Interference and Oxidation Processes in Graphene on Copper

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Contrary to initial expectative, graphene does not prevent the oxidation of copper; it actually favors the formation of copper oxide (1). Many aspects remain unclear in this oxidation process as whether the mechanism depends on the copper characteristics, the properties of the formed oxides or its long time evolution. Moreover, though an enhancement of the graphene Raman signal has already been reported in this system (2), it has not been analyzed in detail since a characterization of the oxide is lacking.

We report, analyze and simulate the Raman enhancement effect, up to 60 fold, of graphene/copper system after long oxidation time under ambient conditions. The simulations provide the possibility to obtain the copper oxide thickness from the ratio of the Cu_2O to graphene Raman intensities. For this study, we chose three kinds of copper as the catalytic substrate for graphene synthesis, a copper film deposited by magnetron sputtering on fused silica substrates and two commercial copper foils, a non-oxygen-free copper and an OFHC copper. The graphene growth was performed at 910 ºC in a low pressure chemical vapor deposition (CVD) system.

A Cu foil was annealed at 250 ºC to form the different copper oxides to be used as reference in order to identify and characterize the oxides formed with time in ambient conditions in the Cu foil after graphene growth. The data obtained with synchrotron X-ray diffraction from the oxidized Cu foil reveal the peaks corresponding to metallic copper and two phases of copper oxide, namely CuO and Cu_2O with a clear prevalence of the second one. The Cu_2O is seen in optical images with different colors depending on the Cu_2O film thickness.

The oxidation of the graphene/Cu foil samples was monitored during 12 months by micro-Raman Spectroscopy. The copper oxide formed after long time at ambient conditions is found to be exclusively Cu_2O according to both Raman spectra and synchrotron x-ray diffraction. The CuO can also be formed by annealing in adequate conditions a Cu foil but such oxide is not detected in Cu with graphene even after a severe oxidizing treatment.

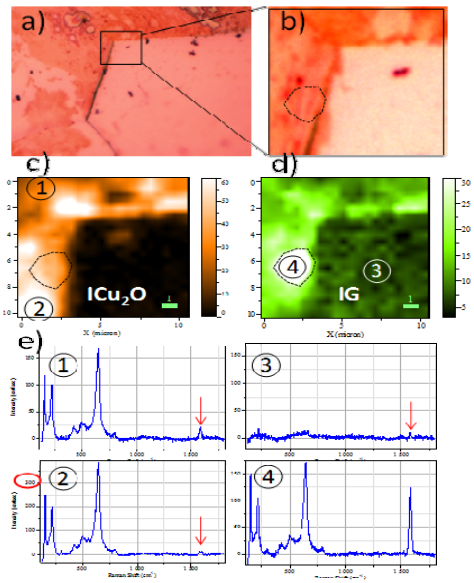

Figure 1: a) Optical image of the graphene/Cu foil surface after 12 months at ambient conditions; b) 10 µm x 10 µm area of the same image; c) and d) Raman images of the 640 cm^{-1} Cu_2O mode and of graphene G peak in the same area as b). e) Raman spectra at the indicated points in c) and d).

A clear correlation between the enhancement of the graphene Raman intensity and the presence of Cu_2O oxide (low frequency peaks) is presented in **Figure 1**. This correlation can be observed for excitation at or above 488 nm when Raman effect in Cu_2O is resonant. At 514 nm the signal is much weaker indicating that the gap of the formed copper oxide film lies in the 2.41 to 2.54 eV range, above that of bulk Cu_2O (2.27 eV). The modifications of the

crystalline structure in the oxide thin layer developed on the Cu surface are most probably at the origin of the gap energy increase. These modifications may have an impact on the refractive index values, which precise knowledge is crucial when performing the simulations of the interference processes occurring in the graphene/Cu_2O/Cu system. The enhancement of graphene G and 2D peaks is evident at all excitations and after our calculations reaches a value of 9 for the G peak. Some correlation between the oxide thickness and the width of the G band can be observed.

In these systems, we have identified regions (see region marked with 4 and its corresponding spectrum in **Figure 1**) where the enhancement factor is as high as 60. This value is well above the calculated one for interference in the graphene/Cu_2O/Cu system. We attribute this large enhancement factor to the interference in a system such as graphene/Air/Cu where our calculations yield enhancement factors as high as 100 depending on the width of the air gap between Cu and graphene. In these regions a drastic reduction of the widths of the G and 2D bands is observed, suggesting that the situation is similar to that of suspended graphene.

References

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