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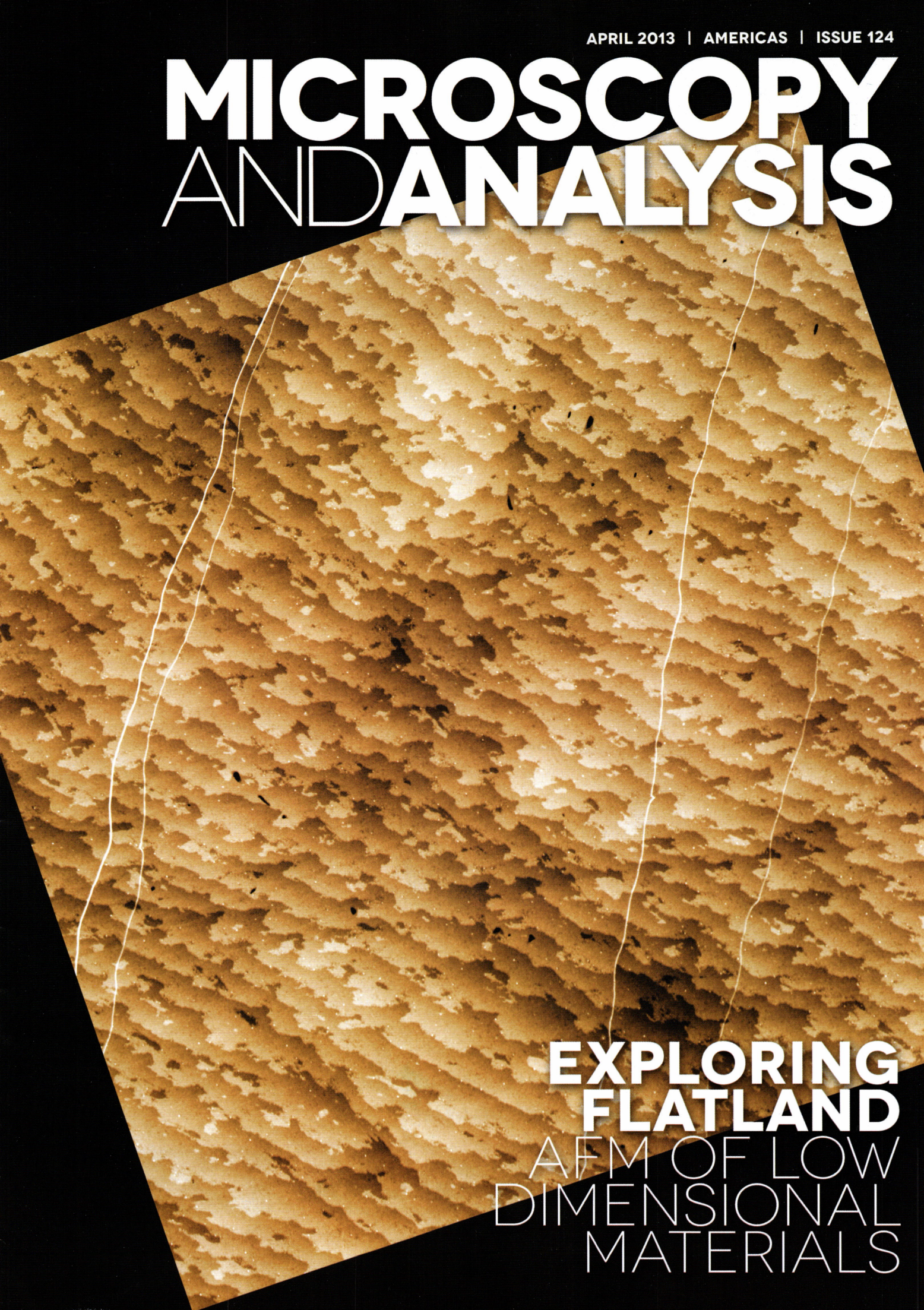
MICROSCOPY AND ANALYSIS



EXPLORING FLATLAND

AFM OF LOW DIMENSIONAL MATERIALS

Exploring flatland: AFM of mechanical and electrical properties of graphene, MoS_2 and other low-dimensional materials

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INTRODUCTION

In 1884, Edwin Abbott Abbott wrote *Flatland - A Romance of Many Dimensions* [1], a mathematical fiction in which he described a whimsical world of only two dimensions. The protagonist of this world is a Square who dreams about a world of only one dimension. To his surprise, he is visited by a Sphere from the three-dimensional world; this Sphere had been observing Flatland from his vantage along the Z-axis. In modern labs around the world today, atomic force microscopy tips - sometimes assumed to be spherical like the three-dimensional character in Flatland - pay regular visits to observe the reduced dimensionality world of graphene and related materials.

The two-dimensional material graphene was first discovered in 2004 [2, 3] and, since then, research into graphene and related materials has grown extremely rapidly. Notably, Dr A. Geim and Dr K. Novoselov of the University of Manchester received a Nobel Prize in 2010 for its discovery. Graphene exhibits the highest known room-temperature carrier mobility [4-7], approximately 25 times the thermal conductivity of silicon [8], and high mechanical strength [22]. Structurally similar monolayers with different atoms behave as semiconductors (MoS_2) and insulators (boron nitride). One-dimensional carbon nanotubes (CNT), equivalent to cylinders "rolled up" from a graphene sheet, approach graphene's thermal and mechanical properties. CNTs are metallic or semiconducting depending on the lattice orientation.

The juxtaposition of impressive mechanical, thermal, and electronic properties makes these materials likely candidates for disruptive technological breakthroughs, in fields spanning high performance and quantum computing, spintronics, energy collection and storage [9], novel single-molecule sensors, terahertz oscillators, nanoelectromechanical systems, and transparent electrodes for touch-screen displays and photovoltaics. Graphene and other low-dimensional materials also offer potential successors to silicon that may take us beyond Moore's law.

We have chosen a few examples that illustrate some of the exciting possibilities for low-dimensional materials as well as highlighting some of the unique insights that atomic force microscopy (AFM) provides in this exploding field of research. AFM is uniquely positioned to provide structural, mechanical, and electrical characterization of graphene and related two-dimensional materials. Some of the utility of AFM simply derives from its impressive height sensitivity. Graphene is a single layer of carbon atoms, so to resolve such a small height requires an instrument with sub-angstrom resolution - a place where the AFM excels, with good AFMs offering height resolution below 10 picometers. Going beyond simple topography measurements, there are a host of mechanical and electrical characterization techniques that rely on the AFM cantilever being able to literally "feel" the mechanical and electrical properties of the material.

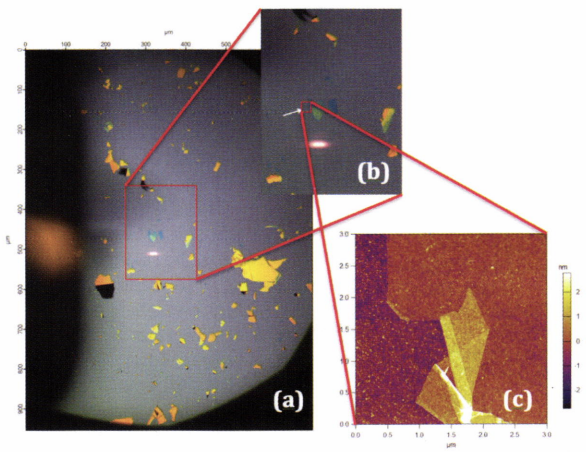


FIGURE 1
(a) Large field optical image, (b) digital zoom and (c) 3 µm wide AFM image of a single graphene layer on SiO_2. Single layers of graphene appear dark blue in the optical image. Note that AFM measurements of graphene thickness on SiO_2 supports vary from 0.35 to 1.4 nm [10-12]

Optical and AFM images acquired with the Asylum Research Cypher AFM

HIGH RESOLUTION TOPOGRAPHY

Locating the interesting parts of a sample to image is one of the first challenges for a microscopist. Integrated high-precision optics allow AFM users to see patches of graphene as thin as a single molecular layer, thereby enabling them to select and scan a region of interest. Figure 1 shows an example of graphene prepared by the "scotch tape" method and imaged topographically [2].

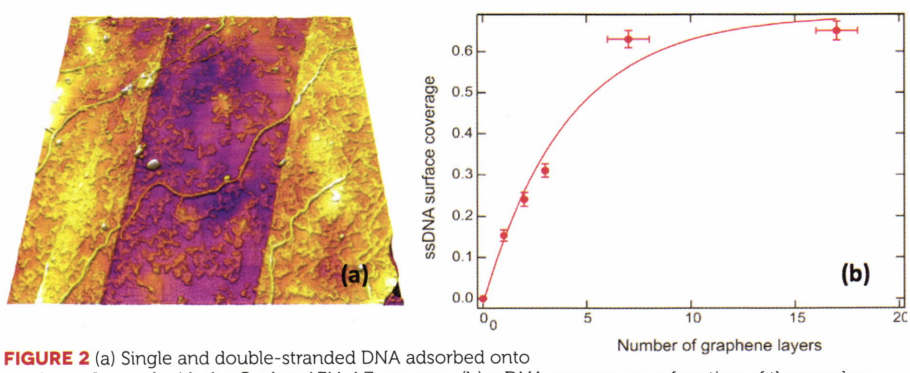


FIGURE 2 (a) Single and double-stranded DNA adsorbed onto graphene. Imaged with the Cypher AFM, 1.7 µm scan. (b) ssDNA coverage as a function of the number of layers of graphene. Imaged with the Cypher AFM. *From Husale et al. [11], used with permission*

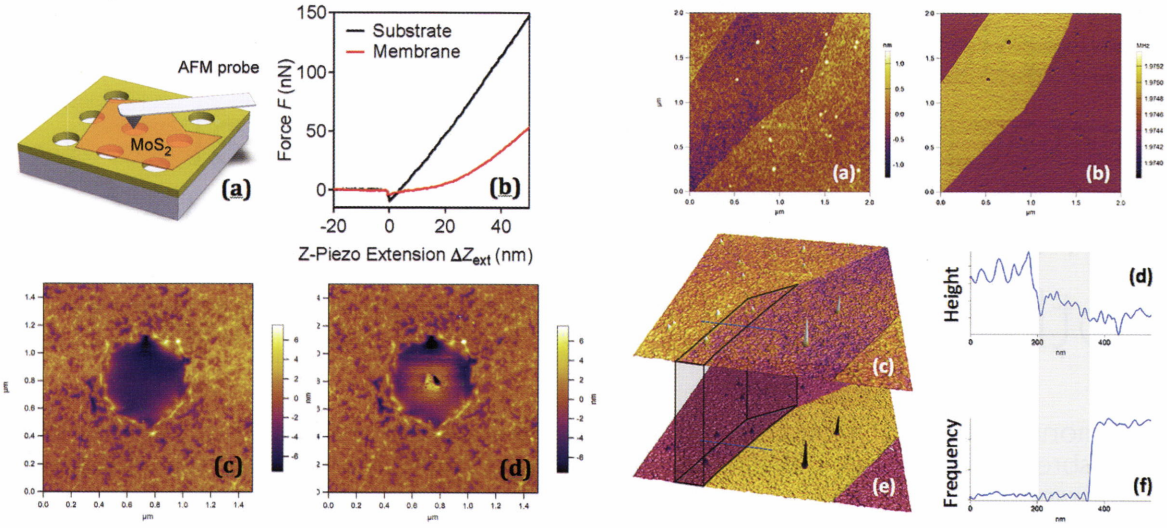


FIGURE 3, right, Suspended MoS_2 membranes and their mechanical failure. (a) Schematic representation of the indentation experiment. (b) Acquired force versus Z-piezo extension curves for the suspended membrane and the substrate. (c) AFM image of a monolayer MoS_2 flake suspended over a hole before the indentation experiment and (d) after it. A hole can be clearly seen in the center of the membrane at the location where the AFM tip punctured it. Imaged with the Cypher AFM.

From Bertolazzi et al. [21], used with permission

FIGURE 4, above right, (a) The topography of a SiO_2 surface with graphene layers. (b) The second mode frequency shift mapped during the topographic measurement of (a), showing a "softer" tip-sample interaction over the graphene. Lower frequency shifts imply a softer surface. Note that this is in apparent contradiction to the expected elasticity of graphene (~1 TPa) [22] being much larger than that of SiO_2 (~100 MPa). (c) The regions outlined in (a), (b) and (e) are where the topography shows little or no height change but where the frequency shift indicates a layer of graphene.

Imaged with the Asylum Research MFP-3D AFM

One of the opportunities of nanotechnology is the construction of nanomachines that can perform a variety of tasks, from seeking out and killing cancer cells to storing data with ever-increasing density to biological and chemical sensing. One of the most popular systems for designing these nanomachines is DNA. With four bases compared to the 22 standard amino acids found in proteins, the rules governing the behavior of DNA are simpler. Inspired by this, researchers have developed a large number of DNA-based nanomachines over the past decade [13-16]. Creating electrical interfaces with these nanomachines is a major challenge and one where graphene shows promise.

In one experiment [17], a mixture of single-stranded DNA (ssDNA) and double-stranded DNA (dsDNA) was absorbed on pristine graphene. The graphene was deposited on a SiO_2 substrate in 1 mM Tris-HCl buffer solution containing 5 mM Mg^{2+} ions. In the image, dsDNA appears as long, relatively thick strands that can be easily distinguished from ssDNA. Somewhat surprisingly, the binding affinity of ssDNA depends on the thickness of the graphene layers as illustrated in Figure 2.

MECHANICAL PROPERTIES

The carbon lattice in graphene has strong, highly directional bonds. The high bond energy means that defects are rare and do not propagate easily through the lattice, as occurs with dislocations in metals. As a result, both the modulus and the strain-to-failure for graphene are exceptionally high. Monolayer MoS_2 has a lower modulus, comparable to stainless steel, yet has a breaking strength 30 times higher than stainless steel. As with graphene, the strength of monolayer MoS_2 is close to the theoretical intrinsic strength of its constituent chemical bonds, indicating a high degree of molecular perfection. Directional bonds also give these materials their layered nature, with unique frictional properties on the surface of the layers.

Because AFM directly touches the surface under investigation, it is the ideal tool to measure the mechanical properties of low-dimensional materials. The flexible cantilever used in AFM acts as a linear spring to convert forces into measurable deflections. The sharp tip enables this to occur with nanometer-scale lateral resolution and sub-nanometer resolution of the indentation depth. By choosing different cantilevers, researchers can access a dynamic range from micronewtons to piconewtons. Forces on the cantilever can be measured quasi-statically or at higher frequencies, in normal bending or torsion, to measure different characteristics of the sample.

FORCE CURVES

Measuring the deflection of the cantilever quasi-statically as a function of the tip-sample separation yields a single-point force measurement known as a 'force curve'. This is directly analogous to conventional indentation [18, 19]. Often, two-dimensional arrays of force curves are made, in a technique known as force volume imaging. The first force curve was reported by Heinzelmann et al. in 1988 [20], two years after the invention of the AFM. This quickly grew into a popular measurement mode, allowing characterization of the full spectrum of tip-sample forces, ranging from (typically attractive) long-range interactions to short-range repulsive interactions. This type of measurement generated much excitement when Lee et al. [22] identified graphene as "the strongest material ever measured." In Figure 3, Bertolozzi et al. [21] have used force curves to test the elasticity and strength of MoS_2 membranes stretched over circular holes in a SiO_2 support. Its mechanical properties make MoS_2 an excellent candidate material for incorporation into flexible and robust electronic devices, including molecular sensors and actuators.

AM-FM VISCOELASTIC MAPPING

AM-FM viscoelastic mapping is an imaging technique that combines the features and benefits of fast, high-resolution tapping mode (also called AM) with quantitative, high-sensitivity frequency modulation (FM) mode. From this technique, we are able to quantitatively derive the dissipation and stiffness of the sample. The topographic feedback operates in normal tapping mode, providing non-invasive, high quality imaging. The second mode drive-frequency is adjusted to keep the phase at 90 degrees, on resonance. This resonant frequency is a sensitive measure of the tip-sample interaction. The stiffer the tip-sample interaction, the higher the frequency shift of the second mode. This frequency shift can then be converted into a quantitative modulus measurement through a variety of mechanical models, e.g. Hertz-Sneddon, Oliver-Pharr, Johnson-Kendall-Roberts (JKR), and Derjaguin-Muller-Toporov (DMT).

Figure 4 shows examples of graphene on SiO_2 imaged with AM-FM viscoelastic mapping. The graphene has a stiffness very different from that of the substrate. The origins of this lower stiffness over the graphene are still not understood. Possible reasons include a water layer between the SiO_2 and graphene or the lower friction of the tip-graphene contact as discussed below.

FRICTION FORCE MEASUREMENTS

Graphene has a very low coefficient of friction which can be exploited using lateral-force or friction-force microscopy to readily locate areas of a surface where there is graphene coverage [23]. This can be useful where the optical properties of a substrate cause difficulties in the identification of graphene using light microscopy, and for many substrates which are too rough to allow unambiguous determination of graphene boundaries

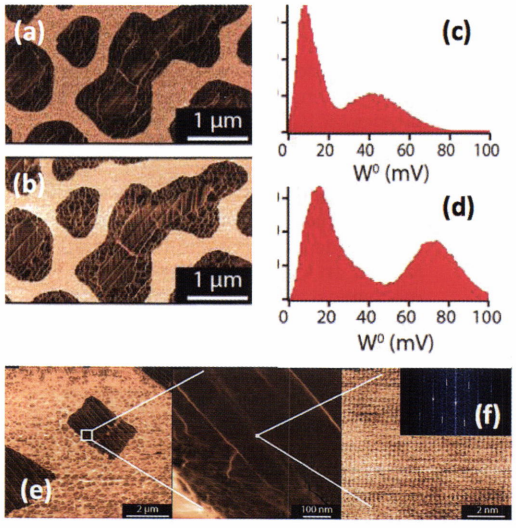


FIGURE 5
Effect of load on friction force: Friction force microscopy (FFM) maps, (a) and (b), and their corresponding histograms, (c) and (d) of graphene on copper taken with contact mode setpoints (i.e. normal deflection) of 6.8±0.1 V, (a), and 11.8±0.1 V, (c). (e) An atomic lattice image of the frictional force (5 nm scan size) and (f) the corresponding Fourier transform showing the expected six-fold symmetry of the graphene surface.

Imaged with the Cypher AFM.

From Marsden et al. [24], used with permission

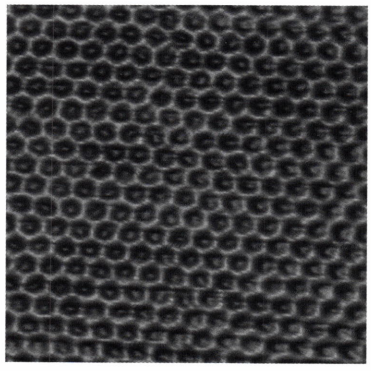


FIGURE 6, above right, Scanning tunneling microscopy image of highly oriented pyrolytic graphite, 5nm scan.

Imaged with the Cypher AFM

FIGURE 7, right, (a) Topography of a biased carbon nanotube (CNT) where the grounded metal electrode is in the upper right corner and the bias is provided by the AFM tip. (b) Measured resistance of the CNT as function of the CNT contour length. (c) Schematic of the circuit. (d) Resistance versus position along the length. The bias voltage was 25 mV.

Imaged with the MFP-3D AFM

by measurements of topography alone.

Figure 5 shows friction force microscopy (FFM) measurements of graphene islands grown on a copper substrate [24]. The friction images were generated by scaling the difference between the trace and retrace lateral-force images by a calibration factor relating to torsional lever stiffness and detection sensitivity. The graphene islands show up clearly as darker regions in the friction images (meaning lower friction), within which terraces and the edges of over-layers can be seen.

It is remarkably straightforward to obtain lattice-resolution images on graphene using FFM. Resolving the lattice allows determination of the relative lattice-orientation of different graphene islands, or of different regions within a single island. Such information can provide useful insights into the mechanics of graphene growth by chemical vapor deposition.

ELECTRICAL PROPERTIES

As mentioned above, graphene and other low-dimensional materials have very interesting electronic properties, making them excellent candidates for a wide variety of next generation electronic components. Because a nanometer-scale conducting probe can be contacted to the sample or hovered less than a micrometer above it, AFM and related techniques such as scanning tunneling microscopy (STM) are ideal methods for probing the local electronic properties of graphene [25-27]. Figure 6 shows an STM image of the top layer of a graphite sample showing the hexagonal lattice. Because the contrast mechanism of STM is exponential, even a crudely prepared tip in ambient conditions can deliver sub-nanometer lateral resolution.

LOW FREQUENCY ELECTRICAL PROPERTIES

A simple way to measure the characteristics of a sample is to complete a circuit between a conductive AFM tip and the sample, and measure the current flowing in that current at a particular bias voltage. This is known as conductive AFM. It requires a sensitive current-to-voltage amplifier; we used the ORCA module from Asylum Research. By ramping the bias, conductive AFM can measure the current-voltage characteristic (I-V curve) – a critical measurement for the development of electronic devices.

A two-dimensional array of force curves can be used to make electrical contact to different points on a surface. For example, the resistance of a nanoscale device can be determined as a function of electrode position. In such measurements, a metal-coated AFM tip plays the role of a movable nanoscale electrode, while a fixed electrode is used to complete the circuit. Figure 7 shows a resistance, R, vs. length, L, measurement of an individual CNT. The measurement reveals $dR/dL = 8\ \mathrm{k\Omega/\mu m}$, in agreement with similar experiments on pristine CNTs [28]. The local nanoelectrode technique has been used to reveal single defects in CNTs (manifested as sudden jumps in resistance) [29] as well as to demonstrate Anderson localization in damaged CNTs (R grows exponentially with L) [29].

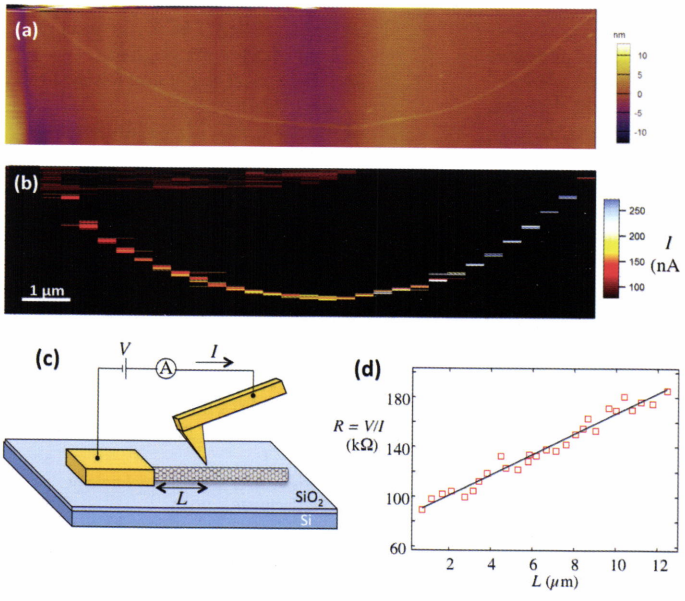
The electronic characteristics of the sample are also revealed in the electric fields above its surface. Two other techniques, scanning Kelvin-probe microscopy (SKPM) and electric force microscopy (EFM), probe these fields by first scanning the sample topography and then floating above it. They use oscillation at the cantilever resonance, typically tens or hundreds of kilohertz, to either measure electric forces (EFM), or null out the contact potential difference (SKPM). In Figure 8, a carbon nanotube on an insulating support is connected to an electrode (white part of image). The EFM phase shows excellent, more-or-less constant contrast resulting from attractive forces. This indicates that the CNT is conductive and has continuity to ground.

HIGH FREQUENCY (MICROWAVE) PROPERTIES

Scanning near-field microwave microscopy (SMM) images the sample permittivity and conductivity using the electric near field formed at a sharp cantilever probe terminating a microwave transmission line [30]. Coupling between a sample and a probe takes place through the capacitance between the probe and the sample, and no counter electrode is needed to complete the circuit. The technique uses microwaves in the frequency range of a few GHz. As an example, the contrast in the SMM image of a single-layer graphene film in Figure 9 appears due to variations of sheet resistance in the film. The bright color corresponds to lower sheet resistance in areas with two and more layers of graphene, and on wrinkles. SMM imaging clearly resolves islands of the second graphene layer on top of the continuous first layer, in contrast to rather minute topographic variations on the sample surface.

CONCLUSIONS

In Abbott's Flatland, things do not end well for the Square. Although the Square embraces the idea of higher dimensions,



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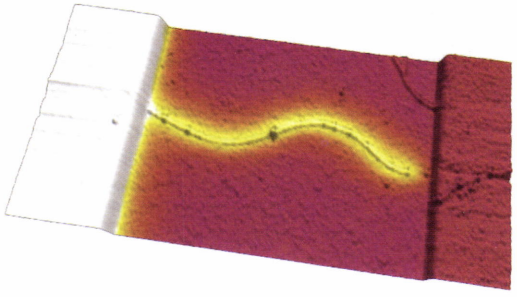

FIGURE 8
EFM phase on topography overlay of a carbon nanotube. In the image, color represents the EFM phase channel. Scan size 2 µm x 1 µm

Imaged with the MFP-3D AFM.

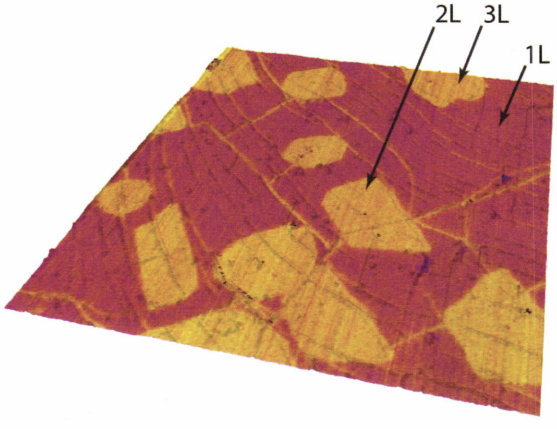

FIGURE 9
SMM image of a large-area graphene sample grown on a Cu foil and transferred onto a Si/SiO_2 substrate. In the image, color represents the SMM phase channel which is overlaid on the rendered topography. 1L, 2L, and 3L denote locations with one, two, and three graphene layers, respectively, as determined from the topographic image. The SMM image was acquired at 5.2 GHz. Scan size is 20 µm x 20 µm

Imaged with the MFP-3D AFM
From Tselev et al. [30], used with permission

the President of Flatland imprisons the Square. The story ends with the Square in prison after seven years, unable to share his revelations regarding higher dimensions and even beginning to wonder if his observations of the third dimension were real.

We expect that the story of AFM measurements will have a happier ending. AFMs have the ability to literally touch materials with a resolution of nanometers or less. Therefore they can image not only the structure of graphene and related materials, but also map many of their physical properties.

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BIOGRAPHY

Simone Bertolazzi has an MSc in engineering physics (2010) from the Politecnico di Milano. Since 2011 he has been a PhD student at the École Polytechnique Fédérale de Lausanne. His PhD project focuses on the investigation of the mechanical and electronic properties of two dimensional materials for application in nanoelectronic devices.

Ethan Minot received his PhD in physics from Cornell University and now leads a research group at Oregon State University investigating the electronic and optoelectronic properties and applications of carbon nanomaterials.

Alexander Tselev received his PhD in materials sciences from Dresden University of Technology in 2000. Currently, he is a Research Assistant Professor at the University of Tennessee Knoxville and works at the Oak Ridge National Laboratory.

ABSTRACT

Low dimensional materials such as graphene are composed of a single layer or at most a few layers of atoms. To resolve the structure of these materials requires an instrument with sub-Ångstrom resolution – a regime where the atomic force microscope (AFM) excels. Going beyond simple topography measurements, there are a host of mechanical and electrical characterization techniques that rely on the AFM cantilever being able to literally "feel" the mechanical and electrical properties of the material. In this paper, we describe several new and existing applications where AFM is used to probe the mechanical and electrical properties of these rapidly emerging materials.

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