Periodically Rippled Graphene: Growth and Spatially Resolved Electronic Structure

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We grow epitaxial graphene monolayers on Ru(0001) that cover uniformly the substrate over lateral distances larger than several microns. The weakly coupled graphene monolayer is periodically rippled and it shows charge inhomogeneities in the charge distribution. Real space measurements by scanning tunneling spectroscopy reveal the existence of electron pockets at the higher parts of the ripples, as predicted by a simple theoretical model. We also visualize the geometric and electronic structure of edges of graphene nanoislands.

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The possibility to produce single layers of graphene [1,2] has opened a fascinating new world of physical phenomena in two dimensions. Graphene has already shown that its charge carriers are massless Dirac fermions [3–7] and that it displays an anomalous integer quantum Hall effect [3–5] even at room temperature [8]. While ultrathin epitaxial films of graphite and even “monolayer graphite” have been grown on solid surfaces by chemical vapor deposition for quite some time [9], the degree of characterization of the films was hampered by experimental limitations [10]. Systems made up of a few graphene layers have been grown on SiC substrates [11,12].

Recently it has been claimed that a free standing isolated graphene layer is intrinsically corrugated [13]. Charge inhomogeneities have also been observed in nominally undoped samples [14]. Thus, so far, structural ripples and charge inhomogeneities have been observed separately.

In this Letter we report on a method to fabricate highly perfect, periodically rippled graphene monolayers and islands on Ru(0001) under ultrahigh vacuum (UHV) conditions. We characterized by means of scanning tunneling microscopy or spectroscopy (STM/STS) the perfection at the atomic scale and the local electronic structure of the rippled graphene monolayer. The periodicity of the ripples is dictated by the difference in lattice parameters of graphene and substrate, and, thus, it is adjustable. We observe inhomogeneities in the charge distribution, i.e., electron pockets, at the higher parts of the ripples. This inhomogeneity can be understood with the help of a tight-binding model which incorporates a periodic potential associated with the structural ripples that induces a shift of the electronic levels and a corresponding charge transfer from conduction to valence bands for some atoms and the opposite in the others. Finally we studied graphene nanoislands that display hexagonal shape with atomically resolved zigzag edges, whose characteristic edge states allow us to determine experimentally the doping of the graphene layer.

The experiments have been carried out in a UHV chamber with base pressure of $4 \times 10^{-11}$ Torr that contains a variable temperature STM and a rear view low energy electron diffraction (LEED) optics. The Ru(0001) crystal was cleaned by cycles of Ar$^+$ sputtering and annealing followed to oxygen exposure and heating to high temperature [15]. The graphene layers were produced either by controlled segregation of C from the bulk of the substrate or by thermal decomposition at 1000 K of ethylene molecules preadsorbed at 300 K on the sample surface. The W tips were routinely cleaned by ion bombardment and annealing. The $dI/dV$ curves were obtained by numerical differentiation of the $I(V)$ curves. We model the graphene electronic bands by a nearest neighbor tight-binding model with parameter $t = 3$ eV, a periodic shift of the carbon $p_z$ levels, and a finite broadening due to the hybridization with the metallic substrate. In order to calculate the density of states, we use a $(30 \times 30)$ unit cell, and a sum over 6 special points in the irreducible sector of the Brillouin zone. Hence, the total number of states included in the calculation is 10800. This is sufficient to resolve local changes in the electron density in the order of $10^{-2} - 10^{-3}$ carriers per carbon atom.

The epitaxial layer of graphene covers completely the surface of the single-crystal Ru substrate over distances larger than a micron (see [16]) and presents a triangular periodicity of 2.4 nm [Fig. 1(a)] that is due to the coincidence lattice of graphene and Ru$_x$, i.e., the lattice of graphene has a size relation with the underlying Ru lattice that implies that 11 carbon honeycombs (0.246 nm) will adjust almost exactly with 10 Ru-Ru interatomic distances (0.27 nm). The weakly interacting (see below), laterally undistorted graphene structure rides on top of the lattice of the substrate, resulting in some C atoms being slightly higher than others. The graphene layer, thus, is rippled in a periodic fashion, with a periodicity dictated by the difference in lattice parameters. Variations of this approach using other experimental conditions can be used to produce...
FIG. 1 (color online). (a) 76 nm × 76 nm STM image of graphene/Ru(0001) showing the decoration of a screw dislocation and a monoatomic step from the substrate. There are also some defects on the rippled structure. (b) 6.5 nm × 6.5 nm atomically resolved image of graphene/Ru(0001). The image was taken with a sample bias voltage of \( V_s = -4.5 \text{ mV} \) and a tunnel current of \( I_t = 3 \text{ nA} \). The image is differentiated along the \( X \) direction in order to see the weak atomic corrugation superimposed to the ripples. The inset reproduces the Fourier transform of the image showing the \((11 \times 11)\) periodicity of the rippled graphene layer. The larger hexagonal pattern corresponds to the C-C distances and the smaller spots to the periodic ripples. (c) Corresponding structural model. (d) Line profile marked with an arrow in panel (b). The atomic corrugation in these conditions is around 5 pm.

graphene monolayers on other single-crystal substrates [17].

Figure 1(a) shows that, in addition to monoatomic steps and dislocations of the substrate faithfully reproduced by the epitaxial graphene, there are also upper part of the ripples that are weaker or even missing completely (see also ref. [16]). Figure 1(b) shows a high resolution topographic STM image of the epitaxial graphene layer, revealing its atomic structure. Unlike STM images of graphite [18], which show normally only one of the 2 C atoms in the surface unit cell, the honeycomb structure of graphene is clearly resolved in the upper part of the ripples with its 0.14 nm C-C distance. The inset in Fig. 1(b) shows the Fourier transform of a larger atomically resolved STM image, indicating that the ripples constitute a \((11 \times 11)\) superlattice with respect to the C lattice. The \((10 \times 10)\) coincidence lattice with the Ru(0001) substrate is revealed in the corresponding LEED pattern (not shown).

The apparent vertical corrugation of the rippled graphene monolayer, as seen with STM, changes with the tunneling voltage, ranging from 0.1 nm (at a sample voltage of −1 V) to 0.02 nm (at +1 V). This indicates the importance of electronic effects. The C-C apparent atomic corrugation inside the honeycomb unit cell is only of the order of 0.005 nm [Fig. 1(d)]. The actual geometric corrugation of the rippled layer can be estimated to be below 0.02 nm from the observed lack of diffracted peaks for a beam of thermal He atoms scattering off the graphene surface [19].

The bonding with the substrate occurs through the hybridization of C \( \pi \)-states with Ru \( d \) states. Photoelectron spectroscopy shows that the layer bonding is not carbidic. Angular resolved photo electron spectroscopy data show that the graphene bands in graphene/Ru(0001) are similar to the ones of graphite, but the bottom of the \( \pi \) band at the center of the Brillouin Zone is shifted down by 1.8 eV with respect to graphite [20]. The small energy shift of the C1s core level with respect to graphite indicates that the charge transfer from the substrate is small, but not negligible; i.e., the graphene layer is doped with electrons by the substrate.

The graphene-Ru interface is atomically well defined. The average interlayer distance for the closely related incommensurate graphene/Pt(111) system has been determined to be rather large (0.37 nm) by means of tensor LEED analysis [10]. First principles calculations in the similar graphene/Ir(111) system have indicated that the average binding (0.2 eV/C atom) is barely strong enough to correspond to chemical bond formation [21]. The incommensurate nature of the graphene monolayer is an additional indication that the interaction of graphene with the substrate is rather weak.

Figure 2(a) shows spatially resolved \( dI/dV \) tunneling spectra, which are roughly proportional to the local density of states (LDOS), recorded on top of the “high” and “low” regions of the corrugated graphene layer. Panel (b) shows the corresponding calculation. The experi-
The observed charge transfer is due to the conduction band is depleted at the high parts of the grade, depleted in the low portions of the ripples, while the empty LDOS is larger at the low regions of the graphene layer. This effect is extremely robust and indicates that the valence band is periodically corrugated graphene layer (see lower panel in Fig. 3). This effect is in agreement with the experiments, the calculations have been performed for an isolated graphene layer in which the effect of the substrate has been considered to result in: (i) a shift of the Dirac point by $-0.3$ eV due to doping; (ii) the introduction of a finite lifetime caused by hybridization of the $\pi$ orbitals with the band of the substrate; and (iii) a $(11 \times 11)$ periodic potential to account for the periodic structural ripples that changes between $-3$ V and $3$ V/2, where $V = -0.3$ eV. This value for the potential gives the better agreement with the experiments. For higher values of the potential, the asymmetry in the calculated DOS is larger than the one found in the experiments. The $\pi$ band in graphene has a total width of $W \sim 6t$, where $t \sim 3$ eV is the hopping between $\pi$ orbitals at nearest neighbor C atoms [22].

In agreement with the experiments, the calculations show that the occupied LDOS is larger on the high regions of the superlattice, where the potential is at a minimum, while the empty LDOS is larger at the low regions of the graphene layer (see lower panel in Fig. 3). This effect is extremely robust and indicates that the valence band is depleted in the low portions of the ripples, while the conduction band is depleted at the high parts of the graphene layer. The observed charge transfer is due to the periodic modulation of the $\pi$ orbitals at the different C atoms. The calculations also reproduce the weaker features at both sides of the Fermi energy that reflect the existence of the periodic superlattice, which induces a folding of the graphene bands in the new $(11 \times 11)$ Brillouin zone. The reconstruction considered here does not superimpose the two inequivalent corners of the Brillouin zone and it does not open a gap at the Dirac energy [23]. The spectrum is split on subbands separated by gaps, away from the $K$ and $K'$ points.

The periodic charge inhomogeneities in the graphene layer can be visualized directly in the real space by imaging the spatial distribution of $dI/dV$ close to the Fermi energy. Figure 3 shows the spatial distribution of the LDOS below and above the Fermi level. The experimental images are in the upper row at the left and the right of the corresponding topographic image. The bright regions correspond to larger LDOS. For a complete set of spatially resolved $dI/dV$ maps versus sample bias voltage see ref. [24]. In our case, the inhomogeneities in the charge distribution are spatially correlated with the ripples in the graphene layer. The reason behind is the periodic modulation of the potential, probably due to changes in the metallic screening from the substrate. It might be possible that the charge inhomogeneities reported in some other graphene samples are also related to some sort of structural corrugations, varying screening or water layers inherent to graphene layers kept under atmospheric conditions.

The growth method described here can also be used to produce different graphene nanostructures, such as nanostripes or nanowires on vicinal surfaces and nanometer wide islands on terraces, as illustrated in Fig. 4(a). The apparent step height of the island in these imaging conditions is 0.15 nm (from the Ru surface to the lower part of the ripples) showing that the graphene layer is indeed only one monolayer high. The inset shows that the islands are

**FIG. 3** (color online). The left and right images in the upper panel are maps of $dI/dV$ at $-100$ meV and $+200$ meV and reflects the spatial distribution of the LDOS below and above the Fermi level, respectively, for an extended graphene layer on Ru(0001). The central image shows the topographic image recorded simultaneously. The lower panel shows the corresponding calculations for the spatially resolved LDOS for a $(11 \times 11)$ periodically corrugated graphene layer.

**FIG. 4** (color online). (a) 10 nm $\times$ 10 nm atomically resolved STM image of a graphene island on Ru(0001). The image was recorded at $V_t = -4.5$ meV and $I_t = 3$ nA. The inset shows an image of the whole island with a lateral size of 47 nm. The images are differentiated in X direction. (b) Spatially resolved tunneling spectra measured on the high (black curve) and low (red curve) areas of the ripples close to the edge of the island and on clean Ruthenium (blue curve). The Ruthenium spectra was offset for clarity.
truncated hexagons with straight edges of a single structural type. It is remarkable that the periodically rippled coincidence lattice goes right to the steps of the islands. In fact in some cases the island step cuts the (11 × 11) arrangement. This confirms that the overlayer of graphene is indeed weakly coupled to the Ru substrate. Further zooming into the island reveals that the atomic geometry of the steps is of the zigzag type.

The relative orientation of the graphene layer with respect to the underlying Ru lattice can be determined by resolving simultaneously both atomic lattices. In order to facilitate the resolution of the weakly corrugated Ru lattice, CO has been adsorbed at saturation in the parts of the Ru surface not covered by graphene. The geometry of the resulting (√3 × √3R30°) structure of CO on Ru(0001) is well known [25], and, thus, the relative orientation of graphene and Ru lattices represented in Fig. 1 has been obtained.

Figure 4(b) shows local tunneling spectra recorded when the substrate is partially covered with graphene. The advantage of this situation is that one can take spectra in the clean Ru patches of the surface, where only a Ru surface state [15] should be detected, and, thus, spurious features from the tip DOS can easily be unraveled. The spectrum recorded on clean Ru patches show indeed only the surface state around the Fermi energy observed on Ru(0001) [15]. The spectra recorded at the center of the graphene islands are undistinguishable from the ones obtained on extended layers (see Fig. 2). The spectra taken at the edges, however, show a new peak at −0.4 eV, particularly intense on the high areas of the ripples, which is related to the theoretically predicted edge state [26], shifted as a consequence of the doping of the graphene by the substrate.

In summary we have grown periodically rippled, highly perfect, spatially extended, graphene monolayers and islands on Ru(0001). The ripples produce a spatial charge redistribution in the graphene observed with spatially resolved dI/dV maps and confirmed with a simple theoretical model. The new periodicity also induce the opening of a series of minigaps by the additional periodic potential. The presence of these minigaps is expected to give rise to new phenomena at low temperatures in the presence of high magnetic fields. We atomically resolve the zigzag edges of graphene islands and use the position in energy of the edge state to determine the doping of the graphene layer. The methods described here can be implemented on many other single-crystal substrates, giving rise to a series of graphene monolayers with different, substrate-dependent, periodic corrugations and, thus, opening the possibility to systematically test the electronic properties of controlled, charge inhomogeneous graphene layers. Methods to transfer the present finding to experimental systems adequate for lateral transport measurements are in progress.

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[16] See EPAPS Document No. E-PRLTAO-100-070805 for a STM 1 μm × 1 μm image of graphene on Ru(0001). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[19] P. Nieto et al. (to be published).
[26] Note that deviations from electron-hole symmetry away from the Dirac energy shift these states away from the neutrality point, see N. M. R. Peres et al. [7].