Electronic and geometric corrugation of periodically rippled graphene epitaxially grown on Ru(0001)

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The growth of large, highly perfect epitaxial graphene monolayers is a prerequisite for most practical applications of this promising material \cite{1,2}. Nanostructuring graphene (in stripes, dots or by periodic potentials), in turn, may reveal new physical phenomena and fascinating applications \cite{3}. Most of these topics can be characterized in detail in epitaxial graphene: a self-organized, millimeter-large, monolayer of graphene grown by soft Chemical Vapor Deposition under Ultra High Vacuum (UHV) conditions on single crystal metal substrate. Graphene epitaxially grown on Ru(0001) displays a remarkably ordered pattern of hills and valleys in Scanning Tunneling Microscopy (STM) images. To which extent the observed “ripples” are structural or electronic in origin have been much disputed recently. Here, combining ultrahigh resolution STM with Helium Atom Scattering (HAS) technique we study the geometric and electronic structure of graphene on Ru(0001).

High resolution STM image of graphene (gr) monolayer shows the characteristic arrays of bumps (the moiré structure due to the difference in the lattice parameter between graphene and substrate) and simultaneously the resolved atomic C structure. The atomic rows are not aligned with the ripples. The misalignment angle $\varphi_{\text{gr, moiré}}=4.5^\circ\pm0.5^\circ$. The rotation between the C and the moiré lattices for gr/Ru(0001) reflects in an amplified fashion the misalignment between the graphene monolayer and the underlying Ru lattice \cite{4}. The moiré superstructure is rotated with respect to the Ru lattice by $\varphi_{\text{moire, Ru}}=5^\circ\pm0.5^\circ$. Due to the magnifying effect of the moiré pattern, that is 9.96 for gr/Ru(0001) system, the misalignment of the C and Ru lattices can be determined with high precision from the observed angles between the moiré superstructure and the Ru or C lattices and it turns out to be $\varphi_{\text{gr, Ru}}=0.5^\circ\pm0.05^\circ$. The STM images measured on this surface present always the same lateral periodicity but depending on the bias voltage the apparent corrugation of the moiré superstructure changes strongly with voltage and can even be inverted, demonstrating its origin in a modulated electronic structure. When imaging occupied states, the apparent corrugation is rather constant (\textasciitilde1Å), as expected because electrons at the Fermi level contribute the most to the tunneling current, but the corrugation decreases continuously when injecting electrons in the empty states of graphene and becomes negative above +2.6 V. This behavior is fully reversible and do not depend on the sample temperature in the range between 4.6K and 300K.

The structural corrugation of the graphene monolayer can be determined by HAS. The advantages of using a beam of He atoms of thermal energy (10-100 meV) as a probe of the surface structure are its combination of low energy with short wavelength, its inert and neutral character and its large cross-section for defects. As a consequence, HAS is a unique non-destructive and surface sensitive technique, with high sensitivity to low mass atoms, such as C, or light adsorbates, such as H \cite{5}. In-plane ($\Phi=0^\circ$) and out-of-plane ($\Phi$ from 0.1$^\circ$ to 15.5$^\circ$) He-diffraction spectra from a graphene overlayer grown on Ru(0001) measured along the $\{1\overline{2}0\}$ direction, with a He beam energy of 43 meV and 30 meV. The intensity of the specularly reflected (0,0) peak depends on the structural perfection of graphene, reaching 25% of the incident beam for highly perfect layers. The relative intensity of the different diffraction peaks with respect to the specular peak determines univocally the corrugation

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function, $\zeta(x, y)$, i.e. the corrugation of the constant charge density contour where the He atoms are reflected. The corresponding corrugation function (comparing the diffraction peaks, normalized to the specular intensity, with the best fits) obtained for the moiré superstructure has a corrugation amplitude of 0.15 Å, one order of magnitude smaller than the value theoretically predicted [6,7] for the aligned graphene overlayer [8].

References


Figures

**Figura 1:** (a) Atomically resolved STM image (13nm x 13nm, $V_s=1$ mV, $I_t=1$ nA) of the graphene monolayer on Ru(0001). The dotted lines highlights the misalignment between the moiré and the atomic C rows. (b) Voltage dependence of the apparent topographic corrugation for many different experimental conditions (tip, tunnelling current, samples and temperatures). Contrast inversion is observed for bias voltages larger than +2.5V.