Nanoanalysis of graphene layers using scanning probe techniques

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Graphene is an almost ideal two-dimensional system. Unlike other two-dimensional electron gas systems realized in silicon or gallium arsenide, the electron wave functions are very close to the surrounding environment. While this causes problems in trying to passivate the surface without reducing the mobility, it does allow direct electrical access to the two-dimensional surface states using scanning probe techniques. In this review, we look at recent advances in the nanoanalytics of the surface and edges of graphene using scanning probe techniques.

Keywords: scanning probe microscopy; graphene; mesoscopic devices

1. Introduction

The prospect of integrating carbon into future nanoelectronic devices continues to generate a great deal of interest in the properties of graphene. Graphene’s superlative electronic properties combined with its compatibility with existing semiconductor processing techniques makes it a serious candidate for applications such as room temperature radiofrequency transistors, novel switches, interconnects and field-effect transistors in digital logic circuits (Geim 2009; Lemme 2009). Its candidacy for entering the post-silicon era is, however, predicated on improving its field-effect mobility, on–off conductance modulation and stability in standard atmosphere (Schwierz 2010). Since these bulk transport properties are ultimately controlled by its local geometrical, crystallographic and electrostatic environment, characterizing graphene at the nanoscale is a powerful way to understand the factors which influence them. In contrast to subsurface two-dimensional electron systems, where the environment is less accessible to nanoscale surface probes, the exposure of the electron wave function in graphene to the environment also provides microscopists with the unique opportunity to probe not only the many-body behaviour of electrons, but also the single-particle
density of states and their *immediate* environment as well. In this review, we look at some of the experiments exploiting this opportunity on graphene sheets and nanostructures.

Before discussing the literature in more detail, it is important to briefly outline what structures we expect to image in graphene. Many of the different physical phenomena associated with graphene stem from the unique electronic bandstructure of a hexagonal lattice of carbon atoms. A tight-binding calculation for the $\pi$ bands reveals that graphene is a gapless semi-metal with linear dispersion around two valleys in the Brillouin zone, where the conductance and valence bands meet at the Dirac point. At zero temperature, the $\pi$ electrons from each carbon atom fill the states up to the Dirac point, where the density of states vanishes. Once isolated from bulk graphite and electrically contacted, the transport properties of graphene flakes away from the Dirac point can be investigated by varying the carrier density via the electric field from capacitively coupled gates (Novoselov *et al.* 2004). Figure 1 schematically shows the structure of a typical back-gated device made from graphene on a Si/SiO$_2$ substrate. Even without intentional doping from the back-gate, carriers can be induced by the spatially disordered electrostatic potential arising from the SiO$_2$ and adsorbed charged impurities (see inset, figure 1), giving rise to puddles of electrons and holes at the charge neutrality point. The conductivity is consequently finite even in the limit of vanishing average carrier density. Without an insulating state the on–off conductance ratio is too low for some of the envisaged applications such as novel switches and field-effect transistors in logic applications. Furthermore,
scattering from inhomogeneities is expected to play a role in limiting the mobility of supported graphene sheets to between 0.1 and 20 m²Vs⁻¹, an order of magnitude less than needed to make graphene competitive when compared with gallium arsenide high-electron-mobility transistors at room temperature (Geim 2009). There is growing evidence to suggest that inhomogeneities in exfoliated flakes are mainly the result of adsorbed charged impurities and out-of-plane corrugations in the graphene atomic lattice, so many scanning probe experiments are performed with the aim of identifying these types of disorder. These include physi- and chemi-sorbed atmospheric gases (Romero et al. 2008; Deshpande et al. 2009), residue from tape used during exfoliation (Moser et al. 2008), monolayers of photo- or ebeam-resist left over from the microfabrication of electrical contacts (Ishigami et al. 2007), trapped charges in the substrate (Deshpande et al. 2009) and molecules such as H₂O trapped between the graphene and the SiO₂ (Zhang et al. 2009).

Another area where local probes are expected to make an impact is in the characterization of patterned nanostructures such as nanoribbons and quantum dots. Over the last few years, patterning graphene into narrow channels has been the primary route to opening up a band gap. It was indeed found that the conductance of nanoribbons can be made vanishingly small within a width-dependent confinement gap (Han et al. 2007), but the size of the transport gap exceeds estimates based on lateral confinement effects alone, and at low temperature the gapped region also contains many sharp conductance resonances (Molitor et al. 2009; Todd et al. 2009). These observations have been described within different theoretical and semi-empirical frameworks, including Anderson localization (Ni et al. 2009), percolation models (Adam et al. 2008), disorder and edge-induced quantum dot formation (Sols et al. 2007), and renormalized lateral confinement (Han et al. 2007). As these mechanisms are distinguished by where localization occurs, we anticipate spatially resolved measurements playing a decisive role in discriminating between them.

2. Comparison of imaging techniques

(a) Scanning tunnelling microscopy

Scanning tunnelling microscopy (STM) is a mature technique for imaging the surface topography of conducting samples with sub-nanometre height and lateral spatial resolution. The physical effect underpinning STM is the exponential increase in the tunnelling current between a biased conducting surface and an atomically sharp metallic tip when brought into close proximity (less than 1 nm). By adjusting the distance between the tip and the surface to keep the current constant, it is possible to image the variations in surface height produced by an atomic lattice. Since the tunnelling current also depends sensitively on the local density-of-states underneath the tip, scanning tunnelling spectroscopy can simultaneously access the local electronic spectra around the vacancies (Rutter et al. 2007) and adsorbed molecules (Ritter & Lyding 2009), which cumulatively determine the mobility and energy gaps measured using bulk transport.

Tunnelling into surface states of exfoliated graphene sheets proved to be non-trivial. The main impediment to obtaining stable STM operation was found to be acrylic residues leftover from lithographic patterning of electrical contacts.

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Subsequent to a post-fabrication cleaning routine, the honeycomb lattice could be imaged with atomic resolution (Ishigami et al. 2007; Stolyarova et al. 2008). This problem has elsewhere been avoided by using a stencil mask for patterning contacts (Deshpande et al. 2009). Another feature of performing STM on graphene is the potential for damaging the tip by crashes with the surface when locating micron-sized graphene flakes, particularly on non-conducting host substrates. An effective solution is to deposit a metallic film around (Stolyarova et al. 2007) or under (Klusek et al. 2009) the flake. This solution is perhaps limited, however, as it does not easily allow a comparison with simultaneously obtained bulk magnetotransport measurements and their explanation in terms of the underlying microstructure. Alternatives to this method include applying the STM to the partially suspended graphene flakes remaining on cleaved graphite (Luican et al. 2009), or using in situ scanning electron microscopy for manual alignment of the tip with the flake (Ishigami et al. 2007).

So far atomically resolved STM images have been obtained of graphene supported by a range of different substrates (graphite, Li et al. (2009b), Luican et al. (2009); gold, Klusek et al. (2009); ruthenium, Vazquez de Parga et al. (2008), Sadowski et al. (2009); silicon carbide, Rutter et al. (2007); silicon dioxide, Stolyarova et al. (2007), Deshpande et al. (2009), Geringer et al. (2009), Xu et al. (2009). Zhang et al. (2009)) in both ambient and low-temperature conditions. STM images of graphitized silicon carbide revealed the presence of atomic defects (Rutter et al. 2007), whereas STM images of SiO₂-supported graphene confirmed the anticipated low density (less than 1 in 10⁵; Xu et al. 2009) of defects and dislocations expected in mechanically exfoliated flakes (Stolyarova et al. 2007). Using local spectroscopy to map the Dirac point, Deshpande et al. (2009) and Zhang et al. (2009) also compared the local curvature of exfoliated graphene sheets with the potential landscape (Deshpande et al. 2009; Zhang et al. 2009). The two were found to be uncorrelated, suggesting that corrugations are not the primary source of potential fluctuations responsible for electron–hole puddles at the charge neutrality point. STM studies of supported graphene invariably report the presence of out-of-plane corrugations, ranging from 0.2 to 3 nm in height and from 10 to 30 nm in lateral dimension (Ishigami et al. 2007; Stolyarova et al. 2007; Deshpande et al. 2009; Geringer et al. 2009; Xu et al. 2009). Such ripples are thought to arise partly from the graphene conforming to the underlying roughness in the substrate and partly from intrinsic rippling (Ishigami et al. 2007; Geringer et al. 2009; Xu et al. 2009), but their contribution to scattering is still debated. Figure 2a shows an STM image of the self-assembly of an organic semiconductor (3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA)) formed on epitaxially grown graphene (Wang et al. 2008). Access to molecular arrangements at this scale is of particular technological interest as a derivative of this molecule (10,12-pentacosadiynoic acid (PCDA)) was used to functionalize graphene for the atomic layer deposition of aluminium oxide (Wang et al. 2008), a candidate insulator for top-gated field-effect devices (Szafranek et al. 2010). The first evidence for edge states, which manifest as peaks in the local density of states, was also obtained by STM of monoatomic step edges on the surface of bulk graphite (Kobayashi et al. 2005; Niimi et al. 2006).

Considering its merits and the pressing challenges associated with optimizing the performance of room temperature nanoribbon field-effect transistors, STM is undoubtedly the characterization tool of choice because it allows the detection
of edge states and adsorbed functional groups, both of which are expected to dominate the transport properties of sub-10 nm-wide nanoribbon devices. In comparison with mesoscopic graphene layers, however, which have a relatively large surface area exposed for study, the application of STM to electrically contacted nanoribbon devices is experimentally more challenging. To date, there is no published STM study of SiO$_2$-supported nanostructures. Several STM studies examining graphene nanostructures on conducting silicon and graphite do, however, offer some insight into the prospects of such a study (Tapaszto et al. 2008; Ritter & Lyding 2009). Using in situ exfoliation of graphite, for example, Ritter & Lyding (2009) were able to identify the armchair and zigzag edges of nanometre-sized platelets and nanoribbons. Figure 2b illustrates spectroscopic measurements of edge states near zigzag edges only, confirming theoretical predictions. In another study, Tapaszto et al. (2008) used an STM tip to etch through single atomic layers on graphite. Figure 2c shows a 2.5 nm-wide nanoribbon etched by this method. The accompanying tunnelling spectra of the nanoribbon show a region of suppressed conductance around zero bias, indicating the presence of a confinement gap. Providing the current experimental challenges with imaging nanostructures can be overcome, we expect the same measurements of edge states and energy gaps on nanoribbon devices to be equally fruitful.

Figure 2. Scanning tunnelling microscopy (STM) imaging of adsorbates, edge states and energy gaps. (a) STM image showing how self-assembled PTCDA is continuous over a step edge on epitaxially grown graphene. The herringbone pattern and the molecular structure of PTCDA are shown in the inset below. (Adapted from Wang & Hersam (2009).) (b) STM image of a (15 nm)$^2$ graphene platelet exfoliated on a silicon substrate. Bias spectroscopy performed at different distances from the zigzag edges reveals an edge state at −300 mV bias. (Adapted from Ritter & Lyding (2009).) (c) A 2.5 nm-wide nanoribbon etched into the surface of graphite using STM lithography (top). Spectrum (bottom) taken over the nanoribbon shows a zero-bias gap ($E_g$) of 0.5 eV. (Adapted from Tapaszto et al. (2008).) (a) Scale bar, 3 nm; (c) scale bar, 1 nm. (b) Zigzag: dotted line, 0 A; dashed line, 4.3 A; thin line, 8.5 A; thick line, 12.8 A.
Scanning gate microscopy (SGM) employs conventional scanning force microscopy techniques to perturb the transport through low-dimensional conducting systems using the electric field from a charged metallic tip. Many of the operating principles behind scanning force microscopy are well established and for completeness we provide only a brief introduction to them here. At the heart of a scanning force microscope is a microfabricated cantilever (typically 100 μm long) whose deflection is measured using an optical or electrical readout. In dynamic mode, the cantilever is mechanically or electrostatically excited at a frequency $f_m$ and brought within a few hundred nanometres of the surface under investigation. A feedback circuit is used to detect the change in the cantilever’s resonant frequency and oscillation amplitude owing to the additional force from the surface. Although the whole cantilever is affected by the surface, a sharp tip at its free end makes the perturbed oscillation particularly sensitive to the nanometre-sized region of the sample just underneath the tip. To perform SGM, a current is driven through the sample and the perturbation of its bulk conductance owing to the presence of the biased tip is recorded as a function of the tip position. Regions that are sensitive to changes in the local electric field, for example, because the current density or field-effect mobility is high there, can then be imaged with approximately 50 nm resolution. Surprisingly SGM has not been widely used to investigate graphene despite its high spatial resolution (Berezovsky & Westervelt 2009; Jalilian et al. 2010) owing to the somewhat poor signal-to-noise ratio achievable at room temperature. This problem stems from the fact that the SGM signal depends on the relative area of the tip-perturbed region to the rest of the sample, which in micron-sized two-dimensional systems such as graphene is obviously rather small (approx. $10^{-4}$). Historically, applications of SGM have thus focused on zero-dimensional and one-dimensional samples such as carbon nanotubes and semiconducting quantum dots, which exhibit large changes in conductance with tip position. Recently AC detection techniques were used to improve the SGM signal from large area graphene devices. Figure 3c shows a series of transconductance images captured at different back-gate voltages using this method. The back-gate voltage both injects carriers into the graphene and moves the Fermi level relative to the Dirac point. The modulating bias on the tip increases or decreases the local current density depending on whether the Fermi level is above (electrons) or below (holes) the local Dirac point, allowing one to map out the mobility, polarity and distribution of charge carriers (see Connolly et al. (2010) for more details.) SGM is likely to become more prevalent in future studies of chemically doped and geometrically tailored devices, especially at low temperature where non-local effects come into play (Berezovsky & Westervelt 2009).

Electrostatic force microscopy (EFM) and Kelvin probe microscopy (KPM) are scanning probe techniques, which can measure stray surface electric fields, usually with less than 100 nm spatial resolution and millivolt sensitivity. By far the most well-known mode of operation is atomic force microscopy (AFM). In AFM, the tip at its closest approach is brought within less than 1 nm from the surface such that the rapidly varying short-range van der Waals and hard-sphere repulsion
dominate the change in the cantilever’s oscillation. In this mode, the cantilever’s frequency shift is used as the error signal of a feedback loop, which adjusts the sample height to maintain a constant frequency shift as the cantilever is scanned over the surface. This allows maps of the surface topography to be generated with atomic resolution. Figure 4a shows a typical atomic force micrograph of exfoliated graphene on SiO₂, confirming the presence of the same nanometre height corrugations revealed by STM. The power of AFM to help optimize host substrates for graphene devices was recently illustrated by a study that revealed atomic-level roughness of graphene on mica (Li et al. 2009a).

As discussed earlier, fluctuations in the local electrostatic potential are also of interest as they contribute to elastic scattering in graphene (Martin et al. 2008). In EFM, the long-range surface force associated with charged impurities can be measured directly, while in KPM a nulling voltage is applied to the sample, allowing maps of the surface potential to be generated in real time (Filleter et al. 2008; Yu et al. 2009). So far these techniques have provided access to the local work function of single- and few-layer graphene on different substrates (Filleter et al. 2008).
Figure 4. Electrostatic force microscopy. (a) Typical AFM image of exfoliated graphene on SiO₂. (Adapted from Geringer et al. (2009).) (b) AFM image (left) showing topography and KPM image (right) showing the contact potential of graphitized SiC. Note the large change in Kelvin probe contrast associated with the bilayer even though it is barely visible in the topography. (Adapted from Filleter et al. (2008).) (c) Topography (i) and EFM phase (ii) of graphene on SiO₂. (iii) Surface potential (ΔV) as a function of graphene thickness (D). Thicker graphene sheets screen the surface potential from the substrate more efficiently. (Adapted from Datta et al. (2009).) (b) Scale bar, 300 nm.

et al. 2008; Datta et al. 2009), the screening and accumulation of charge owing to the electric field from local gates (Lee et al. 2009), and the static electric fields owing to adsorbed charges or multipoles (Chen et al. 2005). Moser et al. (2008) used electrostatic force spectroscopy to measure the nulling voltage at the surface of SiO₂ contaminated by adhesive residues and found a shift of the surface potential to positive values (Moser et al. 2008). Shi et al. (2009) similarly showed that SiO₂ substrates with different work functions control the position of the charge neutrality point. These and other studies have drawn attention to the role played by graphene’s electrostatic environment in producing the random properties of as-prepared devices.

Figure 4b illustrates the variation in surface potential of graphene films epitaxially grown on the silicon-terminated 6H-SiC(0001) surface measured using KPM. Here, the different work functions of single and bilayer graphene lead to pronounced contrast despite only sub-nanometre changes in height. KPM’s ability to assess the quality of uncontacted graphene samples makes it a powerful tool for characterizing large area films of graphene grown on substrates unsuitable for electrostatic gating. Figure 4c is reproduced from Datta et al. (2009), who studied the ability of graphene to screen the electric field from the substrate. The
voltage required to null the change in EFM phase was found to decrease with increasing thickness of the graphene layers, implying that multi-layer graphene is more efficient at screening the surface potential. These measurements suggest that EFM would also be sensitive to the electric field penetration from the silicon back-gate. Since a gap in the density of states around the charge neutrality point modifies the screening properties of graphene, EFM, therefore, offers another method for characterizing the electronic properties of graphene nanostructures.

3. Conclusion

We have reviewed some of the techniques currently used to image nano- and meso-scale topographic and electrostatic features in graphene layers. We illustrated how STM is used to probe the influence of edge lattice symmetries, multi-scale topographic features, atomic structure, edges states and energy gaps, while scanning force microscopy techniques enable one to probe the electrostatic environment and the influence of surface adsorbates at mesoscopic length scales. We note that other techniques such as scanning photocurrent microscopy (Lee et al. 2008; Mueller et al. 2009; Sundaram et al. 2009; Xia et al. 2009), Raman imaging (Stampfer et al. 2007; Freitag et al. 2009; Ni et al. 2009), scanning single electron transistor (Martin et al. 2008) and scanning capacitance microscopy (Giannazzo et al. 2009), while not featuring in this review, are nonetheless equally important in the field. In future, we expect the full arsenal of local probe techniques to be employed to examine the effect of chemical recipes being developed to functionalize large area graphene flakes and for imaging localized states in graphene nanostructures.

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References

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