Aligned Graphene Nanoribbons and Crossbars from Unzipped Carbon Nanotubes

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ABSTRACT
Aligned graphene nanoribbon (GNR) arrays have been made by unzipping of aligned single-walled and few-walled carbon nanotube (CNT) arrays. Nanotube unzipping was achieved by a polymer-protected Ar plasma etching method, and the resulting nanoribbon array can be transferred onto any chosen substrate. Atomic force microscope (AFM) imaging and Raman mapping on the same CNTs before and after unzipping confirmed that ~80% of CNTs were opened up to form single layer sub-10 nm GNRs. Electrical devices made from the GNRs (after annealing in H₂ at high temperature) showed on/off current (I_on/I_off) ratios up to 10³ at room temperature, suggesting the semiconducting nature of the narrow GNRs. Novel GNR–GNR and GNR–CNT crossbars were fabricated by transferring GNR arrays across GNR and CNT arrays, respectively. The production of such ordered graphene nanoribbon architectures may allow for large scale integration of GNRs into nanoelectronics or optoelectronics.

KEYWORDS
Graphene nanoribbon, single-walled carbon nanotubes, aligned, unzipping, plasma etching

Graphene nanoribbons have emerged as an interesting material with a wealth of electronic and spin transport properties [1–6]. Narrow (sub-10 nm) GNRs open up band gaps useful for field effect transistors (FETs) [1–4]. Several approaches have been developed to make GNRs, such as lithographic patterning [5–9], sonochemical methods [1, 10], chemical vapor deposition (CVD) [11, 12], nanocutting [13–15] and unzipping of carbon nanotubes (CNTs) [16–22]. For integration of GNRs into devices, in addition to controlling their width, edge smoothness and quality, it is important to control the alignment of GNRs. Among existing methods, lithographic patterning is capable of fabricating large arrays of aligned GNRs but the width and edge smoothness of GNRs are not well controlled, especially at the sub-10 nm scale. Unzipping CNTs offers a possibility to meet these challenges since much progress has been made on controlled synthesis (alignment, density, length and diameter controls) of CNTs in the past two decades [23–25]. Our previous work demonstrated that GNRs with well controlled width in the 10–20 nm range and smooth edges could be made by unzipping multiwalled carbon nanotubes (MWNTs) using a polymer-protected plasma etching method [16]. Most recently, we developed a new method that produced highly pristine nanoribbons.
by unzipping mildly gas-phase oxidized MWNTs sonochemically in an organic solvent [22]. Thus far, GNRs from unzipped CNTs have lacked the alignment and ordering on substrates required for device integration.

Here, we show that highly aligned, narrow GNRs can be made from an aligned array of single-walled carbon nanotubes (SWNTs) by our polymer-protected plasma etching method (Figs. 1(a) and 1(b)). Aligned CNTs were first partially embedded in a polymer film and the unprotected sides of CNTs were then exposed to Ar plasma. The polymer film served as an etching mask and enabled the longitudinal unzipping of CNTs [16]. The alignment of CNTs was maintained through embedding in the polymer film, unzipping by plasma and transferring to another substrate. Considering the topographic similarity between narrow GNRs and SWNTs, we performed careful atomic force microscope (AFM) imaging and Raman spectroscopic measurements on the same CNTs before and after the unzipping process to obtain spectroscopic evidence of successful unzipping of CNTs into GNRs. Both the obvious decrease in topographic height obtained by AFM and changes in Raman spectra of the same CNTs

Figure 1  GNR array made from CNT array. Schematic illustration of the fabrication of a GNR array (b) from a CNT array (a) by PMMA-protected plasma etching. Typical AFM images of (c) a pristine CNT array and (d) the resulting GNR array. Insets in (c) and (d) are zoom-in images of an individual CNT and GNR, respectively. AFM images of individual GNRs with widths of (e) 8 nm, (f) 4 nm, and (g) 2 nm. (h) AFM image and schematic illustration of CNT–GNR junctions in a partially unzipped tube.
after unzipping confirmed the creation of GNRs. FETs with an individual GNR and arrays of GNRs as channel materials showed on/off current ($I_{\text{on}}/I_{\text{off}}$) ratios up to $10^3$ and 20, respectively. Our method also allowed for the formation of crossbars of GNR–GNR and GNR–CNT for the first time.

The starting materials used were dense (1–2 tubes/μm), uniform, highly aligned arrays of long (~1 mm) CNTs (diameter: 0.6–3.4 nm; ~80% were SWNTs and ~20% were few-walled CNTs and bundles) grown on ST-cut quartz by CVD [26]. We used markers to track specific CNTs through the unzipping process. We first transferred an as-grown CNT array from quartz to SiO$_2$/Si substrates with a sputtered gold marker array by a nano-transfer printing technique [27]. After that, the CNT array was unzipped following a similar procedure to that in our previous work [16]. Briefly, a thin film of poly(methyl methacrylate) (PMMA) was spin-coated on top of the CNT array. After baking, CNTs and gold markers were embedded in the PMMA film. The PMMA/CNTs film with gold markers was then peeled off in a KOH solution. The film was then exposed to 5 W Ar plasma for various times. With the protection of PMMA, only the exposed part of the tube sidewall was etched by the Ar plasma. After etching, the film was contact-printed to another SiO$_2$/Si substrate. Finally, the PMMA film was removed by acetone vapor and followed by calcination at 300 °C for 20 min, leaving the unzipped GNRs and gold markers on the target substrate. The protection of PMMA afforded longitudinal unzipping of CNTs and maintained the alignment of CNTs throughout the whole process; both are critical to the creation of highly aligned GNR arrays.

AFM characterization found that the resulting GNRs were mostly single-layered with average height of ~1.0 nm (Fig. 1(d) and Fig. S-1(b) in the Electronic Supplementary Material (ESM)). The starting CNTs exhibited an average diameter of ~1.4 nm (Fig. 1(c) and Fig. S-1(a) in the ESM). The GNR array maintained the main features of their parent CNT array including high density, good alignment and ultra-long length. The widths of most obtained GNRs fell into the range of 2–8 nm (see Fig. S-1(c) in the ESM). As shown in the AFM images (Figs. 1(e)–1(g) and Fig. S-2 in the ESM), the edges of the GNRs appeared smooth and uniform along their length. GNR–CNT junction-like structures were also observed in some partially unzipped tubes due to nonuniform etching caused by local deformations of the PMMA film (Fig. 1(h)). The etching conditions were critical to the successful unzipping of SWNTs. We found that the optimized etching condition was 5 W (the lowest stable power we could use) for 10 s, which was able to unzip the majority of tubes without introducing many breaks.

By locating specific CNTs with the aid of markers, we obtained AFM images and Raman spectra of the same CNTs before and after plasma etching. As shown in Figs. 2(a) and 2(b), the height of CNTs decreased by ~0.4–0.9 nm after the unzipping process, which indicated that the CNTs were opened up into GNRs by the Ar plasma. We found that the unzipping efficiency was dependent on the diameter of the parent tubes. Small SWNTs (diameter <1.0 nm) were totally etched by the plasma whilst CNTs with a diameter of >2.5 nm were not unzipped under the condition used. All the CNTs with medium diameters (1.0–2.5 nm) were successfully converted into sub-10 nm GNRs. Therefore, the yield of GNRs (~80%) was limited by the diameter distribution of the starting CNTs. Besides the decrease in height, important changes were also observed in the Raman spectra of CNTs after unzipping. The Raman spectra of pristine CNTs showed a strong G-band and no obvious D-band, which indicated the high quality of the starting materials [28]. After the unzipping process, the Raman G-band intensity decreased by ~60% and a strong D-band appeared (Figs. 2(c) to 2(f)). The appearance of the D-band can be attributed to the creation of edges that act as defects responsible for momentum conservation in the double resonance Raman process [29, 30]. The D-band to G-band ($I_D/I_G$) ratio of the GNRs in the array was ~1.5, much higher than for the parent raw tubes (<0.01). The marked increase in $I_D/I_G$ ratio also confirmed that the CNTs were unzipped by our method. We also performed Raman mapping over individual GNRs (see Fig. S-3 in the ESM) and the averaged $I_D/I_G$ ratio of individual GNRs was ~1.5. The averaged $I_D/I_G$ ratio of the sub-10 nm GNRs obtained here was higher than for wider GNRs made by unzipping MWNTs by the same approach due to the much narrower width (2–8 nm) and proportionally higher defect density at the edges [16].
We fabricated FETs on an individual GNR and arrays of GNRs, with palladium (Pd) as source/drain (S/D) metal contacts (channel length $L \sim 100$ nm), a p++ Si backgate, and 100 nm SiO$_2$ as gate dielectric. The resulting devices of as-made single GNRs showed higher resistance and lower $I_{on}/I_{off}$ ratio ($<10^2$) at room temperature than observed for sub-10 nm GNRs made by the previous sonochemical approach [1], which suggested a high defect density in our as-made GNRs. To improve the quality, we carried out thermal annealing aimed at reducing the number of defects on the GNRs generated by the plasma etching process. We found that thermal annealing in 1 Torr of H$_2$ at 800 °C for 20 min improved the electrical properties of GNRs. The $I_{on}/I_{off}$ ratios and on-state conductance improved. Figures 3(a) and 3(b) show a ~2 nm wide
annealed GNR with an $I_{on}/I_{off}$ ratio of ~500 and on-state current of ~500 nA at a bias voltage ($V_{ds}$) of 1 V. We also fabricated FET devices on a small array of aligned GNRs. A FET made of three aligned GNRs showed an $I_{on}/I_{off}$ ratio of 20 and on-state current of 1.5 μA at $V_{ds} = 1$ V (Figs. 3(c) and 3(d)). These results suggested that the sub-10 nm GNRs made by the PMMA-protected plasma unzipping method contained a high defect density, partly due to the ultra-narrow widths of the ribbons. Strategies should be devised to improve the quality of aligned narrow GNRs for practical application in nanoelectronics.

The aligned GNRs were explored as building blocks for constructing complex two-dimensional (2-D) structures. We fabricated crossbar structures potentially useful as logic and memory elements in nanoelectronics [31–33] using GNR arrays. Crossbar arrays of GNRs were fabricated by transferring an aligned GNR array on top of another array with a rotation of 90°. The two layers of GNR arrays formed well ordered square mesh structures as evidenced by AFM and Raman G-band images (Figs. 4(a) and 4(b)). Figure 4(c) shows an AFM image of a GNR–GNR junction. Besides GNR–GNR crossbars, we also made two configurations of GNR–CNT crossbar arrays by transferring GNRs on top of CNTs or CNTs on top of GNRs (Fig. 4(d) and Fig. S-4(a) in the ESM). In the GNR–CNT junction, a ~6 nm wide single layer GNR was placed on the top of a CNT (diameter ~3.3 nm) and induced a radial deformation of ~0.3 nm on the underneath CNT at

![Figure 3](image_url)  
FETs with an individual GNR and a small array of GNRs. (a) Plot of source–drain current versus gate voltage ($I_{ds}$) of a ~2 nm wide single layer GNR probed in air at $V_{ds} = 10$ mV. Inset: AFM image of the GNR–FET. The $I_{on}/I_{off}$ ratio of this GNR device was ~500. (b) Current–voltage ($I_{ds}$) curves for the device in (a) at various gate biases $V_{gs}$ from −30 V to 30 V in steps of 5 V from bottom to top. (c) $I_{ds}$ curve of a FET made on an array of 3 GNRs at $V_{ds} = 10$ mV. Inset: AFM image of the GNR–FET. The width of these GNRs were ~5 nm, ~3 nm, and ~4 nm from left to right. The $I_{on}/I_{off}$ ratio of this device was ~20. (d) $I_{ds}$–$V_{ds}$ curves for the device in (c) at various gate biases $V_{gs}$ from −30 V to 30 V in steps of 5 V from bottom to top.
the cross point (Fig. 4(d) and Fig. S-4(c) in the ESM), which has also been observed in CNT–CNT junctions [34] (Figs. S-4(b) and S-4(d) in the ESM). No obvious deformation was found when the CNTs were placed on top of GNRs (Fig. S-4(a) in the ESM). The successful fabrication of GNR–GNR and GNR–CNT crossbars will make it possible to explore the fundamental properties and possible applications of these junctions.

In summary, well aligned narrow (<10 nm) GNR arrays have been made from CNT arrays by polymer-protected plasma unzipping. Well ordered 2-D architectures of GNR–GNR and GNR–CNT crossbars were constructed. Our approach is compatible with semiconductor processing to obtain GNR arrays. However, future work is required to improve the quality of the narrow GNRs unzipped from small nanotubes for applications in high performance nanoelectronics. Nevertheless, the current work represents the beginning of making GNR arrays from nanotube arrays and opens up a way to large scale integration of GNRs into nanoelectronics or optoelectronics.

**Experimental**

**Preparation of GNR arrays.** Aligned CNTs were transferred from a quartz substrate to a SiO₂/Si substrate with a prefabricated marker array (formed by electron beam lithography (EBL) and sputtering of 30 nm gold) using the procedures described in Ref. 27. Selected CNTs were located with the aid of markers and characterized using AFM and Raman mapping. Subsequently, a PMMA solution ($M_w = 495,000$, 5% in
anisole) was spin-coated on the substrate at 3000 revolutions per minute (rpm) for 1 min and then baked at 170 °C for 2 h on a hotplate. The PMMA film was peeled off together with the CNTs and gold markers in 1 mol/L KOH solution at 80 °C. Then the film was rinsed with water and dried in air. The film was then exposed to a 5 W Ar plasma for 10 s in a plasma reactive ion etching (RIE) system (MRC Model 55) at a base pressure of 40 m Torr. After etching, the film was printed onto a SiO2/Si substrate. PMMA was then removed with the vapor of acetone, leaving the unzipped CNTs and gold markers on the target substrate. Finally, the substrate was calcined at 300 °C for 20 min to remove PMMA residue. To improve the quality of GNRs, the calcined GNRs were annealed in H2 at 800 °C for 20 min at a pressure of 1 Torr.

Characterization of GNRs. AFM images of the GNR were taken with a Nanoscope IIIa multimode instrument in tapping mode. Raman spectra of GNRs were collected with Horiba Jobin Yvon LabRAM HR Raman microscope with a 633 nm He–Ne laser excitation (spot size ~1 μm, power ~10 mW). The step size of mapping was 100 nm and the integration time was 10 s at each spot.

Device fabrication. Before making devices, we first patterned the dense and long GNR arrays within isolated regions using EBL and O2 plasma etching. We then did a second EBL followed by electron beam deposition of Pd (30 nm) and lift-off to fabricate arrays of source- and drain-electrodes on the GNRs. The channel length of these devices was ~200 nm and the width of source and drain electrodes varied from 500 nm and 5 μm for single- and multiple ribbon devices, respectively. The devices were annealed in Ar at 220 °C for 15 min to improve the contact quality. AFM was then used to identify devices with a single or multiple GNR connection. Electrical characterization of the devices was carried out in air using a semiconductor analyzer (Agilent 4156C).

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