Adlayer-Free Large-Area Single Crystal Graphene Grown on a Cu(111) Foil

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To date, thousands of publications have reported chemical vapor deposition growth of “single layer” graphene, but none of them has described truly single layer graphene over large area because a fraction of the area has adlayers. It is found that the amount of subsurface carbon (leading to additional nuclei) in Cu foils directly correlates with the extent of adlayer growth. Annealing in hydrogen gas atmosphere depletes the subsurface carbon in the Cu foil. Adlayer-free single crystal and polycrystalline single layer graphene films are grown on Cu(111) and polycrystalline Cu foils containing no subsurface carbon, respectively. This single crystal graphene contains parallel, centimeter-long ≈100 nm wide “folds,” separated by 20 to 50 µm, while folds (and wrinkles) are distributed quasi-randomly in the polycrystalline graphene film. High-performance field-effect transistors are readily fabricated in the large regions between adjacent parallel folds in the adlayer-free single crystal graphene film.

Chemical vapor deposition (CVD) is currently the most promising method for making large-area graphene since it can produce a large-area film on a Cu foil, which can be transferred to an arbitrary substrate for further study or use.[1] Two exciting challenges for CVD growth are (i) achieving perfect uniformity in the number of layers over a large area (single or double layers, for example), that can be used for consistent (homogeneous) device performance compared to devices that have adlayer regions present, and where these adlayer regions also differ in, e.g., density and size when present in the active regions of devices, and (ii) the growth of single crystal graphene over a large area, because the presence of grain boundaries (GBs) lowers carrier mobility[2] and thermal conductivity,[3] and can reduce the mechanical strength.[4] Large-area single crystal adlayer-free single layer graphene is preferred for fabricating integrated devices, and is also critical for making “stacked graphene crystals” with controlled rotation angles by step-by-step bottom-up assembly.[5]

Cu foil has been used for the reported growth of a large-area “single layer” graphene film.[1b,6] However, adlayers (bilayer or multilayer regions) have always been present in such films.[1b,7] To reduce the number/size of such regions, surface morphology/roughness and cleanliness, crystal orientation of the foil, and growth conditions (H2/CH4 ratio, continuous or pulsed introduction of CH4), have been investigated.[8] It has been reported that the surface roughness of the Cu foil is related to the density of adlayers. Chemical–mechanical polishing was used to smooth the Cu foil surface and suppress the nucleation of graphene and thus the density of adlayers.[8e] A graphene film that was >95% single layer was reportedly grown on an electrochemically polished Cu foil using a low...
methane concentration.\[8c\] In addition to surface roughness, the surface cleanliness of the foil has been discussed. It has been reported that pretreating the foil by oxidizing it in air at 1025 °C led to the growth of single layer graphene with few adlayers. The feedstock for the adlayers has been reported to be organic contaminants adsorbed on the surface of the foil, which can be removed by annealing in air.\[8c\] The crystallographic orientation of the Cu foil has also been reported to affect the growth of graphene—and adlayers. (111) facets reportedly gave faster graphene growth with fewer adlayers compared to facets with other orientations.\[8b,f\] and this was stated as possibly being due to a higher diffusion rate of carbon species on Cu(111),\[8c,9\] and the smooth surface of such facets was also proposed to suppress adlayer formation.\[8b\] Another approach has recently been reported that yielded single layer graphene with very few adlayers by restricting the diffusion of carbon from the backside of the Cu foil using a Ni support substrate.\[10] Although the density of adlayers was suppressed by these strategies, a clear picture of the mechanism(s) for growing few-to no-adlayer graphene by CVD has not been obtained, and a reliable and controllable approach is needed for the growth of single layer graphene that never contains adlayers.

In addition to adlayers, GBs are present in polycrystalline graphene films prepared by CVD where graphene islands with different crystallographic orientations join to complete the film. The growth of graphene from a single nucleus to a large single crystal island has been reported.\[11\] The presence of surface oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on the Cu foil was found to decrease the number of nucleation sites by passivating Cu surface active sites and face oxygen on theCu foil by annealing it in H2 at 1060 °C. After removing the carbon from the as-received polycrystalline Cu foil by annealing it in H2 at 1060 °C, an adlayer-free polycrystalline solid layer graphene film could be grown on it. We have thus shown why adlayers are formed and how to ensure their absence.

The crystallinity and morphology of the adlayer-free single layer graphene film grown on Cu(111) were then investigated. This film is single crystal as indicated by liquid-crystal-assisted polarized optical microscopy (POM), low-energy electron diffraction (LEED) and micro-LEED, and ultrahigh-vacuum scanning tunneling microscopy (UHV-STM). Highly aligned long “graphene folds” were also observed in these films, while “quasi-random” folds and wrinkles were observed on graphene grown on polycrystalline Cu foils, regardless of whether adlayers are present.

With these new graphene samples, we were able to study the scattering effect of adlayers, of GBs, and of graphene folds, by measurements using graphene field-effect transistors (GFETs) that had one or none of these features present in the active region. We found that adlayers, GBs, and folds, all significantly decrease the carrier mobility of the device. By patterning GFETs with the device channel parallel to the graphene folds and using the region between two adjacent folds in the film, thus eliminating adlayers, GBs, and folds, high performance devices with room temperature mobilities of around 1.0 × 10^6 cm^2 V^-1 s^-1 for both holes and electrons were obtained.

**Growth of Graphene on Cu(111) and As-Received Polycrystalline Cu Foils:** CVD growth of graphene was performed on polycrystalline and single crystal Cu(111) foils. The single crystal Cu(111) foil was made from the polycrystalline Cu foil by our contact-free annealing method (Figure S1, Supporting Information). Three different conditions for the growth of a continuous graphene film on either the Cu(111) single crystal foil or the polycrystalline Cu foil were performed with H2/CH4 ratios in the range 100:1 to 1000:1, and a pressure during growth in the range of 2.0 to 30.0 Torr (Figure 1a,b; Figure S2, Supporting Information). For both the single crystal Cu(111) and polycrystalline Cu foils, continuous graphene films were obtained. The graphene films grown on the polycrystalline Cu foils have adlayers (bilayer and multilayer) present over the entire foil (Figure 1b; Figure S2c,d, Supporting Information). It has been reported that GB regions produce a higher density of graphene nuclei than areas away from them.\[8d\] In addition, different orientations of Cu grains were reported to affect the growth of single layer graphene and also adlayers.\[8b,f\] The Cu(111) facet has been reported to facilitate the fast growth of high-quality graphene with fewer adlayers compared to facets with other orientations.\[8b,f\] due to the higher diffusion rate of carbon species on Cu(111).\[9\] However, examination of the adlayers in our graphene films grown on polycrystalline Cu foils shows that the adlayers are randomly distributed.
and show no preference for nucleation in GB regions, and no difference in adlayer size and density is seen for different Cu facets (Figure S3a, Supporting Information). We stopped the growth of graphene on a polycrystalline Cu foil after 5 min in order to examine it before a completely continuous film was formed, and found graphene islands with an areal coverage of ≈70% (Figure S3b, Supporting Information). An adlayer was seen at the center of every graphene island, suggesting that one adlayer was formed at every nucleation site for the single layer graphene, implying that the density of adlayers is the same as the density of nucleation sites when a continuous film is formed. The graphene islands were preferentially nucleated along lines parallel to the rolling direction of the foil. It was also observed that the nucleation of islands was uniformly and randomly distributed over different facets of the Cu foil, as well as the GBs, indicating that both GBs and Cu facet orientation had no effect on the nucleation of both single layer graphene islands and adlayers in our growth conditions. By contrast, graphene films grown on single crystal Cu(111) foils had no adlayers over the entire foil (Figure 1a; Figures S2a,b and S4, Supporting Information) for the same growth conditions, again over a wide processing window. In other words,
we always obtained adlayer-free graphene on our Cu(111) foils but always had adlayers on the as-received Cu foils. We shall discuss this observation in detail later.

Raman spectroscopy was used to characterize the quality, uniformity, and the number of layers in the graphene.[17] Figure 1c–h shows two typical Raman maps of graphene grown on a single crystal Cu(111) foil (adlayer-free) and a polycrystalline Cu foil (with adlayers) using a H₂/CH₄ gas flow of 100 sccm/1 sccm and a pressure of 2.0 Torr. The D band (indicative of disorder and defects)[17] is absent over all areas mapped (Figure 1d,g), so that the graphene with and without adlayers is all high-quality. The width of the 2D band is sensitive to the number of graphene layers.[18] Figure 1c shows a typical Raman map of the full width at half maximum (FWHM) of the 2D band for the graphene grown on a Cu(111) foil. The band has an FWHM of ≈28 cm⁻¹, which is typical for single layer graphene.[18] The uniformity of the map indicates that the entire area is adlayer-free. In addition, two “line” structures were observed in Figure 1c that had a wider 2D band FWHM of ≈35 cm⁻¹, and a stronger G band intensity (Figure 1e) than single layer graphene. A scanning electron microscopy (SEM) image of this region (inset in Figure 1d) shows line structures that are darker than the single layer graphene. These are identified as graphene folds and will be discussed later.

For a graphene film grown on a polycrystalline Cu foil, the Raman map of the 2D FWHM is not uniform (Figure 1f), and can be divided into two: single and adlayer regions. Similar to the adlayer-free graphene grown on Cu(111), the single layer region in Figure 1f has an FWHM of 30 cm⁻¹, but small patches with an FWHM varying from 25 to 50 cm⁻¹ are assigned to adlayer regions. The 2D FWHM of bilayer graphene is sensitive to the stacking orientation of the two layers.[19] Two representative Raman spectra of adlayers are shown in Figure 1h, in which Curve 4 shows a misoriented bilayer region and Curve 5 shows a bilayer region close to AB-stacking.

**Kinetics of the Growth of Graphene Examined by Isotope Labeling:**

The growth of graphene on both Cu(111) and polycrystalline Cu foils was studied by carbon isotope labeling and Raman mapping.[11,g,i,15,20] Figure 2 shows typical Raman maps of graphene islands grown on the two kinds of Cu foils. For this study we used hydrogen (45 sccm) and methane (30 sccm of 0.1% diluted methane in Ar) at 2.0 Torr to obtain graphene islands up to 15 µm in size. The isotope labeling process is shown below Figure 2. Characteristic Raman bands are labeled G₁³ (1523 cm⁻¹), 2D₁³ (2570 cm⁻¹), G₁² (1585 cm⁻¹), and 2D₁² (2675 cm⁻¹), corresponding to the G, and 2D bands of ¹³C and ¹²C graphene, respectively.[15] Hexagonal rings from ¹³C and ¹²C graphene, respectively.[15] Hexagonal rings from ¹³C and ¹²C graphene, respectively.[15] Hexagonal rings from ¹³C and ¹²C graphene, respectively.[15] Hexagonal rings from ¹³C and ¹²C graphene, respectively.[15] Hexagonal rings from ¹³C and ¹²C graphene, respectively.[15] Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively. Hexagonal rings from ¹³C and ¹²C graphene, respectively.

![Figure 2](image-url)
islands grown on the Cu(111) foil (Figure 2b,c). The consistent graphene island shapes suggest that the kinetics remain unchanged during the sequential dosing. The growth rate of an individual graphene island, which can be calculated from the widths of the bands, is almost constant (0.21 ± 0.011 μm min⁻¹, averaged from five graphene islands, Figure S5, Supporting Information). Figure 2f–g shows Raman maps of a graphene island with a bilayer island at its center that was grown on a polycrystalline Cu foil under identical growth conditions to those used for the growth on a Cu(111) foil. In the single layer region, similar rings were observed as for that grown on the Cu(111). Note that the width of the ring in the single layer region is comparable to that shown in Figure 2b, i.e., the growth rate of a graphene island on a polycrystalline Cu foil (0.20 ± 0.012 μm min⁻¹, averaged from five graphene islands, Figure S6, Supporting Information) is similar to that on a Cu(111) foil. For the adlayer region, rings with a constant width were also observed, although they were much narrower than in the single layer region, indicating an adlayer growth rate about half that of the single layer region (0.091 ± 0.0088 μm min⁻¹, averaged from four adlayer regions, Figure S6, Supporting Information). In addition, the growth of the adlayer started at the same nucleation point and stopped with the same number of “isotopically labeled bands” because of the same number of 13CH4 and 12CH4 cycles as the top single layer, which strongly suggests that the adlayer grows at the same time as the single layer.

The stacking sequence of the adlayer with respect to the other graphene layer (which is larger in size compared to the adlayer) when grown on a polycrystalline Cu foil is investigated by using isotope labeling,[21] and we find that the adlayer grows underneath the first graphene layer (see Figures S7 and S8, Supporting Information). This stacking sequence, also known as the “inverted wedding cake” model,[21] seems to play a role in the slow growth rate of the adlayers. The growth of the adlayer is enabled by the diffusion of C species from decomposition of methane into the “nanoCVD chamber” between the top single layer and the Cu surface (why and how this adlayer was nucleated will be discussed later). The extreme “physical confinement” in this chamber results in a lower partial pressure of the carbon species, which results in a decreased growth rate of the adlayer.[15]

Observation of Adlayers, Why they Occur, and How to Eliminate Them: Why is the graphene grown on our single crystal Cu(111) foil always adlayer-free but that grown on as-received polycrystalline Cu foil under identical conditions always has adlayers? It has been reported that organic contaminants adsorbed on the surface of the Cu foil are the feedstock for the growth of adlayers, and oxidizing the foil in air at 1025 °C to burn away organic surface contaminants was reported to be effective for growing a single layer graphene film with few adlayers.[8d] We have also performed ToF-SIMS depth profiling of the 13C intensity after the growth of complete graphene films from 13CH4 (Figure S12, Supporting Information). An increase of 13C content in both the Cu(111) and the polycrystalline Cu foils was observed after graphene growth (Figure S12c,d, Supporting Information), suggesting that carbon also diffuses into the polycrystalline Cu foil under the growth conditions used, although the final amount of carbon inside the polycrystalline Cu foil is lower than before growth (Figure 3a).

ToF-SIMS depth profiling of the 13C intensity after the growth of complete graphene films from 13CH4 (Figure S12, Supporting Information). An increase of 13C content in both the Cu(111) and the polycrystalline Cu foils was observed after graphene growth (Figure S12c,d, Supporting Information), suggesting that carbon also diffuses into the polycrystalline Cu foil under the growth conditions used, although the final amount of carbon inside the polycrystalline Cu foil is lower than before growth (Figure 3a).

The carbon inside the polycrystalline Cu foil was thus identified as the likely reason for the presence of adlayers, since it can diffuse out of the foil at the growth temperature used. At this temperature, the Cu foil catalytically decomposes methane to C3H6 species and/or carbon adatoms, and some fraction of these remains adsorbed on its surface. Graphene nucleates and grows into islands from these adsorbed species and such islands merge to form a continuous graphene film during continued growth.[16a,23] In this proposed mechanism of nucleation by methane, it is suggested that single layer graphene film
without any adlayers can be grown if a “proper concentration” of methane is used in which only nuclei of single layer graphene are enabled. Indeed, it has been observed that the density of adlayers in the graphene film is dependent on the methane/hydrogen ratio used for growth.[7c,24] Based on this assumption, one can imagine that an adlayer-free graphene film could be grown using a “proper” methane to hydrogen ratio, but the fact is that growing an adlayer-free graphene film on Cu foils is very challenging. A recently published paper has presented the growth of adlayer-free single layer polycrystalline graphene on a polycrystalline copper foil by placing the foil in a “suspended configuration,” in which an “equal concentration of methane” on each side of the foil was said to avoid the growth of adlayers from the diffusion of carbon from the backside of the foil.[25] However, our isotope labeling results (Figure 2) clearly show that adlayers are not grown due to diffusion from the backside but that they grow simultaneously with the top single layer graphene. Furthermore, with our as-received Cu foils we do not generate adlayer-free polycrystalline graphene following the method used by these authors, although the adlayer coverage is certainly low. Both of these results suggest that the mechanism proposed by the authors is untenable—we disagree with their suggested mechanism, and discuss this in the Supporting Information.

In addition to the decomposition of methane, the carbon that is already present inside the Cu foil at the growth temperature needs to be considered. A recent paper says that such carbon can form graphene flakes (islands) on a Cu foil surface by diffusing out without any external carbon sources.[26] However, our growth results using $^{13}$CH$_4$ gas suggest that the graphene film (including adlayers) is entirely grown from the methane gas. We thus consider the effect of internal carbon as follows. The carbon diffuses from the interior of the Cu foil to the surface, as shown by the ToF-SIMS depth profile results, and generates “nuclei” for graphene growth leading to adlayers. In other words, for a Cu foil without any dissolved carbon the nucleation of graphene depends only on the dissociation of methane and, under the rather wide range of processing conditions discussed here, single layer graphene without adlayers is always obtained.

Figure 3. a,b) ToF-SIMS spectra of carbon “intensity” inside Cu foils. c) Evolution of CO$_2$ in the combustion analysis of Cu foils. Note that poly-Cu is the as-received polycrystalline Cu foil; annealed poly-Cu the as-received polycrystalline Cu foil after annealing for 18 h as described in the text, and poly-Cu (G) and Cu(111) (G) are the as-received polycrystalline Cu foil and Cu(111) foil after graphene growth on them. d) SEM image of an adlayer-free polycrystalline graphene film grown on an annealed polycrystalline Cu foil. e) Optical image and f) Raman map of 2D band FWHM of adlayer-free graphene films on 300 nm SiO$_2$/Si wafers transferred from annealed polycrystalline Cu foils. g) Raman spectra taken from (f).
layer islands. But in contrast to the situation where the Cu contains a relatively large amount of subsurface carbon, there are two types of nuclei, namely (i) those that grow into islands that ultimately merge to form a continuous single graphene layer and (ii) nuclei that form at the interface between some of these islands and the Cu foil as a result of carbon atoms inside the foil diffusing out to form nuclei at that interface, that then grow into adlayers. For this situation in which the Cu foil contains small amounts of carbon (but not zero), adlayers do not nucleate beneath every single graphene island, and graphene film with a lower density of adlayers will be formed. Indeed, a smaller density of adlayers was observed when growing graphene films on foils with lower amounts of carbon inside them. This will be discussed later.

The carbon inside the Cu foil only participates in the nucleation of the graphene, and the further growth of these nuclei into islands is largely or entirely due to the decomposition of methane. Our experiments with $^{13}$CH$_4$ (Figures S9 and S10, Supporting Information) show that growth after nucleation of both the continuous single layer and the adlayers is from the decomposition of methane because no Raman peak from $^{13}$C-graphene was observed. Indeed, the graphene nucleus consists of only 20–24 atoms and is smaller than 1 nm in size.$^{[27]}$ It not only will not appear in a standard Raman spectrum, but will probably not be observable by tip-enhanced Raman spectroscopy$^{[28]}$ or ToF-SIMS.

Our procedure for making the Cu(111) foil suggests that annealing at 1060 °C in the presence of H$_2$ removes the carbon contaminants inside the foil. We therefore annealed the polycrystalline Cu foil at 1060 °C in a mixed flow of H$_2$ (50 sccm) and Ar (50 sccm) under 1 atm for times of 15 min to 18 h (Figure S13, Supporting Information). A significant decrease of the amount of carbon inside the foil was observed as the annealing time was increased. ToF-SIMS results show that carbon is removed from the polycrystalline Cu foil to essentially the same level as for the Cu(111) foil for all depths when the foil is annealed for longer than 1 h (Figure 3b; Figure S13, Supporting Information). We describe the adlayer-free polycrystalline graphene film grown on these nearly carbon-free polycrystalline Cu foils later.

Combustion analysis is an effective way of quantitatively determining the amount of carbon inside a sample. The sample is heated in an oxygen gas flow by an induction furnace, and any CO$_2$ formed by the combustion of the carbon contaminants is detected by infrared absorption, and through calibration yields the carbon content in the sample.$^{[29]}$ We did combustion analysis on three types of Cu foils: our home-made Cu(111), as-received polycrystalline Cu, and the same polycrystalline Cu foil annealed for 18 h under H$_2$. In the data shown in Figure 3c the peak area corresponds to the carbon content in the foil. Ten samples of each foil with the same 40 µm thickness were combusted and the average carbon content was 5.1 ± 2.0 wt ppm for Cu(111), 5.2 ± 2.2 wt ppm for the annealed polycrystalline Cu, and 18.6 ± 3.0 wt ppm for the as-received polycrystalline Cu foil. As with our discussion of the ToF-SIMS profiling results (Figure 3a; Figure S11, Supporting Information), the Cu(111) foil has very little carbon inside the foil but has adventitious carbon adsorbed on its surface. It has been reported that such adventitious carbon may contain polymeric hydrocarbon species (C–C/C=H), together with minor components containing C–O–C and O=C=O bonds.$^{[30]}$ It has also been reported that a “typical” adventitious carbon film is 0.6 ± 0.2 nm thick and contains carbon and oxygen ([O]/[C] = 0.11 ± 0.02).$^{[32]}$ Considering that most polymers have a density of approximately 1 g cm$^{-3}$, we estimate the carbon content of the adsorbed adventitious carbon layer to be ~2.0–4.0 wt ppm for our 40 µm thick Cu foils, which is comparable to the carbon content measured by combustion analysis of the Cu(111) and annealed polycrystalline Cu foils, also indicating that the carbon content inside these two foils is extremely low, i.e., it can be accounted for as primarily being adventitious carbon on the foil surface. To further test if the carbon content measured by combustion is almost entirely due to adventitious carbon, we measured Cu(111) and annealed polycrystalline Cu foils (ten samples for each) with a thickness of 20 µm by combustion; the measured carbon content values were 9.0 ± 1.5 wt ppm for Cu(111) and 8.7 ± 2.0 wt ppm for annealed polycrystalline Cu, which are almost double that measured for the 40 µm thick foils, further suggesting that the measured carbon content from combustion for these two samples is very likely due to the adsorbed adventitious carbon. If we assume the as-received polycrystalline Cu foil has a similar adventitious carbon content adsorbed on its surface, the combustion measurement allows us to infer a carbon content of ~13.5 wt ppm (~71.4 at ppm) inside that type of foil. Note that this value is much higher than the reported solubility of carbon in solid Cu at 1293 K, namely ~7.4 at ppm.$^{[39]}$ This suggested to us that carbon contaminants inside the as-received polycrystalline Cu foil are not uniformly distributed at the atomic scale. The ToF-SIMS results (Figure 3a) show that there is a carbon concentration gradient in the polycrystalline Cu, usually to a depth of less than ~300 nm. In addition, a much higher amount of carbon was found near the surface than the interior region by energy-dispersive X-ray spectroscopy measurements made on a cross-section of a polycrystalline Cu foil (Figure S14, Supporting Information). We thus concluded that the carbon is mainly in the near surface region of the polycrystalline Cu foil. This carbon is embedded in the Cu foil during manufacture, probably from hydrocarbon-based oil(s) used on the rollers at the high rolling temperatures.$^{[32]}$ What then are the ways the carbon is removed from the interior of the as-received polycrystalline Cu foils to yield foils free of any carbon, at least to the sensitivity levels of our measurements? We have undertaken some further ToF-SIMS surface spectroscopy and depth profiling experiments on the as-received foils prior to any treatment, and also on foils heat treated under (i) H$_2$ or (ii) D$_2$ gas. Details of these experiments are given in Figure S15 of the Supporting Information. From these experiments, we found not only C, but also CH and CH$_2$ species inside the as-received foil, and also that it is likely that some subsurface CH (CD) species are generated by exposure to the hydrogen (deuterium) gas at a temperature of 1060 °C. High-temperature annealing the Cu foil in H$_2$ is an effective way to remove carbon from the foils but it is not the only way. Other methods including mechanical- and/or electrochemical-polishing of the foil to remove the first 300 nm or more where a very high concentration of carbon exists; following this by annealing in a gas such as O$_2$ or water vapor which
can react with carbon to form gaseous species might work as well.

We now consider the growth of graphene on the annealed polycrystalline Cu foils. A decrease in the density of adlayers was observed when growing graphene film on a foil that had been annealed under H<sub>2</sub>(g) for 5 min (Figure S16c, Supporting Information). A further decrease in adlayer density was observed when the annealing time was increased to 15 and 30 min. An adlayer-free continuous single layer film was grown on a foil after annealing for 1 h (Figure S16f, Supporting Information) and on a different foil after annealing for 18 h (Figure 3d–g). These results prove that the density of adlayers depends on the carbon concentration inside the foil, i.e., less carbon (including in the region close to the surface) leads to fewer adlayers and the absence of carbon leads to adlayer-free graphene. The Raman map (Figure 3f) has a uniform 2D FWHM of 26–30 cm<sup>-1</sup>, meaning that the graphene is uniform with no adlayers, and the absence of the D band shows the high quality of this adlayer-free graphene film.

**Experimental Verification of Large-Area Single-Crystal Graphene:**
We studied the crystallinity of the adlayer-free graphene film grown on the Cu(111) foil using micro-LEED, UHV-STM, and liquid-crystal-assisted POM. Cu steps with a height of ≈0.19 nm under the graphene film were observed in the STM images (Figure 4a–c). We checked six random regions over an adlayer-free continuous graphene film coating a 3 cm × 2 cm Cu(111) foil. Three regions are shown in high resolution in Figure 4d–f. The graphene lattice shows the same

![Image of Figure 4](https://www.advancedsciencenews.com)

Figure 4. a,b) Large-area STM images and d–f) atomic resolution STM images of adlayer-free single crystal graphene film on a Cu(111) foil. The insets in (d–f) show the FFT patterns of the STM images. c) Height profile along the white arrow line in (b). g) LEED pattern (beam size ≈1 mm) of an adlayer-free graphene film on a Cu(111) foil. h) Representative LEED patterns (beam size of ≈23 µm) from four different regions of another adlayer-free single crystal graphene film on a Cu(111) foil. i) Distribution of graphene lattice orientation angles determined from micro-LEED patterns at 2500 different positions.
orientation in the three images, as do the fast Fourier transformation (FFT) patterns of the STM images, suggesting that the whole film is a single crystal. Large area LEED (beam size ≈1 mm, Figure 4g; Figure S17, Supporting Information) patterns were taken from four regions of an adlayer-free graphene film coating a Cu(111) foil (1 cm × 1 cm) with all showing only one graphene orientation, suggesting the entire film is a single crystal. LEED patterns with a higher spatial resolution (beam size ≈23 µm) were obtained in six regions of another adlayer-free graphene film coating a 1 cm × 1 cm Cu(111) foil and all had the same orientation (Figure 4h, two of them are not shown), again suggesting that the entire film is a single crystal. A closer examination of the crystallinity and epitaxy of the graphene film on smaller scale was made by micro-LEED measurements on very small selected areas with a diameter of 250 nm. Three randomly selected regions of area 6.20 µm × 6.20 µm were scanned point by point by precisely moving the electron beam so that half the spot overlapped the next spot, in order to interpret any change in the diffraction pattern. This gave 2500 diffraction patterns for each region and these were used to determine the lattice orientation at each point. The three regions showed very similar distributions of the graphene lattice orientation. A histogram of the lattice orientation angles in one region is shown in Figure 4i showing a symmetrical distribution centered at the aligned “0°” orientation (which refers to the most frequently observed orientation angle), with an FWHM of ≈0.4°. We note that these small variations in the graphene lattice orientation do not suggest the presence of GBs between graphene domains. A similar small (FWHM ≈0.4°) distribution of lattice orientations in graphene formed on a Ru(0001) surface has also been observed,[33] even though graphene grown epitaxially on Ru(0001) has only one possible orientation with respect to the underlying Ru(0001) surface.[12a,34] Such small lattice misorientations are thought to be due to point defects formed during the growth. We also note that when graphene is grown on a metal substrate such as Cu and cooled to room temperature, the thermal contraction of the substrate causes compressive stress at the graphene–substrate interface that undoubtedly distorts the lattice.[35] Both of these possibilities may explain the small lattice misorientations (≈0.4°) in single crystal graphene grown epitaxially on, e.g., a Cu(111) foil. We also note that 295 of the 2500 patterns show Moiré patterns (Figure S18, Supporting Information), from which the rotation angle of graphene with respect to the underlying Cu(111) lattice was calculated to be (0.6 ± 0.2)° with a Moiré supercell of a size of (6.3 ± 0.6) nm (Figure S18, Supporting Information). We note that the “misorientation angle” between the graphene lattice and the Cu(111) surface where the graphene is epitaxially grown has been reported in a range from 0° to even 30°, possibly due to different growth conditions and/or the quality of the Cu(111) substrate (such as the density of steps on its surface).[12c-f,36] In our case, we found a misorientation angle of (0.6 ± 0.2)° as discussed above.

We also checked the crystallinity of the continuous graphene films grown on Cu(111) and polycrystalline Cu foils by liquid-crystal-assisted POM.[17] Two batches of samples were studied. Continuous graphene films grown on Cu(111) show a uniform birefringence color across the whole sample, indicating that the film is single crystal (Figure S19b,d, Supporting Information), while graphene grown on a polycrystalline Cu foil is polycrystalline and shows grains with different contrast (Figure S19a,c, Supporting Information).

Parallel graphene “fold” structures (a graphene wrinkle collapsed to form a trilayer-like structure)[12b,38] were also observed in these single crystal adlayer-free graphene films (Figure 1a; Figure S2a,b, Supporting Information) grown on Cu(111), and these are almost certainly due to the thermal contraction of the Cu(111) foil during cooling to room temperature. When cooled from the growth temperature to room temperature the Cu foils contract by about 2%, which causes compressive stress at the interface, compressive strain in the regions where the graphene adheres to the Cu, and also to the formation of wrinkles/folds because the stress is sufficiently high to cause graphene release in those regions.[12d] Our Raman study shows that the adlayer-free graphene film in the fold-free regions has a biaxial compressive strain ranging from 0.1% to 0.5% (Figure S20, Supporting Information). As measured by atomic force microscopy (AFM) (Figure S21b–f, Supporting Information), the fold structure has a height of ≈0.7 nm, which is consistent with the thickness of two graphene layers on top of the existing continuous single layer, indicating a graphene fold. High-resolution SEM images (Figure S21a, Supporting Information) and AFM images (Figure S21b–e, Supporting Information) show that the orientation of the fold is perpendicular to the edge of the Cu steps underneath the graphene. These folds are a few millimeters to 1 cm in length and run over the entire surface of the single crystal Cu(111) foil in the same direction, from one edge of the foil to the other edge, with an average spacing between adjacent folds of ≈20–50 µm and an average width of ≈80–100 nm (Figure S22, Supporting Information). We also studied the fold structure by Raman spectroscopy after transferring the graphene film to a 300 nm SiO₂/Si wafer. From the Raman map in Figure 1c, two graphene folds are observed. It has been reported that the intensity of the G band is proportional to the number of graphene layers,[39] but the G band intensity of the graphene fold is only around twice that of single layer graphene (Figure 1e). This is because the Raman laser spot used is significantly larger than the width of the fold (≈100 nm), so that the Raman signal from single layer graphene also contributes to this spectrum from the fold region, causing a decrease in the intensity. Nevertheless, the graphene fold is still obvious in the Raman map. In comparison, graphene folds with lengths of several to tens of micrometers were also observed in the polycrystalline graphene films with adlayers grown on as-received polycrystalline Cu (Figure 1b; Figure S2c,d, Supporting Information) and those without adlayers grown on annealed polycrystalline Cu (Figure 3d,g), but they are in essentially random directions, likely due to the presence of GBs and the different orientations of the grains in the foil.

Influence of Folds, GBs, and Adlayers on the Electronic Transport Properties of Graphene: Because we have obtained an adlayer-free single crystal graphene film with long parallel folds, an adlayer-free polycrystalline graphene film, and a polycrystalline graphene film with adlayers, it was possible to separately study the possible effects of graphene folds, GBs, and adlayers on electronic transport by measuring GFETs. Note
that all the electrical tests in this study were conducted at room temperature. First, by patterning and testing devices with channel lengths \((L)\) of 2, 4, 8, and 100 \(\mu m\) (Figure 5a; Figure S23, Supporting Information) the carrier mobility \((\mu)\) of an adlayer-free single crystal graphene film was measured. To study the influence of graphene folds, some devices were patterned with the active device channel parallel to graphene folds, and within the region between two adjacent folds. The typical \(I_{SD}-V_{G}-V_{D}\) transfer characteristics are shown in Figure 5d, and Figures S24a and S25a,b (Supporting Information). The carrier mobility was obtained using the well-accepted constant mobility model. The mobility increased with increasing channel length (Figure S25c, Supporting Information). A similar trend has been previously reported for devices made using both exfoliated graphene flakes and CVD graphene films, and has been attributed to the transition from ballistic or quasi-ballistic to diffusive transport as the channel length increased. The average carrier mobility from ten different devices with channel lengths of 100 \(\mu m\) is \(1.1 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) for holes (the highest value being \(1.4 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) and \(9.5 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) for electrons (the highest value being \(1.3 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)), as shown in Table S1 of the Supporting Information. Such high mobilities are due to the high quality of our single crystal graphene film in those regions.

Graphene wrinkles and folds were found to affect the transport of carriers in GFETs. It has been reported that the carrier mobility obtained from a device patterned across two adjacent single crystal graphene islands (interdomain transport) was lower than from a device made inside a single graphene island (intradomain transport), when there is a graphene fold or wrinkle (we have found it a “fold” but in ref. [44] it is called a “wrinkle”) present at the joining region of the two graphene islands.

It was also reported that for a continuous graphene film grown by CVD from which four-probe devices were fabricated and tested, there was little difference in the average electrical resistance of a device “across” a fold compared to a device without a fold. However, it should be noted that the graphene film studied in ref. [38] was polycrystalline, so that the possible effect of GBs on electronic transport needs to be considered. As discussed above, our adlayer-free graphene film is single crystal and continuous and contains parallel graphene folds, but between the folds the graphene has no wrinkles or GBs and this region should provide a better platform to study the influence of graphene folds on carrier transport. Devices \((L = 8 \mu m, \text{Table S2, Supporting Information})\) were patterned along a graphene fold (Figure 5b) and across a graphene fold (Figure 5c). Figure S26 of the Supporting Information shows the typical \(I_{SD}-V_{G}-V_{D}\) transfer characteristics and the mobilities obtained from them are plotted in Figure 5e. The average hole mobility from eight separate devices is \(2.8 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) for the device along a fold, which is very close to that for the device without a fold (average hole mobility of \(3.0 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) obtained from eight separate devices), while it was \(2.1 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (average obtained from eight separate devices) across a fold, perhaps due to carrier-scattering by the fold. For the across fold configuration, we also made devices with a channel length of 100 \(\mu m\), so that they contained four graphene folds “crossing” a single channel (Figure S23b, Supporting Information). Their average hole mobility was \(3.4 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (Table S3, S3).
Supporting Information), about 3× lower than for devices patterned in the fold-free regions (1.1 × 10⁴ cm² V⁻¹ s⁻¹) as discussed above.

We also studied the influence of graphene GBs and adlayers by patterning devices on the adlayer-free polycrystalline graphene film and the polycrystalline graphene film with adlayers. To evaluate the effect of adlayers, we studied and patterned devices with shorter channel lengths (2 and 8 µm), so that the device channel could be considered quasi-single-crystal with zero to two GBs because the average grain size of the film is about 6 µm (Figure S3, Supporting Information). For the adlayer-free polycrystalline graphene film, the average hole mobility from eight separate devices for 2 µm long channels was 1.0 × 10³ cm² V⁻¹ s⁻¹ (close to the value of 1.1 × 10³ cm² V⁻¹ s⁻¹ for the single crystal graphene film) because of the reduced channel length. For the polycrystalline graphene film with adlayers, the average hole mobility from eight separate 2 µm long channels was 5.3 × 10² cm² V⁻¹ s⁻¹ (Figure 5e; Table S4, Supporting Information), i.e., about 47% lower than the value for the adlayer-free polycrystalline graphene film, which suggests that adlayers affect the electronic transport of graphene devices possibly by causing increased backscattering, which has been reported for a single layer graphene film with periodic bilayer stripes in it. A similar trend in carrier mobility was observed for the 8 µm channel devices (Table S2, Supporting Information).

We note from a comparison between single crystal and polycrystalline graphene films that for some reason long channels are better than short channels in identifying the influence of folds, and especially the effects of GBs (Figure 5f). The average mobility was 6.9 × 10³ cm² V⁻¹ s⁻¹ for holes and 6.0 × 10³ cm² V⁻¹ s⁻¹ for electrons (Table S5, Supporting Information) for 100 µm long channels patterned from an adlayer-free polycrystalline graphene film, which are lower than the average values for a single crystal graphene film in the fold-free regions (1.1 × 10⁴ cm² V⁻¹ s⁻¹ for holes and 9.5 × 10³ cm² V⁻¹ s⁻¹ for electrons). This decrease in mobility was due to the presence of GBs and folds. For polycrystalline graphene films with adlayers, the average hole mobility was 2.6 × 10³ cm² V⁻¹ s⁻¹ (Table S6, Supporting Information) for 100 µm long channels, significantly lower than the values for both the adlayer-free polycrystalline graphene film and the single crystal graphene film in the fold-free regions thus showing scattering due to the presence of adlayers, GBs, and folds.

This adlayer-free single crystal graphene film with a high carrier mobility is thus a great candidate for graphene electronic devices because the highly aligned “graphene folds” (that occupy only ~0.3% of the total area of the film) divide the film into regions with a width of ~20–50 µm and a length similar to the dimension of the film, cm or larger, and it is these regions that are free of adlayers, GBs, and folds/wrinkles. The complete absence of these charge scattering centers means a much higher carrier mobility and a more reliable value from device to device.

Because of its uniformity we expect this “perfect” single layer, single crystal graphene to also find use as an ultrathin support material for high-resolution transmission electron microscopy imaging, in optical devices, and as the appropriate graphene to achieve extremely uniform functionalization which leads to many other applications, particularly for sensors of various types.

With respect to the relatively uniform folds that result from graphene growth on single crystal Cu(111) foils, theoretical studies suggested that these may show interesting electronic properties under applied magnetic fields, such as interferometric effects due to the interplay between an externally applied magnetic field and the gauge field induced by the deformation in the fold region. A recent experimental study reports pseudo-Landau-levels induced by a strain gradient induced pseudomagnetic field of about 42 T in a graphene fold. The highly aligned graphene folds we discovered may provide a platform for exploring such phenomena including the zero-field quantum valley Hall effect. Our graphene folds with such consistent uniformity ought to be able to trap small molecules such as C₆₀ to generate graphene-fold-based composite materials with novel optical and electronic properties.

We have found that graphene grown by CVD on as-received polycrystalline Cu foil always contains adlayers which grow under, and simultaneously with, the top layer. We have discovered that it is the subsurface carbon inside the Cu foils that leads to additional nuclei that produce the adlayers. After completely removing this carbon by annealing under H₂ at 1060 °C, an adlayer-free polycrystalline single layer graphene film can be grown on the foil, in a relatively wide CVD synthesis window of H₂/CH₄ ratios and pressures. Additionally, we have obtained an adlayer-free single layer graphene film on Cu(111) foils which have no carbon inside them. This graphene film is single crystal as indicated by LEED, micro-LEED, UHV-STM, and liquid-crystal-assisted POM. Parallel graphene folds up to centimeters in length and with an average separation of ~20–50 µm and an average width of ~80–100 nm were observed in the film. Adlayers, GBs, and folds were observed to significantly decrease the carrier mobility of graphene according to our GFET measurements. To eliminate the scattering effects of adlayers, GBs and folds, devices were patterned with the device channel parallel to the folds and in the region between two adjacent folds in an adlayer-free single crystal graphene film. Since the folds are highly aligned in the large area single crystal graphene film, it was easy to fabricate integrated high performance devices from the regions between the folds, and they had very high electron and hole mobilities.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
adlayer-free, chemical vapor deposition (CVD), Cu(111), folds, single crystal graphene
[32] Private conversation with Dr. Ruolin Zhu of Jiangxi Copper Corporation Limited, one of the largest manufactures of copper foils in the world.