

Probing the distribution of crystallographic charges in graphene membranes : electron holography measurements and DFT modeling

Vittorio Morandi¹, Luca Ortolani¹, Cristian Degli Esposti Boschi¹, Raffaello Mazzaro^{1,2},
Giulio Paolo Veronese¹, Rita Rizzoli¹, Etienne Snoeck³

¹CNR-IMM Section of Bologna, via Gobetti 101, I-40129 Bologna, Italy

²Chemistry Dept. "G. Ciamician", Bologna University, via Selmi 2, I-40126 Bologna, Italy

³CNRS-CEMES, 29 Rue Jeanne Marvig, F-31055 Toulouse, France

morandi@bo.imm.cnr.it

Abstract

Graphene is a fascinating new material [1], and its peculiar properties hold promises for a great technological impact [2]. Around the Fermi energy, the band structure of graphene presents six conical points where the energy dispersion is perfectly linear in the momentum. For this reason, low energy excitations in graphene exhibit a charge conjugation between electrons and holes, and those carriers can be described as a 2D gas of effective massless Dirac fermions [3].

Unfortunately, upon stacking to form a Few-Graphenes-Crystal (FGC), the weak interlayer interaction could induce small valence charge redistribution in the crystal lattice, suppressing the linear dispersion in the band-structure [4]. In particular, in turbostratic FGCs, the interlayer charge redistribution, and hence the electronic structure of the crystal, depend on the rotation angle between the graphenes. For certain orientations, when the lattices are commensurable, graphenes electronically decouple, and the FGC behaves like an individual monolayer [5].

Using transmission electron holography [6], we investigated the redistribution of electronic crystal charges in a turbostratic FGC, showing that, when the lattice of adjacent layers becomes commensurable, each graphene within a turbostratic FGC contributes independently to the total phase shift of the electronic wave-front, with no visible interlayer effect, hence confirming that each layer is electronically decoupled [7].

In this paper we will show improved results achieved on Chemical Vapor Deposition (CVD) grown graphene membranes folded over itself (see Fig. 1), as reconstructed elsewhere [8], confirming the electronic decoupling of turbostratic commensurate stacked membranes (see Fig. 2). At the same time, the combination of the 3D reconstruction methodology reported in Ref. 8, together with the results reported here on the very same flake, opens interesting capabilities to a combined structural-electrical characterization of graphene membranes based on Transmission Electron Microscopy (TEM) interferometric techniques.

Moreover, we will show that electronic density and internal potential energy experienced by an electron can be computed by an ab-initio approach based on Density Functional Theory with high accuracy on single and multiple graphene layers. The computed phase-shift values are in very good agreement with the ones measured by electron holography (see Fig. 3), strengthening the perspectives of the application of the technique, as well as of the computational approach, to more complicated and interesting systems, like functionalized graphene layers.

References

- [1] K. Novoselov et al., *Science*, **306** (2004) 666.
- [2] A.K. Geim et al., *Nat. Mater.*, **6**, (2007) 183.
- [3] A.H.C. Neto et al., *Rev. Mod. Phys.*, **81**, (2009) 109.
- [4] S. Latil et al., *Phys. Rev. Lett.*, **97**, (2006) 036803.
- [5] J. Hass et al., *Phys. Rev. Lett.*, **100**, (2008) 125504.
- [6] H. Lichte et al., *Ann. Rev. Mat. Res.*, **37**, (2007) 539.
- [7] L. Ortolani et al., *Carbon*, **49**, (2011) 1423.
- [8] L. Ortolani et al., *Nano Lett.* **12**, (2012) 5207.

Figures

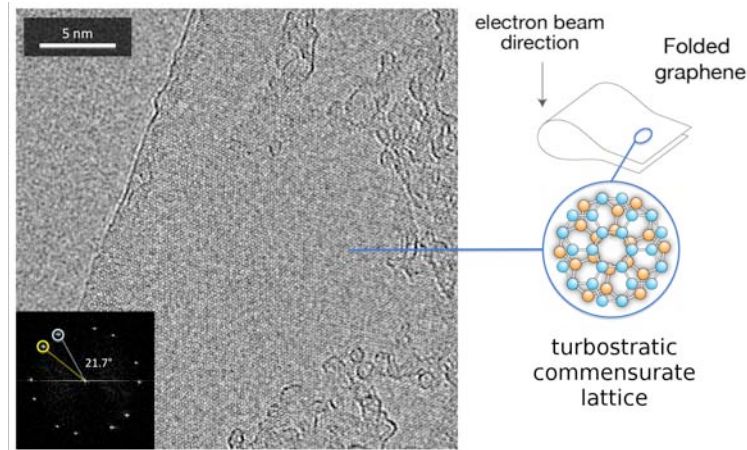


Figure 1: High resolution TEM image, obtained at 100 keV, showing a single CVD-grown graphene flake folded over itself, as reported in the scheme reported on the right (see Ref.8 for details). The two graphene lattice are rotated by 21.7, as shown by the FFT reported in the inset in the bottom left corner, making the stack turbostratic but commensurate.

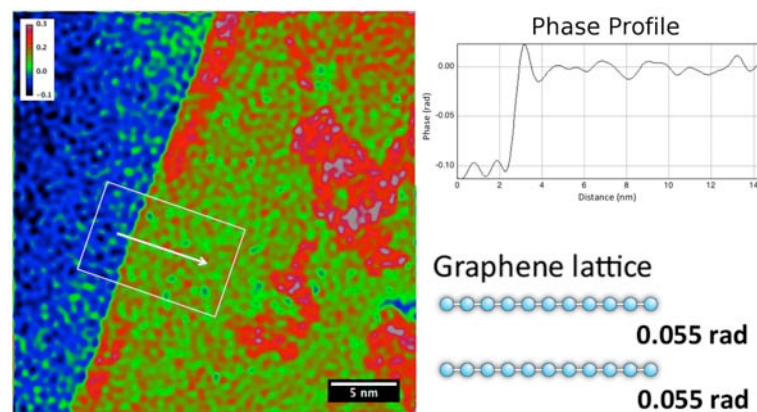


Figure 2: Reconstructed phase map for the folded flake of Fig.1. On the right (top) is reported the phase profile of the region highlighted by the white box, showing a total phase shift induced by the two graphenes traversed by the electron beam of 0.11 ± 0.01 rad., therefore each graphene plane shift the electron phase by 0.055 rad., as shown by the scheme on the bottom right corner.

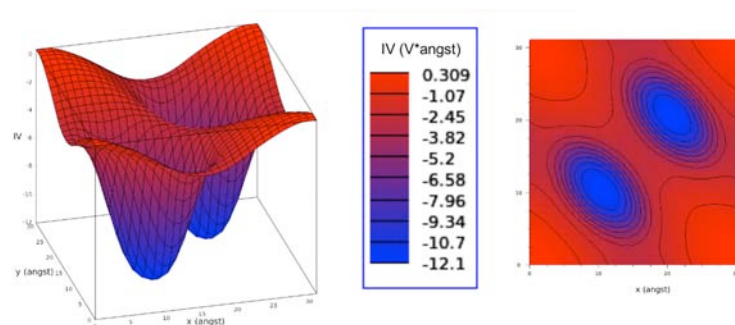


Figure 3: 3D representation (left) and contour map (right) of the integrated (along z-axis) calculated potential for a (single cell) single layer graphene. From the value of the integrated potential it is possible to calculate the phase shift for the given beam energy ($\Delta\phi = (\pi/\lambda)\langle IV \rangle$). The simulated internal potential should be convoluted to take into account the instrumental resolution. The calculated phase for each graphene layer is 0.06 rad.