

Conductivity of nanometer-sized ion tracks in diamond-like carbon films

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Amorphous diamond-like carbon films were irradiated with high-energy heavy ions like 1 GeV uranium or 340 MeV gold. The large energy deposition along the ion track leads to a transformation of the material from insulating diamond-like to conducting graphite-like carbon. The ion tracks form thin straight channels (nanowires) with a diameter of approximately 8 nm and a conductivity of the order of 1–10 S/cm. The conductivity in the tracks is up to eight orders of magnitude larger than in the surrounding material. The surface topography and the conduction properties of these channels were studied with an atomic force microscope. © 2003 American Institute of Physics.

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I. INTRODUCTION

Ion tracks offer the possibility to create structures in the nanometer range and therefore can be used as a tool in nanotechnology. Usually the tracks, e.g., in polymer foils, are etched and subsequently filled with a material different from that of the matrix. In this way, thin wires, tubules, and small devices can be built.¹

If the material change in the ion tracks is sufficiently large, the tracks may be used directly for nanostructuring, without the intermediate etching step. We report here on the creation of thin conducting channels in insulating diamond-like carbon (DLC) films by heavy ion irradiation. Preliminary data were reported before.^{2–4} In this article, we give a detailed description of the properties of the channels, the requirements on energy and type of the ions to create the channels, and on the dependence of the track formation on the DLC parameters.

The phenomenon described here is a single ion effect, i.e., each ion produces a conducting track. The proposed mechanism for the track formation is shown in Fig. 1: The high-energy heavy ion, e.g., 1 GeV U, loses a small part of its energy in the DLC film (thickness 1.3 μm or less) and is finally stopped deep inside the substrate (e.g., Si, the range of 1 GeV U in Si is 53 μm). For this ion type and energy, the energy deposition along the path in the DLC film is approximately constant and is so large that a local heating to several thousand degrees Kelvin occurs. After the cooling down, the material is conducting in a narrow cylinder around the ion path, as seen by local conductivity measurement with a scanning probe microscope. Apparently, in the track a conversion of the material from insulating sp^3 - into conducting sp^2 -bonded carbon has taken place. Transmission electron microscopy (TEM) measurements (see later) show that the

tracks have a diameter of approximately 8 nm. The tracks are continuous through the entire film, since a current is measured between the substrate and the scanning tip.

In other ion irradiation experiments of DLC films,^{5,6} graphitic regions were observed, too. These experiments were performed with low energy ions which stop in a region near the surface of the film. In these experiments the conversion from diamond-like to graphitic carbon is not a single ion effect but rather the result of a high dose implantation process. In addition no well defined structures like long thin filaments, as in the present case, are formed.

It has been proposed to use the track formation by heavy ion irradiation in field emission devices. Investigations are under way.^{2–4} The onset voltages and the homogeneity reached so far are not sufficient for commercial application of this effect. However, improvements are possible and the experiments are being continued. In the course of these investigations, a large amount of information has been accumulated on the ion track formation and their properties. The present article summarizes the results of these studies. The exceptional properties of these conducting channels might be also useful for other applications besides field emission, e.g., they might form parts of nanoelectronic devices on DLC basis.

II. EXPERIMENTAL DETAILS

Two types of amorphous DLC films have been studied in this work. One type was the highly sp^3 -bonded tetrahedral amorphous carbon (ta-C) films provided by different groups and produced either by the filtered arc technique⁷ or by the ion deposition method.⁸ The ta-C layer thickness varied between 40 and 700 nm. The films were deposited on highly n -doped standard silicon wafers. The second type of film was a hydrogenated amorphous carbon layer (a -C:H) produced commercially by plasma-activated chemical vapor deposition

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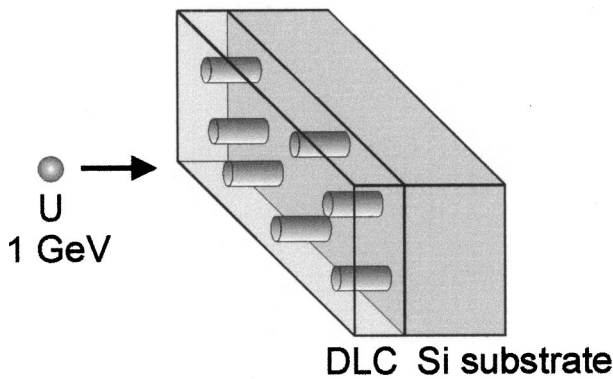


FIG. 1. Schematic production process of conducting ion tracks in DLC films by heavy ion irradiation. Each ion, e.g., uranium with 1 GeV energy, produces a track (indicated by a shadowed cylinder in the figure) in which the material is converted from diamond-like to graphitic carbon. The DLC layer is deposited on a heavily doped Si substrate.

(PACVD).⁹ The 1300-nm-thick *a*-C:H film was deposited on a glass substrate that was covered with a thin indium tin oxide layer working as a backcontact. Finally, an approximately 2- μ m-thick polycrystalline diamond layer on silicon was investigated.¹⁰ The samples were irradiated either with 340 MeV Au ions at the Hahn-Meitner-Institut Berlin (HMI) or with 1 GeV U ions at the Gesellschaft für Schwerionenforschung Darmstadt. The energy of the ions was chosen to be in the range of a few mega-electron-volts per nucleon in order to be in the maximum of the stopping power of the ions.¹¹

The conductivities of the channels obtained with U or Au where approximately the same. The local energy deposition of the ions along the track is apparently sufficient to convert the material from diamond-like to graphite-like in both cases. In an earlier experiment² we had used Xe ions and there lower conductivities of the tracks were measured. The energy deposition of these lighter ions is apparently not sufficient to convert the diamond-like carbon into graphite-like carbon completely all along the track.

The irradiated samples were subsequently investigated with an atomic force microscope (AFM) at ambient conditions in contact mode. A voltage applied between the AFM tip and the substrate allowed a simultaneous mapping of surface topography and current through the film.

III. RESULTS AND DISCUSSION

Figures 2 and 3 show three-dimensional images of the topography (top) and the simultaneously recorded current images (bottom) of two ta-C films with different film thickness, produced by the filtered arc technique. A one-to-one correspondence between the hillocks, which mark the ion impact sites, and the current peaks is clearly seen. The number of hillocks/current spots corresponds to the expected number of ion tracks calculated from the particle fluence of the ion beam. Figures 4 and 5 show the topography and the current for a single ion track together with a line scan.

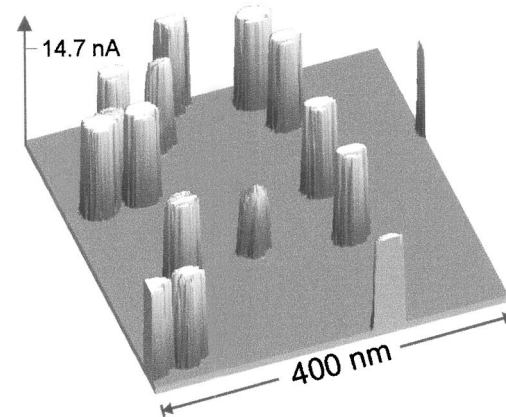
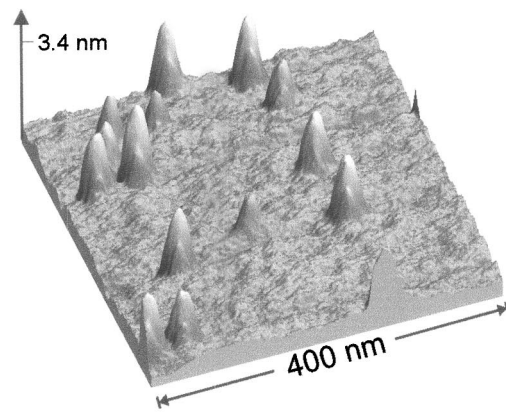


FIG. 2. Topography (top) and current (bottom) image of a 50-nm-thick ta-C film, produced by the filtered arc technique and irradiated with 1×10^{10} U/cm², scan area 400 \times 400 nm². The hillock height (top figure) is approximately 3 nm, the maximum current in the tracks (bottom figure) is 15 nA at 50 mV applied voltage. The AFM tip consisted of a Pt/Ir coated Si needle with a tip radius of 25 nm.

A. Hillocks and track diameter

The height of the hillocks at the ion impact position is typically 2–4 nm, their diameter, seen in the figures, amounts to approximately 25 nm. Since the measured width is strongly influenced by the curvature of the AFM tip, the real diameter is smaller. In the interior of the DLC layers, the track diameter is approximately 8 nm as seen by TEM in Fig. 6.

The contrast in the TEM measurement is due to a lower material density in the ion track area compared to the surrounding regions.¹² The density reduction is consistent with the assumed transformation from DLC ($\rho \sim 3$ g/cm³) to graphite ($\rho = 2.3$ g/cm³). The volume expansion in the individual track leads to a compression of material in the lateral region around the ion track and to the formation of hillocks at the surface. An important prerogative for the track formation is apparently that the amorphous DLC around the track is able to accommodate this compression. This is possible, since the density of DLC is well below of that of crystalline diamond. In crystalline diamond ($\rho = 3.5$ g/cm³), no tracks were observed after irradiation with 1 GeV U ions (see later).

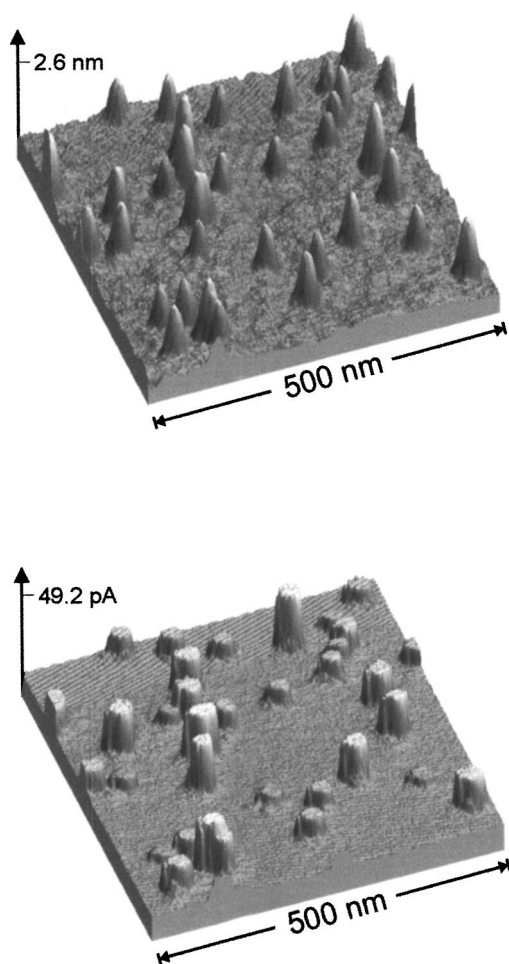


FIG. 3. Topography (top) and current (bottom) image of a 150-nm-thick ta-C film, produced by the filtered arc technique and irradiated with 2×10^{10} U/cm², scan area 500×500 nm². Note the much lower conductance (maximum current 50 pA at 500 mV applied voltage) of these tracks compared to those of Fig. 2. The AFM tip consisted of a Pt/Ir coated Si needle with a tip radius of 25 nm.

B. Electrical conductivity of the ion tracks

We found that the conductivity of the ion tracks depends strongly on the DLC material used. Two examples are shown in Figs. 2 and 3. The samples had nominally similar properties, i.e., the sp^3 content was 70%–80% or higher and they were produced from pure carbon targets. Nevertheless, the currents through the tracks differ by three orders of magnitude and, if normalized to the same film thickness and applied voltage, even by five orders of magnitude. Thus the conversion of the material to graphite in the track is much less perfect in the case of Fig. 3 than in the case of Fig. 2. The reason is probably a difference in the hydrogen content (see later).

We found no explicit dependence of the conductivity on the thickness of the DLC films in the range up to 700 nm. This is not obvious a priori since the volume expansion, necessary for the sp^3/sp^2 conversion, might be easier accomplished in regions near the surface (see hillocks) than deeper inside the film. However, we found that the conductivity of very differently thick films (e.g., the two 50-nm-thick films and the 700 nm film in Table I) is similar. In this case

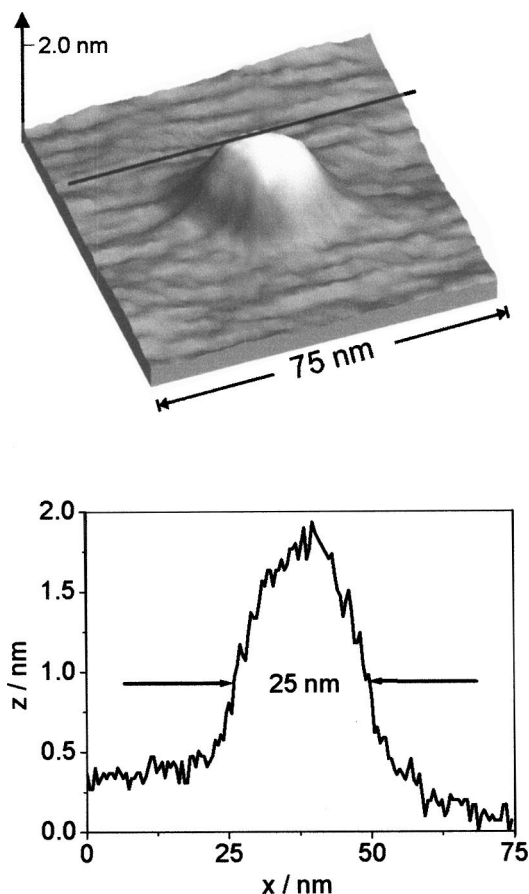


FIG. 4. Topography image of a single track (same sample as in Fig. 3), scan area 75×75 nm². In the lower part a line scan through the hillock is shown. The AFM tip consisted of a Pt/Ir coated Si needle with a tip radius of 25 nm.

the conductivity is even somewhat higher for the thicker film. In other cases also, no correlation between the conductivity and the thickness of the films was found. As seen from Fig. 7, the thinner 150 nm film has very badly conducting channels whereas those of the thicker 500 nm film are well conducting. There is of course also no inverse correlation. We had also very well conducting channels in 40-nm-thick films.

The reason for this independence of the thickness is probably that the volume expansion occurs in the radial direction (except very close to the surface) and that it is therefore independent of the depth in the film. Since the stopping power of these energetic ion is also independent of the depth (at least for films up to several microns), homogeneous track formation can be expected. Inhomogeneities occur only if the material composition, e.g., the hydrogen concentration, varies along the track.

Typical I – V curves for selected single ion tracks from the two different samples of Figs. 2 and 3 are shown in Fig. 7. An ohmic behavior is observed for the well conducting track whereas a strong nonlinearity shows up for the poorly conducting one. The reduced conductance in the later case is probably due to inhomogeneities along the track, i.e., in some parts of the ion channel the conversion from sp^3 to sp^2 is less complete and therefore locally poorly conducting regions interrupt the conducting filament.

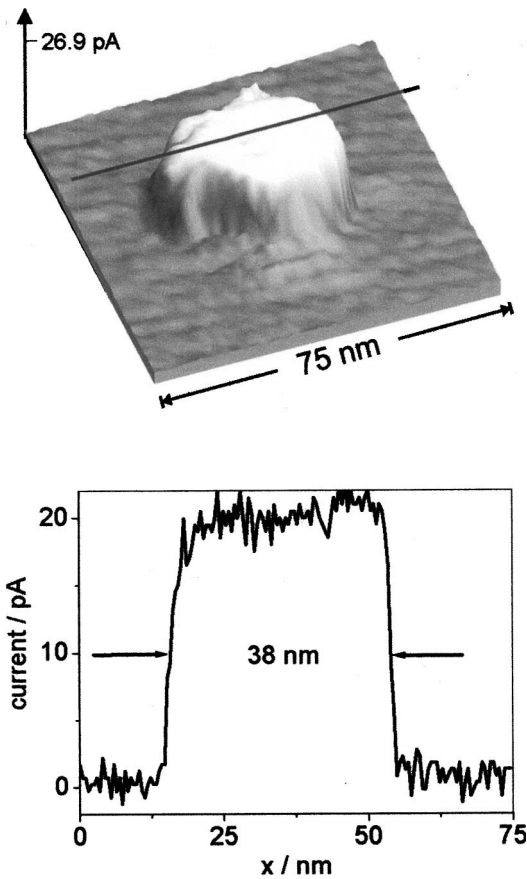


FIG. 5. Current image of a single track (same sample as in Fig. 3), scan area $75 \times 75 \text{ nm}^2$. In the lower part a line scan through the current peak is shown. The AFM tip consisted of a Pt/Ir coated Si needle with a tip radius of 25 nm.

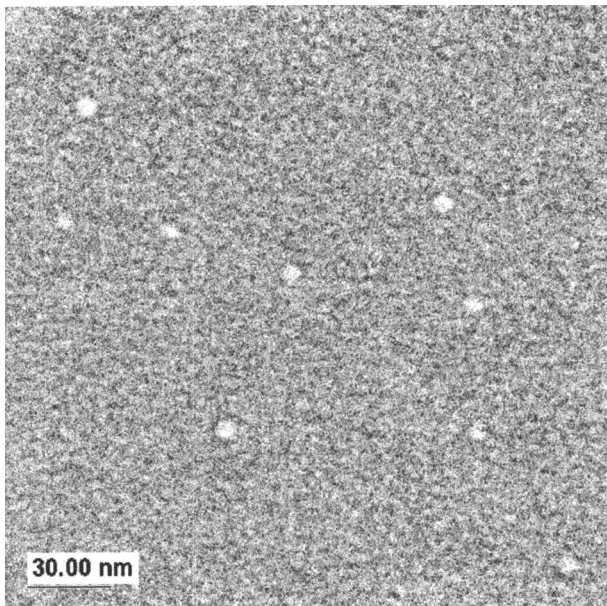


FIG. 6. TEM image of a 50-nm-thick ta-C film, produced by the filtered arc technique and irradiated with $1 \times 10^{10} \text{ U/cm}^2$. The white spots correspond to the ion tracks. Contrast is due to reduced density (less material) in the tracks.

TABLE I. Hydrogen concentration C_H and conductivity σ of the ion tracks in different samples. For the calculation of the conductivity, a track diameter of 8 nm was assumed and in case of nonlinear $I-V$ curves, a medium voltage value was chosen. The sample thickness d and the preparation methods are given: ion dep.=ion deposition (see Ref. 8), filt. arc=filtered arc (see Ref. 7), PACVD=plasma activated chemical vapor deposition (see Ref. 9).

Sample	Method	d/nm	$C_H/\%$	$\sigma/\text{S cm}^{-1}$
1	Ion dep.	700	0.06	9
2	Filt. arc	50	0.8	3
3	Filt. arc	50	4	1.3
4	PACVD	1300	30	0.001

Some more features of the tracks can be seen in Figs. 4 and 5. The height of the hillocks in the topography map (top) is real and is typically 2–4 nm. The apparent shape and width of the hillocks are determined by the AFM tip which had a nominal radius of less than or equal to 25 nm in the present case. The corresponding current spike (Fig. 5) has a larger width than the hillock and is flat at the top suggesting that full conductance is established as soon as some part of the tip comes into contact with the hillock. This observation gives a strong indication that the measured resistance is in-

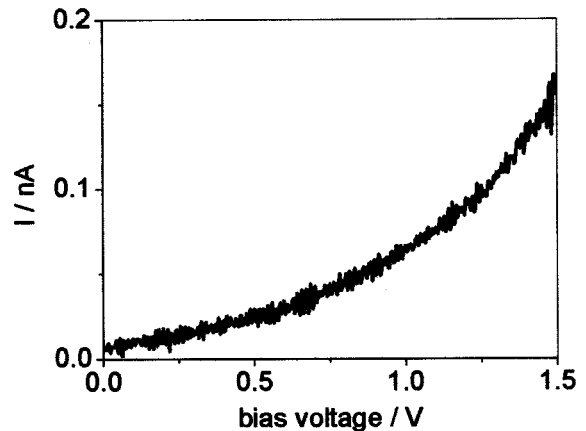
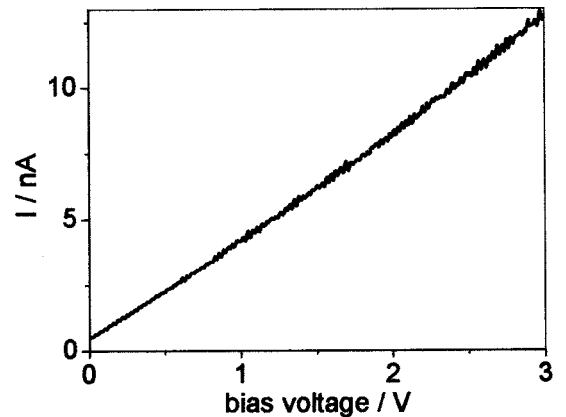


FIG. 7. Current/voltage curve of a single ion track for a well conducting (top) and a badly conducting (bottom) track. Note the different scales. The film for the top curve was produced by the ion deposition method (thickness 500 nm), that for the lower curve by the filtered arc technique (thickness 150 nm).

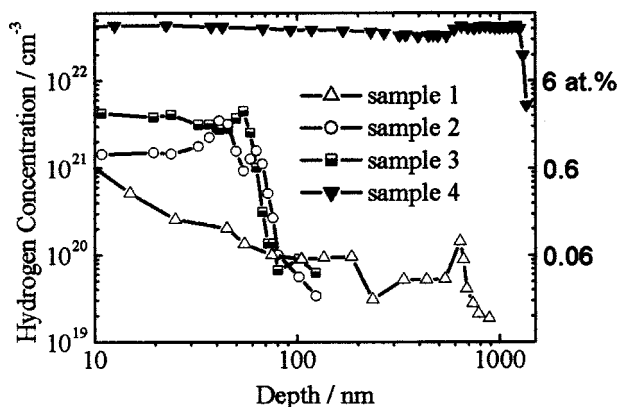


FIG. 8. Hydrogen depth profiles for different DLC films (numbers of the samples are the same as in Table I).

trinsic to the track and is not due to the contact between the tip and the track, since in the latter case a variation of the resistance would be expected due to changes in the quality of the contact.

The observed differences in the heights of the current spikes (see Fig. 3) are probably caused by small inhomogeneities in the material composition along the ion track. Even if these irregularities are small they can have a large effect on the current flow, since a one-dimensional current is very sensitive to weak parts along the line.

C. Hydrogen concentration and conductivity

Amorphous DLC layers contain always some hydrogen even if made from pure carbon. The reason is that hydrogen is taken up from the rest gas in the vacuum chamber during preparation of the layers. The amount of hydrogen in the samples depends on the preparation conditions, in particular on the chamber pressure and the speed of deposition. One may guess that the hydrogen concentration plays a role in the track formation since hydrogen stabilizes the sp^3 configuration of carbon and inhibits the transformation to conducting graphite. This was confirmed by our measurements.

Figure 8 shows hydrogen depth profiles for different DLC samples, measured with the nuclear reaction analysis method.¹³ One observes slight variations of the concentration over the thickness of the samples and a steep drop at the transition to the Si substrate. The overall hydrogen concentration differs markedly in the samples.

Obviously, the ta-C films contain less hydrogen than the a -C:H film. Table I summarizes the results. It can be seen that the conductivity is anticorrelated with the hydrogen concentration, the lower the hydrogen concentration of the DLC films, the higher the conductivity of the ion tracks. For the 1300-nm-thick a -C:H film produced by chemical vapor deposition, a 30 at.% hydrogen concentration is found. Barely any conductance of the tracks is induced by the ion bombardment in this film. For the others, the conductivity is in the same order of magnitude with a tendency to better conductivity for the less hydrogen containing samples. These data show that a hydrogen concentration of up to a few percent is tolerable and does not inhibit the formation of a conducting track.

D. Crystalline diamond films

Crystalline CVD diamond films¹⁰ ($d=2\ \mu\text{m}$) were also irradiated with U ions under the same conditions as described earlier. In crystalline diamond neither hillocks nor conducting channels were observed. The reason is probably that the molten carbon in the ion track recrystallizes in the diamond form due to the high pressure provided by the dense material around the track. Amorphous DLC is less dense and therefore can accommodate the expansion of the material in the track. Such an expansion is necessary for the conversion to graphite.

IV. CONCLUSIONS

Very thin conducting channels with a diameter of approximately 8 nm can be produced in amorphous DLC films by heavy ion irradiation. The length of these conducting channels is given by the thickness of the layers and can amount to several micrometers. The feasibility of making these channels has been demonstrated for layers up to 1300 nm thickness but an extrapolation to thicker films is possible since neither the ion range nor the production mechanism sets a limit below, e.g., 20 μm length. Thus, very large aspect ratios of 100–1000 can be obtained. This may be useful in field emission devices.

The energy deposition of the ions along their path must be very large in order to form these channels. We found that Au and U ions with energies in the maximum stopping power range, i.e., with energies of a few mega-electron-volts per nucleon, form well conducting tracks. The tracks observed with the lighter Xe ions under the same conditions are less well conducting.

The conversion of carbon from diamond-like to graphite-like in the ion tracks depends on the composition of the material. The highest conductivity in the tracks measured so far was approximately 10 S/cm. Compared to bulk graphite ($\sigma=727\ \text{S/cm}$)¹⁴ this value is still almost two orders of magnitude lower but it is much higher than the conductivity of the original DLC films which had a conductivity of typically $10^{-7}\ \text{S/cm}$. Thus, the conductivity ratio for on and off track measurements is eight orders of magnitude.

Hydrogen concentrations in the DLC films beyond several atomic percent as in a -C:H leads to considerable lower conductivities than obtained with almost hydrogen free samples. The possibility to vary the conductance of the channels by varying the hydrogen concentration of the films opens the possibility to design conducting wires with specific properties, e.g., nanowires with tunnel junctions. As a perspective, the conducting ion tracks could form parts of electronic devices build on DLC.

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