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Wrinkle Engineering: A New Approach to Massive Graphene Nanoribbon Arrays

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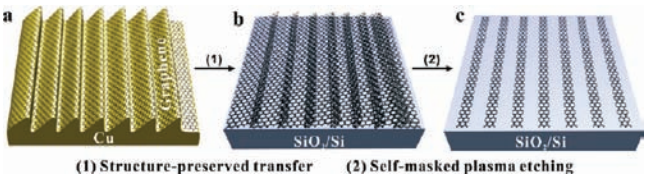
Supporting Information

ABSTRACT: Wrinkles are often formed on CVD-graphene in an uncontrollable way. By designing the surface morphology of growth substrate together with a suitable transfer technique, we are able to engineer the dimension, density, and orientation of wrinkles on transferred CVD-graphene. Such kind of wrinkle engineering is employed to fabricate highly aligned graphene nanoribbon (GNR) arrays by self-masked plasma-etching. Strictly consistent with the designed wrinkles, the density of GNR arrays varied from ~0.5 to 5 GNRs/μm, and over 88% GNRs are less than 10 nm in width. Electrical transport measurements of these GNR-based FETs exhibit an on/off ratio of ~30, suggesting an opened bandgap. Our wrinkle engineering approach allows very easily for a massive production of GNR arrays with bandgap-required widths, which opens a practical pathway for large-scale integrated graphene devices.

Strictly two-dimensional (2D) membranes have a tendency to be crumpled to minimize the total free energy. Intrinsic ripples have been proved to exist on the surface of graphene, a 2D material of sp^2 hybridized carbon atoms.[1,2] Similarly, wrinkles are often observed on graphene grown from chemical vapor deposition (CVD) process.[3,4] For highly corrugated growth substrates, the surface structures can be replicated by the grown graphene film, which collapses into highly wrinkled or folded graphene after transferring onto smooth solid substrates with a suitable transfer medium and conditions.[5,6] Such wrinkled graphenes may exhibit unique properties distinct from homogeneous planar graphene. The ability to engineer the wrinkles or foldings may lead to a better control of graphene morphology and thereby to a deliberate tuning of its properties.

Graphene is intrinsically a semi-metal and, therefore, introducing a bandgap is the prerequisite for graphene-based CMOS electronics. There have been a few approaches for the bandgap opening of graphene,[7−11] among which, formation of graphene nanoribbons (GNRs) is regarded as the most effective pathway.[12] Due to the quantum confinement effect, graphene transforms from semi-metal to semi-conductor as the ribbon width is decreased to several nanometers and the bandgap of GNRs is inversely proportional to the ribbon width.[13] A number of methods have been developed to fabricate GNRs, including conventional electron beam lithography,[14] longitudinal unzipping of carbon nanotubes,[15,16] template-directed growth,[17] and bottom-up organic synthesis.[18]

Scheme 1. Wrinkle engineering for fabricating GNRs array[a]



[a] (a) CVD growth of graphene on nanostructured Cu foil; (b) transfer of graphene from corrugated Cu foil to flat SiO_2/Si substrate by structure-preserved transfer technique; (c) fabrication of GNRs array by self-masked plasma etching.

We report herein a facile way to fabricate high-density aligned GNRs arrays based on the wrinkle engineering of CVD-graphene. Starting from the structural designing of growth substrate as well as the effective control of the transfer process, we have achieved large-area oriented GNRs with a density as high as 5 GNRs per μm and a characteristic width less than 10 nm. With high scalability and massive productivity, our approach opens a practical pathway for large-scale integrated graphene devices.

As illustrated in Scheme 1, our strategy involves three steps, a) CVD growth of single layer graphene on micro/nanostructured Cu foil; b) structure-preserved transfer from growth substrate to flat SiO_2/Si substrate for formation of regularly wrinkled or folded graphene; c) fabrication of GNRs arrays by self-masked plasma etching.

Mechanical processing of Cu foil very easily induces parallel slip lines on the surface along its specific crystalline facet (Figure S1a). In the CVD growth process of graphene at high temperature, these slip lines create surface steps with a height of 20−30 nm and a variable step densities (Figures S1b, 1c). We employed such mechanical slip lines to demonstrate the concept of wrinkle engineering and the fabrication of GNRs arrays. Our CVD growth of graphene was typically conducted in a thermal tube furnace at 1020 °C and 95 Pa (2 sccm H_2, 35 sccm CH_4) on 25 μm-thick Cu foils (Alfa Aesar, item No. 13382) for 20 min. Predominantly single layer graphene was formed on Cu foil, following up the surface steps.[19] Figure 1a shows a typical scanning electron microscope (SEM, Hitachi S-4800) image of CVD graphene on Cu foil with a step density of ca. 5 per μm. Highly corrugated graphene films are easily obtained on such stepped Cu foils.

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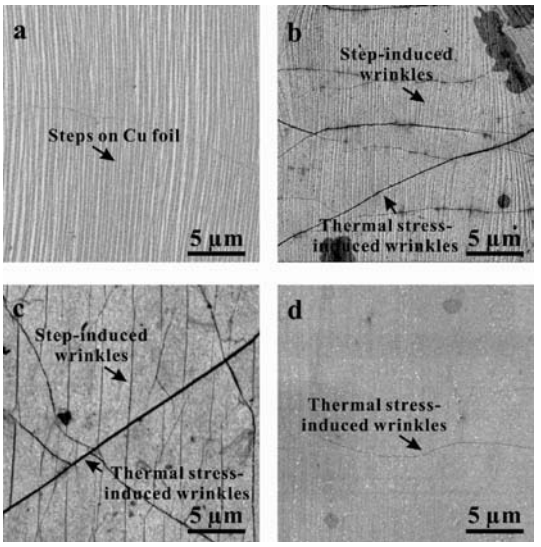

Figure 1. Surface structure-replicated graphene growth and structure preservation/releasing transfer control. (a) SEM image of single layer graphene grown on Cu foil having a step density of 5 per μm. (b) SEM image of highly wrinkled graphene on SiO_2/Si substrate transferred from (a) using PMMA/Au transfer medium. (c) Wrinkled graphene transferred from a Cu foil having a step density of ~0.5 per μm. (d) Graphene film transferred from a Cu foil having a step density of 5 per μm using a conventional PMMA transfer medium with 24 h of soaking treatment in water.

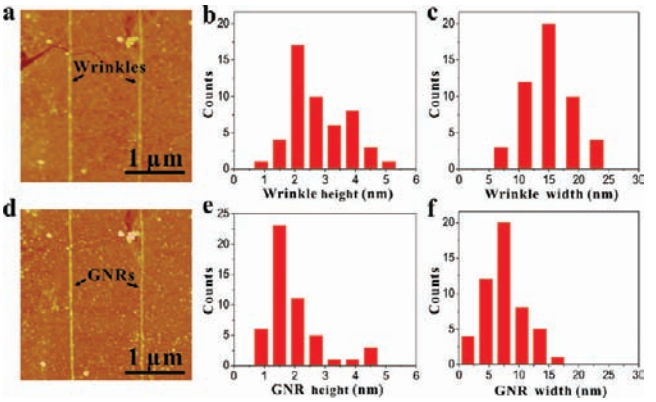

Figure 2. (a, d) AFM images of folded graphene wrinkles and the corresponding GNRs obtained by air plasma etching (30 W, 30 s, SiO_2/Si substrate). (b, c) Histograms of wrinkle height and width on transferred graphene with a wrinkle density of ~3 per μm. (e, f) Height and width distributions of obtained GNRs.

The key factor for wrinkle engineering, to a large extent, depends on the transfer process from growth substrate to target surface. Because of the high flexibility and relatively weak interaction with Cu substrate, the graphene film can well replicate the surface topography of Cu foil. However, such kinds of corrugated graphene structures are mostly released during transfer process.[6] After a large number of trial and error experiments, we found an effective route to preserve these corrugations on graphene. The critical point is to choose a suitable transfer medium, flowable enough to fully replicate the microscopic structures of graphene/Cu foil and rigid enough after hardening to preserve the replicated structures. A 200 nm PMMA film (poly(methyl methacrylate), Microchem, AR-P 679.04, 950,000 MW, 4 wt % in ethyl lactate) with back-coated 80 nm Au layer was found to fit for this criterion. Figure 1b exhibits the SEM image of highly wrinkled graphene film on 300 nm SiO_2/Si substrate, transferred from Cu foil in Figure 1a. Obviously, the surface topographic structures in two figures are highly correlated with each other. With a Cu foil having low step density, the density of wrinkles in transferred graphene film decreases accordingly (Figure 1c). The wrinkle density of transferred graphene can be regulated from ~0.5 to 5 per μm by changing the density of slip lines on Cu foils. It is noted that there are a few irregular wrinkles with higher contrast crossing over the vertical parallel wrinkles, which arise from the well-known thermal expansion effect.[20] On the other hand, when using the conventional flexible PMMA film as the transfer medium together with a prolonged soaking time of PMMA/graphene film in water, the surface step-induced wrinkles can be mostly released as seen in Figure 1d while the thermal expansion-derived wrinkle still exists. In a word, the microscopic surface structures of growth substrate can be replicated by the grown graphene and preserved in the transferred graphene with a designed transfer medium, demonstrating the possibility of wrinkle engineering of graphene with a suitable structural design of growth substrate.

Atomic force microscopy (AFM, Veeco Instrument, Nanoscope IIIA) provides more microscopic information of the wrinkled graphene. Figure 2a shows the AFM image of two typical parallel wrinkles on the transferred graphene on SiO_2/Si substrate. We performed a statistical analysis of 50 parallel wrinkles and summarized their height and width distributions in Figures 2b and 2c, respectively. The wrinkle height falls into a range of 1.1−5.2 nm, with a mean value of 2.8 nm, which could be assigned to various folding structures.[5] The wrinkle width exhibits a narrow distribution with a mean value of 15.8 nm, comparable with the step heights on Cu foil. Obviously, the transferred graphene tends to fold, predominantly into triple-layered wrinkles along the surface steps of Cu foil (Scheme 1b). Such kinds of folded graphene wrinkles provide an alternative route to fabricate GNRs via a self-masked plasma etching technique. Shown in Figure 2d is the GNRs array obtained by exposing the folded graphene in Figure 2a to 30 W air plasma for 30 s. The graphene film was etched away except for the folded wrinkle area, where the top layers were sacrificed and the remaining bottom layer formed GNRs. The statistical height and width data of over 50 GNRs are given in Figure 2e and f. Compared with the original folded wrinkles, the height distribution shifts to a mean value of 1.9 nm, corresponding to a decrease of one to two layers. On the other hand, the widths of thus-obtained GNRs fall into a range of 2.1−16.1 nm with a mean value of 7.4 nm. Apparently, the GNRs are narrower than the original wrinkles, which are attributed to the overetching from wrinkle edges.

Raman spectroscopic measurements give further evidence for the formation of GNRs.[21] As shown in Figure 3a, the unfolded graphene film lost all the Raman spectral features after air plasma etching. In contrast, the folded or wrinkled graphene still exhibits the characteristic D and G bands (Figure 3b) after the same etching treatment. In particular, the D band becomes remarkably enhanced, indicative of formation of graphene nanoribbons.[22] Figure 3c shows the typical GNRs array on SiO_2/Si substrate fabricated by similar plasma etching. By regulating the density of wrinkles with different Cu foils, we can easily change the density of GNRs as seen in Figure 3d and e. The available range of ribbon

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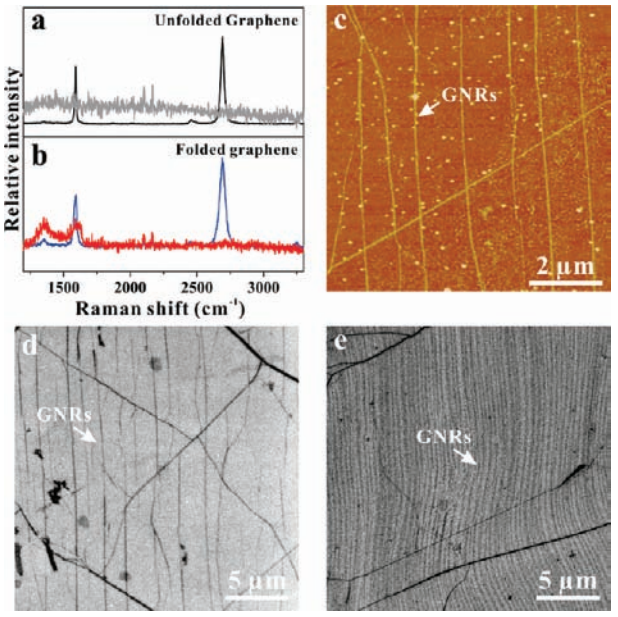

Figure 3. (a) Raman spectra of unfolded single layer graphene before (black) and after (gray) air plasma etching. (b) Raman spectra of folded or wrinkled graphene before (blue) and after (red) air plasma etching. The etching conditions were 30 W, 15 sccm air for 30 s. (c) AFM image of GNRs array on SiO_2/Si substrate fabricated by air plasma etching. (d, e) SEM images of GNRs array with a density of 0.5 and 5 GNRs per μm, respectively.

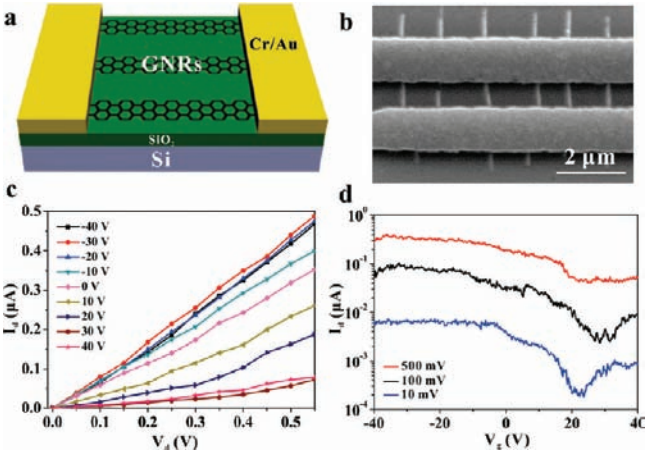

Figure 4. (a) Schematic of a GNRs array FET device with 8 nm Cr/50 nm Au as the source/drain, 300 nm SiO_2 as the gate dielectric and highly doped Si as the backgate. (b) SEM image of a 6 GNRs array device with a conduction channel of ~1 μm. (c) Drain current versus source-drain voltage (I_d–V_d) recorded for the device in (b) under various V_g ranging from −40 to 40 V in a step of 10 V. (d) Transfer characteristics (current versus gate voltage) for the device in (b) at V_d = 10 mV, 100 mV, and 500 mV, respectively.

density was from 0.5 to 5 GNRs per μm. Again, the random ribbons in Figure 3c–e arose from the thermally induced wrinkles.

The electrical performance of thus-fabricated GNRs array was examined by constructing the back-gated field-effect transistors (FETs, Figure 4a). The source/drain (S/D) metal contacts were 8 nm Cr/50 nm Au, made by thermal evaporation and electron beam lithography with a channel length of 1 μm. Highly doped Si substrate with 300 nm SiO_2 dielectric layer was used as the back gate. Figure 4b shows one of the typical FET devices with 6 GNRs in parallel as the conduction channel. Different from the original wrinkled graphene film (Figure S2), the GNRs array exhibited characteristic quantum-confined semi-conducting characteristics as seen in Figure 4c and d. Obviously, the channel resistance is remarkably tuned by gate voltage (V_g) when V_g is changed from −40 to 40 V in 10 V steps. The current–gate voltage curves showed an I_{on}/I_{off} ratio over 30 at V_d = 10 mV, suggesting a bandgap of ~0.1 eV for our GNRs array device,[14] which is also consistent with the previous results.[23] The observed electrical performance is in accord with the AFM measurement results of GNRs width because only GNRs having sub-10 nm width exhibit bandgaps at room temperature.[23] It should be noted that our FETs were based on the GNRs array, in which the I_{on}/I_{off} ratio would be decreased once larger GNRs were involved.[24] By engineering narrower and more uniform wrinkles, GNRs array devices with higher I_{on}/I_{off} ratio can be obtained. The resistivity of our GNRs array is ~56.8 kΩ/sq, which is acceptable compared with the same width of GNRs.[22] Further efforts to obtain better electronic performances of GNRs array should be centered on developing an etching technique.

In brief, we have demonstrated an experimental pathway to engineer the wrinkles or foldings on CVD graphene by designing the microscopic structures of growth substrates together with a suitable transfer technique. Such kinds of wrinkle engineering provide a facile way to produce large-area oriented GNRs array with a controllable density and a width down to sub-10 nm. Different from previously reported techniques, the presented approach is scalable and cost-effective for production of GNRs array, offering a great opportunity to integrate graphene devices.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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