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Invited Talk

The emergence of new ion tract applications

D. Fink[a,*], P.S. Alegaonkar[a,f], A.V. Petrov[a,g], A.S. Berdinsky[b], V. Rao[c], M. Müller[a], K.K. Dwivedi[d], L.T. Chadderton[e]

[a] *Hahn-Meitner-Institut, Glienicker Strasse 100, Berlin D-14109, Germany*
[b] *Novosibirsk State Technical University, Karl-Marx Avenue 20, Novosibirsk 630092, Russia*
[c] *Mangalore University, Mangalagangotri 574199, Karnataka, India*
[d] *Arunachal University, Rono Hills, Itanagar, Arunachal Pradesh 791111, India*
[e] *Institute of Advanced Studies, ANU Canberra, GPO Box 4, ACT, Australia*
[f] *Department of Physics, University of Pune, Pune 411007, India*
[g] *Institute of Solid State Physics, NASB, P. Brovka Street 17, 220072 Minsk, Belarus*

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Abstract

The recent years have brought a renaissance of interest in ion tracks, for the sake of novel applications. This paper summarizes some of the newly emerging possibilities, and the strategies that have been initiated. Only a few applications that are based on *latent* tracks have emerged since then, such as the exploitation of phase transitions, chemical changes, the enhanced free volume along latent tracks, or their capability to trap diffusing penetrants. For contrast, *etched* tracks in both polymer foils and SiO_2 layers appear to have a much greater application potential. Compact rods and tubules as well as dispersed nanosized matter can be embedded within the etched tracks to form the base of various applications. Some of them are summarized, and a few examples are described in detail.

Keywords: Swift heavy ions; Latent tracks; Etched tracks; Galvanic deposition; Chemical deposition; Microtransformers

1. Introduction

With conventional microelectronics approaching to ever narrower sizes at steadily increasing production costs, many small- and medium-sized companies have realized that they will not survive the ever harsher competition and, therefore, look out for alternatives. Just in time, polymeric electronics is coming up with dramatic pace, offering new previously unforeseen applications such as flexible thin-printed transistor electronics, large-size displays, and others, which will soon influence daily life. It appears that ion tracks gain a renaissance of interest in this connection as well. These nanosized structures appear to be capable to cover the bridge between the 'classical' silicon-based, and the new polymer-based electronics. Furthermore, as ion tracks can also be formed in photoresist and SiO_2, which both are the vital components of many silicon-based structures, new silicon/track hybrid structures may be designed. It appears that ion tracks in polymer foils will find a multitude of new interesting applications not only in electronics but also in other fields such as medicine or optics. We want to touch briefly some of them in this communication.

2. Applications of latent tracks

One has to distinguish between the application of latent, i.e. as-implanted ion tracks, and etched tracks. Latent tracks emerge from the primary deposition of high energy (∼MeV to ∼GeV) inside a tiny target volume ('ion track core', $\sim 10^{-15}$–10^{-14} cm^3), and within an extremely short time ($\sim 10^{-17}$–10^{-15} s), by swift heavy ions. These extraordinary transient conditions lead to dramatic modifications of

* Corresponding author. Tel.: +49-30-8062-3029; fax: +49-30-8062-2293.
E-mail address: fink@hmi.de (D. Fink).

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the materials via chemical and structural changes, with accompanying heat and pressure pulses. In spite of repair of much of the primary damage (e.g. the transient breaking of all bonds) during the annealing phase after the ion impact ('thermal spike', $\sim 10^{-12}$–10^{-11} s), quite a number of irreversible changes remain. The cylindrical zones with altered properties where these changes prevail are characterized by a high density of radicals, carbonaceous clusters, new phases (e.g. SiC in case of irradiated polysilanes), amorphization, and an altered free volume. These changes influence many macroscopic properties of the irradiated target material such as its permeability, its refraction index, its conductivity, and others.

Four major strategies for latent track applications show up: (1) exploitation of the modified transport properties along ion tracks, (2) letting metallic atoms or clusters precipitate along the tracks, (3) exploitation of the material's chemical changes, and (4) making use of ion-induced phase transitions (Fink et al., 2002). Little has been done hitherto in these fields. For example, swift heavy ion-irradiated polymer foils are in use as seals to protect sensitive volumes against penetration of ambient dust and moisture while maintaining pressure equilibrium and gas exchange with the ambient. Other concepts such as the doping of latent tracks for electronic purpose (Fink and Klett, 1995), metal clustering along tracks to form conducting wires, the production of SiC needles (Fink et al., 2002; Herden, 2001) for conducting cantilevers in AFM microscopy via radiochemical transformation of polysilanes, and the applications of ion-induced conducting nanowires in diamond (Krauser et al., 2002) or fullerite (Fink et al., 2002) for field emission displays are still in the first experimental stage.

3. Manipulations with etched tracks

Dissolution of the latent track material by suitable agents ('etching') leads to etched track formation. By careful selection of projectile, target, etchant, and etching conditions, etched tracks can be tailored towards any required shape, such as cylindrical, conical, or hyperbolic, transmittent (in thin foils) or non-transmittent. Etched tracks can be filled, in principle, with any material, and the embedded matter can be arranged as either massive wires (also called: 'fibers, fibrilles') or tubules, or it just can be dispersed discontinuously as small nanoparticles along the track length.

The first step of embedding matter within etched tracks is the material's transport towards the required position. This is often accomplished by dissolving the material of interest in a suitable liquid (water or some organic solvent), and then letting this solution to penetrate into the tracks by capillarity. If the liquid is allowed to evaporate within the tracks, then the dissolved matter will supersaturate and precipitate therein as a tubule. Examples for materials which have been already transported in this way into tracks are: KCl, C_{60}, polymethyl methacrylate (PMMA), dyes, etc. The total amount of matter dissolved in the liquid and transported into the tracks determines the final tubule thickness.

The electrodeless (or 'chemical') deposition (ELD) technique (Lincot et al., 1999) falls into this category. Here a high degree of supersaturation of certain metals (Cu, Ag, Au, Ni, etc.) or chalcogenide compounds (e.g. CdS, PbS, Cu_xS, ZnS, CdSe, ZnSe, CdTe, $CuInSe_2$, etc.) is reached by dissolving them in suitable complexing agents such as NH_3, ethylene diamine (EN), nitrilotriacetate (NTA), thiourea (TU), and others. In the presence of nucleation centers on the etched track walls heterogeneous precipitation from these solutions sets in, thus forming tubules of these materials.

Such nucleation centers can be chemically (e.g. by Sn or Pd atoms that have been bond to polymer chains), or physically activated sites (e.g. damage centers after laser or $\sim$keV ion irradiation). Whereas chemical activation techniques and laser irradiation activate the etched tracks over their whole length ($\sim$10 to $\sim$100 μm), $\sim$50–500 keV ion irradiation activates the etched track only up to these ions' range (typically $\sim$0.1 to $\sim$1 μm). This enables axial tailoring of track structures, so that, e.g. circular contacts for sensor materials embedded in the tracks emerge which guarantees full accessibility of the sensors to the ambient.

If no nucleation centers are offered at all, chemical deposition of the aforementioned materials will take place only at intrinsic polymeric surface defects, which signifies the growth of only few dispersed (semi)conducting nanocrystals on the ion track walls. This is beneficial for easy tailoring of the track resistivity to any value by the choice of the crystallite size and intercrystallite distance, via the metal (or semiconductor) precipitation conditions. Eventually such structures show photoresistivity.[1]

In case of insoluble matter, the latter can be transported into the track in the form of colloides. As colloides possess peculiar electronic and optical properties such as a high charge storage capacity, fluorescence, etc., their combination with etch tracks should lead to new challenging applications. Some colloidal solutions are already commercially available,[2] others have to be made in the lab. For example, we produced colloidal solutions of TiO_2 and of $LiNbO_3$ to form nanotubules of these materials in etched tracks. In the latter case, we prepared the 20-nm-sized $LiNbO_3$ particles in a ball mill and, subsequently, dissolved them in amyl acetate.[3] The colloidal solution was fed into the tracks, to form $LiNbO_3$ nanotubules upon annealing.[4] We also should mention a very simple and convenient tool at this occasion: Conducting silver paste penetrates easily throughout etched tracks, thus forming conducting micro/nanowires, if

[1] Hoppe K., Fahrner W.R., Petrov A., Fink D., own results (2002), unpublished.

[2] E.g. SiO_2, offered by Baier Ltd. under the trade name 'Levasil'.

[3] Chemseddine A., Fink D., Heitjans P., Borck D., Petrov A. (1999–2002), own results, unpublished.

[4] Fink D., own results (1999–2002), unpublished.

the etched track diameter is at least ∼5 times larger than the silver particle size.

It is also possible to deposit matter within the tracks by suitable chemical reactions. For example, the insulating polymer polyacrylonitrile (PAN) or the conducting polymer polyethylene dithiophene (PEDT) readily form on the etched track walls by in situ polymerization of the precursor materials. Other examples: tracks can be filled with, e.g. photosensitive AgBr, by letting $AgNO_3$ and NaBr solutions penetrate from both sides of a microporous foil, and react with each other therein chemically, i.e. here the ion tracks act as microreactors.

All above-described processes require hydrophilic, i.e. wetting penetrants. In case of hydrophobic liquids (e.g. liquid metals), pressure injection may be used to force these liquids into the nanopores. Eventually, it is also helpful to modify the wettability of the etched track walls by suitable deposits. For example, liquid Pb/Sn solder readily penetrates easily into tracks (and hence can be used for contacting ion-track-based devices) if a thin Cu layer had been chemisorbed onto the track walls before.

A very common technique is the galvanic deposition of conducting matter within etched tracks. Usually, the microporous foil covers the cathode for that purpose so that the deposited metal or conducting polymer grows throughout the etched tracks from one side to the other, thus forming massive rods. In case that the etched track walls have been made conducting beforehand, the galvanic deposition process can also lead to capped tubule formation.

A principle disadvantage of all manipulation techniques applying liquids is that these liquids penetrate to some extent into the used polymers. Thus, e.g. Ag tubules in polyimide (PI) are always surrounded by a weak halo of Na^+ (from the etchant) and Ag^+ (from ELD) ions that contribute to some additional weak ionic bulk conductivity.

Deposition of matter within etched tracks can also take place from the gas phase, by letting a suitable permeating gas decay towards solid residues such as carbon or silicon, via pyrolytic reactions. As these reactions require high reaction temperatures, only tracks in PI, mica and SiO_2 are useful candidates. Finally, also evaporation leads to a limited deposition of, e.g. metals near the track entrance. In this way, e.g. circular contacts for matter embedded in the tracks can be formed. The disadvantage of this approach is the limited depth that can be reached in narrow tracks by evaporation (in contrast to ELD with low-energy ion-beam activation, see above).

4. Applications of etched tracks

Clearly, the above-summarized multitude of preparatory pathways of ion-track-based structures, and their combination with other techniques, leads to a whole zoo of possible nanostructural applications. For example, by just depositing a suitable contact material (e.g. a semiconductor, fullerite, metal, or indium tin oxide (ITO)) onto a microporous foil with an embedded semiconducting wire, one transforms the nanosized interface to a diode structure—eventually even to a light-emitting one (Granström et al., 1995). Due to their small dimensions, such diodes exhibit quantum effects such as resonant electron tunneling, where the current/voltage characteristics exhibits characteristic local maxima and minima at elevated voltages applied. Capacitive contacting of such a semiconducting wire leads to the formation of field effect transistor-like structures (Chen et al., 2002).

Specially surface-treated metallic nanotubules have been used to control the permselectivity of electrolytes (Martin et al., 2001), and nanotubules with embedded grafted thermoresponsive gels can act as switches for penetrating liquids (Shtanko et al., 2002). Au nanotubules are used as electrodes in miniaturized electrolytic sensors ('Clarc cells') for oxygen determination (Schulz, 2002). By capping of polymeric nanotubules, one can use them as *in vivo* long-time storage vessels for drugs (Desai, 2001). Nanotubules of TiO_2 ceramics act as efficient construction elements in novel miniaturized Li batteries (Nishizawa et al., 1997), and fullerene tubules are useful as temperature, pressure, and humidity sensors (Berdinsky et al., 2001).

Sequential galvanic deposition of different materials leads to axially structured elements, sequential chemical deposition leads to radially structured elements. For example, sequential galvanic deposition of differently semiconducting (i.e. n- and p-conducting) materials, or of metallic and semiconducting wires, e.g. Cu and Se (Chakarvati and Vetter, 1989; Biswas et al., 1999), or Ni and CdSe/CdTe (Klein et al., 1993) give rise to nanometric diodes. Sequential galvanic deposition of different ferromagnetic materials may lead to giant magnetic resonance, GMR (Liu et al., 1995). Sequential *chemical* deposition of different semiconductors, or of metals and semiconductors should lead to the formation of concentric diodes, and metal/insulator/metal structures should give concentric condensors.

Connecting metallic wires embedded in etched tracks with suitable metal contact stripes evaporated (or chemically deposited) onto the surface of the microporous polymer foils leads to the formation of microinductivities (Fig. 1a) and microtransformers. Masks and intermediate production stages of a first prototype magnet are shown in Fig. 1a. Corresponding test transformers show good operation up to ∼1/2 GHz (Fig. 1b), with inductances per winding of 10^{-4} H at 10 Hz and $\sim 2.5 \times 10^{-7}$ H at frequencies between 10^4 and 5×10^8 Hz, and quality factors approaching up to ∼10. First minuaturized ion-track-based transformer is shown in Fig. 1c. Similarly, combining lithography and etched tracks, miniaturized magnetic field sensors based on magnetoresistive ion tracks have been produced by another research group (Hjort, 2002).

First ion-track-based sensors have been developed (Schulz, 2000–2002), especially for oxygen, as some biochemically important materials to be detected react with the enzyme glucose oxidase towards H_2O_2 which is

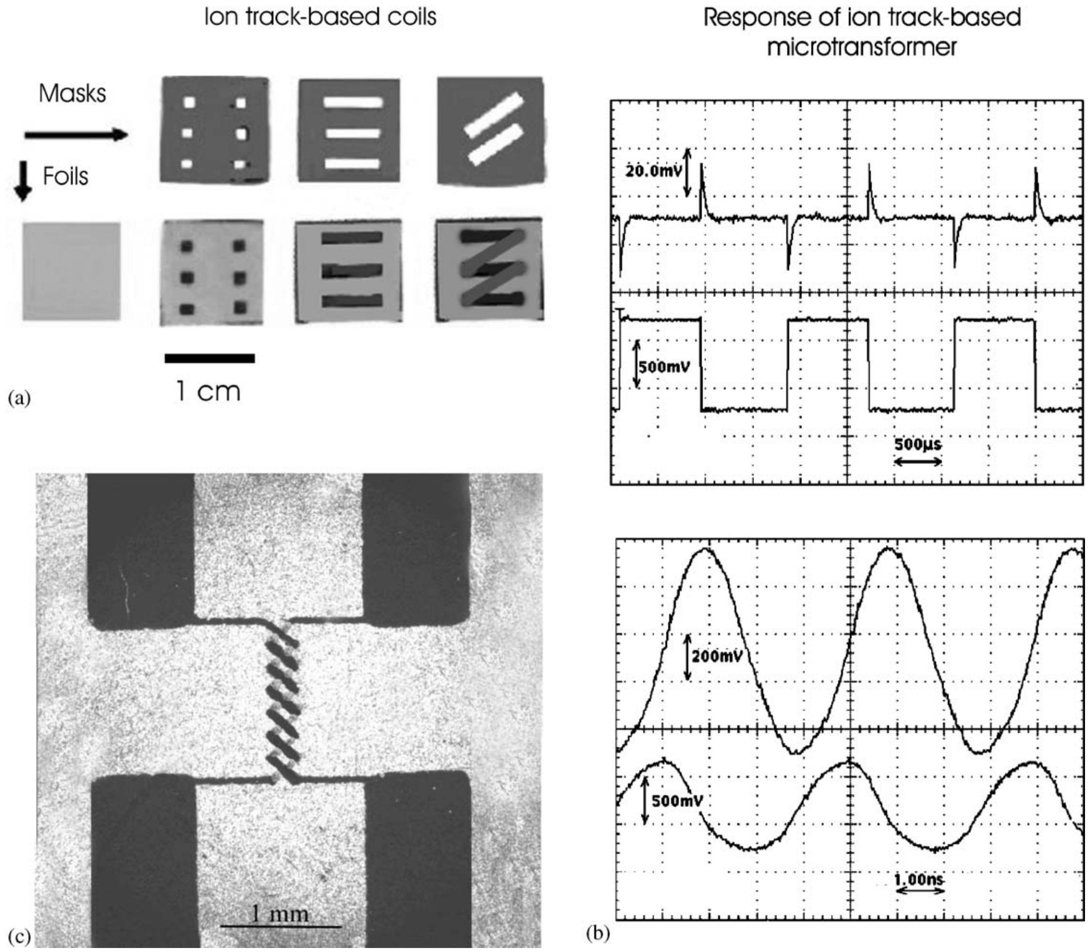

Fig. 1. Ion-track-based magnets and transformers: (a) First prototype magnet with dimensions $6 \times 7 \times 0.02$ mm^3, masks (above) and production steps (below); (b) comparison of input (bottom) and output (top) signals of the transformer prototype, for rectangular and sinusoidal input at different frequencies. Good function is recorded in the MHz range (upper graph), but signal transformation is possible up to the near-GHz range when gradually a phase lag emerges between input and output signals; (c) first miniaturized ion-track-based transformer of $1.2 \times 0.25 \times 0.01$ mm^3 size.

transformed to water by anodic oxidation. Also temperature, pressure, and humidity sensors have been developed with C_{60} as sensor material (Berdinsky et al., 2001).

5. Summary

Etched tracks, eventually in combination with lithography, enable many possibilities for creating novel deep microstructures and nanostructures within polymer foils that are inaccessible by other techniques. Promising first steps have already been undertaken to create basic electronic elements (such as resistors, diodes, condensors, magnets, transformers, or transistors) on this new basis, and whole families of novel sensors for various purposes are expected to come up soon. Apart from this, ion tracks find new applications in fields such as in light and ion-beam micro-optics, in separation technology for waste management and enrichment of precious materials, in food technology where intelligent packings are being developed, and in medicine where advanced sterile bandages, long-time in vivo drug delivering systems, artificial nerves, and numerous biosensors emerge.

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