4$) on a diamond-like carbon (DLC) film. The ion passage transforms $ZnFe_2O_4$ from para- to ferrimagnetic, thus forming a magnetic island in a paramagnetic environment. With a magnetic force microscope (MFM) the magnetization can be measured. This arrangement constitutes a spin filter and can be used in a spin valve application. For a demonstration of spin valve operation, the current between the MFM tip and conducting ion track has to be measured as a function of the polarization of the magnetic island. Ultimately, the MFM tip can be replaced by a self-aligned magnetic metal contact.

Figure 5 shows a proposed design of this structure. The ion track (upper part of Fig.5) is embedded in an insulating matrix and connected with two leads (conducting substrate and conducting AFM tip) to the outside. For a solid-state device, the AFM tip can be ultimately replaced by a self-aligned metal contact as indicated in Fig. 4.

An enlargement of the track region is shown in the lower part of the figure. The approximately 8 nm wide cylinder corresponds to the ion track region. The insulating layers serve as tunneling junctions to the quantum dot (small island). The length of the conductors, insulators and dot are determined by the respective film thickness and can be adjusted to meet the requirements of the specific application.

Since the dimensions of the dot are on the order of 10 nm or less, one is in a regime where quantum effects become dominant. In particular, *single electron effects*, as evidenced by Coulomb blockade, should become observable even at room temperature. The blockade arises from the fact that each additional electron on the dot requires a certain amount of charging energy to overcome the Coulomb repulsion. This effect should be seen as a regular step function in the current-voltage curve.

The structure in the lower part of Fig.5 represents a two-terminal device (diode), the two terminals serving as source and drain, respectively. The addition of a third terminal, the gate, in order to complete the transistor may be achieved by the self-alignment process described above. A possible arrangement is shown in the upper part of Fig.5.

ii) Nano- spin valve

The proposed nano-spin valve structure (Fig.6) consists of a nanometric island of a ferromagnetic material (ion track converted $ZnFe_2O_4$) on top of a conducting ion track. The second magnetic material, required for a spin valve, is the ferromagnetic tip of the scanning probe microscope. As before, the MFM tip can ultimately be replaced by self-aligned contacts.

The two ferromagnetic structures are connected by a tunnel junction consisting of an oxide and/or a vacuum gap. The current through this structure is measured as a function of the magnetization direction of the island, the magnetization of the tip remaining constant (or vice versa). The spin valve effect is evidenced as a difference in currents through the circuit for parallel and antiparallel orientation of the two magnetic entities.

Decreasing the size of these structures to nanometric dimensions increases the sensitivity to few electron spin detection. A final goal would be to reach single spin sensitivity (important e.g. for quantum computer read out) but this is beyond the present possibilities of the method.

iii) Field emission

Cold cathode field emission devices are interesting e.g. as field emitters in flat panel displays. In this case, no individual addressing of the tracks is required since many emitters can be used to form one pixel. Thus the contacting problem is somewhat alleviated.

Enhanced field emission from the conducting ion tracks in DLC is expected due to the high aspect ratio of the emitting structure. Together with a narrow extraction geometry, which can be realized by the self-alignment as shown in Fig.4, an efficient emission structure could be realized.

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