

# A link between corrugation and thermal stability of epitaxial graphene

We report about a novel approach, based on the combined use of synchrotron radiation-based techniques and DFT calculations, to investigate the link between the corrugation of epitaxial graphene on Re(0001) and its thermal stability. Our results prove that graphene on Re(0001) is strongly corrugated, and point out an unambiguous relationship between corrugation and thermal stability. In fact, the high temperature disruption of the carbon network, which is mediated by diffusing vacancies, turns out to be more likely in the buckled, strongly interacting regions of the moiré cell.

In the last few years, epitaxial graphene has attracted a staggering interest in the fields of nanotechnology due to its outstanding properties. It is acknowledged that the strength of the graphene-substrate interaction and its thermally-induced modifications can deeply affect not only the electronic, chemical and geometrical structure of the carbon layer, but also its heat transport properties. In this respect, graphene corrugation plays a key role in determining the properties of the carbon sheet and its high temperature stability. In supported graphene, corrugation arises from the strain caused by the lattice mismatch between the carbon

network and the substrate, which leads to the formation of a moiré long-range periodic superstructure. Our work focuses on the investigation of the properties of epitaxial graphene on Re(0001). The combined use of core level photoelectron spectroscopy and Density Functional Theory (DFT) allowed us to pinpoint a clear-cut link between corrugation and thermal stability and to shed light on the microscopic mechanisms involved in the carbon layer breakup. The single-layer graphene sheet on Re(0001) is uniform and well-ordered on a large scale, as proved by the Low Energy Electron Microscopy (LEEM) images (Fig. 1b).

The C 1s core level spectrum of the graphene-covered surface is reported in Fig. 1d. The spectrum shows two main components, which is typically the hallmark of a strongly-interacting graphene/metal system. *Ab initio* DFT calculations performed on a (10×10)/(9×9) moiré unit cell (according to the stoichiometry suggested by electron diffraction measurements (Fig. 1a)) revealed that the carbon layer is strongly corrugated (Fig. 1c), with C-Re distances ranging between 2.1 and 3.8 Å and a buckling of ~1.6 Å. Interestingly, the computed C 1s core level binding energies of the 200 C atoms in the cell show a clear dependence on the C-Re distance: the closer a C atom is to the metal surface, the higher its Binding Energy (BE) is.

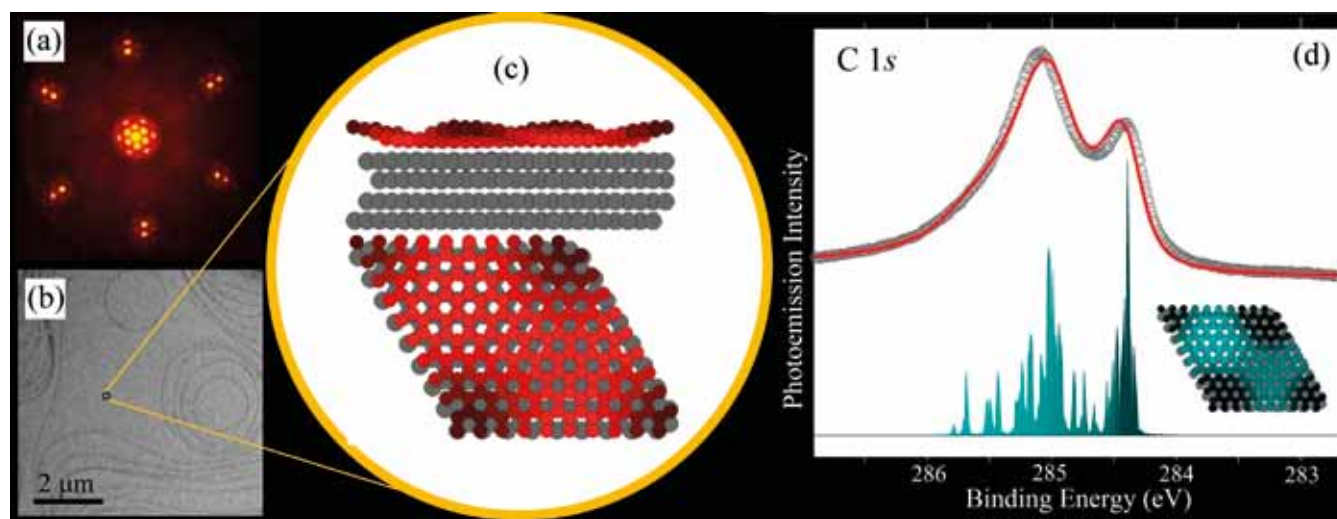


Figure 1. (a) LEED pattern of graphene/Re(0001). (b) LEEM image of the graphene-covered substrate, showing the long-range order of the C film on the surface. (c) Top and side views of the simulated structure (the color scale reflects the C-Re distance). (d) Comparison between the experimental (empty circles) and the simulated C 1s spectrum (solid line); below is shown the calculated spectral distribution originated by the 200 C atoms.

Starting from the calculated BE, we subsequently fitted the experimental spectrum to a convolution of 200 components: the agreement between experimental and theoretical data (Fig. 1d) proves that what lies beneath the two-peak shaped spectrum of graphene is actually an almost continuous distribution of the C-Re distances.

The determination of graphene corrugation provided us the starting point to address the issue of thermal stability.

Annealing graphene to high temperature (>1000 K) leads in the initial stage to a substantial

depletion of the high BE C 1s component, leaving the peak at lower BE almost unaffected (Fig. 2a,b). We performed a series of experiments at different temperatures, in order to monitor the evolution of the high BE C 1s component and measure its temperature-dependent decay rate. From the Arrhenius plot of these data, we estimated an effective activation barrier for C-C bond breakup of  $3.5 \pm 0.7$  eV. In order to shed light on the mechanisms of carbon layer disruption we used DFT. As it turned out, a realistic reaction path

involves the formation of carbon vacancies, which can diffuse at 1100 K from the weakly to the strongly interacting regions of the moiré cell (Fig. 2c). In the presence of diffusing vacancies, the overall barrier for C-C bond breaking in the strongly interacting parts amounts to 4 eV, which matches the experimentally estimated value.

In conclusion, our work highlighted a clear correlation between graphene corrugation and its thermal stability, a key achievement especially in sight of the high temperature applications of supported graphene.

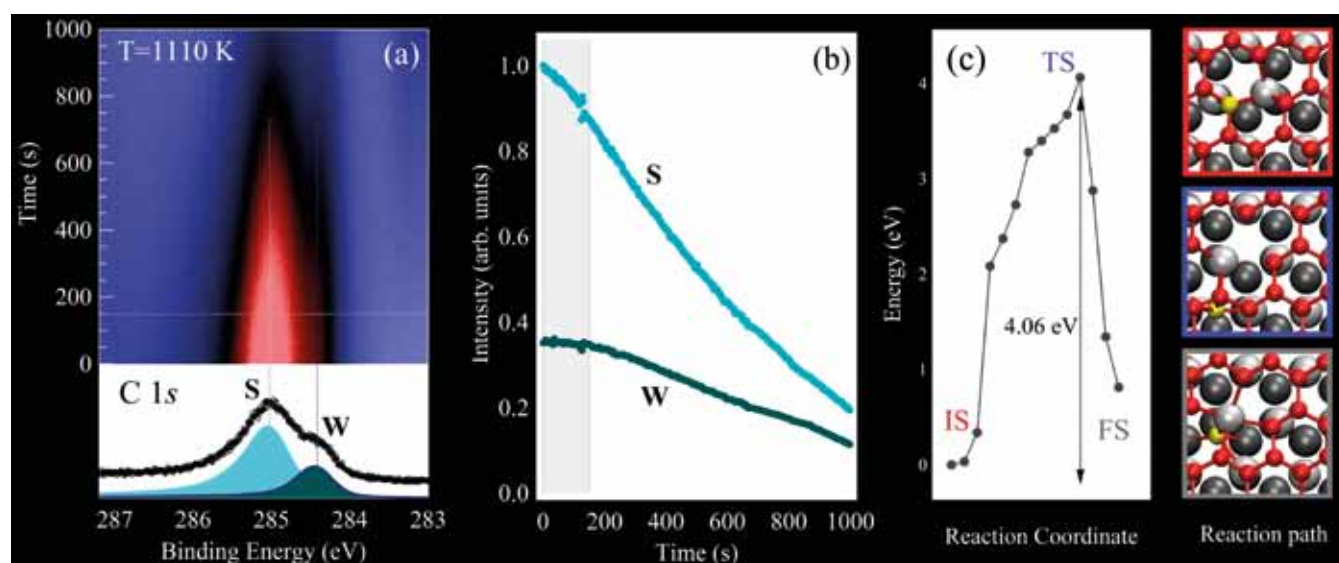


Figure 2. (a) Evolution of the C 1s spectrum during annealing of the graphene-covered substrate at 1100 K. (b) Intensity decay of the two C 1s core level components (S = strongly, W = weakly interacting) during the annealing. (c) Simulated reaction path for graphene layer breaking in the presence of diffusing vacancies. Initial-, Transition- and Final-states are reported.

## ORIGINAL PAPER

E. Miniussi, M. Pozzo, A. Baraldi, E. Vesselli, R.R. Zhan, G. Comelli, T.O. Menteş, M.A. Niño, A. Locatelli, S. Lizzit, and D. Alfè, *Phys. Rev. Lett.* **106**, 216101 (2011)

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