LETTERS

Ultraflat graphene

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Graphene, a single atomic layer of carbon connected by sp^2 hybridized bonds, has attracted intense scientific interest since its recent discovery[1]. Much of the research on graphene has been directed towards exploration of its novel electronic properties, but the structural aspects of this model two-dimensional system are also of great interest and importance. In particular, microscopic corrugations have been observed on all suspended[2] and supported[3–8] graphene sheets studied so far. This rippling has been invoked to explain the thermodynamic stability of free-standing graphene sheets[9]. Many distinctive electronic[10–12] and chemical[13–15] properties of graphene have been attributed to the presence of ripples, which are also predicted to give rise to new physical phenomena[16–26] that would be absent in a planar two-dimensional material. Direct experimental study of such novel ripple physics has, however, been hindered by the lack of flat graphene layers. Here we demonstrate the fabrication of graphene monolayers that are flat down to the atomic level. These samples are produced by deposition on the atomically flat terraces of cleaved mica surfaces. The apparent height variation in the graphene layers observed by high-resolution atomic force microscopy (AFM) is less than 25 picometres, indicating the suppression of any existing intrinsic ripples in graphene. The availability of such ultraflat samples will permit rigorous testing of the impact of ripples on various physical and chemical properties of graphene.

The morphology of high-quality graphene crystals has been the subject of much attention. Detailed electron-diffraction studies of free-standing graphene monolayers[2] indicate the presence of an intrinsic rippling, with ~1-nm-high corrugations normal to the surface appearing over a characteristic lateral scale of 10–25 nm. It has been argued that these corrugations are necessary to stabilize the suspended graphene sheets against thermal instabilities present in ideal two-dimensional systems[9]. A comparable degree of height variation has also been reported in several studies of graphene monolayers deposited on insulating substrates[3–8]. This rippling has been invoked to explain many phenomena observed in graphene, such as the formation of electron–hole puddles[11,12], the suppression of weak localization[10], decreased carrier mobility[22] and enhanced chemical reactivity[13–15]. In addition, theoretical studies of graphene have predicted that graphene ripples will induce fascinating new phenomena, including the enhancement of spin–orbit coupling[16], the generation of an inhomogeneous density of states and the formation of zero-energy Landau levels in the absence of magnetic fields[17–20,23–25].

We report here the fabrication and characterization of high-quality ultraflat graphene monolayers by making use of a mica support that provides atomically flat terraces over large areas. Using high-resolution, non-contact mode atomic force microscopy (AFM) to characterize the morphology, we find that graphene on mica approaches the limit of atomic flatness. The apparent height variation of graphene on mica is found to be <25 pm over micrometre lateral length scales. This flatness, measured with a lateral spatial resolution of 7 nm, appears to be limited by instrument noise and is essentially identical (within 5 pm) to that observed for the surface of cleaved graphite crystals. Our results show that any intrinsic instability of graphene can be fully suppressed by deposition on an appropriate substrate. The availability of such a flat substance provides insight into questions of thermodynamic stability for this model two-dimensional system and also a reference material with which to determine the role of ripples in the panoply of observed and predicted phenomena.

The key to our experiments was the preparation of an atomically flat substrate for deposition of single-layer graphene crystals. For this purpose, we chose mica, a material composed of negatively charged aluminosilicate layers that are linked by single layers of potassium ions[27]. Since cleavage takes place readily along the potassium layer, atomically smooth surfaces with lateral dimensions as large as 100 μm can be routinely produced. Graphene monolayers were prepared by the standard method of mechanical exfoliation of kish graphite[1] on both mica and bulk SiO_2 substrates for comparative studies (see Methods).

We employed amplitude-modulation AFM in the non-contact mode to characterize the topography of the graphene samples. The AFM lateral and height resolution under scanning conditions were 7 nm and 23 pm, respectively. The AFM topographic images displayed in this paper are presented without filtering or smoothing. A third-order line and plane subtraction correction was applied to compensate for scanning drift and image bow. The roughness of the surface was characterized by the standard deviation σ of height distribution and the height correlation length l (see Supplementary Methods).

AFM topographic images acquired for regions surrounding the edges of graphene samples on both SiO_2 and mica substrates are shown in Fig. 1a, b. Histograms of the corresponding height distribution over the $200 \times 200\ nm^2$ regions of the surfaces are presented in Fig. 1c. For the bare SiO_2 surface, the parameters describing the height variation and correlation length (Table 1) are, respectively, $\sigma = 168$ pm and $l = 16$ nm. For the graphene monolayer on SiO_2, we find a comparable (or slightly diminished) degree of roughness, with $\sigma = 154$ pm and $l = 22$ nm, indicating that graphene monolayers largely follow the underlying substrate morphology.

In sharp contrast to these results, our AFM images on the mica substrate exhibit a much smoother landscape. For the bare mica surface, we obtain (see Table 1) $\sigma = 34.3$ pm and $l = 2$ nm. (As discussed below, we attribute the low value of l to residual AFM noise, rather than to physically meaningful features.) Taking the measured value of σ as a guide, the surface of mica is seen to be at least five times smoother than that of the SiO_2 substrate. When placed on such a flat mica terrace, graphene monolayers display an exceedingly flat structure, one quite different from that observed for graphene/SiO_2. This difference can be seen immediately by comparing the three-dimensional presentation of the AFM topographic images in Fig. 2a, b. More quantitatively, for graphene on mica, we obtain $\sigma = 24.1$ pm and $l = 2$ nm. This topography is at least five times smoother than that of graphene on SiO_2. Since the interlayer distance in bulk graphite is 340 pm, with an

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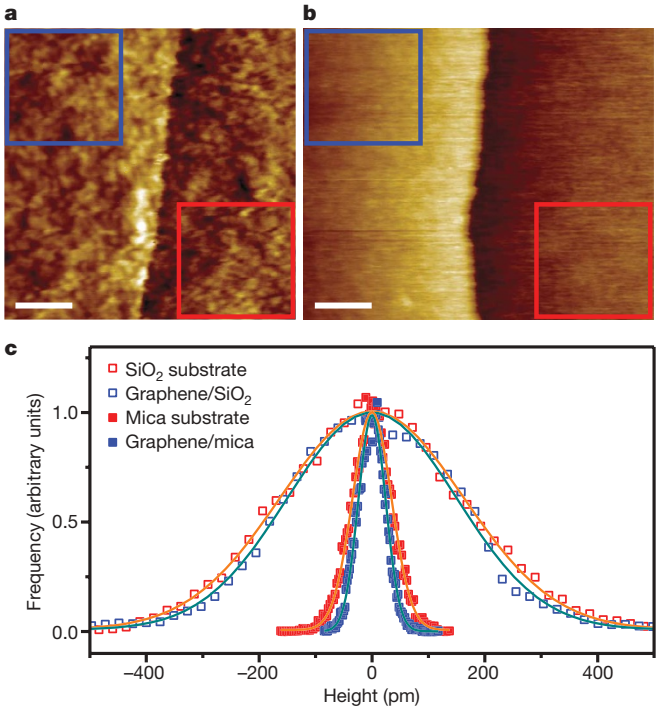

Figure 1 | AFM topographic images of different samples and the corresponding histograms of height. **a**, AFM image of a boundary between a graphene monolayer and a SiO_2 substrate. Graphene occupies the left-hand side of the image and the scale bar is 100 nm in length. **b**, As **a** for a graphene monolayer on a mica substrate. **c**, Height histograms for graphene on mica (solid blue squares), the mica substrate (solid red squares), graphene on SiO_2 (open blue squares), and the SiO_2 substrate (open red squares). The data, corresponding to the regions designated by the blue and red squares in the images of **a** and **b**, are described by Gaussian distributions (solid lines) with standard deviations σ of 24.1 pm, 34.3 pm, 154 pm, and 168 pm, respectively.

observed height variation of only 24.1 pm, we can consider graphene on mica as having reached the limit of atomic flatness with respect to ripples, that is, a height variation that is much less than the diameter of an atom when probed with our lateral resolution of 7 nm (see Supplementary Discussion).

Table 1 | σ and l of the images for different surfaces

	SiO_2	Graphene/SiO_2	Mica	Graphene/mica	Graphite
σ (pm)	168	154	34.3	24.1	22.6
l (nm)	16	22	2	2	2

The discussion of the flatness of the graphene/mica surface given above has been conservative in not attributing any of the observed height variation in the AFM images to instrumental noise. In fact, the results indicate that AFM noise is significant in measurements of flat surfaces. In particular, the correlation length of $l \approx 2$ nm calculated for the mica and the graphene/mica surfaces must arise largely from AFM noise, because any true physical features could only contribute to a correlation length comparable to or greater than the AFM spatial resolution of 7 nm. To address this issue, we made AFM measurements of the topography of cleaved kish graphite (Fig. 2c). The observed topography for the cleaved graphite surface is very similar to that of graphene/mica. Figure 2d compares the height histograms for graphite and graphene/mica. The widths of the distributions are, respectively, $\sigma = 22.6$ pm and $\sigma = 24.1$ pm. If we treat the graphite surface as entirely flat, then the measured standard deviation reflects the instrumental noise. Under the assumption that the instrumental noise adds in quadrature to any true height fluctuations, the values given above constrain the actual roughness of the graphene/mica sample to less than 8.5 pm.

Finally, in assessing the flatness of graphene, possible perturbations in its topography from tip-sample interactions must also be considered. To exclude the possibility that the observed flatness of graphene on mica might be produced through the suppression of ripples by the tip-sample interaction of the AFM probe, our AFM measurements have been carried out in a strictly non-contact mode, that is, one in which the tip/sample interaction was always attractive. Instead of pressing down on the surface at any time, the AFM tip is actually pulling slightly on the graphene sheet (see Supplementary Methods).

Since the discovery of intrinsic ripples in free-standing graphene, there has been considerable discussion of the role of substrate corrugation in determining the morphology of supported graphene

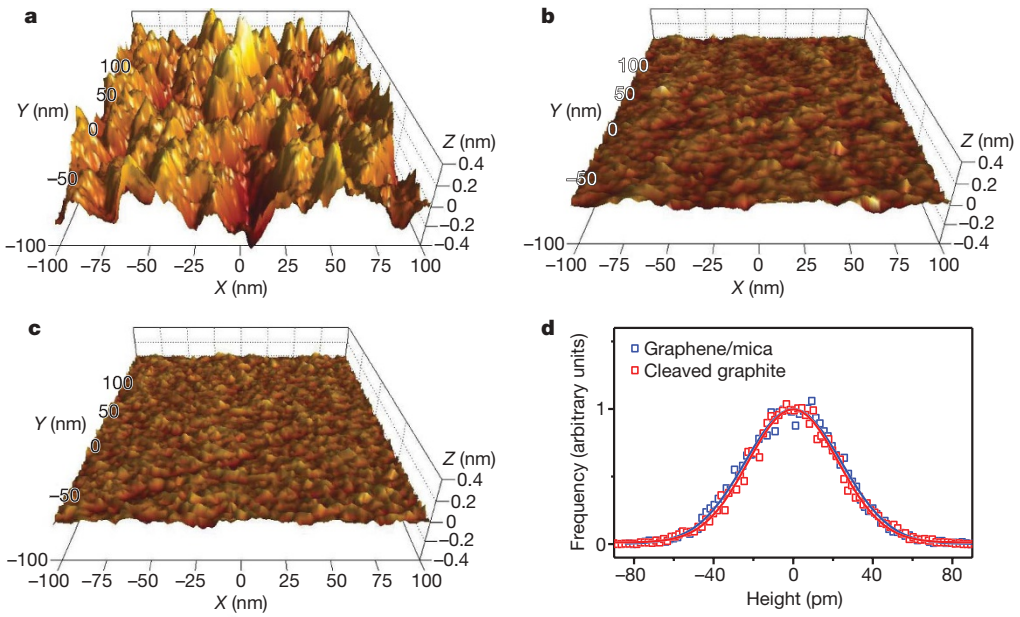

Figure 2 | Comparison of surface roughness for graphene on SiO_2 and on mica, and for cleaved graphite. **a**, **b**, Three-dimensional representations of the AFM topographic data for graphene on SiO_2 (**a**) and on mica (**b**) substrates. The images correspond to the regions in Fig. 1a and b designated by the blue squares. **c**, AFM image of the surface of a cleaved kish graphite sample. Images **a**, **b** and **c** correspond to 200 nm × 200 nm areas and are presented with the same height scale. **d**, Height histograms of the data in **b** as blue squares and in **c** as red squares. The histograms are described by Gaussian distributions (solid lines) with standard deviations σ of 24.1 pm and 22.6 pm, respectively.

monolayers[3–8]. Although the observed corrugation of supported graphene might well be an intrinsic feature[2,9] of the graphene monolayers in the experiments performed to date, a different explanation is equally possible. The roughness of the graphene surfaces may simply reflect the contours of the underlying substrates, which typically exhibit corrugation comparable to that observed in the supported graphene monolayers. Our measurements demonstrate unambiguously that intrinsic ripples in graphene, if they do exist, can be strongly suppressed by interfacial van der Waals interactions when this material is supported on an appropriate atomically flat substrate.

METHODS SUMMARY

Sample preparation. In our study we made use of grade V-1 muscovite mica substrates (15×15 mm^2, from Structure Probe) and produced graphene layers by the standard method of mechanical exfoliation of kish graphite[1]. Mica surfaces are known to be hydrophilic and readily adsorb water and carbon dioxide, as well as hydrocarbons. To minimize the presence of adsorbates at the graphene–mica interface, sample preparation was carried out in a glove box with water and oxygen concentrations below 1 p.p.m. (one part per million). For comparative studies, graphene monolayers were also prepared on bulk SiO_2 substrates. The SiO_2 substrates were carefully cleaned by sonication in methanol and the graphene samples were deposited by the same method of exfoliation of kish graphite, in this instance under ambient conditions. None of the samples described in this paper was subjected to any thermal processing.

Sample characterization. Graphene monolayers were identified on the mica substrate by optical microscopy, which was performed under ambient conditions. Although it is more difficult than for graphene samples deposited on an optimized SiO_2 overlayer on a silicon substrate, we were able to identify graphene monolayers directly by visual inspection. The modulation in reflectivity from a graphene monolayer still amounts to about 5% (Supplementary Fig. 1). Raman spectroscopy was applied for further characterization of the graphene samples[28] (Supplementary Fig. 2). From examination of the 2D mode Raman line, we confirmed the single-layer thickness of all the samples investigated in this paper. Also, the Raman spectra did not show any measurable D peak, indicating the high crystalline order of our samples. Our method of sample preparation was found to produce a significant yield of large graphene monolayers, with characteristic lateral dimensions ranging from tens of micrometres up to ~0.2 mm. The efficient deposition of large graphene single layers is attributed to the flat and clean surface of freshly cleaved mica.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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