Fine tuning of graphene-metal adhesion by surface alloying

E.Miniussi^{1,2}, D. Alfè^{3,4}, M. Pozzo^{3,4}, S. Günther⁵, P. Lacovig⁶, S. Lizzit⁶, R.Larciprete⁷, B. Santos Burgos ⁶, T.O. Menteş⁶, A. Locatelli⁶, and A. Baraldi^{1,2*}

¹Physics Department and CENMAT, University of Trieste, Via Valerio 2, I-34127 Trieste, Italy.

²IOM-CNR, Laboratorio TASC, S.S. 14 Km 163.5, I-34149 Trieste, Italy.

³Department of Earth Sciences, Department of Physics and Astronomy, TYC@UCL, and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, United Kingdom.

⁴IOM-CNR, DEMOCRITOS National Simulation Centre, I-34100 Trieste, Italy.

⁵Department Chemie, Tecnische Universität München, Lichtenbergststrasse 4, D-85748 München, Germany.

⁶Sincrotrone Trieste S.C.p.A., Strada Statale 14 Km 163.5, 34149 Trieste, Italy.

⁷CNR-Institute for Complex Systems, via Fosso del Cavaliere 100, I-00133 Roma, Italy.

*Correspondence to: <u>alessandro.baraldi@elettra.trieste.it</u>

Abstract

Controlling the adhesion between graphene and the metal support requires a thorough understanding of the physical mechanisms responsible for the different degrees of interaction. This is a key step towards the establishment of graphene-based technologies and for the development of graphene heterostuctures in novel electrical and mechanical devices.

It is well known, in fact, that the coupling between supported graphene (GR) and the substrate is responsible for a number of properties of GR-based materials, including the electromechanical properties, contact resistance, and ultrastrong adhesion as well as the electronic transport and heat dissipation in nanoelectronic devices. Several methods, such as the choice of the substrate (1,2), the intercalation of adspecies (2-6) or the creation of an oxide buffer layer (7), have been proven as a possible means of controlling the graphene-metal interaction, though not *ad libitum*. These approaches, in fact, do not enable to precisely control the graphene-substrate coupling strength and come with some significant drawbacks.

Here we show that bimetallic surface alloying provides a viable route for governing the interaction between graphene and metal through the selective choice of the elemental composition of the surface alloy. This concept is illustrated by characterizing the properties of graphene on a model PtRu surface alloy on Ru(0001), with Pt concentrations ranging from 0 to 50%. The specific choice of these two metal relies on the fact that Pt and Ru stand out as two model examples of weakly and strongly interacting substrates, respectively. In fact, GR develops just a weak coupling to Pt, as reflected in the almost flat morphology of the C layer. On the other hand, a strong bonding has been observed for GR/Ru(0001), leading to a significant GR corrugation.

Our study was conducted with a multidisciplinary approach, combining a range of experimental techniques –high energy resolution core level Photoemission Spectroscopy, Low Energy Electron Diffraction and Low Energy Electron Microscopy- and state-of-the-art DFT calculations Our results show that the progressive increase of the Pt content in the surface alloy leads to a gradual detachment of graphene from the substrate, which results from the modification of the carbon orbital hybridization promoted by Pt. Alloying is also found to affect the growth mode and the morphology of graphene, which is strongly corrugated on bare Ru but becomes flat at a Pt coverage of 50%.

Our work is the proof of concept that the employment of binary surface alloys, which are used in many areas of materials science, can provide an unprecedented tool to selectively manipulate the adhesion between GR and the metal.

The proposed method can be readily extended to a range supports, thus opening the way to a full tunability of the graphene-substrate interaction.

References

- [1] A.B. Preobrajenski, M.L. Ng, A.S. Vinogradov, N. Mårtensson, Phys. Rev. B 78, 073401 (2008).
- [2] E. Miniussi et al., Phys. Rev. Lett. 106, 216101 (2011).
- [3] C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov, U. Starke, Phys. Rev. Lett. 103, 246804 (2009).
- [4] A. Bostwick et al., Science 328, 999 (2010).
- [5] P. Sutter, J.T. Sadowski, E.A. Sutter, J. A. Chem. Soc. 132, 8175 (2010).
- [6] A.M. Shikin, G.V. Prudnikova, V. K. Adamchuk, F. Moresco, K.H. Rieder, Phys. Rev. B 62, 13202 (2000).
- [7] S. Lizzit et al., Nano Lett., 12, 4503 (2012).
- [8] J. Wintterlin, M.-L. Bocquet, Surf. Sci. 603, 1841 (2009).