Making the connection

Atomic force microscopy correlates Graphene's functional properties on the nanoscale.

Ilka M. Hermes, Simonas Krotkus, Ben Conran, Clifford McAleese, Xiaochen Wang,
Oliver Whear, and Michael Heuken

The implementation of graphene in devices for nanoelectronics or energy conversion often requires material modifications. However, the local surface inhomogeneities of pristine graphene can affect the uniformity of these modifications. Therefore, accurate nanoscale characterization of the graphene topography in combination with the material's functional properties is essential. Atomic force microscopy (AFM) unites real-space topography imaging with the detection of functional surface properties, including the electrical potential, adhesion, and elasticity.

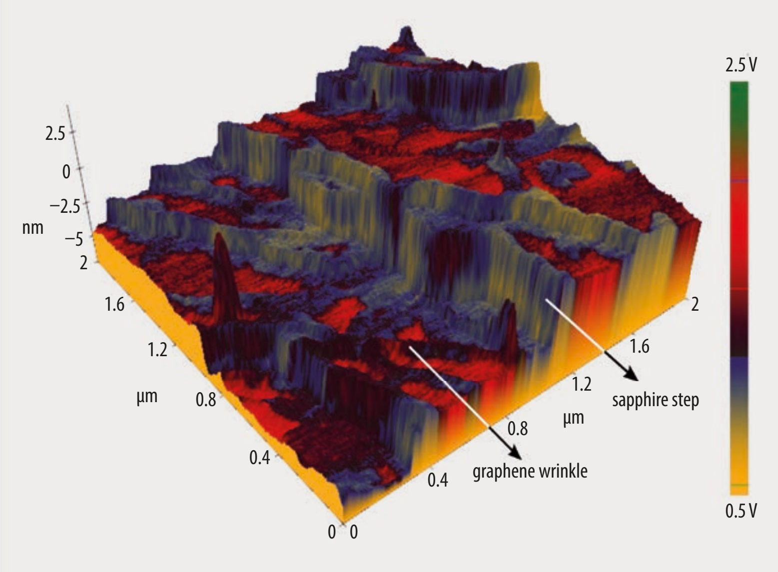

Fig. 1 This 3D overlay of the graphene topography shows the wrinkles and underlying sapphire levels. The surface potential was mapped using sideband KPFM.

When materials are reduced to two dimensions, unique properties emerge. As such, the two-dimensional graphene displays a variety of exceptional physical characteristics, including astonishing charge carrier dynamics, high thermal conductivity, and mechanical strength. Future applications of 2D materials range from flexible electronics to optoelectronics and electrochemical energy storage. Moreover, the low dimensionality and light weight of 2D materials have attracted the attention of nanoelectronics researchers due to the continuous downscaling of electronic devices [1].

Since an industrial application of graphene in electronic devices requires large wafer-scale graphene films, researchers have focused their efforts on improving monolayer growth procedures, with chemical vapor deposition (CVD) on catalytic copper (Cu) as the most common route. However, graphene growth on Cu substrates entails a subsequent transfer onto an insulating substrate, which can damage the monolayer and introduce contaminations. Therefore, a process for direct growth on insulating substrates is an important step to-

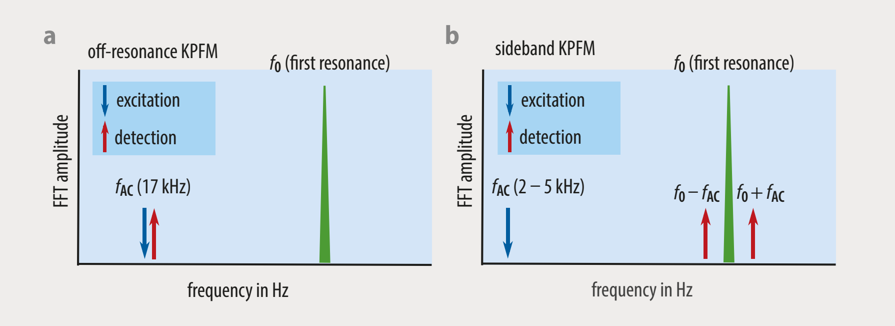

Fig. 2 For off-resonance KPFM (a), the AC voltage modulates the electrostatic force at a frequency well below the first resonance of the cantilever. For sideband KPFM (b), an AC voltage modulates the force gradient introducing two sidebands left and right of the resonance.

wards future graphene applications [2]. In this study, the wafer-scale graphene was grown on LED grade c-plane sapphire in an AIXTRON CCS R&D reactor.

To investigate the morphology and functional properties of this CVD-grown graphene film on insulating sapphire, AFM is ideally suitable. Using sideband Kelvin probe force microscopy (KPFM) available on Park Systems' research NX AFMs, we resolved a heterogeneous surface potential distribution with a distinct contrast between the bulk graphene film on underlying sapphire terraces and graphene wrinkles as well as sapphire step edges (**Fig. 1**). A 3D overlay of topography and surface potential shows a considerably lower surface potential on graphene wrinkles and around sapphire steps than on the sapphire terraces. Furthermore, the surface potential distribution corresponds to mechanical features, resolved via Park Systems' PinPoint nanomechanical AFM. The correlation of the KPFM and the nanomechanical AFM signals indicates a possible connection between the graphene's mechanical and electrical properties, thereby demonstrating the potential of AFM as a holistic characterization technique for 2D materials.

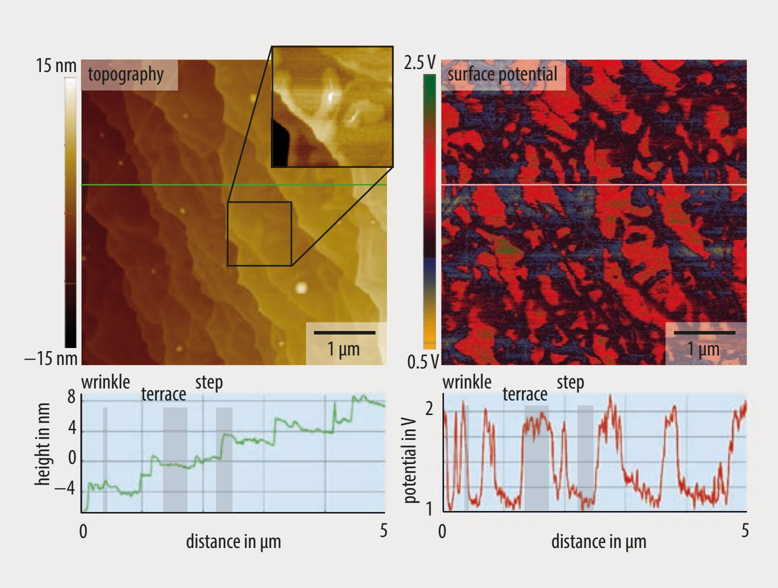

Fig. 3 Sideband KPFM was used to study CVD-grown graphene on a sapphire substrate. The line profiles of topography (green) and surface potential (red) show a correlation of both signals with clear potential contrast between underlying sapphire steps and terraces as well as graphene wrinkles.

Surface potential imaging

KPFM captures the surface topography simultaneously to the surface potential. For this, an oscillating conductive cantilever scans the surface, while applying an AC voltage to detect changes in the electrostatic force between tip and sample caused by local variations of the surface potential [3]. To minimize the detected electrostatic force, a DC bias counteracts the contact potential difference between tip and sample at each point of the scan. Based on the applied DC bias, the surface potential distribution of the sample is reconstructed in the KPFM signal. If the work function of the con-

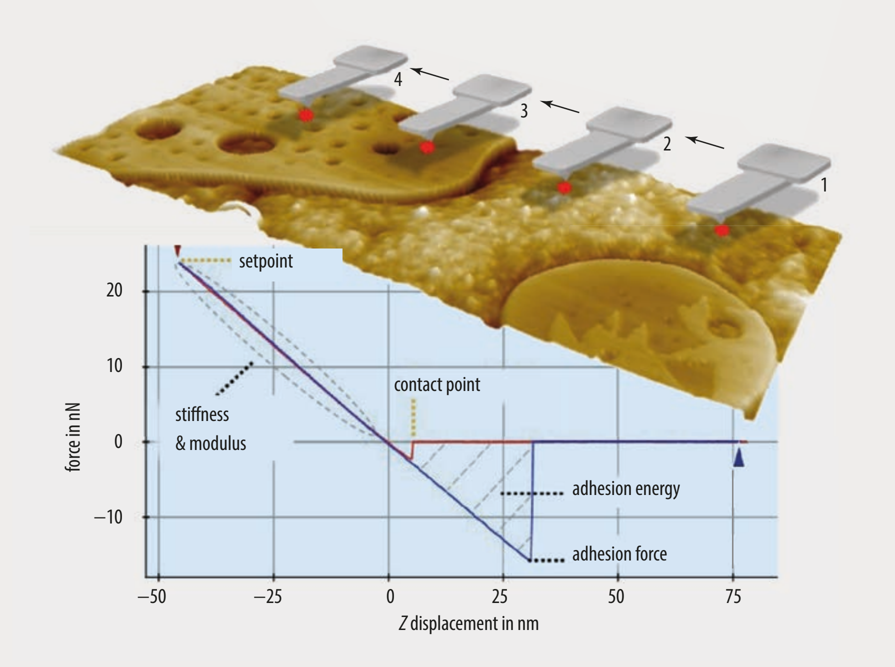

Fig. 4 In Park Systems' PinPoint AFM, the tip approaches the sample and retracts at each pixel before moving to the next pixel, as indicated by positions 1, 2, 3 and 4. The resulting force curves and their automated analysis allow real-time imaging of nanomechanical properties including adhesion force, elastic modulus, and deformation.

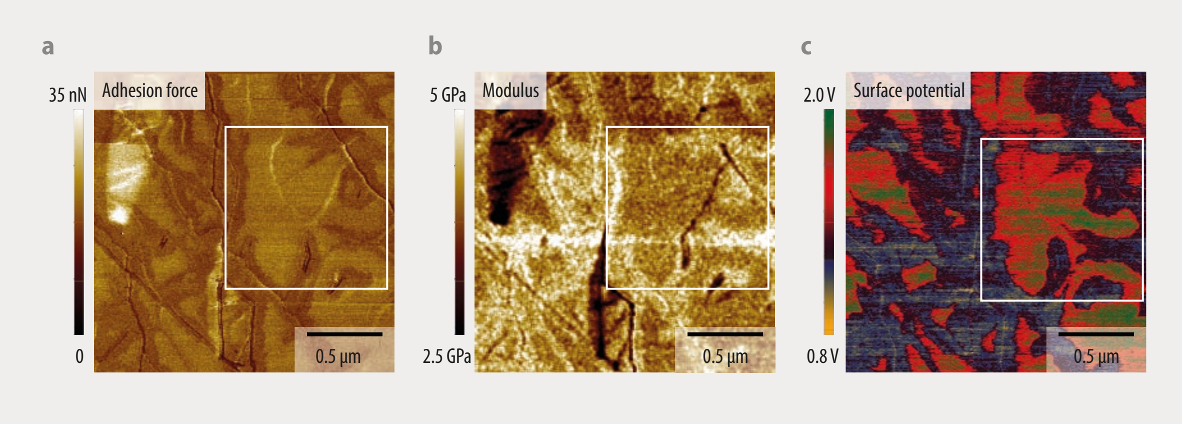

Fig. 5 Adhesion force (a) and modulus (b) of graphene on a sapphire substrate were recorded using Park Systems' PinPoint nanomechanical imaging, surface potential (c) with sideband KPFM. The white box highlights a sapphire terrace with higher adhesion force, modulus, and surface potential than the surrounding sapphire steps.

ductive tip is known, the potential distribution can be converted into the work function distribution of the sample. For the resolution and accuracy of the surface potential in KPFM, the detection method of the electrostatic force is decisive.

In the widely applied off-resonance KPFM, the AC voltage modulates the electrostatic force at a frequency far from the resonance of the cantilever, used for topography imaging (**Fig. 2a**). The electrostatic force is detected via the oscillation amplitude at the AC frequency. By applying a DC bias that matches the potential difference between tip and sample the amplitude at the AC frequency and therefore the electrostatic force is nullified. However, the dependence of the KPFM signal on the long-ranged force lowers the sensitivity: non-local interactions between sample and cantilever overlay the local signal, which in turn affects the spatial resolution and accuracy of the surface potential measured via off-resonance KPFM [3].

To improve the resolution and accuracy of the KPFM signal, Park Systems has implemented an easy-to-use sideband KPFM mode in their NX research tools. In sideband KPFM, a low-frequency AC voltage (2 – 5 kHz) is applied to the tip to modulate the electrostatic force gradient. The modulated force gradient introduces frequency sidebands left and right of the cantilever resonance (**Fig. 2b**). Analogous to off-resonance KPFM, the feedback of sideband KPFM nullifies the amplitude of these sidebands by applying a DC bias matching the potential difference at each measurement position. By detecting the short-range force gradient instead of the force, long-range crosstalk decreases, and the lateral resolution and local potential sensitivity improve significantly [3].

By measuring sideband KPFM on a CVD-grown graphene film on a sapphire substrate, we resolved a distinct potential contrast that directly correlates with the topography of the sample (**Fig. 3**). The topography signal showed underlying sapphire terraces and varying step heights of up to 3 nm as well as graphene wrinkles with heights between 0.5 and 2 nm. Interestingly, each sapphire terrace featured finer substructures with elevations of 0.6 nm in proximity to the step edges.

The simultaneously recorded surface potential displayed a clear contrast between two discrete states: we observed a low potential state at the position of the elevations close to the sapphire steps as well as on the graphene wrinkles, and a high potential state on the bulk film on underlying sapphire terraces. For the wrinkle we detected a potential contrast of around 0.5 V with respect to the bulk film on sapphire terraces [4]. The potential on the elevations close to the sapphire steps, on the other hand, differed by around 0.7 V from the potential of the bulk film on the terraces.

Correlation of surface potential and nanomechanics

In addition to KPFM we imaged the sample's nanomechanical properties at the same position using Park Systems' PinPoint AFM. This method provides accurate and quantitative nanomechanical images via fast force spectroscopy mapping (**Fig. 4**): the cantilever approaches and retracts at each pixel of the entire scan area to simultaneously acquire 3D topography and nanomechanical information of the sample surface. At each pixel, the XY scanner stops, and high-speed force-distance curves are acquired with well-defined control of contact force and contact time between the tip and the sample. The automated analysis of each force curve allows for real-time visualization of sample deformation, elastic modulus, and adhesion force simultaneously to the topography imaging.

The nanomechanical signals acquired via PinPoint AFM showed a distinct contrast between the underlying sapphire terraces and the steps and graphene wrinkles (**Fig. 5**). As such, the elevations in proximity to the sapphire steps, which also featured a decreased surface potential, exhibit a lower adhesion force and a higher modulus. This suggests that the graphene film becomes harder at these positions. On the sapphire terraces, on the other hand, the adhesion force increases and the modulus decreases. The correlation of the nanomechanical properties with the surface potential and the sample topography indicates a possible connection of the material's mechanical and electrical properties.

Summary

The combination of different functional AFM techniques including sideband KPFM and PinPoint nanomechanical imaging available on Park Systems' research AFMs allows a holistic and in-depth characterization of 2D materials as demonstrated on a wafer-scale CVD-grown graphene film on sapphire. The measurements showed a distinct correlation of all measurement signals indicating a connection of graphene's electronic and mechanical surface properties. Characterizing the highly localized mechanical and electronic properties of 2D materials enable a tailored development for future nanoelectronics applications.

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Authors

Ilka M. Hermes, Park Systems Europe GmbH, Mannheim, Germany; **Simonas Krotkus**, AIXTRON SE, Herzogenrath, Germany; **Ben Conran, Clifford McAleese, Xiaochen Wang, Oliver Whear**, AIXTRON Ltd, Cambridge, United Kingdom; **Michael Heuken**, AIXTRON SE, Herzogenrath, Germany