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Citation: *Appl. Phys. Lett.* **85**, 5376 (2004); doi: 10.1063/1.1829381

View online: <http://dx.doi.org/10.1063/1.1829381>

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Catalyst consumption during growth of carbon nanofilaments on Pd seeds

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(Received 9 February 2004; accepted 7 October 2004)

Carbon nanofilaments are produced at 600 °C by catalytic decomposition of acetylene on palladium nanoparticles. We observe that nanofilament length is limited to a few hundreds of nm when the size of Pd germs is less than 10 nm, possibly due to the incorporation of Pd atoms during growth. We propose a growth model, supported by first-principles calculations which show that Pd atoms are stable when adsorbed on graphene and that a charge transfer occurs, modifying significantly the electronic properties. © 2004 American Institute of Physics. [DOI: 10.1063/1.1829381]

Understanding the growth mechanism of carbon nanostructures is of primary importance for a number of applications. Catalytic growth from metallic nanoparticles is used in many processes to produce different kinds of nanotubes or filaments,¹ which could serve as field-emission sources, conducting fillers in polymers, or reinforcing elements in composites. The catalytic chemical vapor deposition (CCVD) method has been used to synthesize carbon phases since the works of Baker *et al.*² Pyrolytic graphene layers can be grown on flat transition metal surfaces, whereas filaments can be produced from particles of the same metals. When the particle size is limited to a few tens of nanometers, nanofilaments or nanotubes can be synthesized, their morphology being dependent on the experimental conditions, i.e., gas nature and flux, metallic element (usually Ni, Co, Fe, and here Pd,^{3–6}) substrate, and temperature. It seems well established that the diameter of the metallic growth germs determines the average diameter of the nanofilaments, and a number of observations suggest that the crystallography and shape of the germs influence the filament microtexture.⁴ The most popular theory of CCVD growth relies on the archetypal model of Baker and Harris,² which states that carbon atoms, produced at the surface of the catalytic particle by decomposition of the gas, are dissolved as interstitials in the metal lattice of the particle. After reaching a critical concentration, a graphene layer forms at the particle surface, initiating filament growth. In this view, the term catalytic is often used to evoke the role of metallic particles, which are presumed to be unaffected by the filament growth and to serve only as a buffer for the diffusing carbon atoms (beyond their catalytic role for gas decomposition). Growth can continue as long as carbon atoms are provided to the catalytic particle. In such a model, metal atoms are implicitly supposed to diffuse very slowly compared to carbon atoms, so that pure carbon filaments are formed out of the metallic germs. Besides this model and numerous works supporting it, we have found a number of reports stating that metallic germs go through a solid–liquid transition before growth starts, which would ex-

plain why metal particles are often found inside the nanofilament core.⁷ This transition would occur at a temperature much lower than the bulk melting point, suggesting nanosize effects. However, no direct experimental proof of this transition have been reported. Surface melting above 600 °C, leading to coalescence, has been reported by Wang *et al.* for 8 nm diameter Pt nanoclusters.⁸

In this work, isolated, nm-diameter palladium clusters are deposited by plasma sputtering on Si substrates covered with SiO₂ native oxide (see details in Ref. 9). We use such substrates to grow small-diameter nanofilaments at low temperatures (≤ 600 °C) by catalytic decomposition of acetylene. We find that nanofilament diameters are never as small as expected based on the diameters of pristine Pd clusters. In fact, fast diffusion of metal atoms occurs even at a few hundred degrees, which increases the diameter of the Pd nanoparticles.⁹ Transmission electron microscopy (TEM) observations show that, in some cases, large Pd inclusions (larger than the pristine clusters) are found inside the filament core, which shows that atomic diffusion is very fast indeed. Annealing the substrates in N₂ at the growth temperature shows that a bimodal cluster distribution forms in a few minutes, due to coarsening. Bigger particles keep growing at the expense of the smaller ones.¹⁰ Starting from nm-diameter clusters, we are able to grow 40 nm-diameter filaments after annealing. The correlation between particle and filament diameters can be established once annealing is taken into account.

In a series of experiments, a small amount of Pd ($\approx 10^{14}$ atoms/cm²) is deposited at the surface, in order to produce Pd nanoparticles with an average diameter less than 10 nm once coarsening is taken into account. After growth on these substrates, we observe that filament length remains limited to a few hundreds of nanometers, whatever the deposition time. This is observed by scanning electron microscopy (SEM) on substrates (Fig. 1), and TEM after scratching the deposit (Fig. 2). This experimental fact can be explained by the rapid poisoning of the catalyst. We suggest here that in fact the Pd nanoparticle is partly consumed during growth, so that the catalytic activity of the particles is reduced, as their active surface decreases during root growth,

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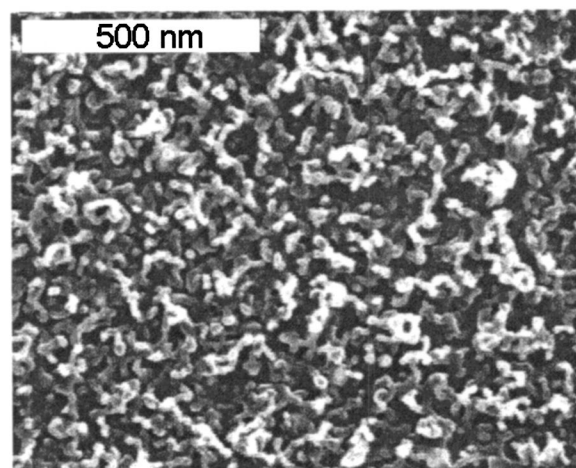


FIG. 1. SEM picture showing short filaments grown from Pd nanoparticles.

as illustrated in Fig. 3. Two mechanisms can contribute to the catalyst consumption: First, the adsorption of Pd atoms at the graphene surface, which is an energetically favorable situation as shown below by first-principles calculations; and second, the trapping of small Pd clusters escaping from the germ surface during growth (see Fig. 3). It is to be noted that the average diameter of the Pd nanoparticles observed by TEM after growth is much smaller than the diameter of the nanofilaments, which also supports our growth model. Such a model supposes a quasi-liquid state of the particle during growth, or a very fast diffusion at the surface. The presence of Pd impurities is supported by electron spin resonance (ESR) experiments and first-principles calculations.

Unlike Co, Ni, or Fe which are ferromagnetic, Pd is a paramagnetic metal. This allows us to perform ESR measurements on the as-grown samples, without the perturbation of a ferromagnetic signal. Pure graphitic materials show a sharp intense line, owing to the weak spin-orbit coupling with carbon atoms. Arc-grown multiwall carbon nanotubes exhibit a signal similar to that of graphite. In contrast, our *herringbone* or *stacked-cup* shaped samples do not show a resonance, which indicates that the spin-lattice relaxation time is drastically decreased. A disordered herringbone structure precludes the ballistic transmission of charge and spin, which occurs in single-shell nanotubes, since transport must proceed by hopping from one cup to another. The absence of an ESR signal must therefore be the result of relaxation on

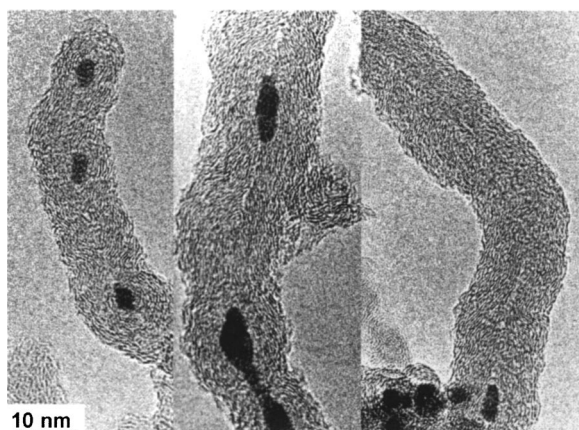


FIG. 2. TEM pictures of short filaments. Catalyst nanoparticles are seen encapsulated in graphene layers.

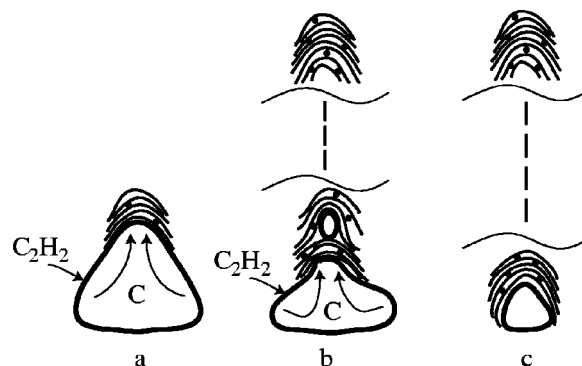


FIG. 3. Sketch of nanofilament growth. Dots represent Pd atoms adsorbed on graphene. Germ size decreases during growth due to incorporation of Pd in the carbon network.

Pd impurities incorporated in the filaments. As shown below, this assumption is supported by calculations of the electronic states of model graphene-Pd systems. Note that the presence of Fe impurities in nanofilaments have been observed recently by Kiselev *et al.*¹¹ using electron energy loss spectroscopy.

In order to assess the stability of Pd in a carbon network, a crucial ingredient of our growth model, we have performed first-principles calculations on several graphitic systems containing Pd atoms. The simulation was carried out with the ABINIT package,¹² using norm-conserving pseudo-potentials,¹³ and a plane-wave basis set with a maximal cutoff energy of 50 Ha. The atomic positions were relaxed, until the atomic displacements were inferior to 0.0005 nm. The charge^{14,15} on the adsorbed Pd atom is +0.13, and is transferred to the first and second neighbors on the graphene sheet.

The first model considered is a planar sheet of graphene (60 atoms), with a palladium atom either adsorbed at the center of a hexagon, or substituted in the carbon lattice. The substituted atom buckles severely out of the plane by 0.15 nm, whereas the adsorbed Pd sits 0.19 nm above the plane. In the first case, the C—Pd bond length is 0.20 nm, and in the second 0.24 nm, indicating a much weaker bond. Both structures were tested in spin-polarized initial configurations, but neither demonstrates a magnetic moment. The substitutional graphite is unstable by −2.5 eV, whereas adsorbed Pd is stabilized by 1.1 eV with respect to separated graphene and metallic Pd. This suggests the strong affinity of the carbon lattice for Pd atoms, which can stay wedged between graphite sheets in order to maximize their adsorption energy.

The curvature-induced hybridization of the π and σ orbitals of graphite can change both electronic structure and reactivity. In order to check this effect, we impose a wavelike geometry to the sheet, where the curvature at the crest of the wave corresponds to the radius of a (10,10) nanotube (1.4 nm). The distance between periodic images above is increased to 1 nm to render their interaction negligible. Only the Pd and its first- and second-nearest neighbors are allowed to relax. Binding is enhanced, the positions under and over the wave being stabilized by 2.3 and 2.4 eV, respectively, and the substituted atom being unstable by −1.8 eV (these energies refer to a wave of carbon, to account for the strain energy).

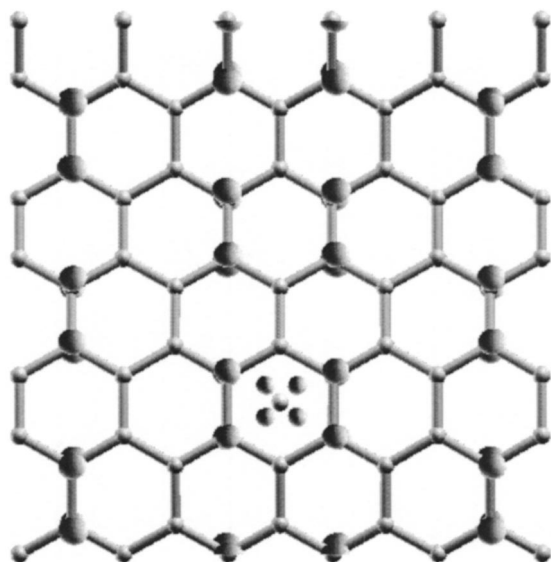


FIG. 4. Pd atom adsorbed on top of a wave of graphene. Electron isodensity surface for one eigenstate 0.38 eV below the Fermi level.

Finally, we consider the effect of adsorbed palladium on the electronic states of the graphene wave. The states near the Fermi energy are composed of atomic d states on the Pd, hybridized with carbon π states. As can be seen in Fig. 4, electronic states contain concentrations of electrons on Pd and on the whole carbon network. The overlap between these orbitals and the π -conduction electrons will be very strong. Even though the Pd atom is not in a ferromagnetic state, electron spins will scatter easily on the heavy atom, as it presents a strong spin-orbit interaction, which is a usual relaxation mechanism for conduction electron spins.¹⁶ These results confirm that the absence of an ESR line can be explained by the presence of Pd atoms, incorporated in the nanofilament during growth.

The various models proposed so far in literature for filament growth do not include modification and consumption of the metallic germs by atomic diffusion and trapping. Although it is certainly a second-order effect, we suggest that a realistic model should take this effect into account. The particle structure modification may have important conse-

quences on the growth (structural defects in the tube can occur due to this effect), particularly for nm-size germs.

One of the authors (J.C.C.) acknowledges the National Fund for Scientific Research (FNRS) of Belgium for financial support. This work was carried out within the framework of the European COMEL-CAN project (No. HPRN-CT-2000-00128), the Belgian Program on Inter-university Attraction Poles (PAI5/1/1), and the Action de Recherche Concertée of the Communauté Française de Belgique. Another author (J. P. S.) acknowledges T. Cacciaguerra, C. Andreazza (CRMD), and A. Richard (Centre de Microscopie Electronique de l'Université d'Orléans). M. Castignolles and A. Loiseau are thanked for fruitful discussions on CVD growth.

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