Characterization of Graphene with the NanoWizard® 3 AFM

Introduction

Andre Geim, Konstantin Novoselov and collaborators were the first to publish the production and electrical characterization of single layer graphene, a discovery which was credited with the Nobel Prize in physics in 2010. They produced these 2D crystal structures by mechanical exfoliation of graphite with adhesive tape [1]. Single or few-layer sheets were then transferred onto oxidized silicon substrate for electrical investigation.

In 2013, a group of researchers around Prof. Jari Kinaret were granted a one-billion-euro grant from the European Union for the research on graphene and related materials [2][3]. This large-scale project is aimed to develop new applications, foster scientific advance and lay the foundation for future innovations. Given this increased interest in graphene research we provide some of the measurement results on graphene that were produced with the JPK NanoWizard® 3 AFM system.

Graphene can be produced by micromechanical cleavage as used by Novoselov and Geim to produce graphene samples for fundamental research. Commercial graphene can be prepared by liquid phase exfoliation, mostly involving graphite oxide. Another common method is the epitaxial growth on silicon carbide or other materials. Further production techniques involve anodic bonding, photoexfoliation, chemical vapor deposition, molecular beam epitaxy and chemical synthesis.

AFM is most suited for the characterization of graphene due to its high spatial resolution and the various modes that allow probing different physical properties. The height image gives an overview about the roughness of the graphene layers and the underlying substrate.

The combination with Raman spectroscopy or tip-enhanced Raman spectroscopy (TERS) allows the

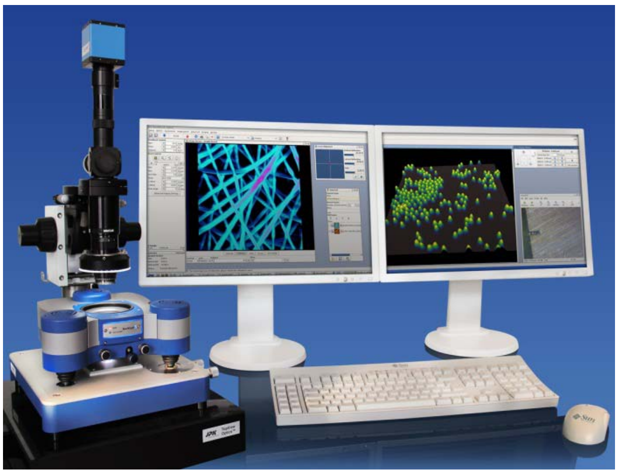
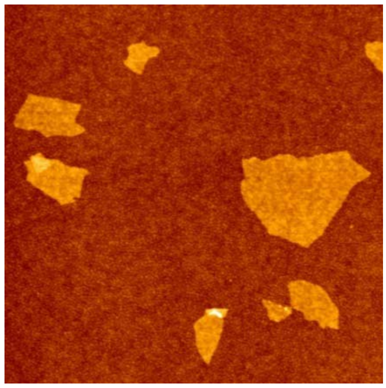


Fig. 1 JPK NanoWizard® 3 NanoScience version with TopViewOptics™

a)



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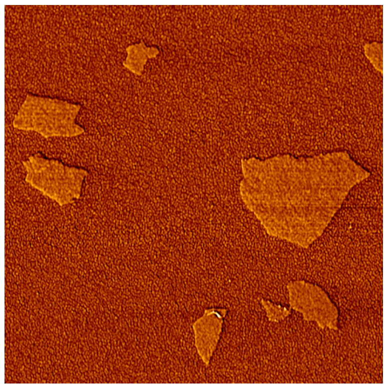

Fig. 2 Graphene flakes on mica imaged in AC mode, scan size: 3x3 µm. a) height image, color scale: 8 nm; b) phase contrast image, color scale: 13°

distinction between different numbers of graphene layers. More properties can be investigated by combining the topography scan with conductive AFM (CAFM), Kelvin probe microscopy (KPM), near-field scanning optical microscopy (SNOM), scanning thermal microscopy and many more. All these modes are available with a NanoWizard® 3 system together with the corresponding accessories.
Here we give a short overview on the studies of graphene with conventional AC mode, JPKs new Quantitative Imaging mode (QI™) and electrical measurements based on contact mode as well as QI™ mode.

Measurement of graphene in AC mode

Fig. 2 shows several graphene flakes distributed across a silicon surface. The flakes which are multilayered graphene sheets mainly appear as flat areas that are ≈1.5 nm high. Higher structures at the edges are due to wrinkles and folds. The flakes are clearly resolved in the height and phase contrast images. In order to determine the exact number of stacked layers, advanced optical methods such as TERS can be employed.

Measurement of graphene in QI™

JPK has released the new Quantitative Imaging mode for the combination of superior imaging quality and simultaneous quantitative data acquisition. While scanning, an entire force curve is recorded at every pixel which can be analyzed to investigate several material properties.
The exact force control in both lateral and vertical direction allows sensitive imaging on loosely attached, brittle and soft samples. Fig. 3 shows some graphene flakes on silicon substrate with overlaps and folds. The adhesion image shows an increased contrast in these areas. The bottom image indicates a decreased stiffness of the wrinkled portions of the flakes as seen in the darker areas.

Conductive measurements of graphene

One of the interesting properties of graphite is the high conductivity due to the delocalized electrons in between

a)

b)

c)

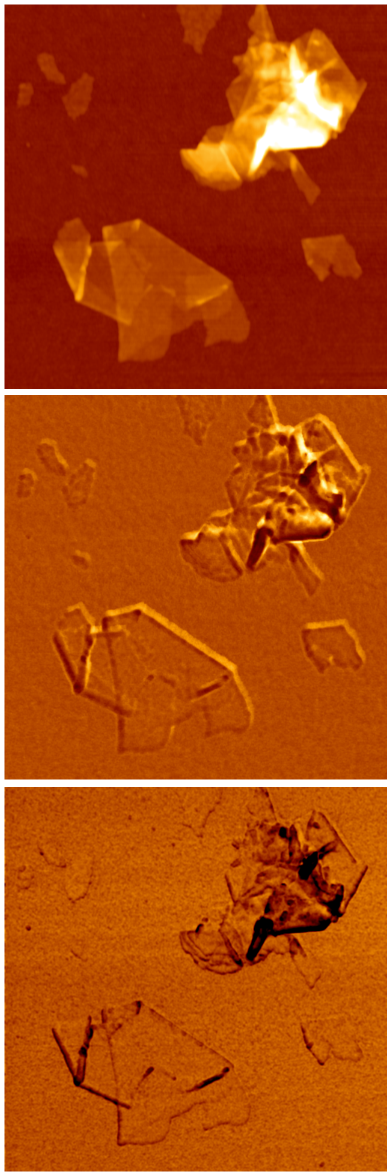

Fig. 3 Graphene flakes on mica substrate, measured in QI™ mode, 2.5µm x 2.5 µm scan size.
a) height image, color scale: 30 nm
b) adhesion image, color scale: 21.3 nN
c) stiffness image, color scale: 1.54 m/N

layers. Single graphene layers, however, show an isolating behavior along the perpendicular direction. This can be seen in the CAFM images in Fig. 4 b) which were recorded in conventional contact mode. The image shows two partially overlapping graphene layers (Fig. 4 a)) on silicon with a vacuum metalized gold-palladium coating. The coating shows a granular structure on the

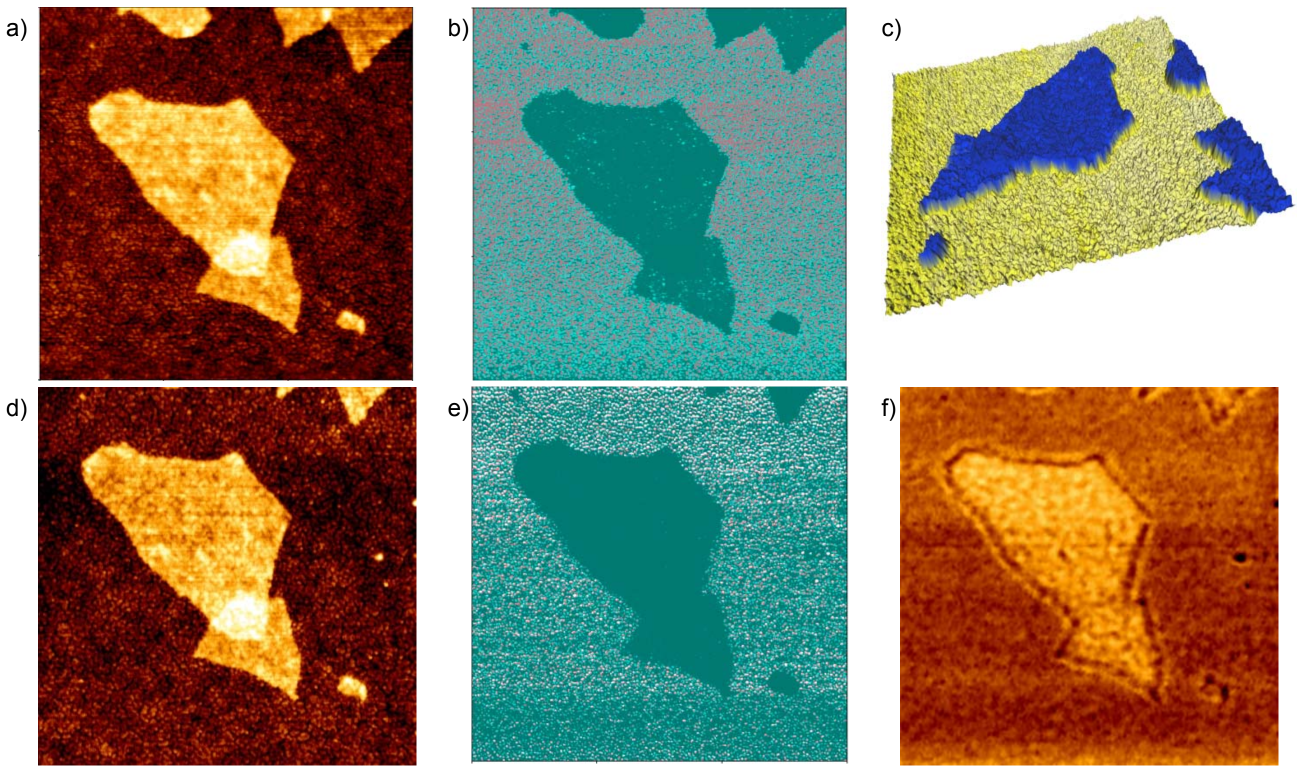

Fig. 4 Two partially overlapping graphene layers in 1.5x1.5 µm scans in a)-c): CAFM in contact mode and d)-f): CAFM in QI™ mode a) height image, color scale: 3.4 nm b) electric current image, color scale: 26.7 nA c) 3D height image with current as color overlay d) height image, color scale: 3.4 nm e) electric current image, color scale: 21.1 nA f) adhesion image, color scale: 7.6-9.3 nN

substrate. Overlaying the three dimensional height image with the colors of the current map shows the exact overlap of non-conducting areas where graphene is present (Fig. 4 c)).

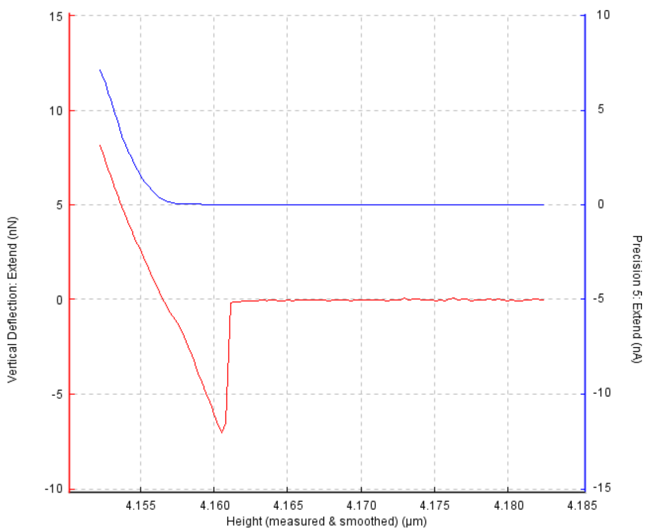

Fig. 5 Example force curve. Red: extend segment, force channel; Blue: extend segment, current channel

Another scan on the same area was done using Quantitative Imaging (Fig. 4 a)). As expected, the two height images are comparable and deliver equivalent information. The height value of each pixel in the image was read out of a force-distance curve. In addition to the topography, the recorded data was analyzed to reveal the conductivity distribution (Fig. 4 b)). An example force curve shows the extend segment for both the Force and current channel (Fig. 5).
In addition, the lowest force of each retrace segment was used to calculate an adhesion map (Fig. 4 c)). It can be seen that the adhesion forces are slightly stronger on the graphene.

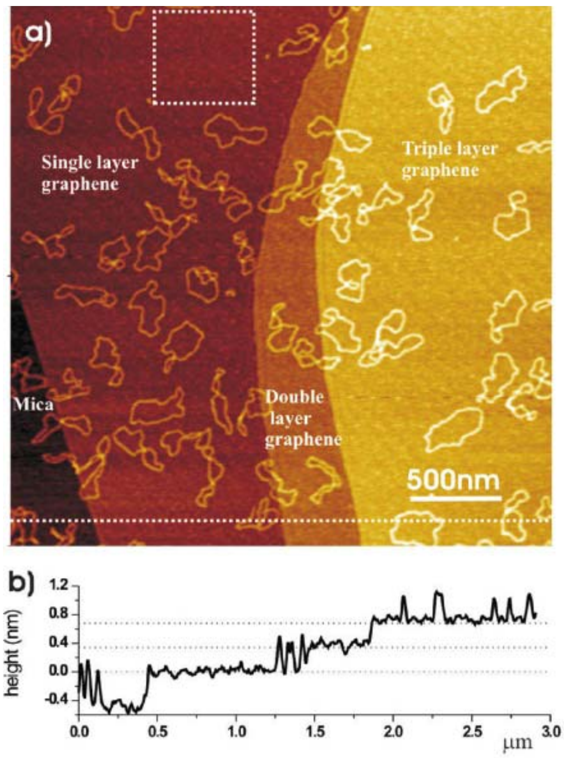

Fig. 6 a) Overview of area showing mica and three different layers of graphene on plasmid ds-DNA, scanned in AC mode. Scan size: 3x3 µm, color scale: 1 nm.
b) Cross section along the dotted line in a) showing the individual layers and the covered DNA.
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Replication of DNA with graphene

In the following application example, graphene was adhered to a mica surface already covered with plasmid DNA molecules. The entire experiment is described in detail in the publication of Severin et.al.[4]. The image in Fig. 6 a) shows part of the mica substrate and three individual layers of graphene which closely follow the shape of underlying DNA molecules.

The scan in Fig. 7 shows a DNA molecule in an area of a single graphene. It was recorded in contact mode with a normal force of 25 nN which is prove of the increased

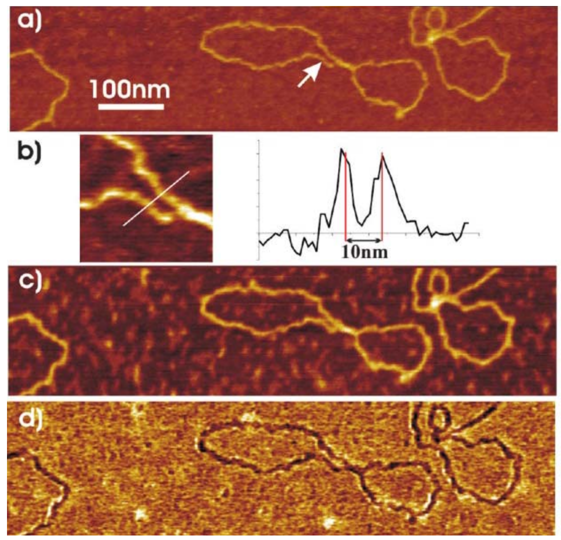

Fig. 7 Contact mode image of six day old sample showing two DNA strands that are 10 nm apart. The DNA is covered by a single graphene sheet. a) height image; b) cross section along two parallel DNA strands; c) AC mode image of same area, recorded with the same tip as the previous image; d) corresponding phase contrast image
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wear resistance of the DNA due to the coverage with graphene. The sample was six days old by the time it was measured showing graphenes impermeability to gases. Further, it was shown that two parallel DNA strands that are only 10 nm apart can be distinguished in the cross section. It was hence shown that graphene closely follows the topography of an underlying molecular structure with high precision. This method may be used as a substitute for lithographic methods in future applications, e.g. in the design of strain engineered graphene electronics.

Literature

[1] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A.: Electric Field Effect in Atomically Thin Carbon Films. Science, 2004, 306, 666-669
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[3] http://europa.eu/rapid/press-release_IP-13-54_en.htm
[4] N. Severin, M. Dorn, A. Kalachev & J.P. Rabe: Replication of Single Macromolecules with Graphene. Nano Letters, 2011, 11, 2436-2439