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Lattice Expansion in Seamless Bilayer Graphene Constrictions at **High Bias**

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Supporting Information

ABSTRACT: Our understanding of sp² carbon nanostructures is still emerging and is important for the development of high performance all carbon devices. For example, in terms of the structural behavior of graphene or bilayer graphene at high bias, little to nothing is known. To this end, we investigated bilayer graphene constrictions with closed edges (seamless) at high bias using in situ atomic resolution transmission electron microscopy. We directly observe a highly localized anomalously large lattice expansion inside the constriction. Both the current density and lattice expansion increase as the bilayer graphene constriction narrows. As the constriction width decreases below 10 nm, shortly before failure, the current density rises to 4×10^9 A cm⁻² and the constriction



exhibits a lattice expansion with a uniaxial component showing an expansion approaching 5% and an isotropic component showing an expansion exceeding 1%. The origin of the lattice expansion is hard to fully ascribe to thermal expansion. Impact ionization is a process in which charge carriers transfer from bonding states to antibonding states, thus weakening bonds. The altered character of C-C bonds by impact ionization could explain the anomalously large lattice expansion we observe in seamless bilayer graphene constrictions. Moreover, impact ionization might also contribute to the observed anisotropy in the lattice expansion, although strain is probably the predominant factor.

KEYWORDS: Bilayer graphene, TEM, strain, constriction, lattice expansion

raphene stands as a unique material for high performance J electronic applications.¹ Both its monolayer and bilayer forms are very attractive for electronic applications. Bilayer graphene can have similar or distinct properties as compared to its monolayer counterpart depending on the angle of rotation between the two layers.² Morozov and co-workers demonstrated that the intrinsic mobility of bilayer graphene is comparable to that of single layer graphene.³ However, unlike single layer graphene, an energy gap can be opened in bilayer graphene in a controlled manner when applying an external electrical field.⁴⁻⁶ Despite the promise afforded by graphene and bilayer graphene as building blocks for electronic devices and circuitry, their actual development to date is limited. In part, this is because the technology to achieve this is still lacking due to the need to structure graphene with high (atomic) precision in a reproducible and controlled manner.⁷ Graphene and bilayer graphene are able to sustain remarkably high current densities;⁸⁻¹¹ however, when structured as long ribbons, lower current densities as compared to large area graphene are obtained due to electron scattering at edges and reduced thermal conductivity.¹² The production of graphene ribbon based devices with ballistic transport is attractive, as it will enable faster devices as well as superior current density

limits. However, our understanding of sp² carbon based nanostructures at high bias is still emerging. In particular, in terms of the structural behavior of graphene or other sp² carbon nanostructures at high bias, little to nothing is known.

To this end, we present an *in situ* atomic resolution transmission electron microscopy (TEM) study of a bilayer graphene nanoconstriction at high bias. We observe highly localized lattice expansion inside the constriction that exhibits a uniaxial component of about 5% and an isotropic component of more than 1% when the constriction width decreases below 10 nm and the current density rises to 4×10^9 A cm⁻². The origin of the lattice expansion is discussed.

Details of the device fabrication can be found in the Supporting Information. The chip with the contacted graphene sample is mounted on a custom-built sample holder for TEM with electrical terminals. For imaging, an FEI Titan³ 80-300 transmission electron microscope with a CEOS third-order spherical aberration corrector for the objective lens is used. It operates at an acceleration voltage of 80 kV to reduce knock-on

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damage. The image acquisition time was 0.5 s. The electrical characterization was performed using a HP 4140B pA meter/DC voltage source. The micrographs are evaluated using the Gatan DigitalMicrograph software with the Triebenberg package.

In Figure 1, a schematic overview of the *in situ* transmission electron microscope setup is presented in which a sheet of



Figure 1. Schematic overview of the setup. (left) Scanning TEM image of the electrodes with a sketch of an overlying graphene ribbon with a central constriction. (right) TEM image of the bilayer graphene constriction at high bias. The inset is the FT of the marked region in the micrograph. The three arrows indicate the directions in which intensity profiles were taken, with the color code used in Figure 3.

mechanically cleaved few-layer graphene is suspended across two free-standing gold electrodes. The use of TEM allows high degrees of structural information about the constriction to be obtained with relatively high temporal resolution while simultaneously gathering electrical data. The electrical setup provides a voltage bias across the electrodes and monitors/ records the current. Upon applying a sufficiently large bias, the graphene begins to crack. The cracking process occurs at the center of the graphene sheet between the electrodes where the temperature rise is greatest. Usually, the cracks initiate from the outside edges more or less simultaneously and propagate toward the center through current induced sublimation of carbon atoms from the crack edges. As the cracks approach the center, a narrow constriction forms. Greater details of the cracking process forming the constriction are available elsewhere,¹¹ so we do not examine this further. Instead, in this study, we focus on the constriction just before failure while under high current densities. The TEM micrograph provided in Figure 1 shows a flake after its width has eroded down from approximately 400 nm to a constriction approximately 2 nm long and 10 nm wide. The edges of the ribbon and crack region are for the most part atomically smooth over a long range and exhibit strong contrast. These features indicate the constriction is bilayer with closed edges (seamless) and is in keeping with previous observations that current induced cracking leads to bilayer graphene with closed edges.^{11,13} Closed edges add stability by reducing dangling bonds¹⁴ and also add mechanical strength.¹⁵ The reflexes observed from the Fourier transform (FT) of the image confirm crystalline graphene and highlight a rotational stacking fault of around 3° between the two layers. This rotation explains the observed Moiré pattern,¹⁶ as well as the periodic contrast bands that are present across the ribbon (see Figure S1 in the Supporting Information). The stacking rotation between the two graphene layers can alter the electronic properties with respect to Bernal (AB) stacked

bilayer graphene. For example, stacking rotations between layers of more than 1.5° are predicted to decouple the two layers, electronically inducing a transition from a parabolic to a linear dispersion, characteristic of monolayer graphene.² Other studies predict a semimetallic behavior with a small indirect overlap of the valence and conduction band for shifted bilayer graphene which does not conform to AB or AA stacking.¹⁷ It is also worth noting that the seamless bilayer constriction is clean, free of unwanted amorphous species, and also highly crystalline which is typical for the current annealing process.^{18,19}

We now turn to examining the graphene constriction's lattice while at a fixed bias of 2.53 V. As previously stated, the current annealing process erodes the constriction with time (e.g., see panels 1-5 in Figure 2). In this case, the constriction width is



Figure 2. Series of micrographs at high bias. The plot shows the measured current through the constriction. The transparent bars indicate when the respective series of color coded micrographs were taken. At time equal to zero, the ribbon failed and the current rapidly dropped to zero (not shown in the plot).

reduced from 11.3 to 7.8 nm. The lower graph in Figure 2 shows how the current drops as the constriction narrows down. Since the bias is constant, in essence, the resistance is increasing and is an indication that carbon atoms are being sublimed. Knowledge of the constriction's dimensions and current allows us to determine the current density, which changes from 24.5 to 28.5 mA μ m⁻¹ for the ribbons shown in panels 1 and 5, respectively. This latter value is equivalent to 4×10^9 A cm⁻², assuming a bilayer graphene thickness of 0.7 nm. These remarkably high current densities are in line with recent reports.^{10,11} Soon after the micrograph aquisition of the constriction shown in panel 5, the nanoribbon fails and the current drops to zero. The average erosion rate of the constriction's width was 0.077 nm s⁻¹, and it allows us to extrapolate the ribbon width at failure, which is ca. 7 nm and would correspond to a breakdown current density of 30 mA μm^{-1} .

The sublimation of carbon atoms from the constriction edges is based on Joule heating. Thus, we might anticipate lattice changes, viz., thermal expansion. Local crystallographic parameters of the bilayer ribbon can be accessed from the FT of the image or selected regions of the image. As an example, the inset in panel b in Figure 3 shows the Fourier transform of the region in the micrograph indicated by the black square. The distances of the spots from the center, i.e., the spatial frequency, represent the directionally resolved lattice parameter (see



Figure 3. The plots show the measured spatial frequencies of each direction separately measured in the FT of the respective TEM micrographs (top) directly in the constriction area (left) and in the lower right corner outside the constriction (right). The solid lines are guides for the eye.

Figure S2 in the Supporting Information for greater detail). To determine the error, we determine the variation from a series of bias free room temperature reference images that were taken with exactly the same imaging parameters used here. The error is about 1% (see Figures S2 and S3 in the Supporting Information). We do this for each of the micrographs collected over the time frame shown in Figure 2. Moreover, we independently examine the constriction and the region just outside by selecting a specific region to obtain the FT, as shown in panels a and b in Figure 3. In the ideal case, the Fourier transform will produce six spots in an isotropic hexagonal configuration due to graphene's 3-fold symmetry. However, in our case, the reflex spots are anisotropic. This anisotropy could be attributed to two reasons. In the first, a distortion of the image due to the aberration correction element may occur.²⁰ The corrector consists of two multipoles in which the first massively distorts the image and the second then reverses the distortion of the first multipole. This process is known to sometimes leave anisotropic image distortions even after an alignment procedure, resulting in an optimized phase plate. Factory alignments aim to keep the distortion below 1%; however, additional distortion can be introduced unintentionally by the user even with an optimized phase plate. However, within a working session, the distortion will remain constant so long as the system is not subjected to a further optimization process. In these studies, no realignment to the C_s correction is applied within a working session so any distortion present can be considered stable.²⁰ The second distortion process is strain, e.g., due to fabrication.²¹ Generally, all free-standing graphene membranes are subjected to a degree of strain and we also expect some strain in our graphene membrane to be the most probable scenario. Because of the anisotropy in the spatial

frequency of the reflex spots, we separate out each of the three directions and plot the (directional) spatial frequency against current density. This is done for two regions; inside the constriction (Figure 3, left side) and outside the constriction (Figure 3, right side). For each of the series for each direction, a least-squares fit is applied to highlight the trend in spatial frequency with respect to the current density (or reduction in ribbon width). In all cases, the spatial frequency is reduced as the current density increases and this corresponds to a relative lattice expansion. Within the constriction (Figure 3, left side), the spatial frequency reduction is noticeably larger in the 11 o'clock direction as compared to the other directions (1 o'clock and 3 o'clock). The 11 o'clock direction is parallel to the direction of the graphene sheet suspended across the gold electrodes, suggesting a tensile strain exists across the electrodes. If the change was solely due to tensile strain, contraction would be observed in the other two directions. However, we observe an additional expansion in all directions and this is concomitant with thermal expansion. Outside the constriction where the current density is much smaller, we expect a cooler region. Indeed, the smaller change in spatial frequency with current density indicates a cooler region. Moreover, the changes outside the constriction are approximately the same in all three directions. This can be expected, since inside the constriction the tension between the electrodes is concentrated in a small area. Similar investigations of the ribbon at an earlier stage where the ribbon width is larger, between 19 and 22 nm, show reduced and more parallel changes in the spatial frequency in keeping with a reduced strain and reduced temperature (see Figure S4 in the Supporting Information). These trends confirm that both strain and temperature changes are involved in the relative lattice changes we observe in the seamless bilayer ribbon. In addition, the spatial relaxation of the two graphene flakes remaining on the electrodes after failure (ribbon rupture) further confirms strain was present (see Figure S5 in the Supporting Information). Within the constriction (Figure 3, left side), the changes in spatial frequency correspond to a relative lattice expansion of around 1-1.5% in the 1 o'clock and 3 o'clock directions and a relative expansion of ca. 4-5% in the 11 o'clock direction.

Extrapolating our in-plane lattice expansion of 1-1.5% with temperature for bilayer graphene from theoretical predictions based on semiempirical interatomic interaction potentials²² yields a temperature between ~4000 and ~5500 K. Estimates based on quasiharmonic approximations for graphite show temperatures of more than 7500 K, while graphene never expands.²³ One can anticipate the temperature estimate for bilayer graphene to lie somewhere in between that for graphene and graphite. Calculations show that graphene melts at <4900 K.²⁴ Since the constriction is highly crystalline (no melting is observed), this reduces our estimation of the temperature window to between 4000 and 4900 K. Assuming a temperature of 4000 K,²² one can extrapolate a thermal conductivity, κ , of ca. 190 W (m K)⁻¹ (see the Supporting Information). This value does not include any changes introduced by strain; however, calculations for single layer graphene with a 5% strain show only a 30% increase in κ .^{25,26} This suggests the change in κ for our bilayer constriction due to strain will be rather limited. In essence, our obtained thermal conductivity is an order of magnitude smaller than the published value of 2800 W (m K)⁻¹ for bilayer graphene²⁷ and other sp² carbon based materials²⁸ (see Figure S6 in the Supporting Information). This implies

that the temperature estimate is too high. On the other hand, if we assume a thermal conductivity of 2800 W (m K)⁻¹, as reported for bilayer graphene,²⁷ a temperature estimate yields a value of approximately 630 K. This is significantly below a previously reported temperature of 2000 K for graphene at high bias.²⁹ In essence, the anomalously large lattice expansion is quantitatively too large to be explained in terms of Joule heating, since state-of-the-art calculations yield values that are too small by an order of magnitude. Thus, the expansion must be due to nonequilibrium effects in the electronic structure. Given the high density of electrons traversing the constriction, a possible nonequilibrium mechanism is impact ionization. Impact ionization is a process in which incoming electrons interact and excite valence electrons into antibonding states. Large expansions have been observed by X-ray diffraction and LEED in doped graphite (1% expansion) and "monolayer graphite" (3% expansion), resulting from charge transfer from bonding states to antibonding states, weakening the C–C bonds.^{30,31} Exciton formation in which electrons transfer from bonding states to antibonding states may result in lattice expansion.³² The production of excitons in graphene through impact ionization is reported to be an efficient process in both graphene^{33,34} and multilayer graphene.³⁵ In addition, highenergy electrons and elevated temperatures are argued to enhance impact ionization rates in graphene.³⁶ Moreover, any expansion that might arise from impact ionization may be anisotropic. In Ge and GaAs, the impact ionization coefficients have been shown to depend on crystal orientation.^{37,38} Thus, we postulate preferential excitation (weakening) of C-C bond electrons parallel to the current (so as to conserve momentum) in our constriction. This, in turn, leads to anisotropic lattice expansion; viz., impact ionization may contribute to the uniaxial lattice expansion we observe. Thus, we argue impact ionization could play a role in both the observed anomalously large lattice expansion as well as its anisotropy.

In summary, we employ atomic resolution *in situ* TEM to investigate the structural behavior of graphene bilayer constrictions at high bias. The studies show a localized lattice expansion in the constriction which increases as the constriction width decreases. For a constriction width below 10 nm, viz., shortly before failure, a lattice expansion above 1% is found. The anomalously large lattice expansion cannot be fully explained by thermal expansion. Impact ionization weakening the C–C bonds could explain the observed expansion. Moreover, the lattice expansion is anisotropic which can be attributed to strain; however, in addition, impact ionization may also contribute to the observed uniaxial lattice expansion, since impact ionization coefficients depend on crystal orientation.

ASSOCIATED CONTENT

S Supporting Information

Details of the device fabrication and calculation of the thermal conductivity are provided. In addition, supporting TEM data on the constriction are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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