

# Temperature-driven changes in morphology and electronic properties of CVD graphene on Ni

*L. L. Patera<sup>1,2\*</sup>, C. Africh<sup>2</sup>, C. Cepek<sup>2</sup>, G. Zamborlini<sup>1</sup>, T.O. Montes<sup>3</sup>, P. Genoni<sup>4</sup>, A. Sala<sup>3</sup>, A. Locatelli<sup>3</sup>, C. Dri<sup>1</sup>, G. Troiano<sup>3</sup>, F. Bianchini<sup>1</sup>, M. Peressi<sup>1</sup> and G. Comelli<sup>1,2</sup>*

<sup>1</sup> Department of Physics, University of Trieste, Via Valerio 2, I-34127 Trieste, Italy

<sup>2</sup> IOM-CNR Laboratorio TASC, S.S. 14 km 163.5 in AREA Science Park, Basovizza, I-34149 Trieste, Italy

<sup>3</sup> Elettra - Sincrotrone Trieste, S.S. 14 km 163.5 in AREA Science Park, Basovizza, I-34149 Trieste, Italy

<sup>4</sup> Department of Physics, Università degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy

\*patera@iom.cnr.it

Chemical vapour deposition (CVD) on metal surfaces is widely recognized as one of the most versatile and promising techniques for large scale production of high-quality graphene films [1]. A plethora of graphene properties can be controlled by tuning the interaction with the substrate. In this context, graphene grown on Ni represents an interesting model system: beside the valuable possibility to grow high-quality flakes at reasonably low temperature (< 600°C), it allows the study of phases with a different substrate coupling [2]. In my talk, I will illustrate how the graphene/Ni coupling can be modified in a reversible way by changing the sample temperature.

Firstly, I will report the tuning of the interaction between the graphene layer and the underlying Ni(111) substrate, from a strong doping to a free-standing behavior. By varying the temperature, it is possible to control the C solubility into Ni bulk, resulting in the reversible formation or dissolution of an interfacial nickel-carbide layer between Ni and rotated graphene domains [3]. Low Energy Electron Microscopy (LEEM), Photo Emission Electron Microscopy (PEEM) and microprobe angle resolved photoelectron spectroscopy ( $\mu$ -ARPES) measurements allowed us to characterize at the meso-scales the morphology of co-existing graphene phases and to probe their electronic structure, directly showing that the interfacial nickel-carbide layer effectively decouples graphene from the substrate (Figure 1).

In the second part, I will show how the temperature drives not only the electronic properties, but also the atomic structure of graphene edges on Ni. Scanning tunneling microscopy (STM) measurements in combination with density functional theory (DFT) allowed a complete characterization of the edge structures of graphene islands on Ni(111) both during growth and after cooling down to room temperature [4]. Fast STM measurements (250 ms/image), acquired during the growth at 470 °C, evidence that at this temperature the edges bend towards the substrate, due to the strong covalent bond with the underlying Ni atoms. When cooling to room temperature, H<sub>2</sub> dissociate on the Ni surface and H atoms bind to the terminal

C atoms, detaching the edge from the substrate. Upon heating to  $T > 300$  °C, *in-situ* STM experiments indicate that hydrogen desorbs, restoring the growth process (Figure 2).

Our results provide a complete picture on how on Ni(111) the temperature control can tune the graphene-metal coupling, thus tailoring its morphological and electronic properties.

1] K. S. Novoselov et al., Nature, 490 (2012) 192–200.

[2] L. L. Patera et al., ACS Nano. 7 (2013) 7901–7912.

[3] C. Africh et al., in preparation

[4] L. L. Patera et al., Nano Letters, 15, (2015) 56–62.

[5] This research was supported by MIUR through Progetto Strategico NFFA, the program PRIN 2010-2011 Project no. 2010N3T9M4 and the program “Progetto Premiale 2012” Project ABNANOTECH.

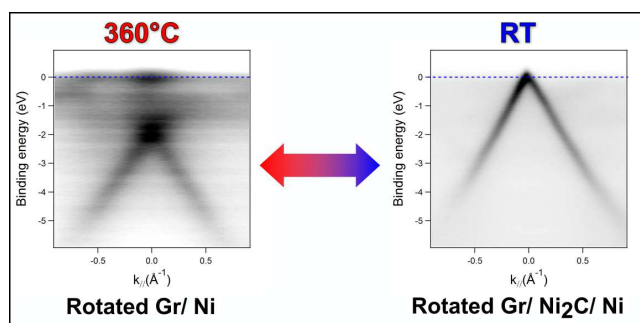


Figure 1:  $\mu$ -ARPES spectra acquired on rotated graphene flakes on Ni(111) reveal graphene Dirac cone changes.

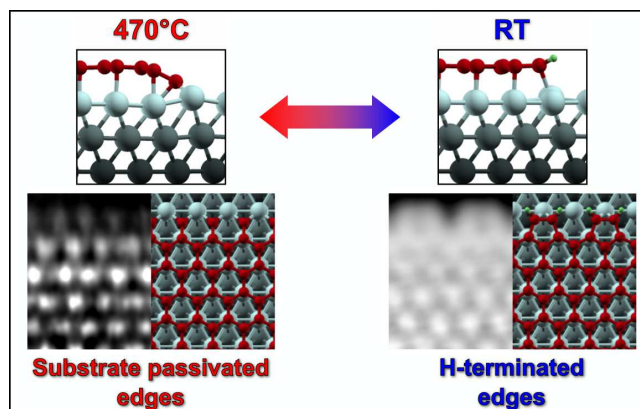


Figure 2: Stick and ball models and high-resolution STM images of graphene edges on Ni(111) imaged at different temperatures.