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Probing Electronic Properties of Graphene on the Atomic Scale by Scanning Tunneling Microscopy and Spectroscopy

Abstract: Atomic scale investigations of the electronic properties of graphene are playing a crucial role in understanding and tuning the exotic properties of this material for its potential device applications. Scanning tunneling microscopy (STM) and spectroscopy (STS) are unique techniques for atomic scale investigations and have been extensively used in graphene research. In this article, we review recent progresses in STM and STS studies of the electronic properties of suspended graphene as well as graphene supported by different substrates including graphite, metals, silicon carbide, silicon dioxide and boron nitride.

Keywords: Graphene; Scanning Tunneling Microscopy and Spectroscopy; Charge Transfer; Charge Carrier Density; Dirac Point; Landau Levels; Edges; Vacancies; Spin-Polarized States; Electron Scattering

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1 Introduction

Graphene, a single atomic layer of sp^2 -hybridized carbon atoms arranged into a hexagonal honeycomb lattice, is the first truly two-dimensional crystalline material with extremely high carrier mobility and has attracted intense scientific interest since it was first isolated and characterized by transport measurements in 2004 [1]. Due to the unique electronic band structure of graphene [2], a linear dispersion with zero gap around the Dirac point, many unusual electronic phenomena have been observed in graphene, including an anomalous quantum Hall effect [3–5], ballistic electron transport at room temperature [6], micron-scale electron coherence lengths [6, 7], novel many body coupling [8], and extremely high carrier mobility [9]. These effects are characteristic of two-dimensional massless Dirac Fermions [2–4]. Besides its unique electrical

properties [1–4, 10, 11], graphene is the strongest material ever measured with a high elasticity [12], a promising transparent conductor with unique optical properties [13], as well as a superior thermal conductor [14]. In addition to that, the electronic properties of graphene can be tuned by functionalizing graphene through hydrogen passivation [15, 16], lithographic processes [17], and other approaches [18, 19]. Therefore, graphene has been considered a promising material for both fundamental studies and future applications.

Since graphene was first isolated by mechanical exfoliation of graphite crystals [1, 20], many approaches have been developed to synthesize large scale graphene including epitaxial growth of graphene by thermal decomposition of the silicon carbide (SiC) surface [6, 21, 22], thermal annealing of the Ru single crystal containing carbon [23–25], chemical vapor deposition (CVD) [26–34], chemical reduction of graphene oxide [35], solid source growth [36, 37], ethylene irradiation [38], and supersonic methane beam [39], etc.

The structures of single-layer and few-layer graphene are the most important factors governing their electronic properties. Single layer graphene has a hexagonal honeycomb lattice, which is composed of two carbon sublattices, as shown in Figure 1(a). Single layer graphene is a semimetal with no bandgap [3, 4]. Most few-layer graphene and graphite are Bernal-stacked, i.e. the “A” carbon atoms in one layer are located above the “B” carbon atoms in its adjacent layer, as shown in Figure 1(b) for Bernal-stacked bilayer graphene and Figure 1(c) for Bernal-stacked trilayer graphene, respectively. However, stacking orders other than the Bernal stacking do exist in few-layer graphene, resulting in significantly different band structures as well as transport properties [40–43]. For example, the ABA (Bernal) stacked trilayer graphene as shown in Figure 1(c) is a semimetal with a tunable band overlap, while the ABC (rhombohedral) stacked trilayer graphene as shown in Figure 1(d) is a semiconductor with a tunable band gap [40, 44–46], which is similar to the AB (Bernal) stacked bilayer graphene [10, 22, 47–49].

The electronic properties of graphene have been extensively studied both theoretically and experimentally. The recent developments in the theory of the electronic

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Fig. 1. (a) Schematic of the hexagonal honeycomb lattice of single layer graphene consisting of two carbon sublattices. The carbon atoms in the A and B sublattices are colored in blue and yellow, respectively. (b) Schematic of the Bernal or AB stacked bilayer graphene. (c) Schematic of the ABA (Bernal) stacked trilayer graphene. (d) Schematic of the ABC (rhombohedral) stacked trilayer graphene.

structure and transport properties of graphene can be found in recent reviews by Castro Neto *et al* [2] and Das Sarma *et al* [50]. Experimental investigations of the electronic properties of graphene have been performed primarily with transport measurements, angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM). These three experimental techniques are complementary to each other. ARPES is a powerful and unique technique for resolving the electronic structure in momentum-space (k -space) [51]. STM has complemented ARPES by resolving the electronic structure in real space [52] as well as in k -space [53].

STM is a unique and powerful technique to detect the structural and electronic properties of materials on the atomic scale [52, 54]. STM measurements are closely related to the local density of states at the surfaces of materials. In particular, scanning tunneling spectroscopy (STS) is capable of measuring energy resolved local density of states with very high spatial resolution. The π -band energy-momentum dispersion relation is approximately linear around the $\mathbf{K}$ points:

$$E = \hbar v_F |\mathbf{k}|$$

where $\mathbf{k}$ is the wave vector measured from $\mathbf{K}$, $\hbar$ is Planck's constant h divided by 2π , and v_F is the Fermi velocity in graphene [55]. The energy-momentum dispersion re-

lation $E(\mathbf{k})$ can be directly observed in ARPES measurements [51]. Based on the above dispersion relation, the density of states close to the Dirac point per unit cell is given by (with a degeneracy of 4 included)

$$\rho(E) = \frac{2A_c}{\pi} \frac{|E|}{v_F^2}$$

where A_c is the unit cell area and v_F is the Fermi velocity [2]. The density of states can be directly measured by STS. The sketches of the energy-momentum dispersion relation and the density of states of graphene are shown in Figure 2. Differential conductance (dI/dV) spectroscopy recorded by STM reflects the spatially and energy resolved density of states at the surfaces of materials. So it is expected that the dI/dV point spectroscopy of graphene exhibits a “V” shape with a local conductance minimum at the Dirac point E_D .

The unique capability of STM, compared to transport measurements and ARPES, is to resolve the spatial distribution of density of states with very high spatial resolution ($<1 \text{ \AA}$ for lateral resolution and $<0.1 \text{ \AA}$ for vertical resolution). For instance, the gap-like feature in differential conductance spectra of graphene, arising from the phonon-mediated inelastic tunneling process, has been observed only in STM measurements due to the high sensitivity of STM to the spatial decay of the electron wave function at a surface [56]. Therefore, STM is a powerful and irre-

Fig. 2. Sketches of (a) the energy-momentum dispersion relation $E(\mathbf{k})$ and (b) the density of states of *n*-doped graphene (green), intrinsic graphene (red), and *p*-doped graphene (purple). The doping of graphene leads to a shift of the Fermi level with respect to the Dirac point.

placeable approach to probing the electronic properties of graphene on the atomic scale.

Atomic scale investigation of graphene is of paramount importance in graphene research. Many macroscopic properties of graphene arise from atomic-scale phenomena and structures. For example, the charge density maps recorded by STM clearly showed the significant difference in charge density fluctuations between graphene/BN and graphene/SiO₂ [57, 58], which provided an atomic-scale interpretation for the significant enhancement of carrier mobility in graphene/BN compared to that in graphene/SiO₂ [58–60]; strong electronic scattering was observed at the domain boundaries of graphene on Cu(111) [26], which most likely contributes to the reduced carrier mobilities of graphene, with numerous domain boundaries, grown on Cu foil compared to those of exfoliated graphene [31]. Exploring the atomic-scale origins of macroscopic properties is crucial for designing graphene-related materials and devices on demand.

In view of the rapid advances in atomic scale investigations of the electronic properties of graphene by STM and STS, it is important to summarize the status of this specific field timely. In previously published articles, Andrei *et al.* reviewed the experimental progress in probing the

electronic properties of graphene by STM, STS, transport, and magneto-transport measurements [61]; Morgenstern reviewed some of the STM and STS studies of graphene on insulating substrates [62]. In this article, we review the most recent research activities that were not covered by previous review articles in this field [61, 62], but some overlaps do exist in order to keep the integrity of this article. Due to the huge amount of research work in this field, it is almost impossible to cover all related studies in one review article. This review focuses on STM and STS investigations of the electronic properties of pristine graphene, as well as those of defective graphene with intrinsic defects, such as edges and vacancies. Studies of graphene growth are not included in this article. Studies of graphene functionalization by adsorption of or doping with foreign atoms or molecules are not included. Our review will start from the suspended graphene, and then focus on graphene supported by different substrates include graphite, metals, silicon carbide (SiC), silicon dioxide (SiO₂) and boron nitride (BN).

2 Suspended graphene

Graphene is only one atomic layer thick, and all carbon atoms are exposed to both surfaces, which leads to the fact that the electronic properties of graphene are extremely sensitive to its surroundings including substrates [63]. In order to avoid substrate-induced perturbations to the intrinsic electronic properties of graphene, devices with suspended graphene have been made and significant improvement in carrier mobility has been achieved [9, 64, 65] compared to traditional devices with substrate-supported graphene [20, 60]. In addition to that, suspended graphene is ideal for investigating some exotic properties in graphene, such as fractional quantum Hall effect [66, 67]. Recent advances in investigating the transport properties of suspended graphene have been reviewed by Andrei *et al.* [61].

Atomic resolution STM images of suspended graphene membranes have been achieved in recent studies [68–71]. In particular, Zan *et al.* obtained the atomic resolution STM images on both monolayer and bilayer suspended graphene membranes, as shown in Figure 3 [69]. For the suspended monolayer graphene, the density of states of *A* and *B* sublattices is identical, as a consequence of which both *A* and *B* carbon atoms are always equally resolved by STM at the same time, leading to a hexagonal honeycomb structure in STM images, as shown in Figure 3(b). In contrast, for the suspended bilayer graphene, the density of

Fig. 3. Atomic resolution STM images on (a) a transition region between suspended monolayer and bilayer graphene, (b) suspended monolayer graphene and (c) suspended bilayer graphene. (Reprinted from Reference [69]).

Fig. 4. (a) dI/dV gate map of suspended graphene membrane at $B = 8$ T. (b) dI/dV spectra for gate voltages varying from 5 to 6 V, taken from the white rectangle in (a). (Reprinted from Reference [70]).

states of A and B sublattices are not identical, which arises from Bernal or AB stacking between two graphene layers. Consequently, the AB-sublattice symmetry is broken and only one of the two carbon sublattices is imaged, leading to a triangular structure in STM images, as shown in Figure 3(c). Similar STM images were observed for graphene on weakly interacting substrates, i.e. a hexagonal honeycomb lattice structure for single layer graphene and a triangular structure for bilayer graphene, as mentioned in the following sections.

The height variation measured on the suspended graphene is larger than that measured on graphene/ SiO_2 , which results from the deformation of the suspended graphene membrane [70]. The electronic structure of the suspended graphene membrane can be tuned by strain engineering, which was demonstrated by Klimov *et al.* in their recent studies [70]. Stable STM measurements on the suspended graphene were achieved by carefully approaching the membrane with very slow scanning speeds to avoid exciting the graphene drumhead. A continuous

tuning of the deformation of the suspended graphene membrane was realized through controlling the competition between the attractive forces from the STM tip, which was attributed to van der Waals forces by Klimov *et al.* [70] and to the electrostatic force by Xu *et al.* [71], and the electrostatic force induced by back-gate voltage.

Gate-mapping STS measurements showed that the electronic structure of the deformed suspended graphene is completely different from that of substrate-supported graphene. As shown in Figure 4, the dI/dV spectra exhibited multiple quartet bands of peaks, which indicated the formation of a spatially confined quantum dot. The STM-tip induced deformation created a localized strain field in the graphene lattice, leading to the generation of pseudo-magnetic fields and thus the formation of a strongly confined quantum dot. It is worth noting that, besides deformed suspended graphene, graphene on SiO_2 also exhibits quantum dot confinement but results from a different cause, i.e. the substrate-induced disorder potential [72].

Despite of obvious advantages of suspended graphene devices in terms of high carrier mobility and the convenience for exploring and utilizing intrinsic properties of graphene, currently there are major challenges confronting suspended graphene devices. For example, the suspended graphene is not mechanically stable under large applied gate voltages [9, 70], which makes it difficult to induce high charge carrier density in devices; and the fabrication of devices with complex geometries is limited by the lack of a supporting substrate for graphene. Therefore, devices with substrate-supported graphene are currently still the mainstream. As the electronic properties of graphene depend sensitively on its interaction with the underlying substrates, it is of great practical and technological importance to measure the electronic properties of graphene on substrates on the atomic scale in order to evaluate the substrate-induced perturbations to graphene and to seek appropriate substrates for graphene in future device applications. In the subsequent sections, we discuss recent advances in STM and STS investigations of atomic scale electronic properties of graphene on different substrates.

3 Graphene on graphite

In STS measurements of Kish graphite and highly oriented pyrolytic graphite (HOPG) in an applied magnetic field, the Landau levels were observed in the dI/dV spectra [73, 74]. In particular, both massless and massive Dirac fermions, originating from monolayer and bilayer graphene, respectively, were first observed in STS measurements of HOPG, which suggested that the surface layers of HOPG are well decoupled from the bulk [73].

In addition to these STS studies of graphite, graphene flakes on graphite were prepared and characterized by Li *et al.* with STM and STS measurements, and it was found that graphene flakes are sufficiently decoupled from the graphite substrate [75]. STM images of graphene flakes exhibit a hexagonal honeycomb lattice structure. A “V” shaped density of states that vanishes at the Dirac point was observed in dI/dV spectra. In particular, a single sequence of pronounced Landau level peaks was observed in dI/dV spectra recorded in a magnetic field, as shown in Figure 5(a). The relationship between the energies of the Landau levels and the magnitude of the magnetic field follows the following equation that is unique to massless Dirac fermions, as shown in Figure 5(b).

$$E_n = E_D + \text{sgn}(n) \sqrt{2e\hbar v_F^2 |n| B} \quad n = 0, \pm 1, \pm 2, \dots$$

All these observations showed that graphene flakes interact very weakly with the graphite substrate. The only observed graphite-induced perturbation to graphene was a shift of the Dirac point to 16.6 meV above the Fermi energy, resulting from a *p*-type doping by the graphite substrate. More details about measuring the electronic properties of pristine graphene on graphite can be found in the review article by Andrei *et al* [61].

Intervalley scattering patterns have been observed surrounding the point defects on the graphite surface in STM measurements [76–79]. The point defects include isolated adsorbates [76, 78] and vacancies [77–79]. As the surface layers of graphite are well decoupled from the bulk, some electronic properties of isolated graphene are observable on the graphite surface, such as the unique behavior of Landau levels related to massless Dirac fermions and the intervalley scattering patterns. Atomic vacancies can modify the electronic properties of graphene and thus the surface of graphite. Ugeda *et al.* measured the local density of states of the single vacancy on the graphite surface, and found a sharp resonance at the Fermi energy E_F [79], as shown in Figure 6, which was attributed to the formation of a local magnetic moment induced by the single vacancy in graphene. The vacancy-induced local magnetic moment reduces the charge carriers' mobility and at the same time has the potential to induce macroscopic magnetism in graphene.

4 Graphene on metals

The interfaces between the graphene layer and metal electrodes play a critical role in the operation of graphene devices. Therefore, it is of practical importance to investigate the perturbation to the electronic properties of graphene by metal contacts for future graphene device applications. In addition, CVD growth of graphene on metals is currently a major approach to synthesizing large scale high quality graphene. In particular, graphene grown on metals like Cu can be transferred onto other substrates, which provides great convenience for fabricating various graphene devices. The growth behavior of graphene on metals is also closely related to the interactions between the graphene overlayer and the underlying metal substrates.

STM have been widely used to probe the atomic scale interface properties of graphene on different metal substrates including Ir(111) [33], Ru(0001) [23, 80, 81], Ni(111) [80], Co(0001) [82], Pt(111) [32, 34, 39, 80], Cu [26, 38, 83–87], Ag(111) [36], Au(111) [38], etc. The dI/dV spectra recorded by STM reflect the density of states, and thus

Fig. 5. (a) Field dependent dI/dV spectra of graphene flakes on graphite at 4.4 K. (b) The measured square root dependence of Landau level energy on level index and magnetic field. (Reprinted from Reference [75]).

are capable of measuring the energy location and shift of the Dirac point of graphene. It is a usual practice to compare dI/dV spectra with ARPES measurements and/or density functional theory (DFT) calculations in order to identify the Dirac point in dI/dV spectra. Besides probing the density of states and the Dirac point by dI/dV spectra, STM measurements can provide much more atomic-scale information about the interaction between the graphene layer and the underlying substrates.

Based on the strength of the interaction between the graphene layer and the underlying metal substrate, the metal surfaces can be classified into two categories, i.e. weakly interacting surfaces and strongly interacting surfaces. For metal surfaces that interact weakly with the graphene layer, the substrate-induced perturbation to graphene is weak and the characteristic linear energy-momentum dispersion relation of graphene is preserved. The metals falling in this category include Al, Cu, Ag, Au, Pt and Ir [88–92]. In contrast, for metal surfaces that interact strongly with the graphene layer, the characteristic linear π -bands near the Fermi level of graphene is disrupted by the strong substrate-induced perturbation. Co, Pd, Ni, Rh, Ti and Ru belong to this category [81, 88, 90, 92–94]. Although our discussions in this section are for graphene on metal surfaces, the phenomena arising from substrate-induced perturbations also exist in graphene on other substrates, such as SiC, SiO₂ and BN, which will be discussed in the subsequent sections.

4.1 Weakly Interacting Graphene/Metal Systems

In weakly interacting graphene/metal systems, although the substrate-induced perturbation to graphene is weak, graphene can be doped by metal substrates via charge transfer. As a consequence of doping, the Dirac point of graphene shifts with respect to the Fermi level E_F , which can be reflected on the energy-momentum dispersion relation as well as on the density of states of graphene, as shown in Figure 2(a) and 2(b), respectively. For intrinsic graphene, the Dirac point is at the Fermi level. If the graphene layer is n -doped, the Dirac point shifts downward with respect to the Fermi level; and if it is p -doped, the Dirac point shifts upward with respect to the Fermi level. Therefore, the shift of Dirac point is a measure of doping level in graphene as well as of the strength of substrate-induced perturbation to graphene.

The weakness of the interaction between graphene and Cu has been reflected in the following observations in STM measurements. First, multiple moiré patterns were observed for graphene on the Cu surfaces including Cu(111), Cu(100), and Cu foil, which reveals the existence of multiple different orientations of the graphene lattice with respect to the underlying Cu lattice [26, 38, 83, 84]. Second, the strain at the graphene-Cu interface leads to the formation of partial dislocations and surface reconstruction patterns on the Cu foil surface after an annealing treatment of a graphene on Cu foil sample; meanwhile the graphene layer remains intact and no apparent distortions, defects, electronic scattering or moiré patterns were observed in the graphene layer, as shown in Fig-

Fig. 6. (a) STM image of the graphite surface after the Ar^+ ion irradiation measured at 6 K. Size: $17 \times 17 \text{ nm}^2$. (b) dI/dV spectra measured on pristine graphite (black) and dI/dV spectra measured on top of the single vacancy (red) measured at 6 K. The latter exhibits a sharp resonance at the Fermi energy E_F . (Reprinted from Reference [79]).

Fig. 7. (a) STM image of graphene on Cu foil showing the Cu surface reconstruction pattern and the intact graphene overlayer lattice. Scale bar: 5 nm. (Reprinted from Reference [85]) (b) STM image of graphene on Cu(111) at 40 K showing the $(\sqrt{3} \times \sqrt{3}) R30^\circ$ pattern surrounding a point defect, arising from the intervalley scattering in the graphene layer. The unit cell of the scattering pattern is outlined in black. (Reprinted from Reference [38]) (c) STM image of graphene on Cu(111) showing the standing wave patterns on the Cu(111) surface beneath the graphene layer at 40 K. (Reprinted from Reference [38]).

figure 7(a) [85]. The absence of moiré pattern on this sample was attributed to an even weaker graphene-Cu interaction compared to other graphene/Cu samples showing moiré patterns [85]. Third, the intervalley scattering was observed surrounding a point defect in the graphene layer on Cu(111) [38], as shown in Figure 7(b), and at the arm-chair edge of a graphene grain on Cu foil [86]. The intervalley scattering is expected for well-decoupled graphene layers, such as epitaxial graphene on SiC(0001) [7, 95, 96] or HOPG surfaces [76–79]. Fourth, the standing wave patterns related to the Cu(111) substrate were observed through the graphene overlayer, as shown in Figure 7(c); while the defects in the Cu(111) substrate were not found to cause the intervalley scattering in the graphene overlayer [38].

As a consequence of the weak graphene-Cu interaction, although the characteristic linear π -bands struc-

ture near the Fermi energy is preserved, the graphene layer is doped by the Cu substrate via charge transfer, which was verified by dI/dV spectra, ARPES and DFT calculations. The dI/dV spectra measured on a graphene/Cu(111) sample surface revealed that the electronic states on the underlying Cu(111) surface extend above the graphene overlayer [26], as shown in Figure 8. This phenomenon was also revealed by the observation of the standing wave patterns, which corresponds to the scattering of the surface state electrons of the underlying Cu(111) substrate, through the graphene overlayer in STM measurements [38]. A local conductance minimum at around 0.35 eV below the Fermi level E_F is also exhibited in the dI/dV spectra of graphene overlayer on Cu(111), as shown in Figure 8, which arises from the electronic states of the graphene over-

layer [26]. The correlation between this observed local conductance minimum and the Dirac point was carefully discussed [26]. ARPES measurements revealed a Dirac point at around -0.3 eV for both graphene/Cu(111) and graphene/Cu(100) [97]. STM measurements of the standing wave patterns on graphene/Cu(111) by Martínez-Galera *et al.* revealed a downward shift of the Dirac point [38]. Sławińska and Zasada performed first-principles calculations of graphene/Cu(111), obtained a Dirac point at -0.427 eV and suggested that the observed local conductance minimum at around -0.35 eV in dI/dV spectra is indeed the fingerprint of the Dirac point [98]. The dI/dV spectra of graphene on Cu foil recorded by Tian *et al.* revealed that on their sample the electronic states of the Cu surface are efficiently screened by the graphene overlayer, which was attributed to an even weaker graphene/Cu interaction on this sample compared to that on other graphene/Cu samples [85]. Based on these STM, ARPES and DFT studies, the graphene layer is *n*-doped by the Cu substrates and consequently the Dirac point shifts downward with respect to E_F .

Strong electronic scattering was observed at the boundaries between different graphene domains on the Cu(111) surface in STM measurements [26], which most likely contributes to the decrease of carrier mobility for graphene, with numerous domain boundaries, grown on Cu compared to exfoliated graphene [31]. Indeed, graphene with larger domains exhibited higher carrier mobilities, as evidenced by electrical transport measurements [99, 100]. It is encouraging that significant progress has been made towards growing graphene with large single crystal domains [99–102].

Graphene interacts weakly with Pt, which has been evidenced by the existence of multiple moiré patterns, resulting from multiple graphene domains with different orientations relative to the underlying Pt substrate [34, 80, 90, 103–105]. DFT calculations and ARPES measurements of graphene/Pt(111) indicated a Dirac point at 0.30 eV above E_F , indicating *p*-type doping of graphene by the underlying Pt substrate [103, 106]. Regarding STS measurements, different dI/dV spectra have been obtained for graphene on Pt(111) [107, 108].

Levy *et al.* reported that dI/dV spectra measured on the flat graphene patches on Pt(111) exhibited no clear signatures of the graphene Dirac point, as shown in Figure 9(b); while dI/dV spectra measured at the boundary between the flat graphene and the nanobubbles exhibit features of Dirac point consistent with ARPES measurements, as well as a gap-like feature centered at E_F that was attributed to the phonon-mediated inelastic electronic tunneling process [107]. In particular, Landau level

quantization was observed in a sequence of dI/dV spectra measured in a line across a graphene nanobubble on Pt(111), as shown in Figure 9(c), which arises from giant strain-induced pseudo-magnetic fields in excess of 300 Tesla in highly strained graphene nanobubbles formed on Pt(111) [107]. Similar phenomena were recently reported by Yan *et al.* who observed the Landau level quantization of the strained graphene bilayer in a large pseudo-magnetic field of ~ 100 Tesla [109].

The dI/dV spectra of monolayer graphene on Pt(111), recorded by Ugeda *et al.*, exhibited a clear dip at around 300 meV above the Fermi energy accompanied by a “V” shaped rise at both sides, as shown by the red curve in Figure 10(b) [108]. This dip has an energy that coincides with the Dirac point energy determined by DFT calculations [106] and ARPES measurements [103], and thus was attributed to the Dirac point of graphene/Pt(111) [108]. Single carbon vacancies in a monolayer graphene on Pt(111) were generated by Ar^+ irradiation, and subsequent STS measurements in Figure 10(b) showed that the electronic properties of carbon vacancies in graphene/Pt(111) are quite different from the ones found for carbon vacancies in a well-decoupled graphene layer [79, 108]. The electron scattering surrounding the point defects in graphene on Pt(111) is nontrivial and the $(\sqrt{3} \times \sqrt{3}) R30^\circ$ pattern, which is expected for well-decoupled graphene layers due to intervalley scattering, was not obvious in STM images but can be measured through 2D Fourier transform [108]. Although graphene/Pt(111) is a weakly coupled system, the presence of vacancies was found to increase the coupling between the graphene layer and Pt(111), which gives rise to a rapid decay of the localized state and the quenching of the magnetic moment associated with carbon vacancies in freestanding graphene layers [108].

Multiple moiré patterns have been observed in STM and LEED measurements of graphene on Ir(111) [110, 111]. ARPES measurements of graphene on Ir(111) clearly display a Dirac cone with the Dirac point shifted to 0.10 eV above E_F [89]. However, the features of Dirac point were not observed in dI/dV spectra recorded on graphene on Ir(111) [112, 113]. Decker *et al.* investigated the structural and magnetic properties of cobalt-intercalated graphene on Ir(111) by using spin-polarized STM [114]. They observed a site-dependent variation of the local effective spin polarization, as shown in Figure 11, which was attributed to a site-dependent magnetization of the graphene [114].

The weak graphene-Au interaction has been revealed by several observations in STM and STS measurements. First, multiple moiré patterns were observed for graphene on the Au(111) surface [38]. Second, the intervalley scattering was observed surrounding a point defect in the

Fig. 8. STS measurements of a graphene/Cu(111) sample. (a) dI/dV point spectroscopy recorded on the graphene layer and that recorded on Cu(111). (b) Spatially resolved dI/dV spectra recorded along a straight line across two graphene-Cu boundaries on the sample surface. The spectra between the two arrows were recorded on Cu(111). The spectra below the yellow arrow and those above the blue arrow were recorded on the graphene layer. (Reprinted from Reference [26]).

Fig. 9. (a) STM image of graphene monolayer patch on Pt(111) with nanobubbles. Inset: Atomic-resolution STM image of a graphene nanobubble showing distorted honeycomb lattice. (b) dI/dV spectra of bare Pt(111), flat graphene on Pt(111), and the center of a graphene nanobubble. (c) Sequence of eight dI/dV spectra recorded in a line across a graphene nanobubble on Pt(111). (Reprinted from Reference [107]).

Fig. 10. STM and STS measurements of monolayer graphene on Pt(111) with point defects at 6 K. (a) Atomic resolution STM image of graphene on Pt(111) with carbon vacancies induced by 140 eV Ar^+ irradiation. (b) dI/dV spectra on a carbon vacancy (blue) and on pristine graphene/Pt(111) (red). (Reprinted from Reference [108]).

Fig. 11. (a) STM image of the graphene/Ir(111) surface with four cobalt-intercalated regions. The line profile was taken at the bottom of the scanned area showing the difference between the graphene/Ir(111) and the graphene/Co/Ir(111) moiré corrugations. (b) STM image of a cobalt-intercalated region. (c) Spin asymmetry map of the region shown in (b). (Reprinted from Reference [114]).

graphene layer on the Au(111) surface [38]. Third, the standing wave patterns related to the Au(111) substrate was observed through the graphene overlayer [38]; and the Fermi wavevector (k_F) derived from the standing wave patterns suggested that a significant change is not expected in the energy position of the Dirac point [38]. Fourth, dI/dV measurements indicate that the Dirac point of graphene on the Au(111) surface is located at $\sim E_F$ [38], which indicates that no appreciable doping of graphene exists for graphene/Au. DFT calculations show small shifts of the Dirac point for graphene on Au [88, 92, 115–117]. ARPES measurements show that an intercalated Au layer can electronically decouple graphene from the substrate for graphene on Ru(0001) [118], graphene on Ni(111) [119, 120], and graphene on SiC [121].

Recent STM and STS studies of graphene nanoribbons (GNRs) on Au(111) revealed interesting phenomena about the edge states and band gap of GNRs [122–125]. Tao *et al.* measured the edge states of GNRs that were produced by unzipping carbon nanotubes on a clean Au(111) surface [122]. Two edge-state peaks, the energies of which are below the phonon-assisted inelastic onset, have been observed in the dI/dV spectra of chiral GNRs recorded at 7 K [122], as shown in Figure 12(b). The measured amplitude of the edge-state peaks decays exponentially from the GNR edge to the interior of GNR [see Figure 12(c)], and oscillate along the GNR edge with a period corresponding to the periodicity of the chiral edge [122]. The measured energy gap of GNR edge states shows an inverse correlation with GNR width [122], which is qualitatively in agreement

Fig. 12. (a) Atomic resolution STM image of the terminal edge of a GNR. (b) dI/dV spectra of the GNR edge measured at different points along the black line in (a). (c) The amplitude of edge-state peaks at the points where the spectra in (b) were measured. (Reprinted from Reference [122]).

with a prior investigation of electron transport in lithographically patterned GNR structures [17]. Their further theoretical calculations show that the observed energy-split peaks in dI/dV spectra arise from lifting the degeneracy of the edge states by the electron-electron interactions that lead to the formation of spin-polarized edge states and opening up a gap at $E = 0$ in pristine GNRs [122]. Due to the existence of a curvature, the terminal edge of the GNR is little affected by the underlying Au substrate and manifests its intrinsic electronic properties including edge states and phonon-assisted inelastic electron tunneling [122]. In contrast, the feature related to phonon-assisted inelastic electron tunneling disappears in the flat interior of the GNR due to increased electron tunneling to the Au substrate [122].

GNRs on Au(111) have also been fabricated by surface-assisted coupling of molecular precursors and subsequent cyclodehydrogenation [123–126], and characterized by STM and STS measurements [123–125]. Among these studies, the localized electronic states related to the localized zigzag edges were observed in dI/dV spectra measured near the ends of armchair GNRs (AGNRs) [123, 125]. The measured band gaps of the 7-AGNR and 13-AGNR on Au(111) are 2.3 eV and 1.4 eV, respectively, which are smaller than the predicted 3.7 eV for a free-standing 7-AGNR and 2.4 eV for a free-standing 13-AGNR, which has been ascribed to screening by the Au substrate [124, 125]. The measured width dependence of the band gap of GNRs

is in agreement with theoretical predictions [127–129]. Ruffieux *et al.* pointed out that the interaction of GNRs with the Au substrate is weak based on the small hybridization of the electronic bands of GNRs and Au(111), the absence of charge transfer and the unperturbed valence band as measured by ARPES [124]. In addition, the weak GNRs-Au interaction was also suggested as the origin of the asymmetry of the measured band gap with respect to the Fermi level E_F of Au(111) [124]. Koch *et al.* measured the conductance through a single GNR by pulling the GNR off the Au(111) surface. The observed voltage-dependence of conductance was found to be closely related to the atomic scale structure and electronic states of the GNR [123]. One interesting observation in all these STS measurements is that the measured LDOS of the conduction and valence band edge states are strongly localized at the edges of GNRs, which has not been well understood yet [123–125].

The weak interaction between graphene and Ag has recently been revealed by STM and STS measurements [36, 130]. First, the dI/dV spectra recorded on large scale graphene layer on Ag(111) are significantly different from those recorded on the bare Ag(111) surface [36], as shown in Figure 13(a). Second, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern induced by intervalley electron scattering was observed at the armchair edges of large scale graphene overlayer on Ag(111) [36], as shown in Figure 13(b), as well as of AGNRs on Ag(111) [130]. Huang *et al.* measured spatially resolved dI/dV spectra of AGNRs on Ag(111), and observed

Fig. 13. (a) dI/dV spectra of the graphene layer on Ag(111) (blue) and dI/dV spectra of the bare Ag(111) (red). (b) Atomic resolution STM image showing the electron scattering pattern near an armchair edge of graphene on Ag(111). (Reprinted from Reference [36]).

an energy shift of the electronic bands of AGNRs, which has been attributed to the charge transfer between AGNRs and Ag(111) [130]. ARPES results of graphene on Ag are not available yet, but would be important complementary data to the reported STM/STS results for determining the electronic band structure of graphene on Ag.

4.2 Strongly Interacting Graphene/Metal Systems

In strongly interacting graphene/metal systems, the characteristic linear π -bands near the Fermi level is strongly modified by the substrate-induced perturbation, as a result of which the Dirac point is not preserved in these systems.

For single layer graphene on Ru(0001), a strong perturbation to the electronic structure of graphene by its underlying Ru substrate was observed [23–25, 81, 131]. STM measurements revealed that the strong substrate-induced perturbation leads to a spatial redistribution of density of states of graphene near E_F and a broken AB sublattice symmetry [23, 25, 81]. ARPES measurements indicated that the graphene π -bands near E_F are completely disrupted due to the strong substrate-induced perturbation [131]. The dI/dV spectra measured for single layer graphene on Ru(0001) by Sutter *et al.* show an electronic state at around 0.2 eV below E_F , which was also observed in ARPES measurements, and pronounced modulations of local density of states near E_F [81]. Similar dI/dV spectroscopy has also been obtained by Pan *et al.* [23] Marchini *et al.* observed two states at -0.4 eV and $+0.2$ eV in their dI/dV spec-

troscopy and interpreted them as the edges of a gap resulting from the bond formation to the Ru substrate [25].

The strong perturbation to single layer graphene by the underlying Ru(0001) substrate, can be significantly reduced by intercalating a silicon layer between graphene and Ru(0001), which was supported by the following experimental observations [132]. First, the graphene π -bands were observed on graphene/Si/Ru(0001) in ARPES measurements with a Dirac point at 0.26 eV below the Fermi energy. Second, The dI/dV spectroscopy [see Figure 14(c)] measured for graphene/Si/Ru(0001) shows a local conductance minimum at -0.26 eV, whose energy location is the same as that of the Dirac point as measured by ARPES, and a gap-like feature around E_F , which has been attributed to the photon-mediated inelastic electronic tunneling. Third, the intervalley scattering patterns [see Figure 14(b)] were observed surrounding the point defects on graphene/Si/Ru(0001), which reflects that the graphene layer is well-decoupled. In addition, the intercalation of Si represents a promising approach to integrating graphene with Si, which remains the most important material in current semiconductor industry, as well as to *in situ* preparing a structure for electrical gating of graphene with a Si dielectric layer.

Although the single layer graphene is strongly coupled to the underlying Ru(0001) substrate, it acts as an active buffer layer for subsequent graphene layers. The graphene π -bands were observed for bilayer and trilayer graphene on Ru(0001) in ARPES measurements [131]. All graphene layers beyond the first layer interact weakly with the Ru(0001) substrate, and consequently the characteristic linear Dirac-like dispersion of isolated graphene is pre-

Fig. 14. (a) STM image showing the Si intercalation between graphene and Ru(0001). Size: 25 nm $\times$ 25 nm. (b) STM image of Graphene/Si/Ru(0001) showing the electron scattering patterns surrounding the point defects. Size: 10 nm $\times$ 10 nm. (c) dI/dV spectra of Graphene/Si/Ru(0001) showing a local conductance minimum at -260 mV and a gap-like feature around the Fermi energy. (Reprinted from Reference [132]).

served. The residual doping due to the charge transfer from the Ru substrate leads to a shift of the Dirac point from E_F to -0.50 eV for bilayer graphene and -0.30 eV for trilayer graphene, respectively [131]. The dI/dV spectroscopy measured for bilayer graphene shows a local conductance minimum at around -500 meV [81], as shown in Figure 15(c), which has been associated with the Dirac point at -0.50 eV as measured by ARPES [131], and a gap-like feature around E_F , which was attributed to the phonon-mediated inelastic electronic tunneling [56, 81]. The width of this gap, ~ 125 meV, is significantly wider than that observed in the dI/dV spectra measured for graphene on SiO_2 , 67 meV [56], which was rationalized by considering that the inelastic electronic tunneling process is assisted by the in-plane K_2 phonon instead of the out-of-plane K_6 phonon [81]. In addition to that, in contrast to the broken AB sublattice symmetry observed for the first layer graphene on Ru(0001) [see Figure 15(a)] due to strong substrate-induced perturbation, a symmetric honeycomb lattice was observed in STM images of bilayer graphene on Ru(0001) [see Figure 15(b)], indicating that the second graphene layer is well decoupled from the Ru substrate and recovers the properties of freestanding monolayer graphene [81]. It is worth noting that the function of single layer graphene as a buffer layer has been utilized to study the intrinsic properties of molecules in STM measurements [133, 134].

Graphene/Ni(111) and Graphene/Co(0001) interfaces are of particular interest. First, there is a small lattice mismatch ($<2\%$) between graphene and the two surfaces, which enables the growth of graphene without moiré patterns. Second, Ni and Co are ferromagnetic metals that are commonly used in spintronics. No moiré pattern was observed for graphene on Ni(111) and only one set of lattice was observed in LEED measurements, which indicate that carbon atoms in the graphene layer bond strongly one-to-one with the underlying Ni surface atoms [80]. Murata

et al. observed hexagonal and striped moiré patterns on the (111) and (110) facets of Ni islands, respectively; and their STS measurements indicate that the graphene layers are metallic on both Ni(111) and Ni(110) facets, which are attributed to a strong hybridization between the d -bands on Ni and the π -bands of carbon [135]. The linear π -band dispersion for graphene on Ni(111) can be restored by the intercalation of alkali metal [94] or Au [119] between the graphene layer and the underlying Ni(111) substrate. The dI/dV spectra recorded for graphene on Co(0001) show three primary features at -0.37 eV, $+0.25$ eV, and $+0.64$ eV, which arises from the strong electronic coupling between the graphene π -states and Co d -states at the interface [82].

As discussed above, the interaction between graphene and metals can be evaluated from many phenomena, such as moiré patterns, standing wave patterns, intervalley scattering, Dirac point, etc., which can be precisely detected by STM and STS measurements. The perturbations to graphene induced by metal contacts are critical in designing and fabricating future graphene devices. Atomic scale investigations by STM and STS, complemented with ARPES measurements and DFT calculations, are playing a critical role in detecting and tuning the perturbations to graphene by metal substrates.

5 Graphene on silicon carbide

Epitaxial growth of graphene by thermal decomposition of the SiC surface has been proposed as a potential route to graphene-based electronics because of its compatibility with mainstream planar processing [6, 10, 21, 22, 136]. In addition, wafer-size homogeneous layers of graphene have been obtained by annealing SiC in a dense noble gas environment at atmospheric pressure [137]. For epitaxial

Fig. 15. (a) Atomic-resolution STM image of single layer epitaxial graphene on Ru(0001). (b) Atomic-resolution STM image of bilayer epitaxial graphene on Ru(0001). (c) dI/dV spectra of single layer graphene (red) and bilayer graphene (blue) on Ru(0001). (Reprinted from Reference [81]).

graphene on SiC(0001), studies have reported the ability to tune the electronic structure of bilayer graphene via reversible adsorption and desorption of hydrogen [15, 138], and on decoupling graphene from the substrate via oxidation [139].

Many efforts have been taken to unveil the interfacial structure of epitaxial graphene on SiC(0001) with the focus on the geometric structure of the $(6\sqrt{3} \times 6\sqrt{3})R^\circ$ reconstruction. This $6\sqrt{3}$ reconstruction on SiC(0001) was first studied by van Bommel *et al.* in 1975 [140], and has been interpreted with different models [141–149].

The observed triangular lattice in STM images of bilayer and multilayer graphene is consistent with the Bernal (AB) stacking of the individual graphene layers and resolving only one sub-lattice for the given scanning bias [150]. Lauffer *et al.* observed both AB stacking and AA' stacking for bilayer graphene, Bernal stacking (ABA...) and rhombohedral (ABC...) stacking for trilayer and multilayer graphene [151]. The coexistence of Bernal-type stackings, ABAB and ABAC, and rhombohedral-type stackings, ABCA and ABCB, has been observed in ARPES measurements [152].

The dI/dV spectra of graphene on SiC show a local minimum or a gap-like feature around E_F [7, 151, 153]. The dI/dV spectra recorded by Brar *et al.* show a gap-like feature with a width of ~ 100 meV around E_F for both monolayer and bilayer graphene [153]. Three possible explanations for the gap-like feature were proposed initially [153] and one of them, the opening of new electron tunneling channels due to inelastic electronic coupling to surface excitations, was found to be the mechanism in later studies [56, 154]. Lauffer *et al.* measured the dI/dV spectra of few layer graphene with different thicknesses on SiC, as shown in Figure 16, and observed local conductance minima at -0.31 eV for bilayer graphene, -0.19 eV for trilayer graphene, and -0.13 eV for quadlayer graphene, respec-

tively, which are in agreement with the position of the Dirac point as observed by ARPES [22, 152, 155, 156].

Fig. 16. dI/dV spectra of few layer graphene with different thickness on SiC(0001). (Reprinted from Reference [151]).

Landau levels were observed for multilayer graphene (10 ± 1 layers) on SiC by STS measurements [157]. The measured Landau level energies scale as $\sqrt{B}$, which is an indication of massless Dirac fermions in graphene, as shown in Figure 17 [157]. The topmost layer of epitaxial graphene on SiC performs as an isolated sheet of graphene, which was attributed to the presence of rotational stacking faults between the graphene layers that can effectively decouple the electronic structure of the layers [158].

Electron scattering patterns were observed in STM measurements for graphene on SiC, including near the armchair-oriented edges of graphene [7, 95, 96, 159]. Similar scattering patterns have also been observed in STM measurements near the armchair graphene edges on Cu foil by Tian *et al.* [86], near the grain boundaries of graphene on SiO₂ by Koepke *et al.* [160], and for graphene armchair edges on Ag(111) by Kiraly *et al.* [36]

6 Graphene on silicon dioxide and boron nitride

Silicon dioxide (SiO₂) and boron nitride (BN) are currently commonly used dielectric substrates for graphene in view of the convenience for investigating intrinsic properties of graphene as well as for fabricating back-gated graphene devices. Recent STM and STS studies of graphene on SiO₂ were discussed by Andrei *et al.* [61] and by Morgenstern [62] in their respective review articles. Here we focus on the commons and differences in the electronic properties of graphene on two different insulating substrates, SiO₂ and on BN, based on recent STM and STS measurements.

High resolution STM images have been achieved for graphene on SiO₂ [56, 161–165] as well as on BN [57, 165]. The measured root-mean-square (RMS) surface roughness of graphene/SiO₂ is 1.5 – 5.0 Å (~1.5 Å, 60 nm × 60 nm [56]; ~1.5 Å, 30 nm × 30 nm [58]; ~1.9 Å, 250 nm × 200 nm [161]; ~5.0 Å, 10 nm × 10 nm [162]; ~3.5 Å, 195 nm × 178 nm [164]; ~2.2 Å, 100 nm × 100 nm [165]). In contrast, the RMS surface roughness of graphene/BN is 0.02–0.30 Å (0.02–0.17 Å, 20 nm × 20 nm [57]; ~0.30 Å, 100 nm × 100 nm [165]). The graphene layer primarily conforms to its underlying substrate surface [164], and the atomically flat BN surface is much smoother than the amorphous SiO₂ surface, which leads to the observed significant reduction in RMS surface roughness of graphene/BN compared to graphene/SiO₂. Ishigami *et al.* observed the coexistence of both triangular and hexagonal honeycomb lattices in atomic resolution STM images of single-layer graphene on SiO₂, which has been attributed to strong spatially dependent substrate-induced perturbations to graphene electronic states [161]. Stolyarova *et al.* observed the hexagonal honeycomb lattice for single-layer graphene on SiO₂ and the triangular lattice, arising from the three-fold symmetry due to Bernal (AB) stacking, for multi-layer graphene on SiO₂ [162]; and no prominent signs of substrate-induced perturbations to graphene were observed in their STM measurements [162]. Zhang *et al.* and Luican *et al.* also observed the hexagonal

honeycomb lattice for single-layer graphene on SiO₂ [56, 58, 163]. The hexagonal honeycomb lattice was observed for graphene on BN in STM measurements [57, 165].

STM and STS measurements of graphene/SiO₂ and graphene/BN have revealed interesting electronic properties of graphene including phonon-mediated inelastic electron tunneling [56, 57], charge puddles [57, 58], charge carrier dependence of Landau levels [163], and localization resonances in high magnetic fields [72].

The dI/dV spectra of graphene on SiO₂ recorded by Zhang *et al.* showed a prominent gap-like feature that is pinned to the Fermi level (E_F) while changing the electron density in graphene, which has been attributed to a suppression of electronic tunneling to graphene states near E_F and a simultaneous giant enhancement of electronic tunneling at higher energies due to a phonon-mediated inelastic tunneling to the graphene Dirac point, as shown in Figure 18 [56]. Such gap-like features have also been observed earlier in the dI/dV spectra recorded on both monolayer and bilayer graphene on SiC [153], and later in the dI/dV spectra recorded on graphene on BN [57], near the edge of graphene nanoribbons (GNRs) on a clean Au(111) surface [122], on bilayer graphene on Ru(0001) [81], and on graphene/Si/Ru(0001) [132]. It is worthy to mention that the STM tip calibration was found to be very important for obtaining the gap-like features in the recorded dI/dV spectra of graphene [56]. Theoretical studies by Wehling *et al.* corroborated the explanation that such gap-like features in the dI/dV spectra of graphene are induced by the phonon-mediated tunneling [154].

Charge carrier density plays a key role in the operation of many devices. Investigating the phenomena related to charge carrier density is of paramount importance for future graphene device applications [166, 167]. Atomic scale STS measurements show that the graphene Dirac point (E_D) shifts energetically with respect to E_F while changing the charge carrier density in graphene by a back gate [56, 57]. Charge carrier density inhomogeneities affect Dirac fermion behavior and thus the performance of future graphene devices. The spatial charge carrier density inhomogeneities in graphene have been obtained for graphene/BN [57] and graphene/SiO₂ [58] by measuring the Dirac-point map, $E_D(x, y)$ and converting it into a charge-density map, $n(x, y)$, through the relation $n(x, y) = E_D^2(x, y) / \pi (\hbar v_F)^2$, where v_F is the Fermi velocity in graphene. The measured charge density roughness is $8.2 \times 10^{10} e \text{ cm}^{-2} \text{ rms}$ in the graphene/SiO₂ charge density map [58] and $2.3 \times 10^{10} e \text{ cm}^{-2} \text{ rms}$ in the graphene/BN charge density map [57], respectively. These measurements reveal that charge density fluctuations in graphene/BN are significantly reduced com-

Fig. 17. (a) Field dependent dI/dV spectra of multilayer graphene on SiC showing Landau levels. (b) Landau level energies versus square root of Landau level index n and magnetic field B . (Reprinted from Reference [157]).

Fig. 18. (a) Atomic resolution STM image of a graphene flake on SiO_2 . (b) dI/dV spectra of graphene on SiO_2 for different gate voltages. (c) Mechanism for the phonon-assisted inelastic tunneling process. (Reprinted from Reference [56]).

pared to the scenario in graphene/ SiO_2 , as shown in Figure 19. The charge density fluctuations are induced by charged impurities above and below the graphene layer, leading to a reduction in carrier mobility [59]. Therefore,

the measured charge density maps [57, 58] provide an atomic-scale interpretation for the significant enhancement of carrier mobility in graphene/BN compared to that in graphene/SiO₂ [58–60], which exemplifies the importance of atomic scale investigations to the studies of macroscopic-scale properties of materials.

The carrier mobilities in graphene/SiO₂ are limited by its roughness [161], the presence of trapped charges [168] and SiO₂ surface phonons [169]. The atomic scale measurements of charge carrier density in graphene suggest that BN is an ideal substrate for investigating the intrinsic properties of graphene and also for future graphene device applications. Xue *et al.* also observed the significantly reduced charge inhomogeneities in graphene/BN by STM/STS [165]. Due to the improved electronic quality of graphene on BN, the fractional quantum Hall effect [170], unconventional quantum Hall effect in tri-layer graphene [171] and ballistic transport at room temperature [172] have been observed in BN-supported graphene devices. The carrier mobilities in graphene/BN reach $140,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ near the charge neutrality point [60], $125,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature and $275,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 4.2 K [173].

The Landau level quantization was observed for graphene on SiO₂ in STM and STS measurements in a magnetic field [72, 163]. Compared to graphene on conductive substrates, graphene on insulating SiO₂ is convenient for controlling the charge carrier density in graphene with a back gate, and thus the dependence of Landau quantization on the charge carrier density can be measured. Abrupt jumps of the Fermi level into different Landau levels, arising from the filling of Landau levels by gating, were observed in gate-dependent dI/dV spectra measurements of graphene on chlorinated SiO₂ [163] and graphene on SiO₂ [72], as shown in Figures 20(a) and 20(b), respectively. Luican *et al.* made a detailed discussion on the dependence of Landau level quantization on the charge carrier density [163]. Jung *et al.* observed a quartet of charging peaks in dI/dV spectra taken in high magnetic field, as shown in Figure 20(b) [72]. The four-fold peaks were identified as single-electron charging phenomena arising from Coulomb blockade effects in a graphene quantum dot on the SiO₂ surface, which is a consequence of substrate-induced disorder. These localization resonances were not observed in graphene on chlorinated SiO₂, as shown in Figure 20(a), the most likely reason for which is the reduction of substrate-induced disorder by chlorination of the SiO₂ surface. More details about graphene on chlorinated SiO₂ can be found in the review article by Andrei *et al.* [61]. As BN has recently proved an ideal substrate for graphene [60], it will be very interesting to characterize the

Landau level quantization of graphene on BN by STM and STS measurements.

7 Outlook

As reviewed above, the electronic properties of graphene can be explored with STM and STS on the atomic scale through the measurements of moiré patterns, stacking orders, defects, electron scattering patterns, Dirac points, Landau levels, charge carrier density dependent properties, etc. with high spatial resolution. In addition to the above mentioned research activities, STM and STS have also been used to investigate other properties of graphene including, for instance, growth process, functionalization, magnetic and optical properties. Since its invention in 1981, STM-related techniques have been experiencing a rapid development in virtue of integrating other techniques with STM. Nowadays STM measurements can be performed at variable temperatures, down below 50 mK and up above 1000 K, and with a variable external magnetic field up above 10 Tesla. Integrating optical techniques with STM allows the investigation of light-matter interaction on the atomic scale. The continuing expansion of STM capabilities, such as spin-polarized STM [174, 175], allows clarifying some scientific problems that cannot be resolved by using other experimental techniques [176]. Therefore, STM and STS studies of graphene are expected to continue playing an important and irreplaceable role in advancing our knowledge of this fascinating two-dimensional material.

The interaction of graphene with its various environments is the basis of the fabrication and application of this wonder material, which means that suspended graphene and graphene on various substrates have their respective advantages and applications. For example, the graphene/metal interfaces are generally important for the electrode contacts of graphene-based devices; graphene on Cu has an advantage in growing transferable centimeter-scale single crystal graphene domains [100]; the moiré patterns of graphene on Ir(111) and on Ru(0001) are excellent templates for growing monodisperse transition metal clusters for catalytic applications [177–180]; and atomically precise GNRs can be grown on Au(111) and Ag(111) surfaces with surface-assisted coupling of molecular precursors and subsequent cyclodehydrogenation [123, 125, 126, 130]. Therefore, the interaction of graphene with its surroundings remains a practically important topic in future STM and STS investigations.

Fig. 19. Charge density maps measured on (a) graphene/BN and (b) graphene/SiO₂. The minima and maxima marked in the color scale bar are the minima and maxima of the respective images. (Reprinted from Reference [57]).

Fig. 20. (a) dI/dV gate map of graphene on chlorinated SiO₂ in a magnetic field of 12 T. (Reprinted from Reference [163]). (b) dI/dV gate map of graphene on SiO₂ in a magnetic field of 8 T. (Reprinted from Reference [72]). In both maps, each vertical line corresponds to the dI/dV spectra taken at a particular gate voltage.

As mentioned above, further experimental investigations are required in order to fully understand the electronic properties of GNRs supported on various surfaces. In particular, future STM and STS measurements of GNRs on BN are expected to reveal the intrinsic electronic properties of GNRs. In addition, the magnetism induced by spin-polarized edge states of graphene remains a rich area for future research. Theoretical calculations predict that the spin-polarized edge states at different edges correlate with each other, leading to opposite spin-polarization at the two edges of GNR [181], alternating spin-polarization for the edges of hexagonal graphene islands [182], and the same spin-polarization for the edges of triangular graphene islands [181, 182]. The magnetic and spin-related

phenomena at the graphene edges can potentially be detected by spin-polarized STM techniques, which have allowed the direct observation of spin structures with atomic resolution [174–176].

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