Etching and narrowing of graphene from the edges

Xinran Wang and Hongjie Dai *

Large-scale graphene electronics requires lithographic patterning of narrow graphene nanoribbons for device integration. However, conventional lithography can only reliably pattern ~20-nm-wide GNR arrays limited by lithography resolution, while sub-5-nm GNRs are desirable for high on/off ratio field-effect transistors at room temperature. Here, we devised a gas phase chemical approach to etch graphene from the edges without damaging its basal plane. The reaction involved high temperature oxidation of graphene in a slightly reducing environment in the presence of ammonia to afford controlled etch rate (~≤1 nm min⁻¹). We fabricated ~20-30-nm-wide graphene nanoribbon arrays lithographically, and used the gas phase etching chemistry to narrow the ribbons down to <10 nm. For the first time, a high on/off ratio up to ~10⁴ was achieved at room temperature for field-effect transistors built with sub-5-nm-wide graphene nanoribbon semiconductors derived from lithographic patterning and narrowing. Our controlled etching method opens up a chemical way to control the size of various graphene nano-structures beyond the capability of top-down lithography.

Graphene has attracted much attention as a novel two-dimen-
sional system with great potential in future electronics develop-
ments¹,². Narrow graphene nanoribbons (GNRs) have
been used as semiconducting wires in field-effect transistors (FETs) that have high on/off ratios at room temperature³-⁹. Of the various methods used to produce narrow GNRs, including chemical sonication² and unzipping of carbon nanotubes⁵-¹⁰, top-down lithographic patterning of a large pristine graphene sheet into GNRs is appealing for large-scale device integration². To date, patterning methods have only produced arrays of GNRs with widths down to ~20 nm (except for short, narrow constrictions³) because of the limits of lithography resolution⁷,⁸, but GNRs narrower than ~5 nm with sufficiently large bandgaps are needed for room-temperature FET operation³-⁶,¹¹-¹³. Here, we demonstrate a gas-phase chemical approach to etching graphene from the edges without damaging its basal plane. The reaction involves high-temperature oxidation of the graphene in a slightly reducing environment, resulting in controlled (~≤1 nm min⁻¹) etching. We fabricated ~20–30-nm-wide GNR arrays by electron-beam lithography, and subsequently narrowed the GNRs using the gas-phase etching process. When GNRs narrowed to ~≤5 nm were used in GNR-FETs, bandgap opening related to quantum con-
struction occurs, enabling graphene from the edges to narrow the ribbons down to <10 nm. For the first time, a high on/off ratio up to ~10⁴ was achieved at room temperature for field-effect transistors built with sub-5-nm-wide graphene nanoribbon semiconductors derived from lithographic patterning and narrowing. Our controlled etching method opens up a chemical way to control the size of various graphene nano-structures beyond the capability of top-down lithography.

To devise a gas-phase chemistry process for etching and narrow-
ing graphene from the edges without creating defects in the basal plane, we investigated chemical etching of few-layer (~≤3 layers) mechanically exfoliated graphene on a 300-nm SiO₂/Si substrate under various oxidation conditions at high temperatures (Fig. 1 and Supplementary Figs S1,S2; see Methods for experimental details). We varied the partial pressure of O₂ and introduced Ar, H₂ or NH₃ as a dilution gas or to provide a reducing environment. We found that etching of the graphene was highly dependent on the gas mixture and reaction temperature, as well as on the number of layers of graphene (Supplementary Table S1). At 750 °C, ~100 mtorr of O₂ diluted by ~1 torr of Ar or H₂ gave an etch rate of ~3–5 nm min⁻¹ (~6–7 nm min⁻¹) for single- (double-) layer graphene (Supplementary Fig. S1). Interestingly, when using ~100 mtorr O₂ with ~1 torr 10% NH₃ in Ar as additive, we observed a considerably slower etching rate of ~2–2.5 nm min⁻¹ (~4 nm min⁻¹) for single- (double-) layer graphene (Supplementary Fig. S2). We then reduced the O₂ partial pressure to ~25 mtorr with a view to achieving slower etching. Under ~25 mtorr O₂ and ~1 torr H₂, the etching rate at 800 °C was ~3–3.5 nm min⁻¹ (~3.8–5 nm min⁻¹) for single- (double-) layer graphene (Supplementary Fig. S1). By introducing NH₃ into the system, we found that the etching rate was further lowered to less than ~1 nm min⁻¹ under ~25 mtorr of O₂ in ~1 torr of 10% NH₃ in Ar (Fig. 1, Supplementary Fig. S1 and Table S1). A slow etching rate is highly desirable for the controlled etching and narrowing of graphene and GNRs down to the ~≤5 nm regime.

We observed that graphene etching occurred predominantly at the edges and proceeded inwards isotropically (Fig. 1, Supplementary Figs S1,S2). As a result of the presence of bond dis-
orders and functional groups at the edges of the graphene, the chemical reactivity of the edge carbon atoms was higher than the perfectly bonded sp² carbon atoms in the basal plane¹⁴. Consequently, the graphene sheets were etched uniformly from the edges under controlled oxidation conditions. Holes or trenches were occasionally observed to have formed in the graphene due to etching that had initiated at point defects or line defects, respectively, within the graphene plane (Fig. 1d–f, Supplementary Fig. S1)¹⁴-¹⁶. Certain line defects were visible under atomic force microscopy (AFM), including wrinkles (Fig. 1d), although not all defects were observed by AFM (Supplementary Fig. S1a–d,e). Importantly, Raman spectroscopic mapping and imaging revealed that etching from the edges did not damage the basal plane of the pristine graphene, as indicated by the absence of the defect-related Raman band (D band) in the plane of the graphene sheets following etching (for example, Fig. 1g–i, Supplementary Fig. S2c,d). We observed redshifts of the Raman G band of graphene after etching in both O₂/NH₃ (Fig. 1i) and O₂/Ar conditions, which could not be fully explained but could be due to strain in the graphene sheets, indicated by the formation of the wrinkles sometimes observed following the high-temperature reaction process (Fig. 1e, Supplementary Fig. S1b,e)¹⁷,¹⁸.
Figure 1 | Gas-phase chemical etching and narrowing of graphene sheets. The etching conditions were \( \approx 25 \) mtorr O\(_2\) in Ar at 800 °C for 1 h. a,b, Graphene sheet imaged by AFM: as-made (a) and after etching (b). c, Overlay images before (yellow) and after (red) etching, with uniform etching from the edges observed at an etching rate of \( \approx 0.5 \) nm min\(^{-1}\). d-f, Another set of graphene sheet etching data. A wrinkle with high strain (bright strip) on the as-made graphene was etched away to form a trench. Etching rate, \( \approx 0.8 \) nm min\(^{-1}\). Note that new wrinkles (bright lines in e) were observed after the reaction, probably caused by thermal effects. g–i, Raman G band mapping of the graphene sheet in d and e before (g) and after (h) etching. i, Averaged Raman spectra from the graphene plane in g and h. The 2D band can be fit into 4 Lorentzians for both as-made and after-etching cases, indicating two-layer graphene both before and after etching\(^{21}\). No obvious D band is observed after etching in the plane of the graphene.

Figure 2 | Lithographically patterned GNR arrays and junctions. a, Schematics of the fabrications process. b, AFM image of a \( w \approx 20 \) nm GNR array at \( \approx 200 \) nm pitch. c, High-resolution AFM image of a \( w \approx 22 \) nm GNR array at \( \approx 500 \) nm pitch. d–g, AFM images of various GNR structures including alphabetic characters and zigzag junctions.
Our graphene etching process involves O₂ oxidation of graphene into CO or CO₂. During etching, O₂ molecules exothermally dissociate and form bonds with dangling carbon atoms at defect sites and edges. The slower etching rate observed under the NH₃ environment was attributed to in situ NH₃ reduction of oxygen groups formed during graphene oxidation. Our recent work on the reduction of graphene oxide suggests that NH₃ is more effective than H₂ in reducing oxygen groups in graphene oxide, and the NH₃ reduction effect could impede the oxidation of graphene when mixed with oxygen. It was also interesting that, under the same reaction conditions, thicker graphene sheets were etched more quickly than thinner ones (Supplementary Table S1, Fig. S2), a finding that is similar to earlier observations made for thick graphite. This also could not be fully explained, but could be due to the synergistic effects of oxygen groups at the edges of adjacent layers leading to self-catalysed etching at the edges of multilayer graphene.

As a control, we heated graphene in pure ammonia, and did not observe any etching effects (Supplementary Fig. S3). We succeeded in narrowing the GNRs uniformly from ~20 to ~8 nm (Fig. 3a,b). However, further narrowing generally resulted in breaks due to edge roughness and width variations in the as-patterned GNRs. By over-etching, we obtained ribbons with widths as narrow as ~20 nm, with most GNRs evolving into discontinuous segments down to less than 5 nm in width. Some of the segments were sufficiently long to be useful for integration into FET devices for electrical measurements (Fig. 4d). Edge roughness in as-made GNRs created by lithographic patterning is currently a limiting factor in producing long, uniform ultra-narrow GNRs over large areas.

We next fabricated GNR arrays by lithographic patterning, and used our gas-phase reaction to narrow the as-made ribbons to a width of several nanometres. GNR arrays were fabricated by electron-beam lithography and Ar plasma etching of exfoliated graphene on a 300-nm SiO₂/Si substrate (Fig. 2a; see Methods for details of the fabrication process). Rather than using the electron-beam resist as the etch mask, we instead used thin (~6.5 nm) Al lines (defined by a single-pixel electron beam) (Fig. 2a; see also Supplementary Information). The widths of the GNRs were measured by AFM with finite tip size deconvolution. The as-patterned GNRs had widths as narrow as ~20 nm, with a mean edge roughness δw = (w_{max} - w_{min})/2 < 5 nm (Fig. 2b-g). The edge roughness was caused by random fluctuating factors in the lithography and plasma etching processes. Lithographic patterning using Al as an etch mask is versatile, enabling graphene to be patterned into various structures with high reproducibility and consistency. For example, we easily fabricated alphabetic characters and junctions using GNRs with w ~ 20 nm (Fig. 2d-g); these could form interesting structures with which to study electron transport along the various crystallographic directions of graphene.

To create GNR-FETs with a high I_{on}/I_{off} ratio at room temperature, GNRs with w ~ 5 nm and sufficiently large bandgap (E_{g} > k_{B}T ≈ 26 meV) were required. We narrowed down the as-made w ~ 20 nm GNRs using the 0.5–1 nm min⁻¹ etching condition (25 mtorr O₂ in 1 torr NH₃/Ar at 800 °C). (It was found to be difficult to narrow the GNRs with good width control in several control experiments using other conditions; Supplementary Fig. S3.) We succeeded in narrowing the GNRs uniformly from ~20 to ~8 nm without obvious breaks along the ribbons (Fig. 3a,b). However, further narrowing generally resulted in breaks due to edge roughness and width variations in the as-patterned GNRs. By over-etching, we obtained ribbons with w ~ 5 nm, with most GNRs evolving into discontinuous segments down to less than 5 nm in width. Some of the segments were sufficiently long to be useful for integration into FET devices for electrical measurements (Fig. 4d). Edge roughness in as-made GNRs created by lithographic patterning is currently a limiting factor in producing long, uniform ultra-narrow GNRs over large areas.

We carried out Raman spectroscopic measurements on the as-made and narrowed GNRs (Fig. 3c,d). For as-made GNRs with w ~ 20 nm, several pronounced peaks were observed, including a D band (~1,340 cm⁻¹), G band (~1,590 cm⁻¹), D' band (~1,620 cm⁻¹) and 2D band (~2,670 cm⁻¹) (Fig. 3c). The intensity ratio between the D and G bands, I_D/I_G, was ~1–2. The presence of defect-related D and D' bands was attributed to the edges of GNRs, because no D band was observed in the parent graphene sheet.

For a GNR with w ~ 20 nm, ~1% of the carbon atoms are at the edges, resulting in D and D' bands as expected. We observed lower I_D/I_G ratios in wider GNRs (see Supplementary Information; Fig. S7), consistent with reduced edge effects. After narrowing to less than ~10 nm, the intensity of the G and 2D bands of the graphene reduced, the I_D/I_G ratio increased, and the G and D' peaks were broadened to form a single and up-shifted G peak (Fig. 3d). These changes in the Raman spectra were a...
result of a higher percentage of the atoms being edge atoms in narrowed GNRs. The $I_{on}/I_{off}$ ratios of our narrowed GNRs were larger than similar-width GNRs derived chemically\(^4\), suggesting a higher degree of edge roughness and disorder in the former.

We fabricated electrical devices with as-made and narrowed GNRs with Pd source and drain electrodes and heavily doped Si back-gate (see Methods). At room temperature, the devices comprising as-made $w \approx 20 \text{ nm}$ GNR and GNR arrays typically showed $I_{on}/I_{off}$ current ratios of less than $\sim 3$ (Supplementary Fig. S4)\(^{5,6,8}\), indicating insufficient bandgap (compared to $k_BT \approx 26 \text{ meV}$) for room-temperature FETs. The bandgap of a perfect GNR is predicted to scale inverse linearly with GNR widths, and $E_G \approx (0.3-1.5 \text{ eV nm})/w$ (nm) depending on the orientation and edge configuration of the ribbons\(^{12,13}\). For GNRs narrowed down to $\sim 10 \text{ nm}$, we observed an $I_{on max}/I_{on min}$ ratio of $\sim 10$ at room temperature (Supplementary Fig. S5). Using long GNRs narrowed down to $w \approx 8 \text{ nm}$ with good continuity (Fig. 3b), we fabricated a FET comprising an array of GNRs arranged in parallel and with interdigitized electrodes as contacts (Fig. 4a). We observed a high $I_{on}/I_{off}$ ratio of up to $\sim 50$ at room temperature, and an ‘on’ state current of $\sim 20 \mu\text{A}$ ($\sim 40$ times that of single-ribbon devices) at $V_{ds} = -500 \text{ mV}$ (Fig. 4b,c) with $\sim 40$ GNR sections (channel length $\approx 160 \text{ nm}$).

For GNRs narrowed down to the $w \leq 5 \text{ nm}$ regime, because of limitations resulting from discontinuity in the ribbons, we fabricated devices only on single ribbons rather than with parallel arrays. Figure 4e,f presents room-temperature $I_{on}-V_{gs}$ and $I_{off}-V_{ds}$ characteristics of a GNR-FET with $w \approx 4 \text{ nm}$ GNR (see Supplementary Fig. S6 for another example). The device exhibited ambipolar transport in air with $I_{on}/I_{off} > 1 \times 10^4$ (Fig. 4e), clear evidence of bandgap opening through lateral quantum confinement\(^4,6,11-13\). This is the highest room-temperature $I_{on}/I_{off}$ ratio reported for GNRs derived from lithographic patterning\(^4,6\). In vacuum, the device shows an intrinsic n-type behaviour, with the threshold voltage shifted to the negative gate voltage side due to desorption of physisorbed species including oxygen\(^23\). Based on ambipolar $I_{on}-V_{gs}$ characteristics, we estimated the bandgap of the GNR to be $E_G \approx 0.4 \text{ eV}$ from $I_{on}/I_{off} \approx \exp(E_G/2k_BT)$, because the off-state current was thermally activated over a body-Schottky barrier of $\sim E_G/2$ (ref. 8).

In conclusion, we have developed a process for controlling chemical narrowing of graphene to yield quantum confined structures. Parallel GNR arrays were used to create graphene FETs with high ‘on’ currents and a high on/off ratio of $\sim 50$ at room temperature. Single ribbons based on lithography were narrowed to below $\sim 5 \text{ nm}$ to afford on/off ratios of $\sim 1 \times 10^4$. On the single-ribbon basis, our narrowed GNRs exhibited lower ‘on’ currents than our previously reported chemically derived sub-10-nm GNRs on the same 300-nm SiO$_2$ substrate\(^3\). The narrowed lithography-derived GNRs showed rougher and more disordered edges, as reflected from Raman spectroscopy data. Edge disorder caused scattering effects that contributed to the low ‘on’ currents of the GNR devices\(^24,25\). There were variations between the devices, such as doping, probably due to differences in the detailed edge structures. Clearly, the success of our approach is currently limited by the edge roughness introduced in the patterning process, and much

Figure 4 | FETs from lithographically patterned and chemically narrowed GNRs and parallel GNR arrays. a, AFM images of a $w \approx 8 \text{ nm}$ GNR-array FET (top panel, the same array as in Fig. 3b) with interdigitized electrodes used to contact $\sim 40$ GNRs in parallel (channel length, $\sim 160 \text{ nm}$). Bottom panel, enlarged image of the device. Source (S) and drain (D) contacts are marked on all images. b, Room-temperature $I_{on}-V_{gs}$ characteristics of the GNR-array FET in a, probed in air. The $I_{on}/I_{off}$ ratio is $\sim 50$. c, $I_{on}-V_{ds}$ characteristics of the same device in a, probed in air. From top to bottom, $V_{gs} = -40$ to $50 \text{ V}$ in steps of $10 \text{ V}$. d, AFM images of as-made and narrowed GNRs with breaks along the ribbon. The highlighted part is less than $5 \text{ nm}$ in width, and was used to make a GNR-FET. e, Room-temperature $I_{on}-V_{gs}$ characteristics of the GNR-FET fabricated from the GNR in d. The device demonstrated an $I_{on}/I_{off}$ ratio greater than $10^4$ when probed in air and in vacuum. $V_{gs} = 10 \text{ mV}$ for both curves. f, $I_{on}-V_{ds}$ characteristics for the device in e, but probed in vacuum. From top to bottom, $V_{gs} = 40$ to $-30 \text{ V}$ in $10 \text{ V}$ steps. Inset: AFM image of the GNR-FET.
effort should be directed in the future towards making smooth edges by either improving the lithographic patterning processes or by developing novel chemical means to perfect the edges. Some recent experiments have demonstrated the promise of making graphene and GNRs with atomically well-defined edges by using anisotropic etching 27–30, which could be combined with narrowing to produce long, uniform sub-5-nm GNR semiconductors to produce high-performance graphene transistors for potential digital applications. This could lead to an appealing future for graphene, in particular because chemical narrowing of GNRs with well-defined crystallographic orientations could yield semiconducting GNRs with desired edge structures.

Methods

Preparation of mechanically exfoliated graphene, microscopy and spectroscopy characterizations, and lithographic patterning of GNRs. Graphene sheets used in etching experiments under various conditions were mechanically exfoliated from highly oriented pyrolitic graphite (HOPG) in a vacuum of ~ 300-nm SiO 2 /Si substrate using Scotch tape 31. Subsequent annealing in ~ 2 torr H 2 at 800 °C for ~ 15 min was carried out to clean the substrate and graphene sheets. AFM and Raman mapping were then used to characterize the graphene sheets before and after the gas-phase reaction. Raman mapping was carried out by a Horiba Jobin Yvon LabRAM HR Raman microscope with 633-nm laser excitation (spot size ~ 1 μm; power ~ 5–50 mW). We used a step size of 100 nm and accumulation time of 4 s to map the graphene sheets. The graphene sheets used for patterning the GNRs were mechanically exfoliated on a thermally grown ~ 300-nm SiO 2 /p++ Si substrate with pre-patterned Ti/Au markers and were annealed at ~ 600 °C for ~ 15 min (Ti/Au markers melt at higher temperatures). We used an optical microscope to locate few-layer (~3 layers) graphene sheets and then carried out Raman spectroscopy to determine the number of layers. We spun ~ 70-nm poly(methyl methacrylate) (PMMA) with a molecular weight of 950 kDa as the electron-beam lithography resist. Single pixel lines were exposed in a Raith 150 system in the Stanford Nanofabrication Facility with an acceleration voltage of 10 keV and line dosage of 650 μC cm−1. Wider GNRs could be made by exposing areas instead of single pixel lines. Development was carried out in cold (4 °C) 1:3 methyl iso-butyl ketone:isopropanol solution for 75 s to provide a good edge roughness in the resist profile 32. A 6.5-nm thick Al film was then electron-beam evaporated, followed by standard lift-off. Argon plasma etching was carried out in an MPC plasmaetcher for ~ 20–30 s (depending on the number of layers of graphene), under an Ar flow rate of ~ 10 cm 3 min−1, chamber pressure of ~40 mtorr and plasma power of ~10 W. After plasma etching, the chips were soaked in 0.1 mol l−1 KOH water solution for ~2 min to remove the Al lines. We then annealed the chips in ~ 2 torr H 2 at 600 °C to clean resist any residues from the substrate.

Gas-phase chemical etching of graphene in a vacuum furnace. Gas-phase etching of the graphene sheets and narrowing of the GNRs were carried out in a vacuum furnace connected to a mechanical pump, with a base pressure of ~15 mtorr. Note that a leak-free vacuum system was essential to achieving high reproducibility in the etching results. From experience, we have found that the etching rate is sensitive to the detailed configuration of the vacuum furnace and may vary in different systems. The vacuum level in the furnace was monitored by a Millipore CML series cryogenic vacuum probe station connected to a turbo pump. The base pressure of the system was ~1 × 10−8 torr.

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References


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Author contributions

X.W. and H.D. conceived and designed the experiments. X.W. performed the experiments and analysed the data. X.W. and H.D. co-wrote the paper. Both authors discussed the results and commented on the manuscript.

Additional information

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