Influence of Interfaces on the Transport Properties of Graphite revealed by Nanometer Thickness Reduction

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Abstract
We investigated the influence of thickness reduction on the transport properties of graphite microflakes. Using oxygen plasma etching we decreased the thickness of highly oriented pyrolytic graphite (HOPG) microflakes from \(\sim 100\) nm to \(\sim 20\) nm systematically. Keeping current and voltage electrodes intact, the electrical resistance \(R(T)\), the magnetoresistance (MR) and Raman spectra were measured in every individual sample and after each etching step of a few nm. The results show that \(R(T)\) and MR can increase or decrease with the sample thickness in a non-systematic way. The results indicate that HOPG samples are inhomogeneous materials, in agreement with scanning transmission electron microscopy images and X-ray diffraction data. Our results further indicate that the quantum oscillations in the MR are not an intrinsic property of the ideal graphite structure but their origin is related to internal conducting interfaces.

1. Introduction

Experimental results of the temperature dependence of the electrical resistance of bulk highly oriented graphite samples of good quality reported in the literature show usually a metallic-like behavior. This behavior, together with Shubnikov-de Haas oscillations, were taken as evidence for the existence of a three dimensional Fermi surface and the band structure of graphite was proposed using tight binding calculations with up to seven free coupling constants [1]. In the last years, however, new experimental results on graphite bulk and mesoscopic graphite samples have shown that the temperature dependence of the resistance [2, 3, 4] and the resistivity [4, 5] have a thickness dependence incompatible with the assumed metallic- or semimetalliclike behavior. High resolution X-ray diffraction (XRD) data and scanning transmission electron microscopy (STEM) pictures of highly ordered pyrolytic graphite (HOPG) as well as natural graphite samples revealed a system far from being homogeneous and single phase [6], as assumed in most of the common literature in the past. The existence of two stacking orders, Bernal and in a smaller amount rhombohedral, the interfaces between those orders and the interfaces between twisted crystalline regions around a common \(c\)-axis [7, 6], make usual bulk graphite samples an inhomogeneous system, structurally as well as electronically.

A recently published study on the temperature dependence of the resistance of more than twenty samples of different origins and thicknesses obtained in four different laboratories, provided a semiquantitative explanation for a rather complicated temperature behavior [5]. The simple model assumes three different resistors in parallel: One from the Bernal and one from the rhombohedral stacking orders and a third one due to interfaces [5], a model similar to the one proposed in [8] but including the rhombohedral stacking contribution. The samples with different thicknesses were prepared in those studies by exfoliation [2, 3, 4, 5]. It means that each sample after reaching a given thickness, was electrically contacted with four electrodes to measure the resistance. The resistivity vs. thickness of those samples reveals a clear tendency, namely,
Towards an increase by reducing the thickness. The observed increase in the resistivity is not related to an extra disorder produced during the sample preparation process, as Raman measurements indicate [5]. For a thickness below \( \sim 100 \text{ nm} \), the temperature dependence of \( R(T) \) tends to be more semiconducting-like [4, 5].

A closer look at the reported thickness dependence of the resistivity [4, 5] reveals a certain scattering around the main tendency. This scattering is much larger than the experimental errors and, as we will show in this work, is related to the inhomogeneity of each graphite sample. This knowledge is of importance if one wants to compare the behavior of nominally “similar” samples prepared from the same or different batches.

To clarify this point further, let us use as an example a STEM picture of a HOPG sample with grade A (rocking curve width \( \sim 0.4^\circ \)), as studied in this work, see Fig. 1. This STEM picture was taken with the e-beam parallel to the graphene planes of the sample. The different grey colors indicate either different stacking and/or twisted crystalline regions around the common \( c \)-axis. As pointed out in recent studies [4, 8, 5] some of those interfaces show a metallic (and/or superconducting) behavior (see [6] for a review). Therefore, if the current input and voltage electrodes are localized, as usual, at the top free graphene layer of the sample, due to the large anisotropy in the resistivity \( \rho_c \gg \rho_{c,b} \) the near surface region at the top of the sample provides the main contribution to the measured voltage.

In other words, if an interface due to, e.g., twisted graphene layers (as clearly measured in early studies [9]), is located under the top surface layer, the measured voltage will be smaller than in the case where such an interface is localized deeper in the sample interior. This is expected because twisted graphene layers [9, 10, 11, 12, 6] as well as at the interfaces between Bernal and rhombohedral stackings [13, 14] show a fundamentally different and higher density of states than ideal Bernal stacking. This is basically the reason for the existence of higher conductivity most of the relatively large and thick graphite samples show [8, 5, 6].

On average and from the STEM pictures obtained in HOPG samples of ZYA grade, the density of interfaces is of the order of \( \sim 2 \times 10^{-3} \), which means \( \sim 2 \) interfaces every 103 graphene layers. However, STEM pictures, obtained at relatively low electron energies of the order of 30 keV, have two restrictions: On one side they have a finite resolution, which does not always allow us to recognize interfaces between regions twisted with a very small angle. On the other side those STEM pictures scan in general only a very small part of the whole HOPG sample, roughly \( \sim 1 \mu \mathrm{m}^2 \) area of a region parallel to the \( c \)-axis. The measured samples, however, are several microns long. Within this length, even for a constant density of interfaces, interfaces exist at different distances from the surface. This fact together with the grain boundaries that exist at the end of the single stacking regions, see, e.g., the STEM picture in Fig. 1, mean that the input current does not always flow at one single and short interface closest to the surface, but it can flow through different interfaces at different locations. Etching a few nm from the surface can or cannot remove most of the interfaces that affect the measured voltage. In other words, the observed changes in the resistance may appear as due to a larger interface density.

From XRD data [7] we know that the percentage ratio between the rhombohedral and Bernal stacking orders is < 5% to \( \sim 20\% \) in bulk samples of the selected ZYA grade sample. From STEM pictures we guess that the layers of the rhombohedral stacking order can have a thickness between a few nm to 20 nm, whereas the Bernal stacking can have a thickness between a few tens of nm to \( \gtrsim 400 \text{ nm} \). As will be clear in the discussion, although our phenomenological model fits extremely accurate the

Fig. 1: Transmission electron microscope pictures of a thin lamella taken from the same batch as the samples measured in this study. The sketch around the picture shows the position of the electrodes at the top graphene layer. The usual width and length of the microflakes were a few micrometers with thickness below \( \sim 100 \text{ nm} \), see text for more details.
temperature dependence of the resistance $R(T)$, it is not possible to estimate the absolute thickness of the layers from the experimental data but the ratio between the two stacking orders.

The main aim of this work was to study the behavior of the resistance as a function of thickness by thinning the samples in steps of a few nanometers. In this work we not only studied the changes in the resistivity and its temperature dependence but also the magnetoresistance. In contrast to all other published studies we investigated this behavior without changing the corresponding electrodes. This allowed us to observe a clearly sample dependent behavior of the resistance with thickness and, in some cases, even a non-monotonous one. A gentle oxygen plasma etching procedure was used to decrease systematically the sample thickness between the protected voltage and current electrodes. The appearance of disorder at the sample free surface generated during the etching process was investigated by means of confocal Raman spectroscopy. The overall results support the view that the graphite samples are, electronically speaking, highly inhomogeneous with an important contribution from internal interfaces.

2. Experimental procedures

The mesoscopic graphite samples used for our experiments were obtained from a bulk HOPG material from Advanced Ceramics, with a rocking curve of 0.4° and metallic impurities in the ppm range [15]. The flakes were produced using a rubbing method already described in previous publications [4]. After pre-selecting the flakes with an optical microscope they were attached on the top of silicon substrates capped with 150 nm thick insulating silicon nitride ($\text{Si}_3\text{N}_4$). After further selection of suitable samples, electron beam lithography was used to print the structures for the electrodes, which were sputtered with a bilayer of Cr/Au with a thickness of $\approx 5$ nm and $\approx 30$ nm, respectively. The main contact area of the electrodes was at the top of the sample. Although the Cr/Au deposited film can touch part of the edges of the flakes, the results presented in this work indicate that the main part of the current input takes place at the large top electrode area.

Oxygen plasma etching was employed to reduce the thickness of the samples. The etching was done using passive oxygen plasma etching (ZEPTO), with a gas flow of $\approx 80$ sccm. Experiments were performed at a pressure of $\approx 1.1 \times 10^{-2}$ mbar. The oxygen plasma was generated by a microwave generator at a power of 50 W and a frequency of 13.56 MHz. Samples were exposed to the oxygen plasma for different times. The longest treatment time in a single step was $\approx 6$ minutes, with exception of the last step for sample GF2. Figure 2 shows the measured thickness of six different mesoscopic flakes as a function of the total exposure time to the oxygen plasma. We obtain a similar etching slope $\approx 0.7 \pm 0.1$ nm/min for all the samples within the exposed total time and the used parameters.

When placing the sample plus substrate into the oxygen plasma chamber, the whole substrate including the sample as well as the electrodes would be exposed to the plasma. In order to avoid the destruction of the electrodes through the oxygen etching, part of the sample and the electrodes needed to be protected with an insulating material. We deposited 150 nm insulating SiN$_x$-layer on the top of a part of the sample by means of plasma enhanced chemical vapor deposition (PECVD). SiN$_x$ is insulating and stable enough to be used as protection for the contacts against oxygen plasma etching. Even after several etching processes, the SiN$_x$-layer remained unchanged and its protecting purpose retained. Only a window without the SiN$_x$-layer was left (using electron beam lithography with PMMA), in order to etch the samples between the electrodes afterwards, see Fig. 1.

The temperature dependent resistance and magnetore-
tance of the samples were measured in a commercial He cryostat, within a temperature range of 2 to 310 K and maximum applied magnetic field of ±7 T. Low noise resistance measurements were performed using an AC bridge (Linear Research LR-700), with the current kept constant at 5 μA.

The structural quality of the mesoscopic graphite samples before and after etching process was investigated by Raman spectroscopy measurements. For this purpose, a confocal micro-Raman microscope was used (alpha 300+, WITec) with an incident laser light with λ = 532 nm and a maximum power of 35 mW.

A conventional atomic force microscopy (AFM) device (Veeco, D-3000) with standard AFM tip (r = 30 nm) was used to measure the surface roughness. The resolution of the device is limited by the tip radius and it is not possible to resolve point defects.

3. Experimental results

In the following subsections we present and discuss the experimental results, starting with the Raman results in Section 3.1. With this method, we are able to show that the as-received samples are defect-free. The Raman results obtained after the first thickness reduction show the presence of defects at the near surface region. This defect contribution, however, does not change with further thinning and therefore it is not the reason for the observed changes in the resistivity presented in Section 3.2, and also not in the magnetoresistance in Section 3.4.

3.1. Raman spectroscopy

Raman spectroscopy (RS) is a powerful method used to investigate the structure of carbon-based materials [16, 17, 18]. With RS it is possible to investigate samples having micrometer lateral size and thicknesses from a single layer graphene to bulk samples. The experimental results of some selected samples are shown in Fig. 3(a). The effect of the etching process on the Raman spectra is shown in Fig. 3(b) for the case of sample GF2. According to literature [16], the most intense peaks in the Raman spectra of graphene and graphite are expected at ≈1580 cm⁻¹ (the G-peak) and at ≈2700 cm⁻¹ (the G’ peak). The G-peak is due to the doubly degenerate zone center E₂g mode while the G’-band is due to the second order of zone-boundary phonons. An open question at the beginning of Raman spectroscopy in graphite was, whether or not it is possible to detect disorder [19, 17]. This question was answered with the observation of the D-peak at ≈1350 cm⁻¹, which is related to the disorder present in the material [17, 20].

It is important to emphasize that the Raman results of the as-received samples do not show any evidence of disorder, see Fig. 3(a) and also [5]. After the first etching, a small peak, the D-peak, at ω ≈ 1350 cm⁻¹, appears and remains without changes during all the etching steps in each sample, see Figs. 3(b) and 4(a).

In other words, the etching process results in the appearance of the D-peak; the other peaks do not change after successive oxygen plasma etching within experimental resolution. Previous Raman studies on graphene [21], where the formation of the disorder peak as a function of oxygen plasma etching was investigated, introduced the intensity ratio I_D/I_G as a parameter to quantify the results. We have obtained this intensity ratio from our measurements and we compare them with those from the literature, see Fig. 4(b).

It was shown that after two-oxygen plasma pulses I_D/I_G ≈ 0.5 and the magnetoresistance shows weak-localization effects [21], which is typical for low-disorder single-layer graphene [1]. In our case and after the first
etching, the intensity ratio $I_D/I_G$ remains nearly constant with a ratio value at least one order of magnitude smaller than the ones reported [21]. Thus, from our Raman results at all etching steps the observed disorder peak corresponds to a very low density of defects, located at the sample surface. This was already observed at the edges of graphene sheets on the top of graphite samples [23]. As we describe above, this disorder at the surface does not change with further etching procedure and therefore is not responsible for the occasionally not systematic changes of the resistance and magnetoresistance of the investigated samples.

3.2. Resistance measurements

The results of the temperature dependence of the resistance of some of the samples, before and after thickness reduction, are presented in Figs. 5 and 6. The results of the other samples are included in the supplementary information. Comparing the results of the untreated samples, different temperature dependences of the resistance can be observed, although all samples were obtained from the same initial HOPG bulk material. Some samples show a metallic-like behavior over all temperature range, such as GF2 (Fig. 5(a)), others exhibit a maximum and minimum, i.e. like a combination of metallic and
semiconducting contributions, e.g., sample GF3 shown in Fig. 5(b) and GF8 in Fig. 6(a). In addition, there are some samples with only a semiconducting-like behavior, as sample GF10 (Fig. 6(b)). Considering that the samples are made of the same initial material, that the same experimental procedures were applied and that the spatial dimensions are also comparable (see Table 1 for detailed information), the overall results already suggest that the HOPG sample cannot be considered as a homogeneous material.

A dependence of the estimated resistivity \( \rho \) \((T = 300 \text{ K})\) on sample thickness is shown in the inset of Fig. 5(b) for sample GF3. The resistivity decreases after the first etch and then increases reducing the thickness, indicating that the resistivity of the HOPG graphite bulk cannot be taken as intrinsic. This kind of behavior of \( R(T) \) and the thickness dependence of the resistivity was already reported in the literature with samples of similar quality but different initial materials and each sample with different current and voltage electrodes [24, 3, 4, 25, 5]. We note that the estimate of the resistivity is done in general using the whole total thickness of the sample. This approach can, upon sample, be misleading if the electrodes are mainly at the top of the sample. Due to the large anisotropy in the resistance, only a smaller part of the total top thickness contributes to the measured voltage. Decreasing the thickness, different internal regions from the rest of the sample start to contribute to the measured voltage leading to the rather anomalous behavior shown in Figs. 5 and 6.

The results for sample GF2, see Fig. 5(a), indicate a behavior close to that expected for a homogeneous sample, i.e. the resistance increases after each thickness reduction, the resistance recovers the initial values at temperatures \( T > 20 \text{ K} \); at low temperatures \( R(T) \) behaves different compared to the initial state. An interpretation and more detailed discussion of the changes in the temperature dependence of the samples will be given in Section 4.

The changes of sample GF8, see Fig. 6(a), are more complicated. After the first thickness reduction, \( R(T) \) changes notably. Moreover, at temperatures below 150 K the resistance decreases. A significant change is observable after the third thickness reduction, where the resistance is reduced and thus less than after the second etching. In the case of the sample GF10, see Fig. 6(b), \( R(T) \) behaves semiconducting-like above 40 K. After the first etching, \( R(T > 50 \text{ K}) \) increases and at \( T \lesssim 30 \text{ K} \) the resistance remains nearly constant.

Figures 7(a–d) show the change of the resistance with thickness at 5 K and 300 K. Clearly the resistivity is not

Table 1: Overview of some of the investigated samples and their dimensions, in the as-received state. The thickness of the samples was measured using atomic force microscopy, and the other two dimensions correspond to the area between the electrodes used to measure the electrical resistance.

| Sample | Width (µm) | Length (µm) | Thickness (nm) |
|--------|------------|-------------|----------------|
| GF2    | 6.8        | 9.5         | 85             |
| GF3    | 5.3        | 5           | 50             |
| GF8    | 6.7        | 5.6         | 72             |
| GF10   | 8.3        | 3.8         | 35             |

Fig. 6: Resistance vs. temperature of samples GF8 (a) and GF10 (b), before and after etching. GF8 shows a varying behavior after each etching and GF10 is an example of a sample with a semiconducting-like behavior. The lines are results of the fits using Eq. (1).
simply inversely proportional to the thickness. From previous measurements in thin enough samples [4, 5], where the influence of the interfaces can be assumed to be minimal, we estimate within ~ 15% the intrinsic resistivity $\rho(5K) \sim 960 \mu \Omega \text{cm}$ for ideal graphite with Bernal stacking. This is indeed the case for sample GF10, see Fig. 7(d), which results we take to estimate the resistivity of nearly ideal graphite with a Bernal stacking order. The error bars (in green) in Figs. 7(a–c) indicate the expected resistance values at the lowest thickness and at 5 K, were the samples single Bernal phases. We note that these estimates of the resistance assumes that the measured voltage comes from the whole sample thickness. This assumption is expected to be reasonably correct in thin enough samples where the amount of interfaces and/or inhomogeneous regions in parallel do not contribute substantially. In Fig. 7(d) we show the estimated resistance vs. thickness assuming the intrinsic resistivity mentioned above. Interestingly, the measured resistance at the smallest thickness matches the calculated one (dash-dotted line in the figure) and the behavior at largest thickness is nearly proportional to the expected $1/t$ but shifted downwards by a constant value of $\sim 100 \Omega$.

From all these results we can roughly estimate a penetration depth of $\sim 20$ nm for the input current in ideal graphite. However, this estimate should be taken with care because, even without interfaces, lattice defects and grain boundaries in the sample can still increase effectively this penetration.

3.3. Surface roughness measured with AFM

Another possibility to check for the defective state of the surface before and after oxygen plasma etching is provided by AFM. For sample GF3, AFM was used also to measure the height and the root mean square (RMS) of the surface roughness of the sample. The results are as follows: In the as-prepared state the RMS=3.4 nm; after the 1st etch RMS=2.5 nm; after the 2nd etch RMS=2.1 nm; after the 3rd etch RMS=2.2 nm and after the 4th etch RMS=2.2 nm. These values indicate that the passive oxygen plasma etching does not increase the surface roughness. Moreover there is no correlation between the RMS and the electrical resistance, see Fig. 7(b). This is actually expected for a passive plasma etching process, where two oxygen radicals are formed in the plasma, $O^+$ and $O_2^+$. The resulting compounds, CO and CO$_2$, are then

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**Fig. 7:** Resistance measurements of four of the investigated samples as a function of the thickness at 5 K and 300 K. The error bars at the upper left in (a–c) denote the expected resistance value for the graphite samples with the smallest achieved thickness with Bernal phase and without interfaces. The dash-dotted line in (d) represents the resistance calculated assuming a constant resistivity of $\rho(5K) = 960 \mu \Omega \text{cm}$ for sample GF10 and its error bar applies to the whole curve within the displayed thickness scale.
removed by the flow of the process gas and the vacuum pump. There is no acceleration towards the sample, i.e. the reaction happens only at the surface. The removed C-atoms result in dangling bonds at the surface, which can be measured with Raman spectroscopy, see Section 3.1 and Fig. 4. Our AFM device does not allow us to measure point defects with atomic resolution.

3.4. Magnetoresistance

The in-plane MR was measured before and after reducing the thickness at different constant temperatures and for fields applied always normal to the graphene layers and interfaces. The results at $T = 5$ K of some of the investigated samples are plotted in Fig. 8. All samples regardless of the thickness show a positive MR, before and after etching. In case of a single graphene layer the formation of defects after O-plasma etching [21] is the cause for a negative MR measured at low magnetic fields and low temperatures as a sign of weak localization (WL). A similar WL contribution and negative MR were observed in few-layers graphene and interpreted as a consequence of defects present in the sample [1, 2]. To verify any contribution of WL in the MR of our samples, we have performed low field measurements with small field steps in all samples at $T = 5$ K, before and after etching. We did not observe any negative contribution to the MR. This result indicates that the surface disorder produced by the etching does not influence notably the MR, see Fig. 8 and corresponding figures in supplementary information. Considering that this surface disordered layer should have a much larger resistance than the graphene and its underlying interface layers, it is expected that its contribution to the total resistance in parallel is negligible.

The MR as a function of the sample thickness, i.e. after etching, follows a general behavior, namely, when the resistance is smaller the MR is enhanced. The results of the sample GF8 is a good example to demonstrate this behavior, compare the results in Fig. 7(c) and Fig. 9(c). Early results [4, 25] showed that the MR in thick enough samples is larger compared to thinner samples. Taking into account the internal microstructure of the samples, from these studies one concludes that an important part of the measured MR is directly related to the influence of a large number of metallic-like interfaces between crystalline regions. Similarly, our results can be understood assuming that at a certain etching process the defect- or interface-free crystalline layer becomes very thin and the contributions of the underlying interfaces increase, see Section 4 for details. This suggests that the main contribution to the large MR comes from internal interfaces or thin defected regions. Further etching removes the interface completely and the resistance increases whereas the MR decreases. We note that the MR of graphite is extremely anisotropic [27], a fact that speaks for the contribution of 2D regions.

In this work we have also investigated the MR at different temperatures, ranging from 5 K to 300 K, before and after each etching step. In Fig. 9 we have plotted the MR at $\mu_0 H = 7$ T vs. thickness of some of the investigated samples. In general, the MR decreases, with reducing the sample thickness, as in samples GF2 and GF10, Fig. 9.
Fig. 9: Magnetoresistance at $\mu_0H = 7$ T of the investigated samples presented in Fig. 7 at different temperatures as a function of the sample thickness.

(a) and (d). However, this behavior is sample dependent because the change of the MR with thickness depends on whether an interface remains near the surface region. The MR results of sample GF3, which show a large decrease in the MR after the first etching and a recovery afterwards, (Fig. 9(b)), and the results of sample GF8 with its large oscillatory behavior (Fig. 9(c)) are clear results that support the idea that metallic interfaces formed between crystals strongly dominate the general electric transport properties. Further results of other samples can be seen in the supplementary information. In agreement with the main conclusions obtained in earlier studies [4, 28, 25], the whole MR results of the different microflakes before as well as after etching, indicate the non-intrinsic origin of the MR.

The large MR in graphite is observed only at fields normal to the graphene layers and interfaces. At fields applied parallel to them, the MR actually vanishes. The very small, still measurable MR can be quantitatively explained taking into account a small normal field component. This component is due to an intrinsic misalignment between the interfaces and applied field, measured through the finite rocking curve width, added to any extra but small experimental misalignment [27].

Finally, we would like to note that the observed effects are not related to a ballistic contribution [29], which would be the case if the electron mean free path is of the order or larger than the sample size parallel to the graphene and interfaces layers. In the case of ballistic transport the MR is notably smaller in comparison to larger samples [30, 31]. If the ballistic transport overwhelms the diffusive one, the MR increases with temperature in contrast to the behavior obtained in all our samples, see Fig. 9. This is expected because the length and width of our samples are larger than the mean free path of the conduction electrons ($\ell < 3 \mu m$ [29]) within the graphene layers as well as at the interfaces, in the whole temperature range [29].

3.4.1. Shubnikov-de Haas oscillations

Shubnikov-de Haas oscillations (SdH) as well as de Haas-van Alphen oscillations in the transport properties and in the magnetization as a function of field were considered in the past [1, 32] to build a Fermi surface for 3D graphite with different contributions of electrons and holes of different effective masses. However, trans-
It is also observed that the oscillation amplitude follows the field derivative of the MR obtained for sample GF2 at 5 K. The SdH oscillations are clearly seen at all etching steps. After the first etching step with the resulting thickness of 46 nm, see Fig. 10(b), a remarkable experimental fact that clearly indicates the non-intrinsic origin of the SdH oscillations. After further etching the SdH oscillations recover and maintain a similar amplitude to thickness of 37 nm, similarly to the MR, see Figs. 10(b) and 9(b).

The behavior observed in sample GF10 is similar to the one reported in previous studies [2, 33], i.e. the SdH oscillation amplitude tends to decrease the thinner the graphite sample, see Fig. 10(c). The non-systematic change of the MR with thickness observed in sample GF8, see Fig. 9(c), is also seen in the SdH oscillation amplitude, see supplementary information, supporting the direct correlation between the value of the MR and the SdH oscillations amplitude.

The results obtained from, e.g., sample GF3 (see Fig. 10(b)) appear to indicate identical carrier densities in the as-received and also after the 2nd etching step. But this is not quite correct. In order to find the $1/B$-frequencies one should use FFT on the whole SdH oscillations curves, because the changes are rather small. For the as-received sample we find 2 main frequencies: $(0.231 \pm 0.003)T^{-1}$ and $(0.120 \pm 0.002)T^{-1}$. After the first etching we get $(0.215 \pm 0.005)T^{-1}$ and $(0.101 \pm 0.002)T^{-1}$ for all other etching steps. Thus, there are differences, though small. Note that the MR is sensitive to the paths with the largest conductivities. Those can be located at the regions of relatively large and similar density of states observed in the moiré patterns formed between twisted layers [9, 11, 35, 6].

**4. Discussion**

In the last years and with the help of scanning transmission electron microscopy (STEM), it has been shown that HOPG is composed of many crystalline regions with aligned $c$-axis [4] but, either with different $a$-$b$-axes orientations (i.e. twisted) with similar stacking orders on both sides of the interface, or different stacking orders.
Recently, it was reported that in HOPG as well as in natural graphite rhombohedral stacking is present with a concentration $\approx 10\% \ldots 20\%$ [7]. This phase influences the transport properties of the whole sample [5] and its interfaces with the Bernal phase may show superconductivity, as last studies suggest [13, 14, 7, 36, 6, 37]. The formation of metallic-like regions within interfaces is not a new concept and was already observed in many oxide materials, even superconductivity was found but at very low temperatures [38, 39].

The crystalline regions inside HOPG bulk have a lateral size in the order of a few to tenths of micrometer and a thickness varying from ten to hundreds of nanometers [30, 4, 28, 36]. We note that the usual thickness dependence of the resistivity in metallic-like systems, such as Cu [40] or Ag [41], can be described with the theory of Fuchs-Sondheimer (FS) [42, 43], which considers the influence of scattering processes at the sample surface. This, however, is not the case for a material consisting of stacked layers, such as graphene sheets, where each single sheet is already conducting [44, 45]. In other words, the graphite structure cannot show this surface scattering because the $c$-axis conductivity is several orders of magnitude smaller ($\sigma_c < 10^{-5}\sigma_{a-b}$) than along the graphene layers. That means that conduction electrons (and holes) do not have an appreciable momentum component parallel to the $c$-axis of the graphite structure. The conduction occurs along the graphene sheets, at which surface scattering does not exist. The absence of weak localization in the MR also indicates that the transport does not occur at the surface. Further, within the Fuchs-Sondheimer model the Matthiessen rule has to be applicable. The electron mean free path in thin graphite flakes was found to be of the order of micrometer and for samples much thinner than $\sim 50\, \text{nm}$ [31, 29]. This implies that the conduction is in plane, i.e. parallel to the surface. If the Fuchs-Sondheimer model would be valid, the mean free path cannot be much larger than the thickness of the samples. Note further that the resistance of the disordered surface layer should be similar to the one of an amorphous carbon layer. In this case, its contribution to the total resistance (in parallel to the interfaces and graphene layers) is negligible. This is actually supported by our experimental results where the surface disorder measured by Raman and AFM, see Sections 3.1 and 3.3, does not change with further etching procedure and therefore cannot be responsible for the systematic as well as non-systematic changes of the resistance.

On the basis of early [4] and recent [8, 7, 6] findings regarding the internal structure of graphite, a simple parallel resistor model was proposed to describe $R(T)$, considering the different contributions from the crystalline structures and the interfaces [5]. In this work, we use this model to describe the results of $R(T)$ of the sample in the as-received state and after each thickness reduction step, in order to find some hints on the correlations between the different contributions and the thickness behavior described above.

The model we use assumes that the total measured electrical resistance $R(T)$ consists of three contributions in parallel, one originating from the interfaces ($R_i(T)$) and the other from the crystalline parts, i.e. Bernal ($R_B(T)$) and rhombohedral ($R_r(T)$) stacking orders. The total resistance is formulated as [8, 5]:

$$R(T)^{-1} = R_i^{-1}(T) + R_B^{-1}(T) + R_r^{-1}(T).$$ (1)

The interface contribution is assumed to behave metallic-like with a linear and a thermally activated exponential
term as discussed in [8]:

$$R_i(T) = R_0 + a_i \left[ R_1 T + R_2 \exp \left( \frac{-E_g}{k_B T} \right) \right]. \quad (2)$$

This relation slightly deviates from the originally used in [8, 5]. The reason is that we would like to have a prefactor $a_i$ that provides the weight of this contribution, independent of the constant residual resistance term $R_0$.

The crystalline semiconductinglike contributions for rhombohedral and Bernal stacking orders are given as usual:

$$R_i(T) = a_1 \cdot T^{3/2} \cdot \exp \left( \frac{+E_{g1}}{2k_B T} \right), \quad (3)$$

$$R_B(T) = a_2 \cdot T^{3/2} \cdot \exp \left( \frac{+E_{g2}}{2k_B T} \right). \quad (4)$$

Although we do not differentiate between electron and hole carriers to understand the temperature dependence of the resistance, the Hall data of different graphite samples clearly indicate the existence of both carriers and should be taken into account [46, 6]. The coefficients $R_0, R_1, R_2, a_1, a_1$ and $a_2$ as well as the activation energy $E_a$ and the gap energies $E_{g1}$ and $E_{g2}$ are free parameters we obtain from the fits to the experimental curves. A detailed discussion of the parameters in terms of their origin and the fitting procedure can be found in [5]. In the present work, we use those equations and correlate the fitting parameters to the changes in the resistance after the thickness reduction.

Before we describe the results of the fittings to the experimental curves, it is instructive to plot the results of $R(T)$ of samples GF2 and GF8, see Figs. 5(a) and 6(a), in a normalized way, i.e. $R(T)/R(300)$ vs. $T$, see Fig. 11. Through this normalization we can realize better and discuss the changes in the temperature dependence produced by reducing the thickness of the flakes. The temperature dependence of the resistance of sample GF2 remains practically unchanged at the first thicknesses, i.e. from $t = 85$ nm to 76 nm. However, at the last two thicknesses 72 nm and 50 nm, see Fig. 11(a), the sample shows a smaller ratio $R(4)/R(300)$ and less metalliclike behavior, i.e. there is a clear flattening of $R(T)$ between $120 \text{ K} \lesssim T \lesssim 250 \text{ K}$. This systematic change of the normalized $R(T)$ with thickness is not observed for sample GF8, see Fig. 11(b) and Fig. 7(c), although one gets the impression that both samples show similar trends. The reason for this apparent similarity can be understood when we realize that upon sample thickness the interfaces, which provide the metalliclike contribution (see Eq.(2)), can be partially removed from the superficial region or, after further thickness reduction, a new interface starts contributing.

As an example, we discuss the fittings to the experimental normalized curves of samples GF2 and GF8. From the fits to the experimental curves of $R(T)$ in the as-received states of the samples, continuous lines in Figs. 5 and 11, we get the parameters given in Table 2. Those parameters are kept fixed for all other curves obtained at different thicknesses. In other words, the fits to the curves obtained after etching are done leaving free only the weight prefactors $a_1, a_1, a_2$ and the residual resistance $R_0$. We can observe that the fits (continuous lines in Fig. 11) using Eq.(1) and with merely three free parameters, describe very well all the experimental results. The fixed parameters, i.e. the parameters, which were shared among the etching steps and obtained through the fitting, have usually an error of the order of 1%. The strength of our analysis is based on the fact that we can reduce the amount of free parameters through sharing them among different curves taking into account the physics behind.

$$\begin{array}{|c|c|c|}
\hline
\text{Parameter} & \text{GF2} & \text{GF8} \\
\hline
E_{g1} (\text{meV}) & 105 & 113 \\
E_{g2} (\text{meV}) & 33 & 41 \\
E_a (\text{meV}) & 8.4 & 6.3 \\
R_1 (\Omega/\text{K}) & 2.3 \times 10^{-3} & 1.2 \times 10^{-3} \\
R_2 (\Omega) & 0.85 & 0.41 \\
\hline
\end{array}$$

Table 2: Activation $E_a$ and semiconducting gap energies $E_{g1,g2}$ of the selected samples. $E_{g1}$ and $E_{g2}$ are the energy gaps of rhombohedral and Bernal stacking orders, see Eqs. (2,3). The parameters were obtained by fitting to Eq. (1) the experimental $R(T)$ curves in the as-received states, before any etching process. The typical uncertainty we get for the parameters is $\sim \pm 10 \%$. For a brief discussion on the errors see main text.
relative decrease of the weight of the rhombohedral phase with respect to the Bernal one. When an interface is removed, i.e. at $t = 72$ nm, we get a clear decrease in $a_i$ with a further decrease in the ratio $a_1/a_2$, see Fig. 12(a). The obtained weight factors for sample GF8, see Fig. 12(b), indicate also that a correlation exists between the increase or decrease of the interface contribution with those from the ratio between the minority rhombohedral stacking order and the majority Bernal; note that the ratio $a_1/a_2 \sim 0.1$ is in agreement with XRD studies [7]. This correlation is somehow expected if at least some of the interfaces are between the two stacking orders. In other words, removing the region where an interface contributes to $R(T)$ implies removing, relatively speaking, mainly the minority rhombohedral phase.

In the case of sample GF10, the interfaces contribution is diminished in comparison to the other samples, as expected due to the small thickness. Till the third etch the ratio $a_1/a_2 \approx 0.08 \pm 0.02$. We note that the low temperature behavior was used to fix $R_0$ and $R_1$ ($a_i$ was fixed at 1). The data in the whole temperature range were then fitted in the usual way, with the energy gaps and the activation energy taken as shared parameters ($E_{g1} = 104 \text{ meV}$, $E_{g2} = 41 \text{ meV}$, $E_a = 4 \text{ meV}$). After the fourth etch, we clear recognize that the behavior of the sample changed dramatically, especially at low temperatures. To get a reasonable good fit of the data for the thinnest sample we had to leave all parameters free. The parameters obtained from the fit process suggest that there should be a negligible rhombohedral contribution to the electrical transport, together with a clear change in the energy gap of the Bernal phase ($E_{g2} \sim 17 \text{ meV}$) and in the activation energy ($E_a \sim 51 \text{ meV}$). In the supplementary information we compare the results of the fits to the data of sample GF10 with and without including the contribution of the rhombohedral stacking at all thickness. The obtained differences between the different fit approaches and the experimental data indicate that the contribution of the minority rhombohedral stacking is necessary, expect for the sample with $t = 19$ nm, see supplementary information.

5. Conclusion

We have investigated the electric transport properties of a series of mesoscopic graphite samples obtained from the same initial bulk HOPG material. The investigated microflakes are similar in lateral dimensions but with slightly different thicknesses. By means of a gentle oxygen plasma etching procedure and the protection with SiN the electrodes for the resistance measurements, we were able to investigate with high precision the influence of thickness reduction on each sample individually. Our results show that one can obtain different temperature dependence upon initial sample and/or thickness. The reason for the observed changes with thickness is due to the heterostructure of the graphite bulk samples. This heterostructure is the reason for the occasionally large changes in the SdH oscillations amplitude.

Our results also indicate that those oscillations are not intrinsic of the graphite ideal structure and should not be taken as evidence for a 3D Fermi surface. By fitting $R(T)$, we confirm the presence of both stacking orders with semiconducting energy gaps similar to previously reported in the literature [5, 47, 48]. Regarding the reasons for the apparent failure of the well-established models [49, 50, 51, 52] to predict the obtained energy gaps, we note that they all have difficulties to model the van der Waals interaction between graphene layers and they do not include electron-electron or spin-orbit coupling interactions as modern theories do. We further note that these well-established models do have several free parameters that were obtained from the comparison with experimental transport data without considering the interfaces contribution, see [6] and Refs. therein.

Fig. 12: The weight coefficient due to the interfaces $a_i$ (right y-axis) and the ratio of the weight coefficients of the rhombohedral and Bernal stacking orders $a_1/a_2$ (left y-axis) vs. the corresponding sample thickness for samples GF2 (a) and GF8 (b), obtained from the fits to Eq. (1) setting all parameters of Table 2 fixed.
The magnetoresistance shows also evident changes induced by the thickness reduction, indicating the significant role of the interfaces, specially at low temperatures. Raman spectroscopy confirms that our samples are free from defects in the as-received state. After thinning using oxygen plasma etching, a small peak related to defects appears. We correlate this peak to the defects produced within the first layers on the sample surface and from the edges, produced during etching. The overall results indicate that the amount of surface defects present in the samples after gentle oxygen plasma etching is too small to affect the transport and they are not the origin of observed changes in $R(T)$ or in MR. Our results provide new convincing evidence indicating that the transport properties of bulk graphite are not intrinsic, they depend strongly on the amount of interfaces present in the material, and the two stable stacking orders of graphite.

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Supplementary Information of: "Influence of Interfaces on the Transport Properties of Graphite revealed by Nanometer Thickness Reduction"

1. Temperature dependence of the resistance and magnetoresistance at $T = 5$ K at different etching steps for samples GF4, GF6 and GF7

In the main article only the results of four samples were shown and discussed, but during this work we have investigated three more samples, which will be presented in this supplement. In Figs. 1–3 the results of samples GF7, GF6, and GF4 are presented. For all samples the magnetoresistance MR is plotted in (a), and the temperature dependence of the resistance $R(T)$ in (b), at different etching states, i.e. the same sample after etching and characterized with the thickness written in the panels (a). The lines are the fits using the parallel resistor model, as explained in the main article. The insets in the panel (b) show the corresponding MR at 5 K in a smaller field range.

After a few nanometer decrease of the thickness, the value and the temperature dependence of the resistance $R(T)$ change. But, as we described in the main article, the changes depend very much on the sample, although all the samples were obtained from the same bulk HOPG sample. This fact can be easily realized comparing the $R(T)$ curves among the samples GF7 and GF6 or GF4, see Figs. 1(b) and 2(b) or 3(b). The interesting fact of sample GF7 is that the absolute value and the temperature dependence of $R(T)$ do only slightly change below 75 K, whereas at higher temperatures the changes are not monotonous, similar to sample GF8 (see Fig. 6 in the main article).

The MR at 5 K shown in the panels (a) of Figs. 1, 2 and 3 shows a behavior similar in all samples, i.e. it decreases the larger the resistance, validating again the conclusion that the MR and the $R(T)$ are influenced by certain interfaces located near the surface region. We note that at 5 K the influence of defects can be observed through the weak localization (WL) effect. This was indeed reported in graphene and few-layers graphene [1, 2]. The plots in the insets show no signs of WL in the MR, neither in the as-prepared state nor after thickness reduction. These results also indicate that the transport measurements are not influenced by the surface disordered layer produced by our gentle oxygen plasma treatment.

2. Magnetoresistance at different constant temperatures before and after thickness reduction

The Figs. 4 and 5 show the magnetoresistance measured at different constant temperatures of the samples GF3 and GF10 in the as-prepared state (a), and after the last thickness reduction (b). We show the results of these two samples as examples of all investigated samples in this work. From the results we can conclude that in general the thinning of the samples results in a reduction of the MR.
Supplementary Figure 1: (a) Magnetoresistance at $T = 5$ K and (b) temperature dependence of the resistance at different thicknesses for sample GF7. The results of the as-prepared sample are always from the sample with the largest thickness. The lines shown in (b) are the corresponding fits using the parallel resistor model as explained in the main article.
Supplementary Figure 2: Similar to Fig. 1 but for sample GF6.
Supplementary Figure 3: Similar to Fig. 1 but for sample GF4.
Supplementary Figure 4: Magnetoresistance of sample GF3 measured at different constant temperatures in the as-prepared state (left picture) and after the fourth etching (right picture).
Supplementary Figure 5: Similar to Fig. 4 but for sample GF10.
3. Shubnikov-de Haas oscillations of sample GF8

Figure 6 shows the field dependence of the first field derivative of the MR obtained for sample GF8 at 5 K, see Fig. 8(c) in the main text. The SdH oscillations are clearly seen at all etching steps. Their amplitude changes with thickness as the MR at the same temperature, see Fig. 9(c) in the main text.

4. Contribution to the temperature dependence of the minority rhombohedral phase to the resistance of sample GF10

In Fig. 7(a) we present the temperature dependence of the resistance of sample GF10 at different thickness with the best possible fits including the rhombohedral phase (3R) and in (b) without it. As explained in the main text, the best fits are found when both stacking orders and an activation term in $R_l$ are taken into account, see Eq. (1) in the main text, up to the third etch. The linear term is still present with $R_1 \approx -0.04 \pm 0.006 \Omega/K$ for all samples up to the third etch. To fit the data obtained for the thinnest sample after the fourth etch, the rhombohedral phase was not needed. However, a clear change in the energy gap $E_{g2}$ and activation energy $E_a$ had to be used, see main text.

We have also tried to fit all the results of sample GF10 without the rhombohedral phase, see Fig. 7(b). In this case the Bernal energy gap and activation energy $E_a$ were taken as shared parameters and the other parameters were left free. Using standard values for the Bernal energy gap and for the activation energy as starting values, the best possible fits were obtained with a reasonable value for $E_{g2} \sim 57$ meV (including the fourth etch), but the contribution of the activation energy term tends to vanish ($R_2 \to 0$). Taking the energy gap value $E_{g2}$ as free parameter, i.e. not shared among all curves, did not improve the result. As can be seen in Fig. 7(b), the fits show larger deviations especially at low and high temperatures.

For a better comparison between the fit results, in Fig. 8 we have plotted the normalized residuals $\Delta = R(T)/R(T = 310 \text{ K})_{\text{data}} - R(T)/R(T = 310 \text{ K})_{\text{fit}}$, with (a) and without (b) the rhombohedral stacking. It is obvious that the deviations are much larger for the case where the rhombohedral stacking was excluded at all thicknesses $t > 19 \text{ nm}$. We have also tried to manually change the parameters for a better fit, including setting $R_1 = 0$, yet all trials resulted in even larger residuals $\Delta$. Note that although in both approaches in (a) and (b) we do not include the rhombohedral contribution in the fits at $t = 19 \text{ nm}$, the difference of the residuals $\Delta$ between the two and for this thickness is due to the different values used for the energy gap $E_{g2}$. We may therefore conclude that our fit procedures indicate that the rhombohedral contribution is necessary to fit the data up to the third etch of sample GF10.
Supplementary Figure 6: First derivative of the resistance with respect to the magnetic field of sample GF8 at different etching steps and calculated from the curves shown in Fig. 8(c) in the main text. The y-scale is similar for all the curves, which have been shifted vertically for clarity.
Supplementary Figure 7: Temperature dependence of the resistance of sample GF10 at all thicknesses. The fit curves in (a) were obtained taking into account the two stacking orders and in (b) without the rhombohedral (3R) stacking.
Supplementary Figure 8: Normalized residuals $\Delta = R(T)/R(T=310\text{ K})_{\text{data}} - R(T)/R(T=310\text{ K})_{\text{fit}}$, including (a) and without (b) the rhombohedral stacking (3R). A value of $\Delta \approx 0.01$ means about 1% deviation. See similar curves for different samples in [3].
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