Structure and Electronic Transport in Graphene Wrinkles

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Supporting Information

ABSTRACT: Wrinkling is a ubiquitous phenomenon in two-dimensional membranes. In particular, in the large-scale growth of graphene on metallic substrates, high densities of wrinkles are commonly observed. Despite their prevalence and potential impact on large-scale graphene electronics, relatively little is known about their structural morphology and electronic properties. Surveying the graphene landscape using atomic force microscopy, we found that wrinkles reach a certain maximum height before folding over. Calculations of the energetics explain the morphological transition and indicate that the tall ripples are collapsed into narrow standing wrinkles by van der Waals forces, analogous to large-diameter nanotubes. Quantum transport calculations show that conductance through these “collapsed wrinkle” structures is limited mainly by a density-of-states bottleneck and by interlayer tunneling across the collapsed bilayer region. Also through systematic measurements across large numbers of devices with wide “folded wrinkles”, we find a distinct anisotropy in their electrical resistivity, consistent with our transport simulations. These results highlight the coupling between morphology and electronic properties, which has important practical implications for large-scale high-speed graphene electronics.

KEYWORDS: graphene, fold, wrinkle, electronic transport, ripples

The advance of a new generation of very high speed graphene electronics 1−8 depends upon understanding and controlling the interaction of graphene with the surroundings, especially the supporting substrate.9−11 Graphene obtained by chemical vapor deposition (CVD) on metals 12−15 is emerging as a powerful platform for graphene electronics with wafer-scale compatible fabrication. However, carrier mobilities in CVD graphene are smaller than for exfoliated graphene,12−15 and the limiting electron scattering mechanisms in these large-scale graphene wafers are not well understood. Recently, several studies have reported on the polycrystalline nature of CVD graphene and the associated electrical resistances due to grain boundaries,16−19 which can be significant. Fortunately, improvements in current state-of-the-art growth techniques have led to large micrometer scale grain sizes.16−18 Hense, in typical submicrometer graphene devices electron scattering mechanisms at length-scale much smaller than the grain size are likely responsible for the inferior carrier mobilities.

A particular issue for CVD graphene is the presence of wrinkles. These are formed by differential thermal expansion, as the metal contracts more than the graphene during postgrowth cooling, leaving an excess area of graphene.20−24 Wrinkles are still present after transfer to the device substrate, as can be clearly seen in SEM images. Figure 1a shows such an image on a SiO2/Si substrate. The dark lines correspond to the graphene wrinkles, since these regions reflect fewer secondary electrons. The same features are also reflected in the Raman images. Figure 1b shows the Raman G band intensity map of the same graphene area shown in Figure 1a. It displays the total intensity of the G phonon band. There are clear line features in the phonon spectrum at the same locations as the features in the SEM image. The total G band intensity is higher at the wrinkles due to the extra layers of graphene as compared to the surrounding area.25 In Figure 1c, we show a map of the ratio of the Raman D to G band intensities. We note that there is no corresponding line feature in the D to G ratio map at the position of the wrinkle, indicating that this feature is not a line defect, such as grain boundary that gives rise to an increased D band.18 26 A TEM cross-sectional image of such a wide graphene wrinkle is shown in Figure 1d. The width of this wrinkle is about 50 nm. The profile of TEM intensity in the boxed area is shown in the inset. The multilayer structure of the wrinkle clearly shows that it is not a standing wrinkle but a folded structure.20

More quantitative information about the wrinkle distribution is obtained using AFM with “SuperSharp” tips. Figure 2a,b shows the AFM images of a wide graphene wrinkle (∼135 nm) and a narrow graphene wrinkle (∼16 nm). The AFM heights of the marked region in panels a and b are shown in Figure 2c and are about 0.9 and 3.8 nm, respectively. Figure 2d gives the statistical distribution of the wrinkle heights as a function of their width. The wide wrinkles all have similar height, roughly 1 nm, but they exhibit a broad range of widths. In contrast, the narrow wrinkles are taller and have a broad distribution of
heights, ranging roughly from 2 to 6 nm. Their width is apparently below the resolution of our AFM.

Little is known about the factors determining the distribution of wrinkles, which may depend on the details of CVD growth and subsequent transfer. However, previous studies have already yielded insight into the morphology of individual wrinkles. Figure 2e–g shows three distinct morphologies: panel e is the simple ripple geometry usually assumed;23,27 panel g is the recently identified folded geometry;20 and we propose an intermediate geometry, panel f, a "standing collapsed wrinkle". The sequence of shape is easily understood at the qualitative level, as arising from the competition between elastic bending and van der Waals binding.20,32 The ripple structure minimizes the bending distortion. However, when there is a large amount of excess material, collapsing it to form bilayers or folding it to form trilayers provides additional van der Waals binding, at the cost of progressively increased bending. For a given structure, the binding increases with length, while the bending energy is constant (roughly proportional to the number of sharp bends), leading to the sequence of shapes.

To better understand the energetic competition and resulting morphologies, we perform total energy calculations, including the van der Waals binding and elastic bending and assuming a variational form for the geometry. The only material parameters are the bending stiffness $\kappa$ and the van der Waals binding energy $\beta$ (for details see Supporting Information). We use the value $\kappa = 1.4$ eVÅ3,34 for the bending stiffness of graphene, and $\beta = 40$ meV per carbon atom32 for the van der Waals adhesion energy between the graphene sidewalls. When the excess graphene length (i.e., the graphene length compared to the substrate length) is greater than $L_{\text{m}} \approx 24(\kappa/2\beta)^{1/2} \approx 16.3$ nm, we find that the "folded" structure (Figure 2g) has the lowest energy. Below this, the standing collapsed wrinkle (Figure 2f) has lower energy. The height of the "standing wrinkle" at the transition (i.e., the maximum height) is about 8.4 nm, very close to $L_{\text{m}}/2$. Taking into account the uncertainties in AFM of flexible structures and in the parameters $\kappa$ and $\beta$, this estimate is consistent with the experimental value found above of 5–6 nm.

For electronic devices, the most important issue for graphene wrinkles is their impact on transport. Here we address this both experimentally and theoretically. For "folded wrinkles", we systematically measured the electrical resistivities both along the fold and across it, using four-probe devices as illustrated in Figure 3a,b. Their averaged resistances, herein denoted as $\langle R_{\text{fl}} \rangle$ and $\langle R_{\text{ac}} \rangle$, respectively, are plotted in Figure 3c,d as functions of the gate voltage $V_{\text{g}}$ and compared with resistances of the control (flat) devices $\langle R_{\text{f}} \rangle$. The resistances involving the fold structure exhibit an interesting anisotropy: (i) $\langle R_{\text{fl}} \rangle$ is smaller than $\langle R_{\text{f}} \rangle$, especially when biased near the charge neutrality point. (ii) $\langle R_{\text{ac}} \rangle$ shows no difference from $\langle R_{\text{f}} \rangle$ within error. We cannot directly measure the resistance of standing wrinkles, because their high density precludes contacting them individually. Hence, each device with the folded wrinkles has a control device constructed beside it, which measures the resistances associated with these smaller background wrinkles. $\langle R_{\text{fl}} \rangle$, $\langle R_{\text{ac}} \rangle$, and $\langle R_{\text{f}} \rangle$ are obtained by averaging over dozens of these devices.

In general, folds could trap impurities that act as dopants or scatterers, affecting the resistance. Such extrinsic effects would depend on the details of processing. Our measurements suggest that trapped impurities are not a significant factor here, see Supporting Information. We therefore address theoretically the intrinsic resistance of folds, without any such impurities or defects. Electrical transport along folded wrinkles can be
analyzed using a simple diffusive transport model. Roughly speaking, the folded wrinkle can be viewed as a strip of trilayer graphene. Neglecting hybridization between layers, the electrostatic problem for the trilayer can be solved self-consistently. The resulting carrier distributions within each layer are plotted in Figure 4a. Due to nonlinear charge screening, the carriers are almost all confined to the bottom layer for large $V_g$, while the carriers are more equally distributed when the device is biased near the charge neutrality point. The transport coefficient (i.e., the mobility) is commonly seen to improve with decreasing carrier density, and we confirm this behavior in our own devices (see Supporting Information Section 6). Therefore the charge redistribution in the trilayer structure should improve its effective carrier mobility relative to that of monolayer graphene at a given electrostatic doping. We confirm this by quantitatively modeling the experiments as shown in Figure 4b (see Supporting Information Section 3). The largest difference in electrical resistance between $\langle R_f \rangle$ and $\langle R_0 \rangle$ occurs at the charge neutrality point, when charge redistribution in the trilayer graphene is most effective.

Electrical transport across folded wrinkles, however, cannot be explained with the simple diffusive model above. The excess length associated with the fold and its reduced doping would both increase the resistance. If this were the controlling physics, the resistance would be an order larger than what is experimentally observed, see Figure 4c. This discrepancy can be reconciled by taking into account an additional conduction pathway via interlayer tunneling across the collapsed bilayer graphene, which can reduce the larger resistance associated with the density-of-states bottleneck.

To estimate the role of interlayer tunneling in limiting the resistance, we performed quantum transport simulations based on the nonequilibrium Green’s function method. Since we are also interested in the resistance of standing wrinkles, we perform calculations for the simpler geometry of Figure 2f, but for varying excess graphene lengths spanning the range from standing to folded geometries. For both geometries, we expect reduced doping in the raised graphene areas, reflecting the poor coupling to the gate due to its geometry for the standing wrinkle or due to screening by the bottom graphene layer for the folded wrinkle. For simplicity, we treat these regions as undoped, giving an upper bound on the resistance. The resulting room-temperature resistances are shown in Figure 5a as a function of the length $\lambda$ of the collapsed bilayer region. Depending on the orientation of the wrinkle, the bilayer could have some rotated alignment, but we focus on the simpler case.
with zero misorientation, where the stacking depends only on sliding of one layer over the other. We show the average resistance and range for different bilayer alignment.

The most striking feature of Figure 5a is that the resistance depends only very weakly on the excess graphene length. The reason is seen in Figure 5b, which shows that much of the current flows between graphene layers at the base of the wrinkle, rather than flowing through the whole length. To verify this interpretation, we repeat the calculations with the graphene sheet cut at the top of the wrinkle. Despite totally blocking the direct intralayer pathway, the change in resistance is minor. We expect the interlayer transport to be similar for folded wrinkles, since it occurs largely near the base. Thus, our calculations suggest a resistance on the order of $\sim 200 \, \Omega \mu m$, which is relatively independent of $\lambda$, for either type of wrinkles. The resistance observed in our experiments is also very small, below the experimental accuracy, consistent with the small calculated value.

In conclusion, we reported experimental and theoretical measurements of collapsed graphene wrinkles, and compared these. The calculated energetics based on competition between the elastic and van der Waals energies is consistent with the experimental observation of a maximum wrinkle height of $\sim 6 \, \text{nm}$, substantiating our physical picture of the structure of standing and folded wrinkles. Our transport experiments on these folded wrinkles yield a distinctive anisotropy in the fold.
resistivity consistent with our model. We conclude that this anisotropy arises because transport along and across the folded wrinkles are limited by different transport effects: diffusive transport of the charge distributed across the multilayered folds, versus local interlayer tunneling across the collapsed region. From an applications standpoint, the former degrades the on−off ratio, while the latter can contribute a significant resistance to the overall device, of the same order as typical graphene contact resistances.41,42 Our study therefore identifies a source of electrical performance degradation in CVD grown graphene, and highlights the subtle interplay between morphology and electronic properties. It also underscores the importance of a better fundamental understanding of the formation and engineering of wrinkles.

Methods. The method we used in this work to prepare monolayers of graphene is based on CVD of graphene on Cu and is similar to the method described in ref 13. A Cu foil (25 μm thick, 99.98%, Alfa-Aesar) was placed in a 1 in. diameter quartz furnace tube at low pressure (10^-6 Torr). After evacuation, the Cu foil was heated to 1050 °C in vacuum. At this temperature, the sample was exposed to ethylene (6 sccm, 6 mTorr) for 10 min. The sample was then cooled down under vacuum. PMMA resist was spin-coated on top of the graphene layer formed on one side of the Cu foil. The Cu foil was then dissolved in 1 M iron chloride. The remaining graphene/PMMA layer was washed with DI water, 1 M HCl, and DI water and transferred to the Si/SiO2 substrate. Subsequently, the PMMA was dissolved in hot acetone (80 °C) for one hour. The substrate with the transferred graphene was then rinsed with methanol and dried in a stream of nitrogen.

Subsequently, metal alignment marks were formed by lift-off and graphene Hall-bar structures were fabricated by photore sist patterning and O2 plasma etching. Following that, SEM, AFM, and Raman characterization was performed, and then source/ drain and sensing terminals were formed using Ti/Pd/Au metallization and lift-off. The SEM measurements were obtained at 3 KV. The Raman G band intensity is summed in the frequency range of 1480 to 1700 cm^-1 and the D band intensity is summed in the frequency range of 1253 to 1450 cm^-1. The AFM images were taken in the tapping mode with “SuperSharp” silicon tip. The tip radius is less than 5 nm. For TEM analysis, the sample was prepared using dual-beam focused ion beam and imaged in a JEOL 3000F TEM operated at 300 eV.

**REFERENCES**


**ASSOCIATED CONTENT**

*Supporting Information*

Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Notes

The authors declare no competing financial interest.

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