HRTEM STUDY OF GRAPHENE GROWTH MECHANISM ON NICKEL THIN FILMS

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As the study of the physical and chemical properties of graphene widens, potential applications of this material emerge in very different domains, from microelectronic devices to large scale flexible electronics and biological sensing [1, 2]. As a consequence, the need large scale production process of graphene raised. To date, CVD growth on transition metals appears as the most promising pathway to overcome this technological barrier [3]. In the case of the use of nickel as catalyst, where carbon has a significant solubility, such a growth process includes at least two elementary steps: (1) carbon diffusion into the metal, and (2) graphene precipitation at the surface. Here, we use transmission electron microscopy to analyze the precipitation process in detail. In order to precisely control the carbon content in the metal layer, as well as the uniformity of its in-plane distribution, we introduce and dissolve carbon in nickel thin films by ion implantation and annealing at 725^oC or 900^oC [4].

200 nm thin Ni films are e-beam evaporated on silicon substrates. These samples are then implanted with carbon ions at a 80 keV. This implantation energy is calculated in order to assure that all the implanted carbon is in the nickel film. Implanted doses correspond to integer multiple of the carbon density of a graphene monolayer (3.8×1015 C atoms/cm^2). Doses used in this study range from 8x1015 to 32x1015 C atoms/cm^2. The samples were then annealed under vaccum ($\sim10?5$ mbar) using different starting and stopping temperatures . Graphene formed on top of the Ni film were characterized by Raman spectroscopy before the Ni film was etched away and the graphene film was transferred on TEM grid. Thin cross-sections of the samples with the supporting substrate, the nickel film and the graphene film were also fabricated.

During the heat treatment, most of the carbon appears to join grain boundaries and then through the latter, diffuse towards the surface, from which graphene layers then grow laterally on top of the Ni films (Figure 1). The overall process leads to non-uniform distributions of relatively large single crystals of graphite.

In parallel, we also observe continuous layers of nanocrystalline graphene, probably the result of direct surface segregation. We propose a scenario for these two phenomena (Figure 2) and routes for improving one or the other.
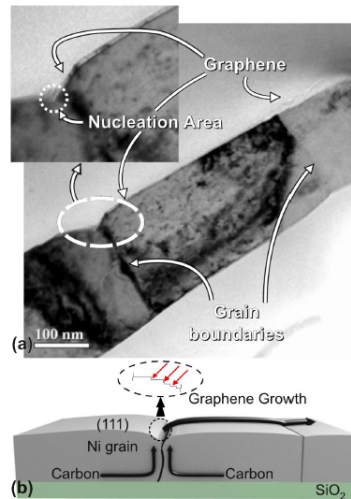

Figure 1: TEM cross-section of graphene or graphite on nickel grains. Sample implanted with the 4-GL dose, annealed at 900°C for 30 min, slowly cooled to 750°C, then quenched. (a) TEM image showing the connection between a nickel grain boundary and graphene layers at the surface of the film. (b) Schematic representation of the nucleation and growth mechanism of graphene over nickel. Nucleation preferentially occurs in regions of high curvature of the (111) grain surface, where the step concentration is high (red arrows in the inset of b), and graphene subsequently grows parallel to the grain surface.
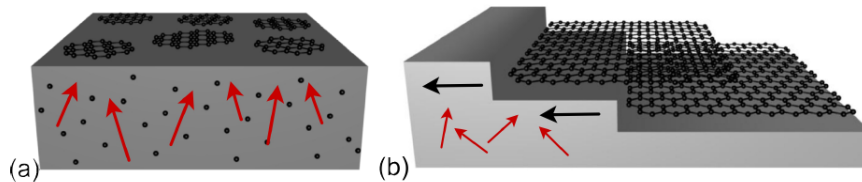

Figure 2: Two types of growth processes starting from carbon atoms dissolved into Ni: (a) growth of nanocrystalline graphene after surface segregation of carbon atoms, (b) lateral growth of high quality graphene.

References [1] Soldano, C. et al. Carbon. 48 (2010) 2127-2150.
[2] Geim, A. K. Science. 324 (2009) 1530-4.
[3] Bae, S. et al. Nature Nanotechnology. 5 (2010) 574-578.
[4] Baraton, L. et al. Nanotechnology. 22 (2011) 085601.