In situ electron microscopy observations of graphene growth from metal films

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Graphene can be obtained by different methods including mechanical exfoliation of graphite, surface decomposition of silicon carbide, chemical vapor deposition (CVD) of carbon-containing gases on suitable substrates, different chemical methods, or carbon segregation from solid solutions. For methods involving growth on metals, as in CVD and carbon segregation, the underlying principle implies the transformation of carbon from gas or solid solution to graphene. Therefore, in order to fully understand graphene growth we must consider how and under what conditions such transformations occur.

Here we show that single-and few layers graphene can be grown by annealing metal films supported on amorphous carbon films, the latter acting as the carbon source. The process involves the uptake of carbon by the metal films followed by graphene nucleation and growth on the metal surfaces. The process has been carried out in a Transmission Electron Microscope (TEM, JEOL 2100F) allowing for image acquisition with high spatial resolution during the growth process at high temperature [1].

Polycrystalline films with thicknesses and crystallite sizes of ~ 10 nm of Fe, Co or Ni were deposited over 20 nm thick amorphous carbon films in a cathodic sputtering chamber. The specimens where then heated in vacuum inside the TEM (~ 10^{-5} Pa) up to temperatures of 750°C while the induced transformations were observed. As the temperature was raised, ripening of the metal crystals occurred, leaving uncovered areas of the carbon film. Above ~ 600°C, the uncovered carbon film showed domains of single- and few layers graphene, proving that that the amorphous carbon had undergone a transformation to graphene which was catalyzed by the metal. A further increase of temperature led to ongoing ripening of the metal and areas of ~ 0.01-0.02 μm^2 of free-standing graphene were obtained (see figure, top).

During this work a second method to visualize the formation of graphene *in situ* has been developed. We have found (work in preparation) that by electron irradiation of the interfaces between the metal crystals and the amorphous carbon film at high temperature, it is possible to induce the migration of the metal atoms towards the amorphous carbon, and so to induce growth of a metal lamella on the carbon film. The inherent instability of such a thin lamella of ~ 20 nm width and tens of nanometers in length leads to a sudden retraction of the lamella towards the crystal from where it has grown after a certain length has been exceeded or after a further increase in temperature. Again, the uncovered area reveals graphene domains (see figure, bottom).

We put forward an experimental approach based on the solid-state transformation of amorphous carbon to graphene by a catalytically active metal. In addition, we show that it is possible to “pattern” graphene areas of 10-20 nm in width by making use of the interaction between metals and amorphous carbon under an electron beam. The process has been carried out in a Transmission Electron Microscope (TEM) which allows for *in situ* recordings of the complete growth process, involving the transformation of amorphous carbon into graphene via a catalytically active metal.

References

[1] Julio A. Rodríguez-Manzo, Cuong Pham-Huu and Florian Banhart, ACS Nano, (2011), accepted for publication.

Figure

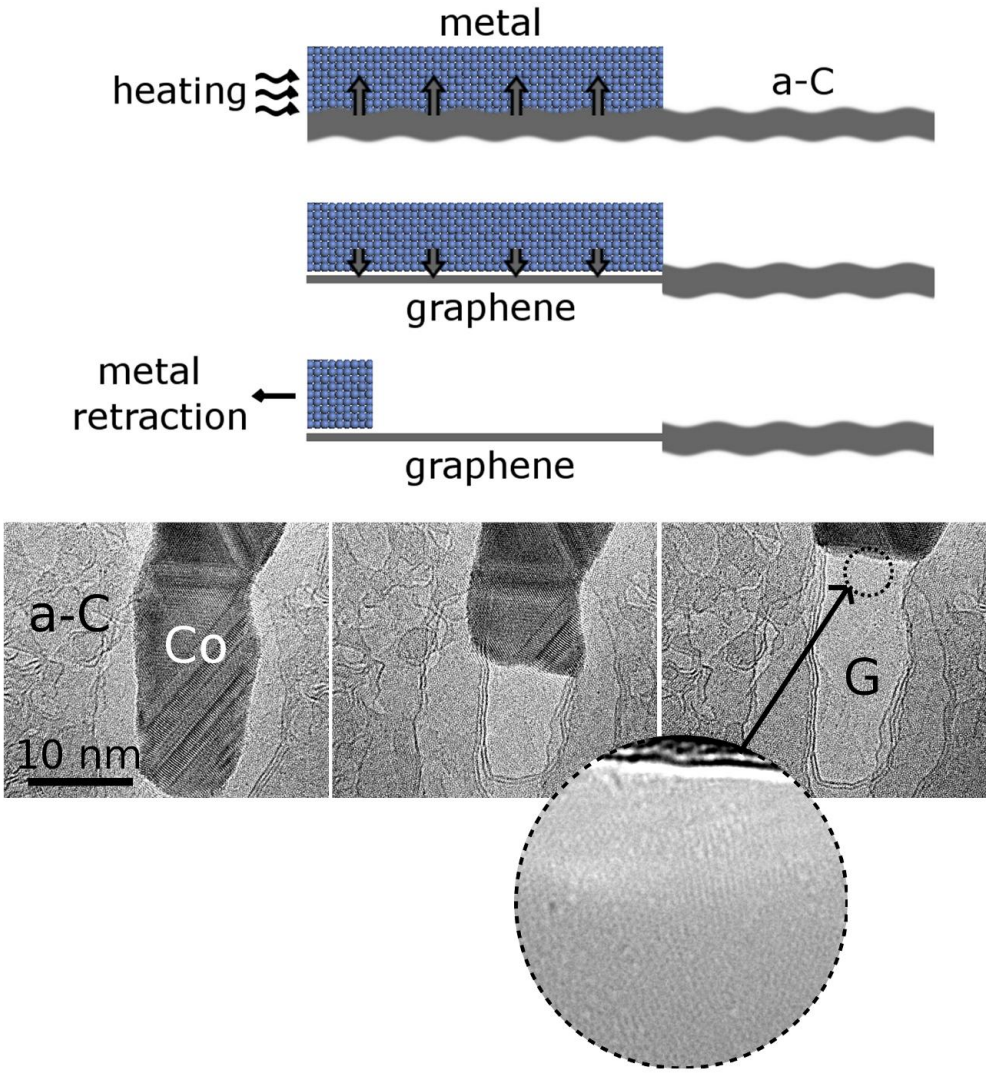

Figure 1: (Top) Scheme of graphene growth from a metal- carbon bilayer system. Carbon uptake in the metal is induced by an increase in temperature. This process is followed by graphene growth at the metal surface originally in contact with the amorphous carbon. Finally, metal retraction driven by ripening uncovers graphene domains. (Bottom, left to right) Top view of metal retraction from a graphene lamella. The inset shows how the amorphous carbon is graphitized next to the metal catalyst. Labels a-C, Co and G stand for amorphous-carbon, cobalt and graphene, respectively.