

Metal-Graphene Interaction Studied via Atomic Resolution Scanning Transmission Electron Microscopy

Q.M. Ramasse¹, R. Zan^{2,3}, U. Bangert² and K.S. Novoselov³

¹SuperSTEM Laboratory, STFC Daresbury, Keckwick Lane, Daresbury WA4 4AD, U.K.

²School of Materials, The University of Manchester, Manchester M13 9PL, U.K.

³School of Physics and Astronomy, The University of Manchester, Manchester M13 9PL, U.K.

Graphene, just one atom layer thick, has spurred a flurry of investigations into its structural properties, morphology and chemistry [1,2]. The interaction between metal atoms or clusters and graphene, in particular, is of great interest. For instance, a better understanding of the influence of metal contacts on the macroscopic electrical transport properties of graphene could have enormous repercussions on its practical applications in devices. To date, our knowledge about this interaction is mainly based on theoretical calculations. The preferred positions of foreign atoms on graphene have been calculated for a wide range of metals. So-called H-sites (centre of the hexagon) are predicted mainly for alkaline metals, such as K and Na, as well as for Ti and Fe; T-sites (directly on top of the carbon atoms) for Au, Cu, Ni, Sn and F, whereas Pt, Cr, Cl, S, O, N and P are expected to bind strongly to B sites, the bridge sites on top of carbon-carbon bonds, as illustrated on fig. 2d [3,4].

However, experimental exploration of the metal-graphene systems is still limited, with electron microscopy observations being practically non-existent. The recent advances in atom-by-atom chemical analysis using annular dark field scanning transmission electron microscopy [5] provide the perfect tool to confirm unambiguously the predicted positions of metal atoms in the hexagonal graphene structure. We apply here a combination of simultaneous Z-contrast and STEM bright field imaging at 60kV on a Nion UltraSTEM100 to a series of graphene membranes prepared by either mechanical cleavage or CVD growth, upon which varying thicknesses of Au, Fe, Cr or Ni were deposited [6]. Electron energy loss spectra confirmed independently the chemical nature of the observed ad-atoms and provided insight on the local changes in electronic structure.

This investigation of transition metals and gold on graphene revealed systematically that clean single-layer graphene surfaces do not retain any significant amount of atoms of these species (notably none in the case of gold). All metals, whether as isolated single atoms or as small agglomerated clusters, appear to reside almost exclusively in the patches of hydro-carbon surface contamination, ubiquitous even in the cleanest graphene membranes: fig. 1. This behaviour may have drastic consequences for macroscopic electrical transport properties in graphene, suggesting that charge transfer from mono-layer graphene into metal contacts proceeds, in the largest part, across a macromolecular layer (hydrocarbons). Individual Au and Fe atoms could be observed, however, on clean, much thicker few-layer graphene surfaces and found to reside on top of carbon atoms, and on top of C-C bonds, respectively. Chromium appears to interact more strongly with mono-layer graphene and was observed to catalyse the dissociation of C-C bonds under the electron beam, even at 60kV acceleration voltage: fig. 2. Bonding of singular Cr-atoms to graphene, possibly via lattice defects, could be a precursor for the high frequency nucleation of Cr-clusters, which, in contrast to Au, provide more continuous contact throughout the membrane, and hence the importance of role of a Cr-‘wetting layer’ in forming electrical Au-contacts on graphene can be understood.

References

- [1] K.S. Novoselov et al., *Science* 306, 666 (2004).
- [2] A.K. Geim and K.S. Novoselov, *Nature Materials* 6, 183 (2007).
- [3] K.T. Chan, et al., *Physical Review B* 77, 235430 (2008).
- [4] D.W. Boukhvalov and M.I. Katsnelson, *Applied Physics Letters* 95, 023109 (2009).
- [5] O.L. Krivanek et al., *Nature* 464, 572 (2010).
- [6] R. Zan et al., *NanoLetters*, Articles ASAP, DOI: 10.1021/nl103980h (2011).

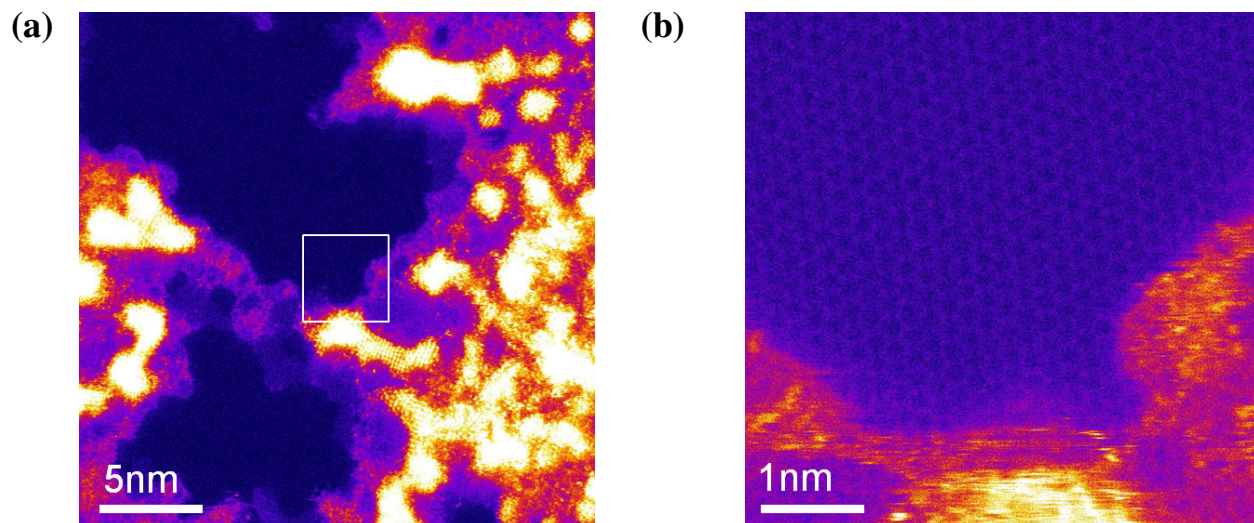


FIG. 1. (a) Raw HAADF image taken at 60kV of large clean monolayer graphene patches surrounded by hydrocarbon contamination, on top of which Ni clusters are aggregated (verified by EELS); (b) Raw HAADF close-up of the region highlighted in (a), showing how no Ni atoms can be found on pristine graphene.

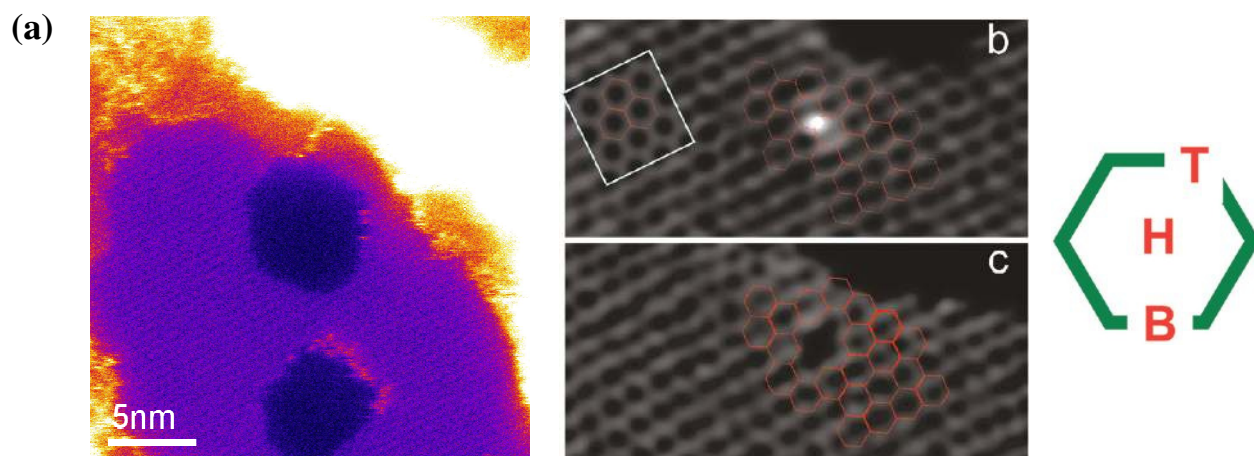


FIG. 2. (a) Raw HAADF image of monolayer graphene patch (dark gray) bordered by hydrocarbons (lighter gray). Cr atoms sit on the hydrocarbon contamination; a chain of Cr atoms can be seen moving from an area of Cr clusters and decorating the edges of holes as those are expanding. (b) Noise-filtered HAADF image of a Cr atom on monolayer graphene; an HAADF image simulation is shown in the inset. (c) Same area as in (b) after repeat scanning, revealing a divacancy where the Cr atom had been. Model structures are overlaid to show the sites of the defects. (d) Schematic of possible adatom sites.