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Different mechanisms of graphenewall nucleation on Fe and Ni particles

J.-L. Maurice,*,1 Z.B. He,1,2 and C.S. Cojocaru1

1Laboratoire de Physique des Interfaces et Couches Minces, LPICM, UMR 7647, CNRS-Ecole Polytechnique, Route de Saclay, 91128 Palaiseau Cedex, France
2Now at EMAT, University of Antwerp, Groenenborgerlaan 171, Antwerp B-2020, Belgium
*corresponding author: jean-luc.maurice@polytechnique.edu

Field-emission devices [1] require that the potential drop be devoted to emission so that the resistivity of the tips must be as low as possible. However, in the case of carbon nanotubes or nanofibres (CNTs and CNFs), the tips are made of graphene layers. In graphite, the resistivity is four orders of magnitude lower in the graphene planes than perpendicular to the planes. Thus real nanotubes – where graphene planes are parallel to the tube axis – are a priori much better fitted to emission than nanofibres – where the graphene planes are at an angle (in that case, the tubular shape is obtained by the stacking of truncated cones, see Fig. 1). Such nano-objects are made by direct-current plasma-enhanced chemical vapour deposition (dcPECVD) with metal nanoparticle catalysts on top. In given growth conditions (see ref. [2]), we have found that iron particles allowed one to obtain real nanotubes [2], while nickel ones did not [3] (Fig. 1). The goal of the present study is to understand how Fe particles would favour real CNT growth while Ni ones would not.

In situ observation of the growth of nanotubes has already been successful for deciphering certain CNT growth mechanisms [4-7]. In the present case, we used in situ annealing of dcPECVD grown CNFs, in a FEI CM 30 working at 300 keV, with a Gatan heating stage, in the temperature range 500-800°C. The nanofibres were deposited on holey carbon grids by scratching the original substrate.

We first explored annealing under electron irradiation as in ref. [6]. We obtained effects with Ni (see Fig. 2a), but not with Fe. We then applied an amorphization treatment to the Fe-CNFs [8], and used amorphous matter to feed the metal nanoparticle with carbon atoms (Fig. 2b). In their as-grown state, both types of nano-objects have graphene planes essentially parallel to the particle surface: the cone angle of the graphene layers is the cone angle of the metal particle (θ in Fig. 1). In the case of Ni, creep of the metal particle brings at places a geometry where graphene planes are almost perpendicular to the local Ni surface: at those spots, the graphene layers get dissolved into the Ni (Fig. 2a, middle). Then, new graphene planes are generated parallel to the surface at another spot (Fig. 2a, right). There is no such thing with Fe: we see no evolution of the particle, unless we start from an amorphized CNF (Fig. 2b). In that case, the amorphous carbon is easily dissolved into the Fe. These dissolved carbon atoms get out of the particle in the form of a new nanotube, where nucleation takes place – partly at least – perpendicular to the Fe surface.

This experiment seems to show that the chemical reactivities at the interface between the metals and end-on graphene planes are quite different in Fe and Ni, which may play a role in the fact that we were able to obtain real nanotubes with Fe and not with Ni.

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Fig. 1. Typical shapes of a carbon nanofibre (left) and of a multiwall carbon nanotube (right). The cone angle $\theta$ has a finite value in CNFs (right) and is 0 in CNTs. The micrograph shows a nanotube obtained at 720°C with a Fe particle on top.

Fig. 2. In situ annealing of CNFs grown with metal on top. At the beginning, graphite layers are parallel to the metal surface. (a) Ni, 750°C: graphene planes that get an angle with the Ni surface get dissolved into the metal (middle), while there is nucleation of new planes parallel to the metal surface (right). (b) Nucleation of a carbon nanotube at the surface of an iron particle by in situ annealing of an amorphized nano fibre at 650°C: graphene planes are extruded from the particle, with a component of growth perpendicular to the local metal surface.