Superlattice effects in Graphene on SiC(0001) and Ir(111) probed by ARPES

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Abstract

We review the angle-resolved photoemission spectroscopy (ARPES) technique and its applications to epitaxially grown graphenes. In particular we discuss the extraction of symmetry-breaking factors associated with superlattice formation due to substrate lattice mismatch. For UHV grown graphene on SiC, which has a quasi-13×13 superlattice (with respect to graphene), no coupling vectors exist to break the chiral symmetry, and a gap at E_D is not observed. For graphene on Ir(111), lattice mismatch induces a well-known Moiré pattern with 10×10 (relative to graphene) symmetry. Despite the fact that chirality should be preserved under this symmetry, energy gaps are found at the main as well as the mini-Dirac crossings. A simple tight binding model that neglects chirality can explain the observed miniband spectrum in graphene on Ir (111).

Introduction

Graphene, a two dimensional layer of carbon atoms arranged in a honeycomb lattice, has been shown in recent years to display an incredible variety of predicted and actual properties [1,2]. Among these properties are zero mass carriers with very high conductivity, ambipolar doping that can be accomplished with ease, optical transparency, and the ability to manipulate its transport character (semimetal *vs.* insulating) by chemical doping. Graphene and its derivatives can be easily fabricated on substrates,

either on semiconductors such as SiC through vacuum annealing [3], or on metals such as copper [4] and nickel [5] by simple chemical vapor deposition or segregation techniques.

Graphene's properties follow from the peculiar band structure of graphene, in particular the linear dispersion of its carriers' energy with momentum [1]. The electronic structure of graphene is also strongly influenced by symmetry-breaking, either by the addition of point-defects which disrupt the symmetry of the lattice [6], or by laying the graphene upon a substrate whose lattice symmetry does not match that of graphene.

Technological development of graphene is often aimed at optimization of transport properties and so transport measurements are essential. There are several reasons why transport properties alone, though, are insufficient for determining the electronic structure. First, while the symmetry, defect energy levels, and band structure strongly influence the transport properties, it is not always unambiguous to work backwards from the transport measurements to learn details about these quantities.

Second, at a temperature T , transport properties are sensitive only to carriers whose energy is within a few times $k_B T$ of the Fermi energy E_F , where k_B is the Boltzmann constant. But, the dispersion and lifetimes of "hot" carriers outside of this energy range can be important as well, especially when studying many-body interactions. Such interactions renormalize the transport properties such as band velocity at E_F , but also manifest strongly for hot carriers. So direct information on these hot carriers is greatly desirable.

In order to augment transport measurements, therefore, we need a flexible tool sensitive to the symmetry, to the energy levels (and their momentum dispersion), and to carriers far away from the Fermi level E_F . Angle-resolved photoemission spectroscopy (ARPES) excels in these areas, and so ARPES has played a key role in the graphene literature.

In this article we will review the electronic structure of graphene, and discuss applications of the ARPES technique to its understanding how environmental factors affect the electronic properties of graphene. In particular, we focus on the effects of the superlattices that can be generated by lattice mismatch between graphene and a substrate.

Electronic Structure of Graphene

Figure 1 illustrates the lattice structure of graphene in real and reciprocal space. The real-space structure (Figure 1a) is characterized by two equivalent carbon atoms on a honeycomb lattice. Although these atoms are chemically indistinguishable (for the moment), we shall label them individually as “A” and “B”. The reciprocal space structure (Figure 1b) is characterized by a similar honeycomb lattice, rotated 90 degrees [7]. In Figure 1b, hexagons represent the conventional Brillouin zone, where the centers are labeled Γ , the corners labeled K and K' and the ellipsoids mark the M points along the Brillouin zone edge between K and K'.

Figure 1. Lattice structure of graphene. a) real-space view of the lattice; the circles represent the carbon atoms, of type A and B which are identical for ordinary graphene. The bond length dimension is given in Å. The center diamond is the real-space primitive cell. b) reciprocal-space view of the lattice; the circles represent reciprocal lattice points K and K'. Equivalent points Γ and M for center and edge of the Brillouin zone are indicated by filled circles and ellipsoids, resp. The diamond represents the primitive unit cell in reciprocal space, while the hexagons are the conventional Brillouin zone. Dimensions are given in inverse Å.

The electronic states can be calculated most simply by using the tight-binding method using Bloch wavefunctions. These wavefunctions are derived by populating each atomic site with a p_z -type orbital oriented perpendicular to the plane. This calculation was first performed by Wallace [7] and a modern explanation is given by Saito [8]. The latter give a closed-form solution to the graphene electronic states as

$$E_{\pm} = \pm t \sqrt{1 + \frac{3}{2} \cos^2\left(\frac{\sqrt{3}ka}{2}\right)} \quad (1)$$

where

$$t = \frac{3}{2} \cos\left(\frac{\sqrt{3}ka}{2}\right) + 4 \left(\cos\left(\frac{\sqrt{3}ka}{2}\right)\right)^2 \quad (2)$$

and a is the lattice constant $1.42\sqrt{3}$ Å, t is the hopping energy between carbon atoms, and s is the overlap integral between A and B atoms. A plot of this function is shown in Figure 2.

The electronic states are represented by two bands, which are labeled by convention π for the lower band and π^* for the upper band. For charge-neutral graphene, the lower band is exactly filled and the upper band completely unoccupied. Defining the Fermi energy E_F as the highest occupied energy level, we find for such a charge neutrality that E_F occurs at exactly where the two bands meet, which is precisely at the K and K' points at the corners of the Brillouin zone in Figure 1. We call the crossing point the *charge neutrality point*, and the energy of this crossing the Dirac energy E_D .

Along the zone boundary (away from K) we observe an energy gap between π and π^* states, whose extrema reach maximum values around ± 3 eV at the center of the zone boundary edge (M point, see Figure 1). Here the bandstructure has a saddle-point shape, which results in a large anomalous singularity in the density of states.

The lack of an energy gap at K and K' points is not an accident but derives from the symmetry of the graphene lattice and is persistent despite the approximation used to solve

the band structure, unless time-reversal symmetry is broken. This can occur, for example, in the presence of spin-orbit coupling, which arises from the interaction of the carriers' spins with the magnetic field associated with their orbital motion. Such a correction can be large at conventional metal surfaces, where local fields are strong and relativistic corrections further enhance the coupling [9,10]. But for graphene, the expected coupling leads to energy gaps on the order of 10s of microvolts [11], which is far too small to be significant in most situations.

Figure 2. The bandstructure of graphene, as calculated by Eq. (1). The upper and lower bands are labeled π^* and π in analogy with molecular orbital terminology. The Brillouin zone boundary is drawn at zero energy with respect to the Dirac energy E_D . Data are plotted for hopping and overlap terms $t=-2.82$ eV and $s=0.129$ eV.

The basic signatures of the graphene band structure are subject to change when the graphene is modified. The most common effect is the introduction of excess or deficit charge through either gate-induced charge accumulation or chemical doping. A modest applied voltage of 50V or so is sufficient to move E_F to around $E_D \pm 0.5$ eV [12,13], which is on the order of 1×10^{13} charges/cm². Larger voltages are likely to lead to breakdown of the gate insulator and so larger deviations of E_F require doping by chemical

means, typically by dopant atoms [14,15] or electrolytic gating [16]. By such means, charge densities on the order 10^{14} cm^{-2} were achieved.

Figure 3. Fermi surfaces for different Fermi energies of graphene, corresponding to hole doping. (a) Fermi contours are calculated for the π band using the third near-neighbor tight binding parameters [17]. The dashed line is the Brillouin zone; the Fermi levels vary from -0.2 eV (small circles around K, K' points, blue) to -3.8 eV (large circles centered on Γ , red) in steps of 0.2 eV. The black contour which passes through the saddle point at

M, occurs at $E_F = E_D - 2.14$ eV. (b) Constant binding energy contours derived from ARPES measurements of a quasifreestanding graphene layer grown on hydrogen-terminated SiC(0001) [18]. Contours map created by summing the spectral function maps for binding energies from 0 to -4.5 eV in 0.375 eV steps. An additional contour map was included for binding energy -2.72, corresponding to the experimental M saddle point energy. The data were collected in one 90° quadrant and symmetrized.

A useful characterization of doped graphene is the Fermi surface measurement, which is defined as the constant energy contour of the bandstructure at the Fermi energy. Figure 3a shows the Fermi surfaces of the π band for various Fermi energies, using the third near-neighbor tight binding parameters of Reich et al [17]. We will see that the ARPES technique can visualize these same contours directly.

In the next section, we will briefly review the ARPES technique, and then discuss some specific examples to show how ARPES can visualize not only the constant energy surfaces (a rather pedestrian measurement) but more importantly show how the more subtle interactions of graphene carriers with the substrate, with dopant atoms, and with each other can affect the electronic structure.

ARPES

The angle resolved photoemission spectroscopy technique has been extensively reviewed [19–21] and so will be only briefly discussed here. Essentially ARPES is a refined version of the ordinary photoelectric effect, as illustrated in Figure 4. Soft x-rays impinge on a sample, in a vacuum sufficiently rarefied (typically better than 1×10^{-10} Torr) to ensure that the samples remain clean of residual gas atoms and molecules. Through optical dipole transition, bound photoelectrons are excited into free electron-like states that are coupled into the vacuum. These free electrons then propagate through the vacuum, to be collected by an angle-preserving lens. This lens transfers the electrons to an entrance slit of a hemispherical spectrometer while preserving the angular distribution. The electrons are then dispersed in energy as they orbit the hemispherical capacitor, leaving a record of both their energy and angle in the exit plane of the hemispheres. By placing an imaging particle detector in this plane, it is possible to record a small segment

of the electronic bandstructure using a video camera or other electronics. This image records energy dispersion as a function of angle of emission, which must then be mapped onto momentum space.

The mapping to momentum space coordinates is easily accomplished after some assumptions are made. It should be noted that in the following we are limiting the discussion to two dimensional electron states at a free surface. The discussion is a bit more complicated when probing bulk (three dimensional) electron states [20,22]. We start with energy conservation, which dictates that the energy of the detected electron is related to the initial state by

$$E_i - E_f = \hbar \omega \quad (3)$$

The absolute value of E_i can be determined by calibrating the measured energy spectrum against the Fermi level of a metal standard. The second assumption is that the final state can be represented by the parabolic dispersion of a plane wave free electron:

$$E_f = \frac{\hbar^2 k^2}{2m} + E_0 \quad (4)$$

where k is the free electron momentum outside the solid and E_0 is a constant. Finally, it is assumed that the momentum projected onto the surface plane, $\mathbf{k}_{||}$, can be related to the total momentum k by

$$|\mathbf{k}_{||}| = k \sin \theta \quad (5)$$

where θ is the angle of electron emission relative to surface normal.

Figure 4. ARPES experimental schematic. Soft x-ray photons impinge on a sample. Electrons (rays at sample) in a plane parallel to the analyzers entrance slit (not shown) are collected and dispersed along circular orbits in a hemispherical capacitor analyzer, to be detected at the detector plane (inset).

At this point, sufficient information is available to convert the measured energy-angle dispersion into the desired energy-momentum bandstructure, within the unknown constant E_0 . This constant is normally constrained by scaling the measured momentum so that band extrema are correctly located at the high symmetry points in reciprocal space.

In ARPES experiments, the choice of the incoming photon source is important. If the best energy resolution is desired, UV lasers excel [23], but with energy range typically less than around 11 eV, the range of accessible momentum $\mathbf{k}_{\parallel}$ is insufficient to reach the K points of the graphene Brillouin zone.

Another common laboratory light source is a UV resonance lamp, with He I radiation (21.22 eV) being the most commonly used. Such sources can have good energy resolution, around 2-3 meV typically, but they have limited flux. Furthermore they are not particularly bright sources, so spot sizes at the sample are not much better than a $\frac{1}{2}$ mm or so. Such a spot is too large to look at small samples, and furthermore, such large

spot sizes can reduce the angular resolution through imaging aberrations in the electron lens. This loss of k resolution can negate the good E resolution, especially for graphene in which the band velocity dE/dk is relatively large.

Synchrotron beamline sources offer a good match between energy resolution (typically 1-20 meV) and small spot sizes (typically 10-100 μm) leading to very good k -resolution (typically $.01\text{\AA}^{-1}$). Furthermore they offer wide tunability (typically 15-100 eV) and so a wide range of momentum space can be probed. Finally, they typically offer high flux, so that statistically robust data sets can be acquired very quickly. A number of new synchrotron light sources have been built or will be built in the next few years, increasing the accessibility of these sources to more experiments.

ARPES Results for graphene

Intrinsic Properties. Exploring the bandstructure of materials is one of the primary uses of ARPES. Figure 3a showed calculated constant energy contours, which may be compared (Fig. 3b) with the results derived from ARPES on a quasi-freestanding graphene layer grown epitaxially on hydrogen-terminated SiC(0001) [24]. Growth of these samples occurs through annealing in high pressure Ar followed by H_2 . Such samples are slightly p -doped i.e. $E_F - E_D < 0$ due to residual interactions with the substrate. Hence, we do not observe the expected point-like distribution of states at the Dirac crossing because those states are unoccupied and therefore not accessible by ARPES. Besides that, we can see the excellent qualitative agreement between the ARPES and predicted contours [17]. However, quantitative differences remain.

The predicted contours [17] were generated using tight-binding parameters that were fitted to *ab initio* local density approximation (LDA) calculations. The main qualitative disagreements are first, the experimental data indicate a saddle (M) point energy of -2.72 eV, which is about 30% larger in magnitude than the predicted energy

(-2.14 eV). This discrepancy is typical for the LDA method, which typically underestimates the bandwidth of metals including graphite [25].

Second, while the predicted contours are in principle infinitely sharp, the actual contours possess a finite width in the momentum plane. This momentum broadening does not reflect the finite instrumental resolution since the data are not resolution-limited (except perhaps for the sharpest features in the data, near the K and K' points). The broadening actually arises from finite lifetime effects caused by many body interactions, mainly due to electron-electron scattering for all energies far E_F [14,26,27].

Third, the intensity of the measured contours is not uniform, rather there is a “dark corridor” (the term coined by Gierz *et al.* [28]) radiating outwards from the K and K' points in which the ARPES signal is weak or extinguished. This was first explained for graphite by Shirley *et al.* [29] and for graphene as arising from the quantum mechanical interference of emission from the A and B atoms of the graphene plane [30,31]. The origin of the interference derives from the variation of wavefunction phase along a closed Fermi contour around the K or K' point. This phase variation is also the origin of the chiral nature of the graphene carriers and therefore the degree to which the intensity is extinguished along the dark corridor can be viewed as a measure of the degree of A-B atom symmetry breaking (as induced, say, by chemical modification of graphene) [30] or indeed the extent to which a carbon layer “is” graphene.

The data in Figure 3b were acquired at relatively high photon energy, near 100 eV. Since this energy is much larger than the ionization potential of the carbon atoms in graphene, the plane wave nature of the final state is more or less assured. But the picture becomes more complicated at lower photon energy, where angular momentum components of the final state become important [28,32–34]. These papers demonstrated that dark corridors can be altered or eliminated altogether by varying the polarization of the light, especially at low photon energy. The inherent chirality of the carriers may still be probed by ARPES, but a fuller analysis considering the photon polarization is needed.

Recently, an approach to analyzing the data using circular dichroism has been successfully used to place a limit on A-B atom symmetry breaking [33].

We have shown that the bandwidth, linewidth, and intensity distribution of electronic states differ in real graphene compared to the ideal model. Although the data presented has been for a quasi-freestanding epitaxial film (graphene grown on H-terminated SiC(0001) as an example), these effects are intrinsic to graphene and would turn up in similar form for a truly freestanding film. Now we discuss what further modifications to the epitaxial graphene electronic structure can be observed as the strength of the coupling to the substrate layer is increased.

Weak Substrate Symmetry Breaking. In contrast to the quasi-freestanding graphene just discussed, a second form of graphene on SiC can be epitaxially grown directly on the substrate by annealing in ultra high vacuum, without the step of passivation of the substrate with hydrogen. Such vacuum-grown films can be grown on either the (0001) or (000-1) faces (i.e. Si or C terminated, respectively), but single-layer control [3], two dimensional electron gas behavior [35] and ARPES bandstructure [14,36,37] were first demonstrated for the Si face. In our experiments, we have grown such samples in ultra high vacuum (UHV), so we refer to them as UHV graphene/SiC(0001). Such samples are characterized by an active graphene-like layer, which is separated from the substrate by an insulating carbon-rich “buffer” layer (see Ref. [38] and references therein) with unit cell dimensions ($6\sqrt{3}\times 6\sqrt{3}$), rotated 30° , relative to the SiC surface lattice. This overall symmetry brings the SiC (0001) surface and graphene lattices, with vastly different lattice constants ($3.08 \text{ \AA}$ and $2.46 \text{ \AA}$, resp.) into registration. Equivalently, the overall symmetry can be expressed as (13×13) with respect to the graphene lattice [3]. (The scale multipliers of 6 and 13 in these lattice scales arise from the fact that along the graphene ΓM direction, the graphene and SiC

atoms are registered every 39 A-B carbon bondlengths, or equivalently every 18 SiC unit cells; the ratio $18:39 = 6:13$).

Figure 5a shows the Fermi surface of such an epitaxial film acquired with ARPES. Since such UHV grown epitaxial graphenes are found to be electron-doped ($E_F - E_D \sim 0.45$ eV, or $n \sim 1 \times 10^{13} \text{ cm}^{-2}$ [14]), the Fermi surface consists of small circular contours at the K points of the BZ. At first glance, the data do not appear to deviate from the isolated graphene result; with a non-linear intensity scale, however (Figure 5b) reveals a set of 6 prominent contours, representing a rosette of 6 new cones, centered on each Dirac cone. These contours have around 40 times weaker intensity than the main bands and so cannot be easily seen in an ordinary, linear intensity scale as shown in Figure 5a. These features have the same relative separation as the rosette spots around the (00) and (10) spots of the low energy electron diffraction (LEED) pattern [3,38], and have similar origin.

Figure 5. Fermi surface of n-doped UHV grown graphene on SiC(0001) [14,18]. (a) ARPES shows small circular Fermi surfaces ($n \sim 1 \times 10^{13} \text{ cm}^{-2}$) at the K points of the graphene surface BZ (dashed line). ARPES data were acquired over one 90° quadrant and symmetrized. (b) Detailed view of BZ corner, with $6\sqrt{3} \times 6\sqrt{3} R30^\circ$ symmetry BZs (with respect to SiC (0001) or equivalently 13×13 (with respect to graphene)). Compared to the first panel, the low intensity part of the color scale has been enhanced to show weak satellite features. The yellow arrow, representing the 6 scattering vector leading to the rosette cones, is the same as the yellow arrow in (c), the reciprocal lattice constant under 6×6 symmetry (with respect to SiC). (c) same data and color scale as (b), with 6×6 (with respect to SiC(0001) Brillouin zones overlaid. The SiC (0001) surface BZ is indicated by the heavy solid line.

In Figure 5b we show the mini-BZs (mBZs) associated with the lowered symmetry $6\sqrt{3} \times 6\sqrt{3} R30^\circ$ lattice (equivalently 13×13 with respect to the graphene lattice). Just as the main Dirac cones occur at three K and three K' points of the BZ, the

mini Dirac cones are centered only on equivalently defined K or K' points of the mBZs. Furthermore, each rosette of mini cones preserves the valley index (whether K or K') of the corresponding central cone. Inspection of Figure 5b shows that combinations of reciprocal lattice vectors of the reduced symmetry lattice can only connect K to K points or K' to K' points of the mBZs. For example, the yellow vector connecting the central to one of the mini cones in Figure 5b is the sum of each of the fundamental reciprocal lattice vectors. Because of this, the chirality of the charge carriers is preserved in the reduced symmetry.

In LEED, the reduced symmetry should lead in principle to diffraction spots at each of the $6\sqrt{3}\times 6\sqrt{3}$ $R30^\circ$ spots, but a scattering structure factor strongly modulates the relative intensity of the spots. Similarly, in a simple tight-binding model of ARPES, a replica band could be expected at each K point of the reduced symmetry reciprocal space. However the intensity of these minibands is limited to wavevectors that provide at which the potential energy landscape has the strongest peaks in reciprocal space [39]. In this case, rather than appearing at the near neighbor (NN) mBZ K points relative to the main Dirac cone, the mini cones appear at the 5th NN K points in reciprocal space. These points turn out to be spaced according to the reciprocal lattice vectors of the 6×6 lattice (relative to SiC) as can be seen in Figure 5c. There we have drawn the SiC BZ and 6×6 mBZ; the correlation of the mini band rosette positions to the 6×6 reciprocal lattice vectors is clear. (It must be noted that the apparent location of the Dirac cones relative to quasi- 6×6 symmetry BZs is not significant because this is not the true symmetry of the system.)

STM analysis of these samples similarly shows that the 6×6 lattice appears to be the important length scale [38,40–42] as far as the electrons are concerned; features with $6\sqrt{3}\times 6\sqrt{3}$ $R30^\circ$ symmetry can be seen only in narrow bias windows and show much disorder whereas 6×6 symmetry features appear strong and regular.

The electronic structure of the buffer layer and the nature of the minibands in the first graphene overlayer are of keen interest and have caused some controversy. The central issue is whether the reduced lattice symmetry also reflects broken symmetry of the system with respect to the A, B carbon atoms in the graphene overlayer. If this were so, then an energy gap could be expected to develop at E_D .

A basic symmetry argument indicates that this should not be the case. The A-B symmetry breaking should only arise when the reduced lattice symmetry couples the main K and K' points of the graphene lattice. As a counterexample, suppose the symmetry (with respect to graphene) was 12×12 instead of 13×13 . In this scenario, there would be a mini BZ centered on both the K and K' points of the 1×1 lattice. Therefore, K and K' points of the 1×1 lattice would both map to the center (G point) of each MBZ. In this case we would be able to connect the K and K' points by a reciprocal lattice vector, and a gap would be expected to open at all of the Dirac crossings. But in the actual 13×13 symmetry, a cone at K cannot be connected to a cone at K' by a reciprocal lattice vector, we can conclude that the A, B atom symmetry is preserved, and no energy gap opens at a main or mini Dirac point.

ARPES data have been used both in support of and against the existence of an energy gap. Bostwick et al reported a gapless energy spectrum at the Dirac point [14], although the energy spectrum near E_D was proposed to be heavily renormalized due to many-body interactions. Figure 6 shows the band structure along the line MK' direction ($k_y = 1.48 \text{ \AA}^{-1}$ in Figure 5b). The renormalization takes the form of a vertical stretching of the intensity in the vicinity of the Dirac crossing; signatures of an energy gap such as a minimum in the intensity at E_D are not observed. Nor could any gap be observed where the main and mini bands cross at higher energy. The absence of these high-energy gaps, which are not forbidden since they occur away from the mBZ boundaries, indicates that the superlattice potential must be very weak in this system.

Secondly, an intensity analysis of the dark corridor (clearly visible in the intensity maps of Figure 5) could be used to limit the size of the gap-inducing symmetry breaking energy to only a few 10's of meV [43]. Subsequent ARPES measurements on quasi-freestanding graphene confirmed that many-body effects on the one hand can strongly normalize the spectrum near E_D but on the other hand preserve the gapless spectrum and chirality of the carriers [24]. Aside from ARPES, Hall effect measurements obtained showed that fully chiral states [44] are obtained. Furthermore, STM measurements did not report AB symmetry breaking [45]. An apparent gap in STM spectroscopy measurements is explained as due to phonon effects [46].

Figure 6. Bandstructure of UHV grown graphene on SiC(0001) along the direction KM' (at $k_y = 1.48 \text{ Å}^{-1}$ in Figure 5b). In addition to the strong central band, weaker minibands are apparent. No gap is observed at the main or mini Dirac crossings (yellow arrows).

Although the $6\sqrt{3}\times 6\sqrt{3}$ $R30^\circ$ symmetry does not necessarily impose a bandgap at E_D *per se*, it is possible that the actual symmetry might depart slightly from this (for example by disordered carbon atom arrangements in the buffer layer) and thus a gap still be induced. In such a situation, A-B atom symmetry breaking might not be obvious in an STM experiment, say, but instead a net asymmetry could accumulate somehow over many unit cells. Such disordered structures were found in large-scale simulations of STM data [45,47]. In addition Ref. [47] predicted that such structures could induce an energy gap was induced at E_D . Such a gap was also found in ARPES measurements by Zhou et al [48] which were interpreted as due to substrate symmetry breaking, although the gap-like feature analyzed in Ref. [48] was later shown to be associated with structural defects [49].

Strong Substrate Symmetry Breaking: Graphene on Ir(111). In contrast to the UHV grown graphene on SiC(0001) just discussed, much stronger substrate-graphene interactions have been observed, and the resulting modifications to the graphene electronic structure may be clearly observed using ARPES. We now consider the case of graphene on Ir (111) [50]. The lattice constants of Ir and Gr differ by 10%, and so the reduced symmetry lattice has symmetry 10×10 (with respect to the graphene lattice) or 9×9 (with respect to the Ir lattice). Strictly speaking, such symmetry, as in the previous case, does not break AB atom symmetry and therefore a gap at E_D is not expected.

STM images of this system [50] reveal that the strain due to lattice mismatch is accommodated by formation of a triangular pattern of long range waves of amplitude greater than $0.3 \text{ \AA}$, which accompanies a moiré interference pattern. The presence of this long-range modulation could be expected to lead to mini-Dirac cones in ARPES [51] in similar fashion to the graphene on SiC.

One of the most interesting aspects of such a system is the possible generation of new Dirac crossings that occur in an otherwise gapped energy spectrum [52]. These Dirac crossings were predicted to occur at the M points of the mini BZs and can occur

only for chiral carriers as in graphene. Furthermore, the group velocity of the carriers can become highly anisotropic, suggesting a new method to control transport properties by generation of an arbitrary superlattice potential. Such a superlattice potential could be generated by lattice constant mismatch to a substrate, but could also be enhanced by deposition of ordered clusters [50,53] by application of an inhomogeneous field, or by rotational misalignment [54].

To establish whether any of this holds true for graphene on Ir, it is therefore interesting to see if such additional mini-cones are observable with ARPES, and furthermore whether new gapless Dirac crossings can be found along the mini BZ boundaries as predicted [52]. Such a study was undertaken by Pletikosić et al. [45] who were able to observe mini cones, and furthermore, sample the electronic structure along the mini BZ boundary. They observed an energy gap at the crossing points between mini-cones and the main Dirac cone, and furthermore, they found evidence for a strong variation in the gap size along the mBZ boundary.

More detailed ARPES studies since followed [53,55–57], in particular constant energy surfaces were acquired in order to locate the mini cones accurately in reciprocal space. A representative example of the data is shown in Figure 7.

Figure 7 shows the relationship between the graphene BZ, the underlying Ir BZ, and the 10×10 -derived mini BZ. Here we follow a different convention than in Figure 5: we show the mBZ to be centered on the graphene K point, despite the fact that we expect the global symmetry requires the mini- and main graphene BZs to be aligned at their respective K-points. By following this convention, we are applying a continuum approximation, in which we assume the superlattice potential is slowly varying compared to the distance between A and B atoms [54,58–61]. Such a model is a necessary simplification to handle arbitrarily incommensurate (through twist, translation, or dilation of graphene's lattice relative to the substrate) systems.

Figure 7 (a-c) clearly show the presence of minibands, consistent with 10×10 lattice symmetry (the distance between main and minicones is within experimental accuracy equal to $1/10^{\text{th}}$ the distance between cones at the main K points). Figure 7 (d) however shows that the chemical interaction between graphene and the Ir substrate is very strong. This is revealed by the disappearance of the mini cone derived features at E_F : as E_F is approached, the graphene bands hybridize with the surface Ir d bands and the

resulting state at E_F has mixed C/Ir character [57]. Similar hybridization with the Ir bands has been observed at deeper binding energies [62] as well.

Figure 8. Constant energy surfaces. (a) Graphene/Ir(111) at binding energy $E_F - 770$ meV where the mini- and main Dirac cones merge. (b,c) model calculated without / with experimental broadening included.

In order to check if there is a gap at E_D , it is necessary to dope the graphene in order that E_D is separated from the Ir bands. This was performed using K [57] or Na [56] atoms, and both experiments showed that there was a gap at E_D on the order of 100-150 meV, implying the system breaks A-B symmetry. This gap is further enhanced up to ~750 meV when Ir clusters are deposited on top of the graphene [56,62]. Since such clusters align very accurately to the underlying Moiré pattern [50], their presence greatly enhances the symmetry-breaking superlattice potential.

Since the Dirac cones are not protected from gap formation in the reduced symmetry of the system, we can conclude that the symmetry must deviate from precisely 10×10 periodicity. The nature of the deviation is not known, but it could be due to small incommensurability away from 10% lattice mismatch, or small twists of the graphene. Indeed, STM measurements showed that rather than 9×9 periodicity, the Moiré pattern displayed $(9.32 \times 9.32) \pm 0.15$ periodicity [50]. Therefore, treating the system in a continuum approximation is probably justified.

Figure 8 (a) shows a constant energy surface of undoped graphene on Ir, where the binding energy (-770 meV) was chosen so that the mini- and main Dirac cones have maximum overlap (data from Ref. [57]). Pletikosić *et al.* showed that the bands in the overlap region are gapped, and that the gap had a strong anisotropy, consistent with strong chirality effects [51]. However, the expected closing of the gap at the M points [52] was not observed. Subsequent studies [56] showed that the gap was more or less isotropic, both for the as-grown system [51], and with enhanced gap due to Ir cluster overgrowth [62].

Here we show that a simple pseudopotential model tight binding model that ignores the effects of chirality but includes trigonal warping of the bands can explain the

observed minigap spectrum. Figure 9 shows bandstructure data acquired along constant k_y lines through (upper panel) the main K point and (lower panel) the minigap K'_1 , K_2 points. (The data in Figures 9 were extracted from the same data set as Figure 8a [57]). The energy gap is readily observed in the lower panel, which was acquired along the mBZ boundary where the gap should be largest. The inset shows magnified data, where the split states due to the energy gap are clearly shown (red arrows). The energy gap is clearly seen at all points from K_2 to K'_1 , although at the latter symmetry point an Ir band (dispersing from lower left to upper right direction obscures the data somewhat).

In our model, we start with the ordinary graphene bandstructure (Eq. 1) and add a single pseudopotential energy component at the 6 smallest reciprocal points of the 10×10 lattice. We fix the hopping and overlap parameters to $t = 2.82$ and $s = 0$, which were previously determined for graphene on SiC [14]. These parameters are very similar to those estimated by fitting the main band over a much larger range of k, E [55]. We assume $E_F = E_D$, so that the only free parameter in our model is the pseudopotential, which was chosen to be 0.085 eV.

The computed bands are in excellent agreement with the observed main and minibands in Figure 9. In particular, the minigapped bands at around -0.7 eV first identified in Ref. [51] are extremely well reproduced by the model. The main discrepancy between the model and the data are that the center of the minigap is predicted to occur at around 100 meV deeper binding energy than the experiment.

Figure 8b,c show constant energy maps derived from the model assuming without/with experimental broadening. The constant energy slices are taken at slightly deeper binding energy (-870 meV) than in Figure 8a, to account for the downward shift of the minigap in the model. The model shows that at this binding energy, the main Dirac band is mostly eliminated, except for the presence of pockets around the K point, but the data do not reveal evidence of new Dirac cones near the M points that were

predicted for chiral graphene superlattices [52]. The experimentally observed intensity at the central mBZ boundary is mostly due to the finite energy width of the states, determined by lifetime effects and experimental broadening, as simulated in Figure 8c.

Figure 9. Bandstructure cuts of graphene on Ir(111) acquired along lines of constant k_y through the high symmetry points indicated in Figure 8a (upper and lower panels). The red lines are results of a pseudopotential tight binding calculation described in the text and lie on or near graphene main/mini bands. The remaining features are attributable to Ir bulk and (111) surface bands. The inset shows a magnification of the bands along the K2-K'1 line, highlighting the energy gap along the mBZ boundary (red arrows). Data are from the same data set as in Figure 8a [57].

Ref. [57] carefully analyzed the experimental bandstructure extracted along the mini BZ contours. A similar analysis was performed for the as-grown system, and also with deposited Ir clusters [62] in which the minigap was greatly enlarged. Both studies

concluded that the experimental minigap was isotropic, at least in the range of momenta where the data were most reliable. (Due to the “Dark corridor” effect, the bands get quite weak in some directions, where interfering bands from the Ir substrate also appear.) Therefore, the conclusion from the present model and the previous ARPES measurements is that graphene on Ir does not possess the correct symmetry to avoid opening gaps at the main or mini-Dirac points.

It should be emphasized that symmetry breaking alone cannot be responsible for opening a gap. For we are free to imagine repartitioning the graphene lattice to any symmetry we care to imagine, but without an external potential, or chemical hybridization to the substrate, no gap can be formed. A complete model of any system would require not only accounting for the symmetry, but also the short-range effects characterized by locally combining the orbitals of different atomic-like symmetry. In the case of graphene on Ir, such hybridization is very strong near E_F , and the graphene bands cannot be described by a simple model, but at the mBZ boundaries, far from most Ir bands, the substrate perturbation is well characterized by a single pseudopotential component at the reduced (10x10) symmetry. This pseudopotential arises not only from the substrate potential felt by the C atoms, but also due to the modulated height of the C lattice.

Conclusions and Outlook

Here we have shown the utility of ARPES to determine many details, especially the symmetry-breaking potentials associated with superlattice formation when graphene is deposited on lattice-mismatched systems. Although many such systems have been examined by transport, there have been relatively few studied by ARPES, mainly due to the difficulty in securing large enough samples. Most ARPES measurements are performed with photon beam sizes on the order of 10s of μm to mm, making it difficult to

measure the bandstructure when superlattice grain sizes are typically much smaller. Notable exceptions are the results of graphene on Ir(111) discussed above—but it should be noted that many other rotational domains have been observed [57] on the same substrate, although typically with grain sizes too small to analyze in detail with traditional ARPES.

Nowadays there are numerous “nanoARPES” experiments being developed or operated that can provide submicron probe beams. The first observation of bands in individual grains of graphite in rotationally disordered graphite [22] showed that the technique was feasible for graphene-related systems. More recently, measurements of single grains of graphene grown on Cu substrates [64] show that much more accurate band parameters can be achieved when compared to measurements over many grains [65].

Removing the restriction of sample size can therefore open up many new families of materials for studies, not only graphene but many other materials besides that can be transferred by micromechanical cleavage methods.

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