Micro-Raman investigation of the coupling to the metal substrate for graphene monolayers deposited by CVD on Cu foil

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Here we report on the results of a Raman micro-spectroscopy characterization of graphene layers grown on high purity copper foil, preliminarily cleaned and chemically reduced by a H_2 treatment. Graphene growth was obtained by exposition of the Cu foil at 1200 K to a mixture of hydrogen (0.5 mbar) and methane (0.5 mbar) for times between 2 and 4 minutes. After deposition, the samples were slowly cooled down to room temperature in an Ar atmosphere (0.1 mbar). The optical microscopy investigation of these samples indicated the presence of differently colored regions, ranging from “light” colored zones, having the color of native copper, to “dark” zones, of brownish color (see micrograph, left side bottom). Interestingly, a similar partition into two different types of regions of comparable size appears also to electron microscopy analysis. In all the “light” zones the Raman micro-analysis, under 633 nm excitation, reveals the occurrence of the graphene monolayer spectral features, of very weak intensity, with the 2D overtone always stronger than the G band. In all these ”light” zones the G band wavenumber is around 1600 cm^{-1}, while the 2D overtone is peaked at about 2660 cm^{-1} (spectrum, bottom center). On the other hand, the “dark” colored zones generally show a Raman spectrum much stronger, while the intensity ratio 2D/G appears even higher (spectrum, bottom left). Moreover, the two observed Raman features are appreciably down-shifted: the G band is peaked even below 1580 cm^{-1}, and the 2D overtone can be found at about 2630 cm^{-1}, under the same 633 nm excitation A tentative interpretation of these Raman findings can be proposed in terms of the different degree of coupling between the copper foil substrate and the graphene layers, due to a different separation distance [1]. The spectrum with weaker intensity and higher peak frequencies can be associated to a graphene monolayer close and tightly coupled to the metal surface, while the spectra with much stronger Raman intensity but showing lower peak frequencies are due to graphene monolayers far away from Cu surface and therefore less coupled to it. As additional experiment, a coupling change between graphene layer and Cu substrate has been locally induced by a proper laser irradiation, on micrometric regions having the laser focus dimensions. In fact, both optical image and Raman spectral features found in these laser-induced dark spots are quite similar to those observed in the film after the post-deposition cooling.

References: [1] Q. Zhou, S. Coh, M.L. Cohen, S.G. Louie, A. Zettl, Phys Rev B **88** (2013), 235431.