Latent Ion Tracks in Polymers for Future Use in Nanoelectronics: an Overview of the Present State-of-the-Art

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Latent ion tracks might turn out to be useful as active elements in future nanoelectronic devices, after appropriate doping. For this salíe, new work has recently been initiated for better ion track characterization, and for understanding the ion track doping mechanism. A review of the present state-of-the-art is given.

I. Introduction

It is known since about half a century ago that energetic ions, after their passage through most insulating materials, modify a certain zone along their trajectory, the so-called latent ion track, which is permanently visible in e.g. the transmission electron microscope (TEM). The possibility to document in this way the existence and fate of individual ions has had a big impact on many fields of science and technology, such as geology, mineralogy, oil exploration, paleontology, medicine, biology, materials science, space science, planetary science, nuclear physics, and nuclear chemistry.

In most cases however, one does not observe nowadays these latent tracks themselves, but instead one makes use of a very specific property of them, which is the enhanced etchability in agressive (mostly alkaline and oxydizing) solutions - a property which may exceed the one of the corresponding bulk materials by orders of magnitude. Thus, by removing the chemically modified and hence sensitive part of the latent tracks, holes are created with diameters in the order of micrometers (so-called "etch tracks"), which are easily visible in optical microscopes, and thus open the way for more rapid ion track registration. Due to the importance of this technology, even an international society has been formed the "Nuclear Track Society"[1], which holds major meetings in different places of the world every two years[1].

Due to the overwhelming success of the use of etched tracks and the difficulties to examine latent tracks instead, interest in latent tracks has gradually decreased in the last decades. Only recently, some new ideas have emerged which led to a renaissance of latent track studies. One of them is related to the possibility of using modified individual (i.e. non-overlapping) latent ion tracks as future electronically active elements of nanometric dimensions in large-scale electronic devices[2]. The possible future use of these latent ion tracks in electronics would meet the trend to increasing degrees of miniaturization in electronics[3] (Fig.1). Apart from this idea, the use of ion irradiation to inscribe submicrometer conducting patterns (with overlapping ion tracks) in insulating polymer matrices is of great interest, and more applications might be found in optoelectronics and membrane technology.

II. The concept of "Single Ion Track Electronics" (SITE)

There exist several approaches to realize electronic elements with smaller dimensions and hence higher storage densities than available nowadays. One attempt, called nanolithography, is crudely spoken - nothing but an extrapolation of today's lithographic mask

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[1] The International Nuclear Track Society (INTS), Secretary: Dr. P.Vater, Phillips-Universitat Marburg, Germany; temporary president: Dr. V.P. Perelygin, Dubna, Russia

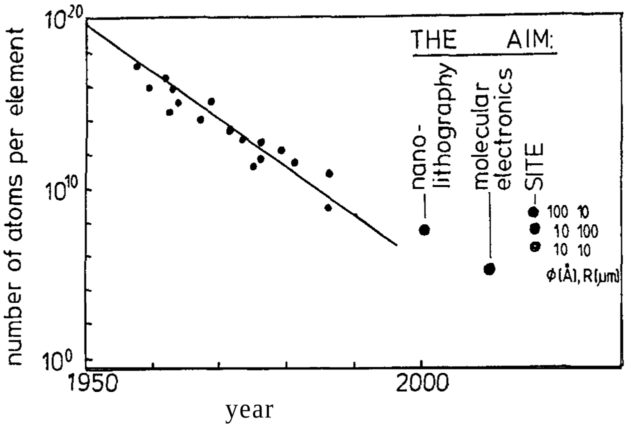

Figure 1: Historical development of the number of atoms needed for a storage device, after Ref. 3. Added are expectation values for nanolithography, molecular electronics, and SITE. For SITE, the different values shown correspond to different track sizes, ranging from: 10 Å track diameter ϕ and 10 μm length R up to: 100 Å diameter and 100 μm length.

techniques to smaller dimensions, by replacing today's light sources by other ones of smaller wavelength, or even by particle beams. Another one, the *molecular electronics*, can be regarded as the attempt to make use of, and to modify God's finest technology - i.e. biology - for human requirements. This approach is characterized by a number of hitherto still quite unusual electronic peculiarities, such as the task to handle two types of charge transport in coexistence - electrons for short range currents, and ions for long range currents -, an aqueous environment, complicated membrane chemistry, parallel data processing, high fault-tolerance, self-assembly and self-reproducibility of the whole system.

Due to the enormous difficulties involved, it is doubtful whether this fascinating technology can be realized in the near future. We have therefore proposed another simpler approach to nanoelectronics by making use of single (i.e. non-overlapping) latent **ion tracks in non-conducting polymers**[2] as active electronic elements. There exist similar approaches, e.g. by filling up *etched* tracks in inorganic solids (such as mica) with semiconducting (e.g.Si)[4] or metallic (e.g. Cu) matter[5], via electrolytic deposition. This technique leads to somewhat larger device sizes as a result of the etching procedure. In this work we shall however concentrate on the use of *latent* tracks in polymers, and not discuss the application of etched tracks further.

We want to make active use of the *modified polymeric material along individual latent ion tracks.* This material is known to be enriched in sp^2 bonds (occasionally e.g. in the form of conjugated double bonds, which exhibit especially high stability[2]), if the tracks have been produced by low energy ions. With increasing ion energy, i.e. with increasing deposited energy density, formation of complex matter such as aromatic or heterocyclic compounds and/or fullerenes along single ion tracks is also observed. This appears to hold for practically all hitherto examined polymers and other organic matter (e.g. for PP, PI, PC, PMMA, PET, PTF, and saccharose), and therefore we dare to make these statements in that generalized way.

The idea to make use of organic materials enriched in sp^2 bonds in polymeric electronics is not new in itself. For example, materials rich in conjugated double bonds - thiophenes and oligomers of thiophenes - have already been used for the production of FET's[7]. Large blocks of sp^2 bond-rich materials are produced in industry by chemical reactions, thermal treatment (pyrolysis), or by irradiation of polymers with UV, X rays, Gamma rays or electrons. What is new here is the use of high energy heavy ion irradiation, so that these materials form small and well-defined structures with relatively sharp borders within an else undisturbed matrix, and thus can be used for future nanometric-size electronics. Most of these above mentioned modified materials with double bonds, phenyl rings or fullerene structures are insulators in their neutral ground states, if considered individually. Bowever, they become semiconducting upon addition or removal of electrons, i.e. upon doping.

It is well-known that after *low energy high dose* ion irradiation polymers transform into highly cross-linked carbon-based networks. Their electronic band structure might possibly be intrinsically semiconducting, so that doping could just act on this basis. In fact, phases of a-C and a-C:H are known to behave as conducting and semiconducting materials[8,9]. It appears however that this type of material modification is restricted to the case of multiple ion-track overlapping, and *does not occur in single ion tracks*: We could demonstrate that single ion tracks exhibit a very poor conductivity, so

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[2] as an example, see the modification of PE by 60 keV O$^+$ [6].

that we can largely exclude the existence of the above mentioned cross-linked carbon-based networks and/or extended phases of a-C or a-C:H.

Therefore, *doping of latent ion tracks* will be of essential importance to activate these tracks electronically. Polymers can be n- and p-doped[10]. Again, this is nothing new by itself - the feasibility of polymer doping for producing electronic devices has been known for a long time[11]: What is new here is that the dopants are expected to act only in the spatially confined ion track regime, but not beyond. In earlier experiments of polymer doping, the dopants have been diffused or implanted at low energies into polymers. In the latter case relatively high ion fluences had been used so that homogeneously modified materials have been formed as the result of multiple track overlapping. For contrast, we are now interested in using ion beams at very low fluences, so that a heterogeneous material results, with individual non-overlapping modified and doped zones (latent tracks) within an else undisturbed matrix.

Proceeding from microelectronics to nanoelectronics imposes onto the device-constructing engineer such well-known problems as the restriction of the overall electric current density to prevent excessive heat development. This restriction implies that only a severely limited number of electrons is allowed to flow through each individual element of such a device per unit time. In order to obtain reliable switching of such a device, the number of passing electrons must be sufficiently high to avoid failure by fatal statistical fluctuations of the electron current through this element. Vice versa, this means that there exists a lower threshold in switching frequency for such an element to enable a minimum number of electrons to flow through this element, before the switching status may be reversed reliably.

From this argumentation it follows that it will be desirable to have an as high as possible overall current density flowing through the nanometric device. Here the application of polymers is, in principle, connected with some disadvantage (as long known in microelectronic) due to their well-known sensitivity to heat. To prevent overheating of the proposed polymeric SITE devices, one could therefore think e.g. at overlaying the electronically active ion track array with a grid of metal-doped ion tracks[5] which, if connected properly with some external cooling facility, will act as heat sinks. The relatively small track-to-track distances in such devices should enable, in principle, efficient heat removal. Further one might think at depositing the relatively thin polymer foils onto a thick metal substrate.

Secondly, there is the question of device stability in SITE. It is well-known that many polymers undergo long-time changes, and that dopants exhibit quite a high diffusivity in pristine polymers. If no precaution was taken, this mobility would readily destroy any newly prepared structural arrangement. There exist however ways to improve this situation. One is the careful selection of appropriate polymeric materials. Another one is to suppress unwanted dopant mobility, which can be done by trapping the dopants at defects along the tracks. Efficient trapping has the consequence that the dopants will migrate from the bulk towards the tracks rather than the other way round, and hence assure device stability.

A favorite class of polymers with very high stability is composed by the polyimides, PI. They have been developed for use in microelectronics where the temperature may reach 400°C or more during processing. The high chemical stability and unusual heat resistance of these polymers are due to the presence of aromatic heterocycles, which brings stability to the polymer skeleton[12]. Another polymer with extraordinary stability in air is poly(paraphenylene), PPP. It can be implantation-doped with e.g. alkali-ions or halogen ions, to produce respectively n-type and p-type semiconductors[13].

Apart from using polymers as carrier materials of the latent tracks, it has been proposed to use *diamond* instead[2,14]. Though this proposal is fascinating due to the many properties which make diamond superior to any other electronic material[2], it is more difficult to realize - diamonds are still less readily available and more expensive than polymers, and thermal doping experiments with diamonds require usually high temperatures up to 1000°C and more. Natural diamond as well as CVD diamond films have been shown to exhibit a strong decrease of resistivity (by up to 10 orders of magnitude) after ion implantation, a behavior similar to that found in the case of polymers[8].

One of the open questions in this connection is the 'riddle' of 'missing' latent ion tracks in diamond - hitherto they have never been observed by TEM. However, there have been performed experiments which point to the existence of an (invisible) zone of defects along an ion's trajectory[2,15] (realized e.g. by decoration of the defects along the tracks of 124 MeV Xe in diamond with postimplanted 300 keV He, and subsequent dopant diffusion at 1000°C[2]) which is capable to trap dopant/impurity atoms, and which we hence might call a 'latent track', by using a somewhat more generous definition of latent ion tracks than it is done usually. Braunstein et al.[9] could reconfirm already long time ago the formation of point defects along ion trajectories in diamond by ion channeling for the low dose ion irradiation case.

Hitherto performed experiments indicate that the principal mechanisms which govern the dopant behavior in ion tracks of diamond and polymers might partly be similar, though differing by orders of magnitude in their absolute values. Therefore one might understand polymeric ion track research not only as a new field by itself, but also as a means to enlarge the principle knowledge of ion track doping in carbonaceous materials which might later be applied elsewhere.

In order to proceed to the proposed SITE in polymers, four basic steps have to be fullfilled:

a) First, we need accurate information about the *geometrical, chemical, structural, and electronic properties of latent tracks* in polymers, and about their *stability*. Only when *a* latent track can be well-characterized in *all* these âspects, reliable tailoring of the latent tracks for specific applications will be possible. For this sake, it is highly desirable to have a comprehensive theory of ion track formation.

b) The process of *ion track doping*, essential for the ion tracks' electronic activation, has to be understood precisely. This involves questions of dopant mobility and trapping and detrapping efficiencies. The dopants should sharply concentrate along the tracks and be depleted in the neighboring region. Diffusion coefficients along the traclrs and in the neighboring bulk material, as well as detailed knowledge about the dopant's modification of the electronic bond structure of tiacks by the dopant are necessary. Again, experiments should be closely accompagnied by theory.

c) A recipe has to be found how to *position the ion tracks in regularly predetermined arrangements.* If no such provision is taken, the tracks will distribute randomly across the target. with the inherent problem of how to contact all these individual elements, and to maintain reproducibility of the whole device.

d) The doped latent ion tracks have to be *contacted* properly, in order to combine them to the predetermined logic circuits.

Hitherto, some work has been invested in the first two points, which will be reviewed below. Nothing has yet been done to answer the questions of track positioning and contacting. There are some ideas - e.g. to make use of microbeams, or to use specifically modified transmission channeling through Moiree patterns for precise track positioning, or of 'writing' conducting connections between the tracks by STM, or by low energy ion beams, but all these ideas still wait for realization.

In the following sections, we shall give an overview of the characteristic ion track properties. Here, we shall look preferentially for general overall trends, and care for details of individual systems only if necessary.

III. Latent ion track characterization

III.1 Geometrical considerations

The shape of a latent ion track is primarily defined by the 3-dimensional distribution of electronic excitation energy, transferred by the incoming projectile to the polymeric target. It could be shown by study of the gas evolution during irradiation that the damage is localized in the tracks of the incident particles[16]. High energy ions follow straight trajectories in a polymer, so that the latent tracks are in general linear (and for parallel ion beams hence parallel) structures with some slight lateral expansion. This is favorable for application to SITE.

Projectile backscattering (resulting in catastrophically deflected ion tracks) can occur only if the target atoms' masses exceed the projectile mass, so that, for application to SITE, heavy ion irradiation is favorable. In this case, also small angle multiple ion scattering and electronic scattering effects are negligible.

The ranges of such projectiles can be described with good accuracy by J.P.Biersack's Monte-Carlo code TRIM[17], or by his analytic code PRAL[18], where the Bethe-Bloch electronic stopping power[19] is applied. They are in a typical order of magnitude of some 10 micrometers for 100 MeV heavy ions, and of some 100 micrometers for GeV heavy ions.

The distribution of energy transferred to the electronic system of the target ("electronic *stopping"*, S_e) is a smooth curve with a maximum shortly before the particles' range and a high but rather constant value in the surface-near area, Fig. 2. It is this effect which determines most of the ion track's properties, such as chemical changes, conductivity etc. (see below).

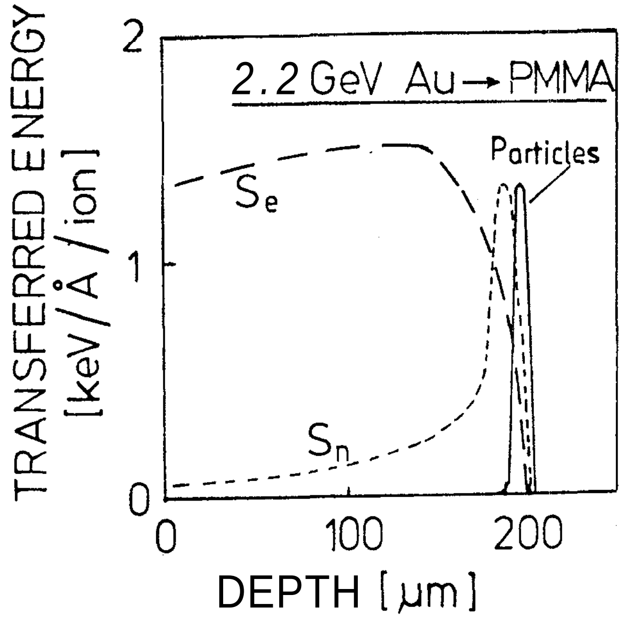

Figure 2: Depth distribution of deposited particles, nuclear and electronic energy transfer, for the example: 2.2 GeV Au ions in PMMA (TRIM calculation[17],[9]).

In contrast, the collisional energy transfer ("nuclear stopping", S_n) is negligible along most of the ion track, except for its very end. Nuclear energy transfer processes usually create less but more stable defects than electronic transfer processes. Therefore they can occasionally gain some importance for trapping of impurities. They also become important with higher degrees of polymeric destruction, when many ion tracks overlap. However, the latter case is not considered here.

The lateral *structure* of an ion track at a certain depth can be described by a number of concentric shells, each shell corresponding to a certain threshold value of transferred electronic energy density, Fig. 3. This picture is probably oversimplified as it is not yet clear whether there really exist sharp energy thresholds for the different effects, or whether these thresholds should better be replaced by broad distributions[3] Thus, these energy thresholds - may they be sharp or smeared out - primarily determine the "effective latent track radii" for the various effects under consideration - e.g. for the dopant mobility, chemical changes, visibility in TEM, etc (for illustration see Fig. 3) - These effective radii may be further enlarged by secondary effects such as e.g. diffusion of the formed radicals. Characteristic values for effective ion track radii are listed in Table 1 including the corresponding references[19-27]. They are only a little dependent on the specific ion and polymeric target under consideration. First attempts have been made to describe the lateral track extension theoretically[28].

III.2 Latent ion track chemistry

At present we are still far away from possessing a thorough overall knowledge about latent track chemistry. There have been a number of scattered 'mosaic stones' in this field, from which one can derive already an overall picture of ion track chemistry, provided that one is courageous enough to fill out the still missing knowledge with a good deal of speculative inter- and extrapolations. This preliminary procedure appears to be justified by the observation that many of the basic radiochemical effects very closely resemble each other for different irradiated polymeric targets, thus allowing for a certain degree of generalization of statements. The materials upon which most of the research work has been based hitherto are common-type polymers such

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[3] Recent TEM and STM pictures of latent ion tracks show structures with astonishingly sharp boundaries, which might be understood as an indication that the thresholds of different ion track properties are rather well-defined.

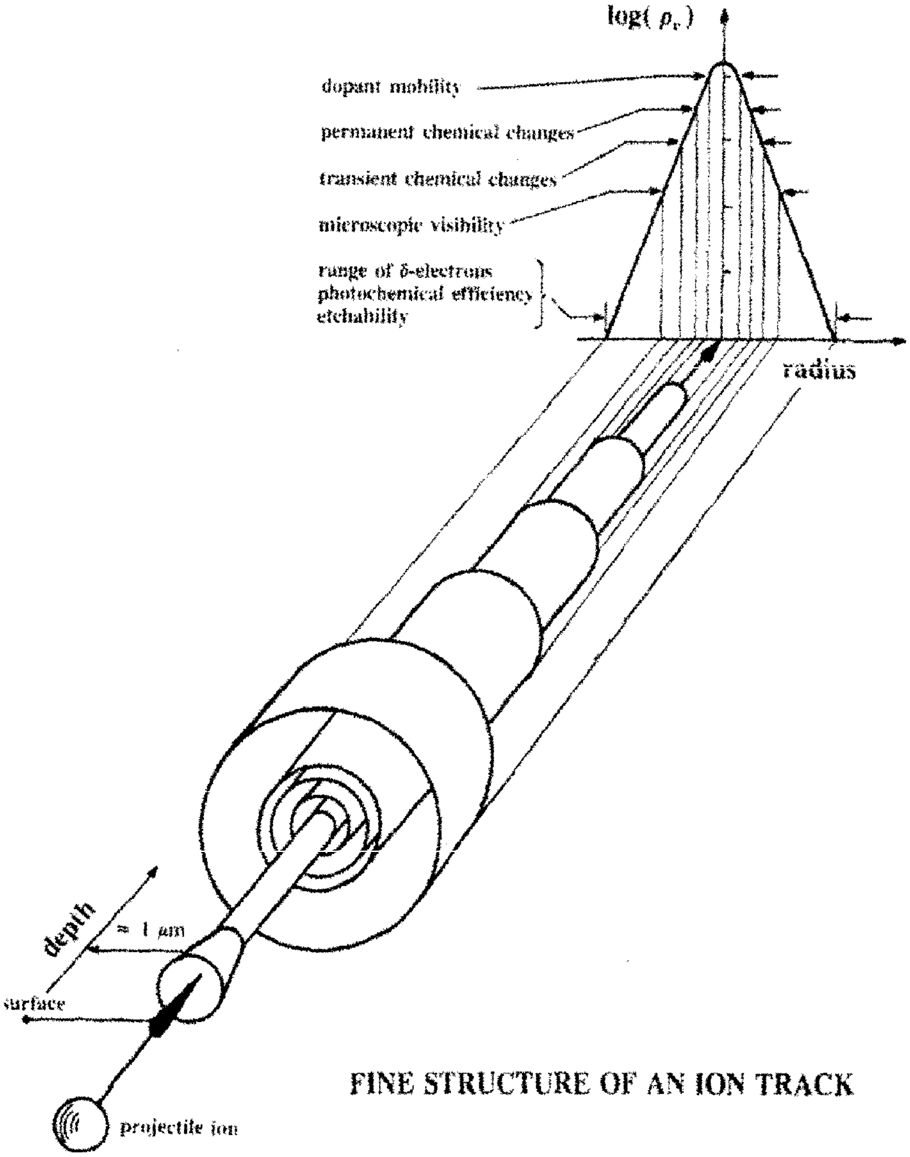

Figure 3: Principle sketch of the lateral structure of an ion.

Table 1 - Some typical values for effective specific properties:

Property	radius [Å]	Comments
dopant mobility	1-3	Ref. [20]
permanent chemical changes	1-3	FTIR results Ref. [21]
water permeation	2-3	for high fluence irradiation
	10	for low fluence irradiation Ref. [22]
alteration of molecular weight; distribution of polymer chains	17-45	for low fluence low energy light and heavy ions Ref. [23]
creation of volatile irradiation products	22	estimated for low energy ions Ref. [24]
intrinsic conductivity	80	low energy ion tracks
	180	high energy ion tracks Ref. [25]
transient chemical changes	160	results from laser induced pulse radiolysis Ref. [26]
transversal etch rate	100-300	Ref. [27]

as foils of PMMA, PE, PP, PI, PC, PET, PTF, PS, or photoresist. Most of the examinations reported in the literature have been performed with low energy ions in the regime of 1 keV to 1 MeV. Hitherto there exists only a marginal number of papers dealing with radiochemistry of ions with MeV to GeV energies, such as e.g. Refs. 29 or 30.

The latent ion track regime is characterized by two effects: (a) destruction of existing components, and (b) formation of new materiais. Chemical bonds in any polymer can be broken whenever the energy transfer to the electronic system of the target exceeds the interatomic bonding energy. The latter is in the range of a few eV only (e.g. H-CH: 4.3 eV, CH_3-CH_3: 3.7 eV [31]). It has been established that upon electronic energy transfer, bonds are not broken at random. Rather, experimental evidence shows that certain selectivity rules which do not only follow bond energy considerations apply. Thus in linear hydrocarbons, C-H bonds are broken more frequently under irradiation than C-C bonds, in spite of the higher bond strength of the C-H bond[31]. Bond breaking will be strongly favored in the core region of a track, where most of the energy is transfered, whereas it will occur only occasionally in the track's penumbra, due to energy transfer densities which are lower by orders of magnitude.

Calcagno et al.[32] have performed optical and rheological examinations of 100 keV H and 300 keV He irradiated PS in the single ion track regime. They derived cross-link production yields of 12 cross links/ion, respectively defect production yields of 100 defects/ion. This corresponds to chemical yields of 0.07, respectively 0.28 defects/100 eV deposited energy. From these observations they concluded that the energy distribution inside the single ion tracks is the controlling factor for the chemical yield.

It has been observed for PVDF modification by energetic heavy ions (1 to 50 MeV/amu O, Kr, and Xe ions at fluences of some 10^{11} to 10^{12} ions/cm^2 [29]) that the major parameter for polymer modification is the projectile atomic number: Destruction is greatest for heavy ions, and it remains stable along the ion tracks in the bulk. For contrast, activated centers introduced by lighter ions tend to migrate towards the surface, where subsequent chemical reactions like rearrangements and readditions can occur between the reactive species and the modified polymer[29]. Applied to our aim of SITE, this means that one should use ion tracks of heavy energetic ions rather tlian of light ones, to obtain best long-time device stability.

Electronic energy transfer processes lead primarily to excitation and breaking of bonds, with the consequences of chain scission, cross-linking, and/or formation of new types of bonds (e.g. C=C), depending on the system under consideration. These effects have long since been studied in great detail. For example, it became possible to distinguish experimentally between interchain and intra-chain bond cross-linking[33]. It was shown that soluble polymers transform into non-soluble gel upon introducing one cross-link per macromolecule[33]. Aromatic polymers irradiated with ions at low deposited energy densities act as efficient 'energy sinks' insofar as the aromatic rings can dissipate a great deal of the excitation energy[32]. However, for ion irradiation of these compounds at higher energy densities (i.e. heavier particles and higher fluentes), the loss of aromatic conjugation is one of the predominant destruction processes[34,35].

Production of a vast amount of volatile irradiation products with subsequent strong gas emission is a characteristic effect of ion track formation in polymers. As the gas emission is a diffusionaliy controlled process, degassing will be strongest at the surface and slowest near the track end. Thus an inhomogeneity in the distribution of residual (i.e. slowly moving, large) volatile components along the ion track will emerge.

With increasing projectile energy the transferred energy density is further increased, until all bonds along the central region of the latent ion track (the so-called *'ion track core3* are broken. Thus a highly energetic ion is capable to produce completely new compounds, with no connection to the originally present ones. The higher the projectile energy - i.e. the higher the *deposited energy density along the ion track core* - the more time it will take for dissipation of the target atoms' excitation energy, and hence the more complex will be the compounds which can be newly formed in this track core.

This has actually been verified (e.g. for 1.5 GeV Bi in Pi, 2.2 GeV Au in PMMA[36,37], 2.1 GeV Dy in HOPG[38,39], and **3** GeV U in saccharose[40]): A large amount of new *(poly)cyclic compounds* emerges from GeV irradiated organic matter - independent from the aromatic or aliphatic nature of the original materials - and even fullerenes are seen to develop (at present, both C_{60} and C_{70} could be identified[40]). Experimental data from GeV irradiated PMMA suggest a threshold in linear energy transfer along the tracks of around 1 keV/Å for the production of polycyclic compounds, corresponding to a threshold energy density in the ion track core of around **3** eV/Å^3. Above this threshold, the production yield of these compounds increases very strongly, as shown in Fig.4. For example, the production yield of the above cited polycyclic compounds formed in GeV irradiated PMMA is of the order of some 10% or more[36,41].

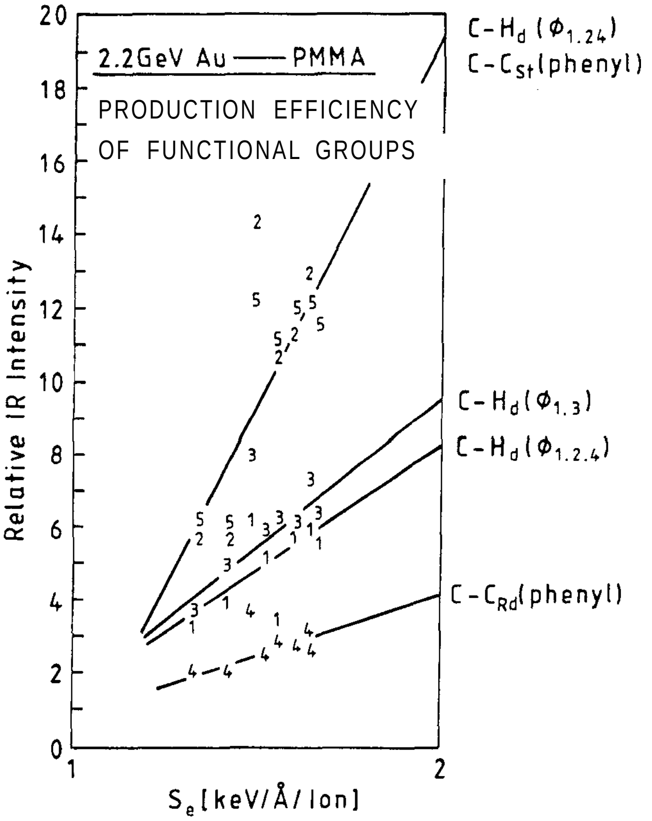

Figure 4: Production yield of polycyclic compounds in polymers as a function of the projectile's linear energy transfer, as verified by specific functional groups in the polymers' FTIR spectra. Shown here for the example of 2.2 GeV Au ions in PMMA[36].

For fullerene formation, the corresponding threshold values could not yet be derived, but they are assumed to lie in a similar order of magnitude.[4] To give the reader a feeling it should be mentioned that a GeV heavy ion impinging into a sugar crystal is capable to create typically some 150 C_{60} and **3** C_{70} molecules along its track[40]. Taking into account the relatively high degree of dilution of carbon atoms in sugar (only about 25% carbon atoms, among a majority of H and O atoms), we should expect that the production efficiency of fullerenes by GeV ions in more carbonenriched material (such as graphite) should be larger by some orders of magnitude. For example, theory predicts some 10^5 to 10^6 C_{60} molecules per ion in GeV-radiated graphite. However this is not yet verified experimentally - present experimental limitations in fullerene detection from ion tracks in e.g. graphite stem from the very low leaching efficiency of these molecules out of the tracks.

There might exist an inverse correlation between the production efficiency of polycyclic compounds and of fullerenes: For GeV irradiated PMMA, where many polycyclic compounds have been found to emerge, practically no fullerene was formed, whereas for irradiated saccharose we found relatively much C_{60} and less new aromatic compounds. It may be that the chemical production paths are influenced not only by the degree of carbon dilution in the presence of high H and O abundance, but also by the mobility (and hence loss) of H- and H-enriched compounds along the ion track regime.

The depth distribution of the production yield of these compounds always follows closely the one of the electronic energy transfer. Only for high doses, when tracks are at least thousandfold overlapping, an influente of nuclear energy transfer processes becomes visible[37].

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[4] The production of fullerenes inside the ion tracks may not be confused with the *sputter-emission* of fullerenes from carbonaceous materials, see e.g. Ref. 42: Here, it could be shown that, upon penetration of an energetic ion into polymers or into fullerite, material is ejected from the surface regime down to a depth of roughly 200 Å of the emerging ion track. Upon penetration of this supersonic jet-like cloud of free neutral carbon atoms through the track surface, adiabatic expansion sets in during which carbon clusters are formed, among which are the above-cited fullerenes. As fullerene formation in an expanding plasma requires a lower energy density than fullerene formation inside highly confined solid matter (but takes longer time), sputter-emission of fullerenes could already be observed for impinging projectile energies as low as some 70 MeV [42], which is about one order of magnitude lower than the assumed threshold for fullerene production inside ion tracks [43].

The hitherto applied technique (FTIR) alone does not allow to distinguish between the different types of ion-created aromatic compounds. Concerning fullerenes, only the two most abundant types, C_{60} and C_{70}, could be identified[40]. In order to improve this situation, a combined chromatograph / mass spectrometer should be used in future.

Theory[43] predicts that the production of aromatic compounds and fullerenes will be restricted to the outer region of the ion track core. Only inside the core the necessary minimum energy density threshold for bond breaking is maintained for a sufficiently long time to enable the formation of aromatic compounds and fullerenes. Furthermore, another threshold condition defines the maximum possible energy density transfer: The newly formed components must be quenched sufficiently rapid after their formation, to prevent excessive decay backreactions. This condition is frequently not fullfilled in the very center of tracks of energetic ions. Thus we are restricted for this special type of radiochemistry in GeV ion implanted polymers to a narrow cylindrical track regime of typically some 30 to 200 Å radius (as calculated by Gamaly and Chadderton[43]).

In the outer regions of the track, competitive chemical reactions which do not require the breaking of all bonds, with only partially destroyed polymers might take place. Thus it has been recently shown by FTIR that aromatic esthers are created together with polycyclic compounds in 2.2 GeV Au ion tracks in PMMA[44]. This aromatic esther formation can be explained on the basis of classical chemical reactions with the original polymer, which has been verified by a simulation experiment[44].

The expected radial variation of ion track chemistry has not yet been verified. It might imply that, on ion track doping, various concentric zones of different electronic conductivities emerge around the ion track core, due to the different chemical compounds created.

III.3 Intrinsic electronic properties

A light modification of the well-known two-point technique for resistivity measurements enabled us to measure lower conductivities than was ever possible before[25,45]. Thus, intrinsic conductivities of single (i.e. non-overlapping) latent ion tracks could be measured for the first time. (By *'intrinsic conductivity'* we mean here the conductivity of as-implanted ion tracks, in contrast to the ion track conductivity after doping). Immediately after the track formation, this intrinsic conductivity seems to decrease rapidly by about at least one order of magnitude, due to the reduction of free electrons (by annealing and eventually also due to oxidation processes - observed for irradiation of PP foils with various ions at some 30 to 100 MeV energies[46]). It turns out that the intrinsic conductivity of a single ion track in e.g. PI in its stationary state (i.e. at least some days after the implantation) is of the order of 10^{-26} ohm^{-1} which means that every second only 1 to 5 electrons pass a single ion track (as determined for about 10 kV/cm electric field strength applied, i.e. still below the onset of electron avanlanches or breakthrough). These data have been derived from a wide range of measurements with different projectiles - from 2 MeV He to 3 GeV U - for low energy deposition rates of 10^9 to 10^{13} ions/cm^2 in commercial polyimide (Goodfellow LTD)[25,45,46].

The overall polymeric conductivity was found to increase proportionally to the ion track density[47]. When all the polymeric target is nearly homogeneously covered with single (but not yet overlapping) ion tracks, the overall polymer conductivity (in the case of polyimide) has risen up to typically 10^{-14} ohm^{-1}cm^{-1}. The conductivity values for other polymers (e.g. PP, PC, PET, PMMA or PTF) are of a similar order of magnitude[45]). Although the intrinsic conductivity of irradiated polymers exceeds the one of unirradiated polymers by some orders of magnitude, these values still lie in the range of definition of insulators (though bad ones): We are still far away from materials with semiconducting or even conducting quality, which only can be obtained after doping. This experience has been indirectly reconfirmed by many authors who studied polymeric conductivity changes after low energy low dose irradiation: ion irradiation at doses below track overlapping "does not produce an appreciable drop in resistivity"[35].

The conductivity of an irradiated polymer becomes isotropic when the ion tracks start overlapping. In this case, the overall polymeric conductivity does no longer increase with fluence, as given in the single ion track case, but remains constant within a fluence range of about 3 orders of magnitude (Fig. 5). For the single ion track case, the conductivity in transversal direction (i.e. from one track to the other) equals the value of the pristine material within our measuring accuracy (shown by us for tracks in PI[45]).

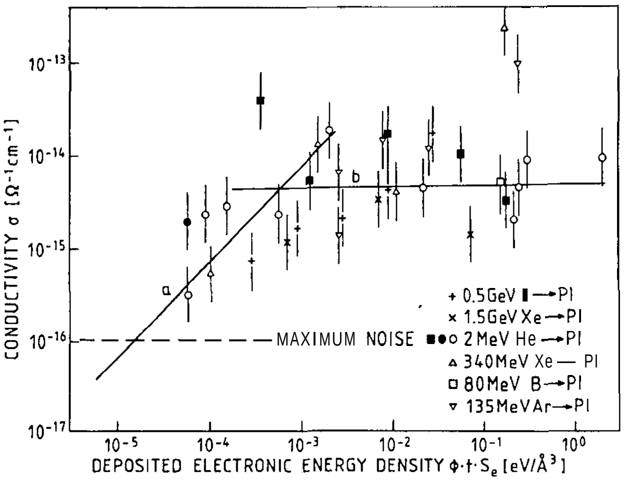

Figure 5: Dependence of intrinsic electronic conductivity in ion irradiated PI on the transferred electronic energy density, for a) the single ion track (SIT) regime, b) the multiply overlapping track (MOT) regime of constant conductivity, and c) the MOT regime of strong conductivity changes. Straight lines to guide the eye, to outline the principle tendency. For even higher transferred energy densities (about 10^{-1} to 10^{0} eV/Å^3), a third regime emerges with extremely high conductivity a a result of carbonization processes (not shown here).

For deposited electronic energy densities exceeding 10^{-1} ev/A^3 (i.e. at roughly thousandfold ion track overlapping) extremely strong chemical and/or structural changes set in, which lead to a dramatic increase in conductivity, until that, at around 10^{2} eV/Å^3 transferred electronic energy density, near-graphitic conductivity has been reached. Extensive experimental work has been performed for this high-dose regime of polymeric destruction in the last decades (see, e.g. Ref. 47). Both conductivity and optical transparency are not only influenced by electronic energy transfer in this regime, but also atomic collisions begin to play an important role[12,21,36,48].

Theoretical models have been derived long ago to describe this conductivity regime, either by a linear model of current transport between localized states[49], or by the process of three-dimensional electron hopping from one conducting island to another[50]. Both models yield the same results, so that an experimental decision between them appears to be rather impossible. A modified concept of electron hopping between conducting aggregates seems to be also a good model for the description of the much poorer *single ion* track *conductivity* (see below).

III.4 **Structural** aspects

The modified polymeric matter inside ion tracks is not homogeneously distributed but exhibits fluctuations in both the carbon and electron density. This has been derived from small angle neutron scattering (SANS)[51], respectively small angle X ray scattering (SAXS)[44,52,53], and from UV/vis. spectra[54], and this is also the basic assumption of the theories on intrinsic polymer conductivity[49,50] - see above. The individual carbon and electron enriched zones appear to have near-spherical, slightly ellipsoidal shapes, their symmetry axes being oriented along the ion track direction[53]. The latter finding resembles earlier assumptions that these inclusions might have a filamentary shape elongated along the track of the incident ions[12].

Typical diameters of the carbon-enriched zones are reported to be 6 to 7 nm (as measured for 50 MeV B tracks in PET at 10^{13} ions/cm^2 by SANS[51]), and the diameters of the electron-enriched zones are found to have sizes of 0.2-4 nm (according to UV/vis. spectrometry, obtained e.g. for some 300 keV He to Ar ions in PS, PE, and PET at fluences between 10^{14} and 10^{16} ions/cm^2 [54], [55]), 5 to 6 nm (as measured for 2.2 GeV Au ions in PMMA at 5 x 10^{10} ions/cm^2 by SAXS[36,44,52]), and 10 to 50 nm according to the conductivity theories (as estimated for some 100 keV heavy ions at fluences around 10^{15} ions/cm^2 [49], [50]). The average distance between these zones is estimated to be 13 nm by SANS[51], and 0.1 to 20 nm from intrinsic conductivity results[49,50]. As those values have been obtained for different implantation conditions (light and heavy projectiles, low and high energies and fluences), a systematic dependence on implantation parameters cannot yet be derived from these data and they just give a feeling for the possible orders of magnitude of this effect. Anyhow, we can conclude that the formation of these aggregates is not a specific high dose effect resulting from ion track overlapping, as the existence of these aggregates has also been verified for the case of non-overlapping single ion tracks[36,52].

Nothing is known about the composition of these aggregates and speculations range from crystalline graphite platelets[12,54,56,57], via giant fullerenes[38], or glassy carbon[56], up to benzoid ring clusters[55], or just simply pitch-and-tar-like matter[51]. Another recently developed idea[43] is to explain these agregates as precipitates of the irradiation-formed fullerenes and/or poylcyclic matter along the ion tracks. The observation of Davenas et al.[12] that conductive polymeric properties after low energy high dose irradiation are always connected to the presence of aromatic or heterocyclic structures in the polymeric precursor appears to be quite interesting in this connection.

It should be pointed out at this occasion that the presently available experimental results derived from UV/vis. spectrometry for the cluster diameters always lead to values smaller than the ones derived from SANS or SAXS. The reason is that the underlying model is based on the assumption that these aggregates stem from diffusional clustering of benzene rings along the track; the observed optical energy gap is then correlated with the number of benzoid rings by a simple formula[55]. This formula would, of course, be invalid if mechanisms other than benzoid ring clustering were responsible for aggregate formation. We have to leave the final decision still open. It has been shown that the growth of these sp^2 clusters is correlated with the loss of hydrogen, the presence of which tends rather to stabilize the sp^3 phase[55].

We do not yet know with certainty whether the carbon-enriched aggregates (as vizualized by SANS) are identical with the electron-enriched ones (as detected by SAXS), though the similarity in geometrical parameters makes this identity highly probable. However we do know that the depth distribution of the size of the aggregates follows the electronic energy transfer curve, hence that the formation of these aggregates stems from electronic processes (shown for 2.2 GeV in PMMA at 5×10^{10} ions/cm^2 [45] from SANS results on B irradiated PET[51]).

ESR measurements on irradiated polymers (specifically shown for 100-300 MeV Ar and Xe irradiated PI and PC) reveal, among other signals, some which depend on the implantation dose. They might stem from broken C-H bonds. For 'old' latent ion tracks (i.e. tracks which had been exposed to atmospheric oxygen for about half a year), a density of about 500 unpaired spins per track was found[45][5].) Combining this result on a still speculative basis with an estimated number of 10.000 carbon- (and electron-) enriched aggregates per track (see above), we arrive at roughly 1 unpaired spin per 20 aggregates. This might indicate that the measured intrinsic polymer conductivity results from a combination of electron hopping between the aggregates, with trapping/detrapping processes (at the unpaired spins) for the electrons inside the aggregates, which would make understandable the low observed intrinsic ion track conductivity. It may be mentioned in this connection that the density of unpaired spins in pure (i.e. undoped) fullerite is also very low (around 10^{-3} spins/molecule), so that even the presence of a major number of fullerenes along the ion tracks would not alter the above given picture.

III.5 Theoretical approach for description of track formation

Several historic models exist for the description of latent ion track formation, e.g. the "Coulomb Explosion Model"[59] and the "Thermal Spike Model"[60]. A Monte Carlo model, based on the Binary Encounter Approximation, has been developed recently to study details of the secondary electron emission and migration inside tracks of heavy charged particles[28]. Unfortunately, this model is at present restricted to a very special case only: the ionic energy deposition in water vapor.

There exists a new model which puts special emphasis on the formation of excited (i.e. non-bound) but neutral target atoms along the ion tracks[43]. We pre-

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[5] This result for energetic heavy ions has to be compared with those of low energy ion irradiation: around 1 spin/ion track for 60 keV O^+ in PE at 5×10^{14} to 5×10^{16} ions/cm^2 [6], respectively for 50 keV C^+ in diamond at 3×10^{13} ions/cm^2 [58].

fer this latter model for an analytic description of the ion track, as it avoids the inherent difficulties of e.g. the Coulomb Explosion model. The latter one assumes that, after bond breaking and ionization of the target atoms by the impinging projectile ion, most target electrons are expelled from the ion track core for a very long time, so that the remaining target ions are free to move away from each other by Coulomb repulsion. In order to explain the absence of immediate electron-ion recombination which would prevent any ion motion at all, the model assumes that

a) all electrons suffer very high energy transfer so that they are capable to move very far away (up to a few micrometers) from the ion track core ('δ-electrons'),
b) the attractive Coulomb field between electrons and ions is shielded by a conducting layer in case of conducting targets, respectively,
c) in case of insulating targets, the electrons - once having lost their kinetic energy - are no longer capable to move back to the ions in the insulating target, but are rather permanently trapped.

Simple formulae, taken from plasma physics, show however that the average target electron gains only little energy and hence migrates only some 10Å (as calculated for the system: 1.5 GeV Dy in graphite in Ref. 43), so that

a) there is no space for building up a shielding conducting layer in a conducting target, respectively
b) the electric field between electrons and ions still exceeds the breakthrough voltage of an insulator so that the electrons cannot be permanently trapped,
c) the recombination time is hence so small (ca. 10^{-14} - 10^{-15} sec) that the target ions have no chance to migrate away from their position by Coulomb repulsion.

The excited but neutralized atoms will gradually return to their ground states via emission of radiation or by electron-phonon coupling, with the consequence of heating the ion track core and its immediate environment. During this time, new chemical bonds are formed between neighboring atoms which may lead to the production of new materials along the track. A precondition for this process is of course that the energy density in the track regime exceeds the threshold energy density necessary for formation of these new compounds. The formation of specific high temperature/high pressure compounds such as fullerenes[6] will be favored as long as the energy density in the track core exceeds their specific formation threshold value, and as long as the lifetime of this hot region exceeds the time required for formation of these compounds. A system of n rate equations can be established to describe the dynamic equilibrium between formation and decay of carbon clusters C, with n atoms each[43]. This process will come to an end when the energy density in the track regime drops below the threshold value for formation of the C, clusters, as a result of heat dissipation by thermal diffusion.

The use of these n rate equations enables one to make predictions for the production yields of the C, clusters, provided that "reasonable guesses" were made for the reaction rate constants in these equations. Applying this approach to the above mentioned case of 1.5 GeV Dy in HOPG, one ends up in some 10^5 to 10^6 predicted fullerene molecules per ion. (This value could not yet be reconfirmed experimentally, as our hitherto applied detection method is by far not yet efficient enough to isolate all formed C_{60} molecules from the track.) It is expected that further work on this model may yield more detailed informations, e.g. on the production yield of fullerenes and polycyclic compounds in organic matter, and on their radial distribution along the track.

IV. Doping of ion tracks

IV.1 Experimental data base

We have seen above that latent tracks of energetic (MeV...GeV) ions in all common polymers contain a number of promising compounds which - though being

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[6] According to the recently derived phase diagram of carbon allotropes[43], fullerene formation is characteristic for the high temperature T / high pressure p regime. This has to be compared with diamond (low T, high p), graphite (low T, low p), and with carbon vapor (high T, low p). In other words, fullerenes and diamond are metastable allotropes under 'normal' conditions (low T, low p).

bad insulators themselves in their neutral ground states - can be readily turned to semiconductors by appropriate doping. Therefore ion track doping is a crucial point in the tailoring of SITE. To this aim, we have to know

a) how to dope the ion tracks,
b) how the dopants distribute along the tracks and the neighboring pristine material,
c) what are the specific changes in the band structure resulting from doping, i.e. what is the most suitable dopant.

It is further important to know how the stability of the ion tracks influences the doping procedure, to have information about the stability of dopants in the ion tracks themselves.

At the moment, there does not yet exist any detailed work about the consequences of ion track doping on the electronic behavior of ion tracks. However we have already some first ideas how the ion track doping process itself proceeds, how the dopants distribute thereupon, and how the ion track stability influences the doping process.

In principle, doping of a solid can be done by *thermal* or ballistic processes. The latter ones can be largely excluded in our case, as the impinging dopant ions would usually introduce additional uncontrolled damage to the target with eventually fatal consequences. The only exception is the so-called *"self-ion track doping"*[61], which means the occasional decoration of a track by the same ion which has formed the track itself before (examples: implantation of 120 keV Li, 90 keV B, and 70 keV F ions into photoresist AZ111, PET, PC, PI, saccharose, epoxy resin, etc., with subsequent self-ion trapping in electronic damage centers[62,66]). This situation is favorable for doping studies due to its simplicity, but it is of no relevance for future applications, due to the low level of doping (one dopant atom per track only, or less).

"Thermal doping" - i.e. the use of diffusional processes for dopant introduction into the tracks - can be performed a) via the gas phase, b) via the liquid phase, or c) via the solid phase. For practical realization of thermal doping from the *gaseous* or *liquid* phases, the ion track containing polymer is exposed to the environmental dopant for a well-defined time and temperature (examples: I indiffusion into PI at 60°C, preirradiated with some 100 keV noble gas ions[67], or diffusion of LiCl solution into PI at R.T. and at 100°C, preirradiated with some 100 keV Ne, respectively 340 MeV Xe ions[68]). This means that the dopant always enters the track via its surface.

In the case of solid phase doping, the dopant can be either deposited as a solid onto the surface of the track containing polymer (e.g. by evaporation), so that it can diffuse subsequently into the polymer through its surface, in the same way as gaseous or liquid dopants do (example: diffusion of Al from evaporated contact layers into polyacetylene[69]). For contrast, easily mobile dopants can also be incorporated homogeneously in the polymer during its production phase (example: Li in Li-grafted PE[20]). Subsequently introduced ion tracks will act as gettering centers so that the mobile dopant atoms will finally concentrate along the ion track (example: 135 MeV Ar or 100 keV He in Li grafted PE at 10^{12} ions/cm^2 [20, 70]).

The transient distribution of dopants along the ion track during the inital doping procedure is determined by the diffusion coefficient of the dopant atoms and the trapping/detrapping behavior of the (intrinsic and ion induced) defects, as well as by their lifetimes; the final dopant distribution is essentially determined by the distribution of trapping centers along (and transverse to) a track. In this connection, the energy of bonding to the traps plays an important role, as dopants may be thermally detrapped from shallow traps, thus resuming their diffusional motion. Not much is known at present about these bonding strengths. A first test experiment (300 keV Li in epoxy resin) indicated that dopants are bound quite strongly to electronic traps, as annealing of the doped samples up to 200°C did not alter the dopant depth distribution markedly[71].

Upon bond breaking, radicals are formed. They are capable to trap mobile reactive natural impurities (such as oxygen) or intentionally introduced reactive dopants (such as Li, B, As, P, Bi etc.) They will not be capable to trap chemically inert impurities or dopants such as noble gases. Once one, or a well-defined number of dopant atoms have been bound to these radicals, the radicals are saturated and no longer chemically reactive. Therefore this type of defect is denoted as "saturable trap" from the point of view of diffusion theory.

The other possible source of defects in a polymer are collisionally (so-called "nuclear") projectile-target interactions. Here, atoms can be knocked away from any point in the polymeric chains, thus introducing bond breaking with some empty space in the target. This additionally available space can be used to accomodate dopants, independently from their chemical reactivity and the chemical nature of the site - i.e. also noble gas atoms can be trapped here. The capability of these defects for dopant uptake is in principle restricted by the available volume, but can be easily enlarged upon widening of this cavity by strain, induced by the dopant atoms present in this cavity. (This case had been discussed extensively, e.g. for He bubble formation in metals[72]). These traps are considered to be large-size potential depressions. These defects are denoted as "unsaturable traps" in diffusion theory. Of course, this distinction between saturable and unsaturable traps appears to be still somewhat schematic, but it is a reasonable simplification to enable first theoretical modelling. As, for swift ions, electronic energy transfer exceeds by far the nuclear energy transfer, nuclear (unsaturable) traps are normally less abundant than electronic (saturable) ones, and hence frequently masked by the latter ones.

The overall amount of trapped dopants is determined by the diffusion coefficient of the impurities and their trapping efficiencies at polymeric defects. If more than one dopant/impurity is present, a competition between the species for chemical bonding will occur. Dopants can be trapped not only at electronically or collisionally induced defects, but also undergo bonding at other dopant or impurity atoms present along the track, or even compensate each other. This type of chemical compensation has been verified e.g. for K^+ and I ions in 15-30 keV K, Na, or I irradiated polyacetylene[10].

The hitherto performed ion track doping experiments yielded two different types of results:

a) After doping of 150 keV F or As tracks in PE with 0.5 mole/l lead acetate solution[73] or with 5 mole/l KI solution[74],[48] at 100 °C, the dopants (as determined by RBS for Pb in the first case, and for I in the latter case) arranged according to the predicted (TRIM)[17] *electronic* energy transfer.
b) After doping of 100 keV Ne tracks in PI with 5 mole/l LiCl solution at 100°C[68], or of tracks stemming from various noble gases in PI with gaseous iodine at 60°C[67] (as determined by NDP for Li in the first case, and by RBS for I in the latter case), the dopants arranged according to the predicted *nuclear* energy transfer distribution.

As immediately after the ions' passage, electronic as well as nuclear defects have been formed (with electronic defects known to be in the vast majority), one has to conclude from these experiments that in the case of irradiated PI these electronic defects have vanished, 'but not (yet) in the case of irradiated PE. In all cases examined, the ion irradiation took place long time (days to years) before doping; hence we can estimate the lifetime of electronic defects in PI to be considerably less than one year, but in case of PE to be much larger than one year. This is, in principle, nothing new. It is known long since that, whereas in liquids or polymers above the glassy transition temperatures T_g the lifetimes of free radicals are extremely short, corresponding lifetimes in polymers in vitreous state may become extremely long (weeks, months,...) and are essentially determined by the temperature: the farther away is the system from its T,, the longer the lifetime of the created defects, due to strongly reduced mobilities and detrapping probabilities of trapped free radicals[31].

Trapped ions and trapped radicals absorb light and may be responsible for more or less transient discoloration[31]. Thus one can study their long-time behavior easily. This has in fact already been done earlier, e.g. for hydrogen irradiated polyimide, where at least two different activation energies for the detrapping process of trapped radicals were found[48]. Regarded from the point of view of polymeric device stability for SITE applications, this means that one should on one side care for polymers with an as high T_g as possible, and on the other hand for as low device operation temperatures as possible. Furthermore one should try to introduce as 'deep' trapping centers as possible, which implies ion track formation with heavy ions rather than with light ones.

At present, it is not yet clear which mechanism determines the annihilation of electronic defects. It is definitely not the indiffusion of oxygen, as was anticipated until recently: Hnatowicz and coworkers[75] could show that oxygen readily had diffused into the above mentioned F or As-irradiated PE, even beyond the irradiated zone, but that the electronic defects for dopant trapping were not affected by this oxidation process[73]. Therefore we tend now to think that the lifetime of electronic defects depends on the material's capability for self-repair, i.e. on the capability for radical recombination, respectively for undergoing cross-linking or forming double bonds.

Trapping centers resulting from electronic energy transfer ("electronic traps", usually free radicals) are occasionally (apparently depending on the polymer; e.g. in PI) metastable due to recombination processes, or due to impurity uptake. In these cases, by recombination or capture of an impurity or dopant atom, the electronic traps might eventually annihilate, so that a subsequently passing dopant atom cannot be trapped any longer by them ("saturable traps"). The much less abundant defects of collisional origin ("nuclear traps") can, in principle, accomodate many dopant atoms (*"un*saturable traps"), so that they might become nucleation centers for dopant precipitation[76], in case that electronic defects have been annihilated already, and a sufficiently large supply of dopant atoms is available.

Thus, tailoring the shapes of dopant distributions appears to be possible: By using appropriate polymers (e.g. PI) and waiting for sufficiently long time, electronic traps have largely vanished, so that subsequently indiffusing dopant atoms will be trapped only at the remaining permanent (nuclear damage) centers. On the other side, "rapidly" introduced dopants (i.e. dopants which arrive at the traps before these ones anneal) will be bound to both electronic and nuclear traps. As the number of nuclear traps is in general much lower than the one of the electronic trapping centers, the dopant depth distributions will then primarily follow the depth distribution of electronic energy transfer. Thus one can use the competition of electronic damage annealing in suitable polymers on one side, and polymer doping on the other side, to sketch the possible recipes for tailoring the dopant depth distributions:

a) **Aim:** Shape *of* dopant depth distribution = shape *of* electronic energy *transfer* distribution: Enable *rapid* dopant diffusion, use any polymer.
b) **Aim:** *Shape of* dopant distribution = shape of nuclear energy transfer *distribution* (near the end of the *ion tracks):* Use appropriate polymeric material (e.g. PI), then wait until metastable electronic traps have vanished, finally perform dopant diffusion.
c) For high energy *heavy* ions, the nuclear trap distribution is near-zero in the surface-near region and non-negligible only near the end of the particles' ranges. Therefore, one will gain *regular* thermal dopant mobility in the *surface-near* track regime, if applying recipe (b) for surface-near polymer regions: use of appropriate polymer - e.g. PI -, and wait for annealing of electronic damage centers).

The latter approach is the basis for all permeation experiments where gases or liquids are transported through thin foils containing latent ion tracks[77]. From this type of experiment, information about the magnitude of the dopant diffusion can be gained via the speed of penetration. For liquid phase penetration, values are found to be in the typical order of magnitude of 10^{-11} to 10^{-8} $\mathrm{cm}^2\mathrm{s}^{-1}$, depending on the polymer, the ion track specification and the ion track density (as derived for 135 MeV Ar and 340 MeV Xe ions in PI ands PC at doses from 10^9 to 10^{12} ions/cm^2 [68]).

In this work, we discuss only the fate of chemically moderately active dopants in tracks, which can bond to defects in these tracks, but do not destroy them further. Enhanced chemical reactivity of dopants leads to the well-known effect of ion track etching, where sensitive molecules in the ion track are either destroyed or dissolved in the etchant, and finally rinsed out from the track with the etchant solution. This etching process thus readily creates an excess of free volume along the latent track, which enhances further dopant/etchant diffusion into the track. Depending on the special circumstances, this diffusion enhancement might be useful for the practical application of deep ion track doping.

Another recipe for dopant enhancement is to treat the ion track with special organic solvents before doping, whereby soluble fragments will leave the track[78].

Further, the amount of dopant which can permeate through the tracks in a given time gives us information about the effective open track radius, respectively cross section, see Table 1. Depending on system and measuring technique, typical effective open. radii of 1 to 10 Å, corresponding to open track cross sectipns of some 10^{-14} to 10^{-13} cm^2 are found (values derived for 100 MeV to 3 GeV heavy ion (Ar to U) tracks in PI, PC, PP, PET, and PMMA for penetration by water and LiCl salt solutions[22]). These "effective" values do however not necessarily give us an information about the real dimensions: an effective open track radius of, say 10 Å, can either mean that there exists a real hole with 100% transmission of 10 Å radius in the track core region, or it might mean that a region of 100 Å radius has an average transmission of only 1%. In general, the latter interpretation of the latent ion track as a porous zone of reduced density with enhanced permeability will be more realistic than the pinhole model, as the polymer destruction by ions usually leaves solid residuals. A remarkable exception is cellulose nitrate which, upon accurate irradiation conditions, decomposes into exclusively volatile reaction products (as demonstrated for 30 keV He to 300 keV Xe at fluences between some 10^9 to 10^{11} cm^{-2} [79]), and hence should form real pinholes along tracks of energetic ions. This has not yet been studied further.

These permeation experiments are usually performed for the stationary flow of gases or liquids through thin films with thickness << track length, long time after the electronic traps have been annihilated. It is recommendable to examine also the track permeation immediately after the track creation. By measuring the exact shapes of the dopant depth profiles along the track as a function of time, one has got a tool to follow the fate of the traps along the considered track regime.

By following the time dependence of a permeation process of water or aqueous salt solution through tracks, one can check for the influence of polymer **swelling** by water uptake of the polymer through the track. Polymer swelling is the result of hydratation, i.e. of a change in the polymer's chemical structure. This is indeed quite an important phenomenon which can decrease the effective track cross section (and hence the track's dopant uptaking efficiency, its conductivity etc.) by orders of magnitude. Observable swelling of e.g. irradiated PI or PC[22] around ion tracks sets in typically some 30 sec... 30 min after the onset of the water permeation, and continues up to 1/2... 5 hours at room temperature - depending on the system under consideration - before it has come to saturation. The amount up to which swelling influences the track's properties differs greatly, depending essentially on the material and the ion track density: reduction of track cross section and conductivity by factors between 2 and 1000 have been found, see e.g. Fig. 6a. Swelling can be even so dramatic that the effective open track radius vanishes. In this case, the only path remaining for the dopant is bulk diffusion. If a strong electric field applied is in this case, one observes repeated current breakthrough pulses along the partly closed tracks, Fig. 6b.

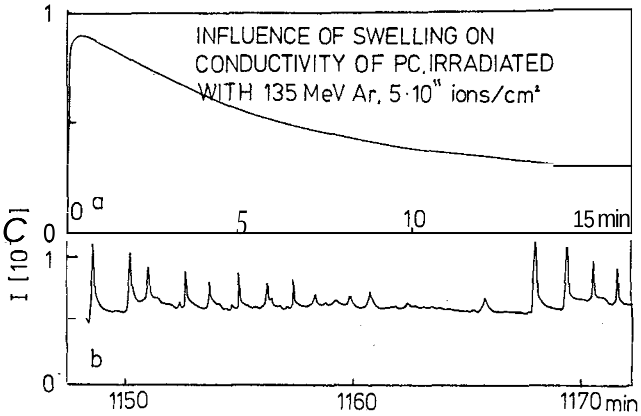

Figure 6: Influence of swelling on the water permeability of ion-irradiated polymers (shown here for 2 μm thick PC, irradiated with 1 x 10^{11} Ar ions of 135 MeV in this case), as determined by conductivity changes: (a) In the first few seconds after exposure to water, rapid water uptake of all the irradiated depth regime occurs through the latent ion tracks which act as 'irrigation pipes'. This is acompagnied by an increase in conductivity of several orders of magnitude. This effect comes to saturation after less than typically a minute. Subsequently, reduction in conductivity sets in, which is ascribed to a reduction in the effective latent track radius for permeation, as a consequence of swelling due to polymeric water uptake. (b) Occasionally the swelling is so strong that the effective latent track radius for permeation nearly vanishes. A sufficently high electric field applied in this case (here: 15 V per 2 μm thickness = 75 kV/cm), periodic breakthrough pulses can be observed.

Whenever an energetic ion impinges into a solid, it will emit Mach's supersonic pressure shock wave in the shape of a cone with opening angle tg $a = v_{\text{sound}}/v_{\text{ion}}$. It is this shock wave which will lead to *plastic deformation* of the polymer in the vicinity of the new ion track, in the way that the open polymeric structure itself as well as also older tracks are compressed. As a result the average effective track diameter decreases with increasing fluence. This has been repeatedly verified by both liquid and gaseous doping experiments (examples: LiCl solution and I vapor permeation into PI and PC[68,67]). From the dose dependence of the effective track diameter for permeation, one can estimate the compressability of ion tracks. It turns out that their compressability is lower by some orders of magnitude than the one of the pristine material[22] - in other words, ion tracks are harder than their environment. Due to the reduction of polymeric free internal volume by the ion-induced target compression, the dopant mobility will in general be reduced as well in tracks as in the pristine polymer itself.

This target compression will also give rise to an enhancement of the overall polymeric density. According to the above model, we should expect the density change to be correlated with the electronic energy transfer. It has been shown however[80] for low energy high dose irradiation (25-250 keV Ar, Kr, and Xe at fluentes of 10^{14} to 10^{16} ions/cm^2) of polystyrene that the densification is mainly due to energy transfer by atomic collisions with the target atoms. It has still to be found out by future experiments in which way the transition from the low energy high dose case to the high energy single ion track case will affect the target density.

There is a close similarity of what we call here "ion track doping" to what chemists use to call "grafting" of ion tracks in polymers. Three standard methods of grafting are available, (a) the consecutive, (b) the simultaneous, and (c) the peroxide methods[81]. In the first case, the polymer P_A is irradiated in the absence of oxygen prior to exposure of the liquid or gaseous monomer M_B which then bonds chemically to form the graft polymer P_AM_B. This corresponds to our hitherto most frequently applied ion track doping procedures from the gaseous or liquid phases. In the second case, the polymer P_A is irradiated whilst in contact with the monomer M_B. This is the counterpart of ion track doping from the solid phase. A potential drawback of this method is the eventually dominant - formation of homopolymers P_BOOH.

In the last case, the polymer is irradiated in the presence of air to produce peroxides P_AOOP and hydroperoxides P_AOOH, which are thermally or photodecomposed in contact with the monomer to form the graft copolymer P_AOP_B. The counterpart of this method in ion track doping would be ion track oxidation during or soon after formation, with subsequent indiffusion and bounding of the dopant.

Grafting has hitherto nearly exclusively been performed after Gamma-, X ray-, or electron beam irradiation. To our knowledge, it has been tried only once after swift heavy ion irradiation[81]. In this case, liquid styrene monomer was grafted by the peroxide technique onto 132 MeV O, 40.7 MeV Xe, and 472 MeV Xe ion tracks in PVDF. Interestingly, it turned out that the overall grafting yield was rather independent from the irradiation dose, i.e. the higher the track density in the polymer, the less the grafting efficiency per ion track. This - for the authors highly puzzling - effect can be easily understood by remembering the strong compaction of both the pristine polymer and neighboring ion tracks during formation of a new ion track: the higher the track density, the smaller will become the available free volume along a track; hence, the lower will be the graft yield.

It would be interesting not only to dope ion tracks with small electrically active ions such as Li^+, B^+, As^+, P^+, etc., but also with larger entities such as C_{60} (in order to increase the fullerene content above the natural production rate), and to see in how far they can be rendered immobile by trapping along the tracks - or in chemist's terminology, by grafting them onto the host polymer along the track. The first step in realizing such experiments is to establish a technique for unambiguous depth profiling of e.g. fullerenes in carbonaceous matter. Such as technique has just been developed by us[82], and we could already show that fullerenes really accomodate along latent GeV heavy ion tracks in PI up to depths of some **3** μm, after doping them with C_{60}/toluene solution at R.T. for 1 day.

Ion track oxidation - applied above for a first ion track grafting experiment - seems to be one of the crucial factors which limits the *stability* of polymeric implanted devices. Recent work[73,75] suggests that indiffusing oxygen preferentially bonds to surface-near polymer zones and to nuclear damage centers, and eventually also to the track-creating projectile ions, provided that they are chemically reactive. After prolonged time, the oxygen may even diffuse towards depths exceeding the ion track length. Not only oxygen, but also nitrogen has found to be eventually incorporated in irradiated polymers (as shown for the case of 2 keV He in PET at 10^{17} ions/cm^2 [83]). It is still unknown whether this finding can be generalized to tracks of higher energetic ions.

There exists another important question in the context of polymeric ion track doping for SITE applications, namely the question of dopant homogeneity. Do the dopants distribute homogeneously along the ion track, or do they eventually cluster at special sites along the track? At the moment, this question cannot yet be answered. Surely, the overall dopant distribution exhibits homogeneity along the ion tracks within the depth resolution of corresponding depth profiling techniques, i.e. typically within a few 100 Å. But this does not exclude possible dopant clustering in the sub-100 Å range. In order to answer this question, it will be necessary to perform small angle neutron (or X ray) scattering measurements on the dopant distribution in tracks, which has not yet been done hitherto.

IV.2 Theory for ion track doping

A first attempt has been made to describe the ion track doping theoretically[76]. For this sake, a set of rate equations has been established to follow the fate of the mobile dopant atoms, the saturable traps and the insaturable traps. The solution of these equations nicely shows that, with increasing fluence, first an excess of saturable traps is produced, which then are filled by the mobile dopant atoms. Once a dynamic equilibrium between creation and annihilation (doping) of saturable traps has been established, insaturable traps grow by capturing more dopant atoms, thus slowly becoming nucleation centers of future dopant precipitations.

This model is valid both for the single-ion-track (i.e. non-overlapping) as for the multiple-ion-track-overlapping case. It has however not yet been expanded to the more realistic case of an irradiated polymer having additional properties such as swelling and/or compaction. As ion tracks are essentially linear structures, dopant mobility in them can be described well by one-dimensional diffusion codes which include source (or sink) terms at the surfaces, and trapping and detrapping at saturable and unsaturable traps. Such a code has been developed recently by us from an older one[62-66], which was based on the mathematical technique of finite differences[84].

It was mentioned above that the diffusional behavior of the dopants will be of crucial importance for the long-term stability of the polymeric SITE devices. In fact, dopant mobility in irradiated polymers differs considerably from the well-known high mobility in unirradiated materials: on one side, radiation-induced polymer compaction reduces dopant bulk mobility considerably, due to the reduction of open volume for diffusion. (This can even lead to the extreme of case of bulk diffusion inhibition, as could be shown by us recently for the example of 135 MeV Ar irradiation of PI at 10^{10} to 10^{12} tracks/cm^2, with subsequent subjection to aqueous LiCl dopant: it was found in this extreme case that no Li dopant could penetrate into the polymer at all, whereas we could accomodate in unirradiated PI nearly up to 10^{19} Li atoms/cm^3 after just 1 h doping at room temperature.)

"Fresh" tracks (where electronic defects still exist) appear to act as quite efficient trapping centers for mobile dopants, thus depleting the surrounding polymer from eventually present dopants. This property efficiently counteracts the tendency of regular thermal diffusion to spread radially from the track all over the matrix. So one should expect that by bonding of the dopants to the electronic defects along the tracks the dopant distribution will gain the required long-time stability. Of course, this has still to be verified experimentally.

V. Summary and conclusion

This is a review about our present understanding of latent ion tracks in polymers, and their possible future application to nanometric electronic technology. In this overview we have tried to underline the basic general trends, and to avoid going into systemspecific details too much. The latter should be done later, when more detailed knowledge has been accumulated. Some progress has been made concerning the knowledge of external and internal geometric track structures, including the influence of compaction, the basic chemical reactions, and the intrinsic conductivity of latent tracks. The principal mechanisms which govern the doping procedure - diffusion, trapping, detrapping, and swelling - are known. Theories have been established for latent ion track formation and for ion track doping.

Based on this fundament, a deeper understanding of latent ion tracks has to be developed now by

1) improving the theoretical models by including all important parameters and less restrictive assumptions,
2) getting more information on the lateral ion track structure - e.g. concerning conductivity and chemistry, eventually by application of tomographic techniques[85,86,87],
3) learning how the composition, size and density of the current-carrying clusters are influenced by decisive parameters such as the deposited electronic energy density along the track, and on the material,
4) getting absolute production yields of polycyclic compounds and fullerenes along the tracks, and knowing which of the many possible polycyclic compounds are specifically created,
5) examining whether dopants in tracks cluster or distribute homoqeneously along them,
6) defining precisely the electronic energy level scheme of ion tracks as a function of their parameteres,
7) understanding the changes in electronic properties upon doping, and
8) handling better the factors which influence degradation and hence ion track stability.

Furthermore, the above proposed ways for precise positioning and contacting of individual ion tracks have to be tested. Only then it will be possible to tailor and arrange ion tracks so that they can fullfill specific requirements and be incorporated in future hyperdense electronic devices as elements of nanometric lateral dimensions.

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