Fabrication and electrical transport properties of embedded graphite microwires in a diamond matrix

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Abstract
Micrometer width and nanometer thick wires with different shapes were produced $\approx$3 $\mu$m below the surface of a diamond crystal using a microbeam of He$^+$ ions with 1.8 MeV energy. Initial samples are amorphous and after annealing at $T \approx$ 1475 K, the wires crystallized into graphite-like structures, according to confocal Raman spectroscopy measurements. The electrical resistivity at room temperature is only one order of magnitude larger than the in-plane resistivity of highly oriented pyrolytic bulk graphite and shows a small resistivity ratio ($\rho(2\,\text{K})/\rho(315\,\text{K}) \approx 1.275$). A small negative magnetoresistance below $T = 200\,\text{K}$ was measured and can be well understood taking spin-dependent scattering processes into account. The used method provides the means to design and produce millimeter to micrometer sized conducting circuits with arbitrary shape embedded in a diamond matrix.

Keywords: embedded microwires, confocal raman, magnetotransport properties

(Some figures may appear in colour only in the online journal)

1. Introduction
Diamond is a natural allotrope of carbon, transparent, insulating and the hardest natural material on earth. Vavilov and coworkers [1] have shown that it is possible to induce graphitization in diamond by ion irradiation. One of the first works trying to change the transport characteristics of diamond showed that one can produce conducting regions by carbon implantation on the diamond surface [2]. The value and temperature dependence of the resistivity of ion implanted diamond layers was found to be similar to that of amorphous carbon produced by sputtering [2, 3]. In a recently published study, micro-channels were fabricated in single-crystal diamond using a microbeam of He$^+$ ions in the MeV energy range [4]. The conductivity of the microchannels was improved substantially by annealing treatment, achieving values similar to polycrystalline graphite [4]. The possibility to create a relatively long conducting path of micrometer or even narrower width inside diamond is interesting for possible electrical device applications where the main electronic circuit remains well protected by the highly insulating and biocompatible diamond matrix.

On the other hand, early studies of 100 keV nitrogen and carbon implanted into nano diamonds, show ferromagnetic hysteresis even at room temperature [5], and recent studies on micrometer small areas on single crystal diamond after irradiation with 2.2 MeV proton micro-beams provided hints on the existence of magnetic order [6, 7]. The authors found that for fluencies below $8.4 \times 10^{17}$ cm$^{-2}$, a very weak magnetic response was observed at room temperature. In both mentioned studies, the origin of the magnetism was related to the defects produced by the irradiation.

In this work, a similar technique as in [4] was used to produce conducting microwires beneath the diamond surface.
using He$^+$ irradiation. After two annealing steps, different degrees of graphitization of the microwire were reached. Our aim was also to check, whether those conducting structures can show some degree of magnetic order. As was shown in several works in the past, defects like vacancies and/or non-magnetic ions within the graphite structure as well as in a large number of materials, can trigger magnetic order even above room temperature, a phenomenon called defect-induced magnetism (DIM) [8]. Therefore, one can expect that a defective graphitic structure, like the one we produce within the diamond structure by ion irradiation and after annealing, may show some magnetic response. The possibility of having conducting and magnetic microwires within a pure diamond matrix provides a further interesting option for future application.

2. Experimental details

2.1. Preparation of sub-micrometer width and millimeter long graphite wires

To produce a graphite-like microwire (GLM) inside diamond, we used a polished single crystal (100) diamond of the company Element Six, with a nitrogen concentration <1 ppm and a boron concentration <0.05 ppm. The diamond sample was produced by chemical vapor deposition (CVD) with dimensions $2.6 \times 2.6 \times 0.3\text{ mm}^3$.

The He$^+$ ion irradiation used to produce the wires in diamond was realized using a very stable high-energy ion nanoprobe in the linear accelerator LIPSION at the University of Leipzig. The wires within the diamond structure were produced with a microbeam of 1.8 MeV energy and an ion current of 2.4 nA.

In our accelerator facilities, using the high-energy ion nanoprobe, we can obtain a sub-micrometer ion beam diameter [9] using a magnetic quadrupole double lens system. Also, to produce the long size microwire inside the diamond, we need a high ion current and energy stability. This two important conditions are fulfilled with the ion accelerator Singletron$^{\text{TM}}$ from the Dutch company High Voltage Engineering Europa [10]. The ability to produce complex two dimensional structures (2D) is obtained with the help of a raster unit, which is located between the quadrupole lenses and the sample. Using a self-made program we can produce any desired 2D structure by deflection of the ion beam. According to our experimental conditions, we can continuously deflect the He$^+$ ion beam within a total area of $(1780 \times 1780)\text{ mm}^2$. As examples, using a beam diameter of about $1\mu m$, a microwire of similar width, see figure 1(a), inside a diamond substrate was produced and after annealing, we have graphitized the wire. As a proof of the ability of our ion nanoprobe to produce complex structures (see also other structures in supplementary information (stacks.iop.org/JPhysD/50/145301/mmedia)), we have prepared a graphitized loop, see figures 1(b)–(d), which can be used to generate small magnetic fields and/or microwave fields in order to manipulate, e.g. the spin states of NV centers in diamond. The images in figure 1 were obtained with a self made confocal optical microscopy implemented with a lens (Olympus MPlanApo 100x/NA0.95), a laser beam with $\lambda = 532\text{ nm}$ and a lateral and depth resolution of $\approx300nm$ and $\approx1\mu m$ respectively. Summarizing, we are able to produce long wires with a width of $\approx1\mu m$ and desired shape. These results show the possibilities to produce 2D graphitized structures inside diamond for future applications.

2.2. Irradiation effects on diamond and annealing treatments

After irradiation of diamond with He$^+$ ions of energy and fluence similar to the ones we used in this work, an amorphous phase is produced at the region where the irradiated ions stop [1]. By annealing at high temperatures, this amorphous carbon region can later be transformed into graphite or back to diamond structure, which is correlated to the density of vacancies produced by the irradiation. There exists an estimated critical vacancy density $N_{0} \approx 10^{22}\text{ cm}^{-3}$ [11] to induce graphitization in the material after ion irradiation at room temperature and after annealing. According to other experimental work and supported by molecular dynamics simulation, the critical density necessary to graphitize the surface [12] was determined to $N_{0} \approx 9 \times 10^{22}\text{ cm}^{-3}$. Raman measurements indicate that after annealing above $T \approx 700\text{ K}$ the graphitization process begins by formation and growth of $sp^2$ bonded nanoclusters [12].

We have irradiated the diamond sample with He$^+$ ions using a fluence of $\phi = 5.5 \times 10^{17}\text{ cm}^{-2}$, which gives a vacancy density $N_{v} \geq 9 \times 10^{22}\text{ cm}^{-3}$ in a specific depth, see figure 2(a) estimated from Monte-Carlo simulation done by SRIM [13].
2.3. Electrical contacts to the Microwire, transport and Raman measurements

The contacts for the electrical measurements have to be done at the surface of the substrate. For this purpose we used a commercial copper grid used for transmission electron microscopy (2000 mesh), having the advantage that the grid has a wedge shape allowing a continuous change of the He\(^+\) ion penetration depth inside the diamond sample, see figures 2(b)–(d). At the surface of the sample and at a distance of \(\approx 450\ \mu m\), square-like contacts with dimension of \(\approx 50 \times 50\ \mu m^2\) were prepared in direct electrical contact with the embedded microwire, figure 2(c). A similar but more complicated method was already used in [4]. Afterwards, the electrodes were made by sputtering of Cr/Au directly at the top of the square-like regions at the surface, after an electron beam lithography process. Finally, the contacts to the chip carrier, where the sample was fixed for the transport measurements, were produced using silver paste and gold wires.

Resistance measurements were carried out using the conventional 4-points method using an AC Bridge (Linear Research LR-700) in the temperature range of 2–310 K. For the current-voltage (\(I-V\)) measurements, we used the Keithley DC and AC current source (Keithley 6221) and a nanovoltmeter (Keithley 2182). The resistance and its magnetic field dependence were measured with a commercial cryostat from Oxford Instruments with a superconducting solenoid that provides a maximum field of \(\pm 8\ T\) perpendicular to the main axis of the microwire.

Raman characterization was carried out at room temperature using a confocal micro-Raman microscope (alpha300+, WITec company) with an incident Laser light of \(\lambda = 532\ nm\), a lateral resolution of \(\approx 300\ nm\) and axial resolution of \(\approx 900\ nm\).

3. Results and discussion

3.1. Raman results

To get information about the structural properties of the measured wire produced inside the diamond sample, we have used CRS, which is probably the only method to get information about the microstructure produced inside the diamond without destroying it. Figure 3 shows the Raman results.

The curve named CR1 in figure 3 was measured at the surface of the as-received diamond sample. The Raman peak at \(\approx 1332\ cm^{-1}\) is the characteristic peak for carbon in the diamond structure. The small bump at \(\approx 1430\ cm^{-1}\) is related to the appearance of disorder at the surface of the sample during the polish process [16]. The curve CR3 obtained after irradiation and the second annealing was measured with the focus at \(\approx 3\ \mu m\) depth from the diamond surface. The results confirm the estimated depth from the SRIM calculations. The results of the curves CR2 and CR3 show three characteristic peaks, one at \(\approx 1332\ cm^{-1}\) corresponding to the diamond structure, a second peak due disorder graphite, the so-called \(D\) peak at \(\approx 1350\ cm^{-1}\). The third and the most important peak for the characterization of graphite structure, called the \(G\)-peak, appears at \(\approx 1580\ cm^{-1}\) as a consequence of the double degenerate zone center \(E_{2g}\) mode.
Our Raman results resemble those obtained in [12], specially for similar annealing temperatures. The results CR2 and CR3 can be very well fitted using Gaussian functions centered at the aforementioned Raman peaks. The results are shown as continuous black lines in figure 3 and describe very well the experimental results. From the fits we get also information about the peak intensity $I_G$ and $I_D$ corresponding to the $G$ and $D$ peak respectively. From these results it is possible to estimate the crystal size $L_a$ using equation (1):

$$L_a(nm) = (2.4 \times 10^{-10}) \lambda_1 \left( \frac{I_D}{I_G} \right)^{-1},$$

which correlates the crystal size $L_a$ with the integrated intensities of the $D$ and $G$ peaks and the laser excitation wavelength $\lambda_1 = 532$ nm. Using this equation, we obtain $L_a = 8 \pm 2$ nm, similar to the results of Rubanov et al using transmission electron microscopy [18], where diamond samples were irradiated with $He^+$ ions using a fluence between $3 \times 10^{16} - 10 \times 10^{16}$ cm$^{-2}$ followed by an annealing for 1 h at 1400 °C.

3.2. Temperature dependence of the electrical resistance

After the first annealing the sample shows (at low temperatures) non-linear $I$–$V$ curves, indicating that non graphitized regions remain in the sample which act like barriers. It has been shown that, whenever a barrier is present between the conducting grains, the resistance $R(T)$ and magnetoresistance (MR) depend on the applied current like in multi-wall carbon nanotubes bundles [19]. Here we do not discuss the $R(T)$ and $I$–$V$ results after the first annealing (see supplementary information) because our interest lies in the behavior of the transport properties in the Ohmic regime, without any influence of potential barriers, this is obtained after the second annealing treatment.

The resistance results after the second annealing are shown in figure 4. The experimental results from 2 K to 315 K are shown as open symbols. The observed temperature dependence is clearly different from the one we obtained after the first annealing treatment. The resistance ratio $R(315 K)/R(2 K) \approx 1.275$ is one order of magnitude smaller than the one after the first annealing, and of the same order as for nano-graphite films [20] and few layer graphene films [21, 22]. The current–voltage curves after second annealing are linear in all measured temperature range and are shown in the supplementary information.

The temperature dependence of the resistance, see figure 4, indicates the existence of two different regions, one below and the other above $T \approx 75$ K. We have identified (see supplementary information) that the dominant mechanism at high temperatures is the so-called Mott variable range hopping (VRH) [23], given as:

$$R_{VRH}(T) = R_0 \exp \left( \frac{T_0}{T} \right)^{1/4},$$

where $T_0$ is a characteristic temperature coefficient defined as: 

Figure 3. Raman results measured at the surface and inside the diamond substrate. The curves CR1 and CR3 were obtained fixing the focus of the Raman microscope at the surface (CR1) on the as-received sample, and in a depth of 3 μm (CR3) after irradiation and second annealing. The curve CR2 was obtained from the measurements at the surface after $He^+$ irradiation and the second heat treatment. The continuous lines through the experimental curves are the fits to the data. The insets show confocal Raman images, in (a) the loop shown in figure 1 can be seen, (b) the image shows a close up of a graphite wire and (c) shows an area perpendicular to the surface, i.e. as a function of the sample depth. The bright part represents the $G$-graphite peak.

Figure 4. Temperature dependence of the resistance (after the second annealing). The inset shows the resistance versus $T^{-1/4}$. The continuous lines are the results of the fits.
and $\xi$ is the localization length, $N(E_F)$ the density of states at
the Fermi level and $R_{ij}$ is a constant prefactor. In order to
fit the resistance over all the measured temperature range,
we need to include an extra transport mechanism in parallel (we
have also checked other configurations, see supplementary
information) given as:

$$R_{\alpha}(T)^{-1} = R_{\text{VRH}}(T)^{-1} + R_m(T)^{-1},$$

with

$$R_m(T) = R_0 + R_aT + R_b \cdot \exp(-E_a/k_B T),$$

a metallic-like contribution, which dominates at low tempera-
tures. The coefficients $R_0$, $R_a$, $R_b$ as well as the activation
energy $E_a$ are free parameters. $R_0$ a residual temperature
independent resistance that we include in the metallic-like
contribution only, provides a saturation of the resistance at
low temperatures. The contribution $R_a(T)$ was already used
to explain the temperature dependence of the resistivity in
bulk graphite [24], few layer graphene samples [22, 25] and
nano-graphite thin films [20]. Its origin is related to certain
interfaces formed between the graphite crystallites. We can fit
the experimental resistance data to equation (4) very well.
The results are shown as continuous lines in figure 4 and the fitting
parameters are listed in table 1.

The inset of figure 4 shows clearly the temperature ranges
where each transport mechanism dominates the electric trans-
port. We have assumed a localization length of $\xi \approx 0.5$ nm [26],
which was estimated for similar samples, by means of spectro-
scopic ellipsometry, Raman spectroscopy and transport meas-
urements. The localization length used in this work is close
to the value of 1.2 nm used by Hauser et al [2]. We estimate
$N(E_F) \sim 2.3 \times 10^{24}$ $\text{eV}^{-1} \text{cm}^{-3}$, which is of the same order as
reported for graphitic materials [27] and multi-walled carbon
nanotubes [28]. Values of $N(E_F)$ of several orders of magni-
tude lower than our result were found for similar ion irradiated
diamond, but these samples were not annealed [2, 29] or even
measured when a barrier was present [29]. Finally, the calcu-
lated resistivity of the GLM is $\rho_{(300 \text{~K})} = 7 \ldots 8 \times 10^{-5}$ $\Omega \text{~m}$, a
one order of magnitude larger than bulk graphite in-plane resis-
tivity ($\rho_{(300 \text{~K})} \approx 0.5 \times 10^{-5}$ $\Omega \text{~m}$) [21, 22, 30] or the resistivity
of few layer graphene ($\rho_{(300 \text{~K})} \approx 3 \ldots 50 \times 10^{-5}$ $\Omega \text{~m}$) [21, 22]
and three orders of magnitude lower than pure amorphous
carbon ($\rho_{(300 \text{~K})} \gg 10^{-2}$ $\Omega \text{~m}$) [31, 32]. However, the GLM
resistivity is comparable to other nano-graphite thin films
prepared by chemical vapor deposition and aerosol assisted
chemical vapor deposition ($\rho_{(300 \text{~K})} = 3 \ldots 8 \times 10^{-5}$ $\Omega \text{~m}$) [20].
From experiments it is known that the resistivity ratio between
the in-plane ($\rho_{\|}$) and out-of-plane ($\rho_{\perp}$) resistivity in graphite
is in the order of $\rho_{\|}/\rho_{\perp} \approx 10^3 \ldots 10^4$ [30, 33], indicating that the
transport in our sample is dominated by the in-plane resistivity.
Further, it means that the produced GLM have nano-crystals
with a preferential c-axis normal to the substrate surface.
The obtained transport characteristics of the produced GLM are
important for future applications, because the resistivity and
its temperature dependence make this GLM interesting to be
used for electronic circuits in a broad temperature range.

### 3.3. Magnetoresponse

To obtain any information of the magnetic properties of the
GLM there are no experimental methods other than transport
because the wire is not only embedded inside the diamond
matrix but also its mass is too small to be measured with
commercial magnetometers. The magneto-transport measure-
ments at different constant temperatures were done with an
external magnetic field applied perpendicular to the current
and main axis of the GLM. The results of the magnetoresistance
$MR$ defined as $MR = [R(B) - R(0)]/R(0)$ are shown in figure 5.

We observe a magnetic field dependence of the resistance,
which is positive at $T = 2 \text{~K}$, and negative in the field range
of $-3 \mathbf{T} < B < 3 \mathbf{T}$ at 5K and 10K. At temperatures $T > 10 \text{~K}$
the $MR$ is negative in all the field range. The positive $MR$
at very low temperatures can be understood as a consequence
of the strong Lorentz contribution. This tends to vanish at
high temperatures. The negative $MR$ can be attributed to a
spin dependent scattering process. Due to the relatively high
temperatures and magnetic field range where the negative
$MR$ is observed, we can rule out weak localization effects.
According to the theory developed by Toyozawa [34] and later
modified by Khosla and Fischer [35], the $MR$ of systems with
localized magnetic moments can be described using the fol-
lowing equation:

$$MR = -P_1 \ln \left(1 + \frac{B^2}{P_2^2} \right) + \frac{P_3^2 B^2}{1 + P_4^2 B^2}.$$
that the experimental results at all measured temperatures, indicating the existence of spin dependent scattering in our GLM, however, this is not an evidence of magnetic order. Similar results were already observed in magnetic samples where the magnetic order was triggered by defects, as in proton irradiated graphite [37], proton irradiated ZnO:Li microwires [38], as well as in samples with magnetic elements like in single walled carbon nanotubes filled with Fe nanorods [39].

The magnetic scattering contribution in our samples can be explained as a consequence of defects present in the disordered graphite structure of the microwire. Because of the preparation method used to produce the microwire, we can rule out the presence of magnetic impurities. The almost zero MR for temperatures \( T \gtrsim 200 \) K opens the possibility to use GLMs in a device under application of high magnetic fields.

### 4. Conclusion

In this work we have prepared a graphitized wire of 1350 \( \mu m \) length and lateral area of \( \approx 15 \mu m \times 130 \) nm inside a diamond matrix by means of He\(^+\) irradiation and heat treatment. After annealing, the resistivity of the microwire is only one order of magnitude larger compared to graphite. Also, its temperature dependence can be well described by the parallel contribution of VRH and a metallic-like conduction, similar has been observed in other carbon based materials. The measured magnetoresistance can be well described by a semi empirical model, which takes into account a spin dependent transport mechanism used to describe the MR of magnetic diluted semiconductors as well as magnetic carbon-based materials, related to the defect-induced magnetism.

In summary, the low resistivity \((\rho(300 \, K) = 7 \ldots 8 \times 10^{-5} \, \Omega m)\), the small resistivity ratio \((\rho(2 \, K)/\rho(315 \, K) \approx 1.275)\) and the very small magnetoresistance, make the graphitized wires inside diamond candidates to be used as circuit elements. Our microwire preparation can be taken as basis for the production and future application of GLMs inside diamonds. For example, a GLM can be used to produce a magnetic field by a loop inside the diamond and thus allows, e.g. further manipulation of NV-centers for future application in quantum computation. Another possibility is the application in biology. Considering that diamond is a biocompatible material, the here used method would enable the design and production of complete electrical circuits that can allow the monitoring of electric signals in situ the human body.

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