

CVD-based techniques for the synthesis of nanographites and nanodiamonds

V. GUGLIELMOTTI^{(1)(*)}, S. ORLANDUCCI⁽²⁾, E. TAMBURRI⁽²⁾, I. CIANCHETTA⁽¹⁾, S. GAY⁽²⁾, T. LAVECCHIA⁽¹⁾⁽²⁾, G. REINA⁽¹⁾⁽²⁾, D. PASSERI⁽³⁾, M. ROSSI⁽¹⁾⁽³⁾ and M. L. TERRANOVA⁽¹⁾⁽²⁾

⁽¹⁾ *NanoShare srl - via G. Peroni, 386, 00131 Rome, Italy*

⁽²⁾ *MINIMA Lab and Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata - Via della Ricerca Scientifica, 00133 Rome, Italy*

⁽³⁾ *Dipartimento di Scienze di Base e Applicate per l'Ingegneria, Università di Roma Sapienza via A. Scarpa, 14, 00161, Rome, Italy*

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Summary. — We report about some Chemical Vapor Deposition approaches used to produce a variety of C- sp^2 and C- sp^3 crystalline nanostructures. The methodologies developed in our laboratories provide custom-made solutions for the fabrication of specific carbon nanomaterials with properties tailored for applications in the field of nanotechnology.

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PACS 81.15.Gh – Chemical Vapor Deposition.

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1. – Introduction

The recent explosion of novel carbon-based nanomaterials make nowadays the carbon phase diagram, which traditionally includes only diamond and graphite, by far inadequate to describe the richness of the carbon solid-state forms [1]. On the other hand, the actual and envisaged applications of nanographitic materials and nanodiamonds in many and different technological fields, stimulated the demand for efficient fabrication routes with an increasing control of deposition procedures [2]. Tailored C nanostructures are nowadays designed and obtained mainly using chemical vapour deposition (CVD)-based apparatuses, where kinetically driven processes promote the creation of novel materials, allowing at the same time to modulate their size, shape, and structure. It has been experimentally demonstrated that the peculiar conditions occurring in CVD reactors enable to

(*) E-mail: valeria.guglielmotti@uniroma2.it



Fig. 1. – Scheme of the MW/RF-PECVD apparatus.

selectively produce in a controlled way $C-sp^2$ nanostructures, such as carbon nanotubes (CNT), astralenes, graphenes, and a variety of differently shaped $C-sp^3$ nanomaterials belonging both to the diamond $Fd3m$ and $F-43m$ space groups [3]. Moreover, from the theoretical side, many efforts by computer modelling have been performed in order to relate plasma chemistry to growth processes and nanostructure formation [4].

However, processes carried out under non-equilibrium conditions often reveal surprises, due to the dynamic competition between concomitant reaction routes. The experimental evidence suggests that many less considered details of already settled synthesis methodologies could be just as important in determining the nature and nanostructure of the final products as the main deposition conditions usually taken into consideration [5]. Previously we have reported the successful growth of a series of interesting nanostructured carbon materials [6-16]. To obtain guidelines for the selective and reproducible generation of carbon nanostructures, our current focus is to analyse the conditions that develop during the processes occurring in CVD reactors and to set-up specific methodologies. For the production of nanographites and nanodiamonds, in our labs various CVD-based apparatuses have been designed and custom engineered. We briefly report the results obtained by using the following CVD reactors, and will illustrate the advantages that they can provide:

- Micro-Waves/Radio-Frequency-Plasma Enhanced CVD (MW/RF-PECVD);
- Hot-Filament CVD (HF-CVD);
- Thermal-CVD (T-CVD).

2. – Experimental

2.1. MW/RF-PECVD. – In the MW/RF-PECVD reactor (fig. 1) the gas phase is excited by MWs (frequency: 2.46 GHz, power: 500 W) coupled to RF (work frequency:

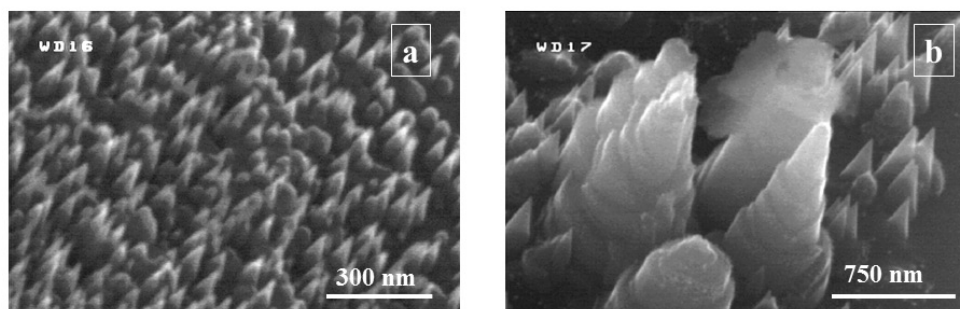


Fig. 2. – SEM images of diamond nanocones arrays.

13.56 MHz, power: 600 W). The gaseous reactants are introduced by a multi-channel flowmeter system. The MW/RF-PECVD works in the pressure range 1–100 mbar and in temperature range 500–1000 °C. The coupling of MW and RF makes it possible to modulate at the best the rates of the growth/etching processes. This technique couples indeed the typical and well-known advantages of MW discharge, such as homogeneity of plasma and high concentration of active chemical species, with the ability to control ion energy by proper biasing of the substrate [17, 18].

The use of such apparatus allows the production of nanosized diamonds, of diamond nanocones arrays [14], of hybrid systems such as CNT on Si nanocones (see fig. 2 and fig. 3) [15, 16].

In this case, the key parameter is the capacitive coupling of MW and RF plasmas along the lines of the electric field and the kinetic energy of the H ions impinging on the growing nanostructures [16].

2.2. HF-CVD. – In the HF-CVD (fig. 4) apparatus a Joule-heated Ta filament ($T = 2200$ °C) provides activation of the reactants, that are gaseous hydrocarbons and hydrogen. Atomic hydrogen is produced at a distance ranging from 2 to 8 mm from the substrate surface. Substrate holder is heated in a temperature range of 600–900 °C.

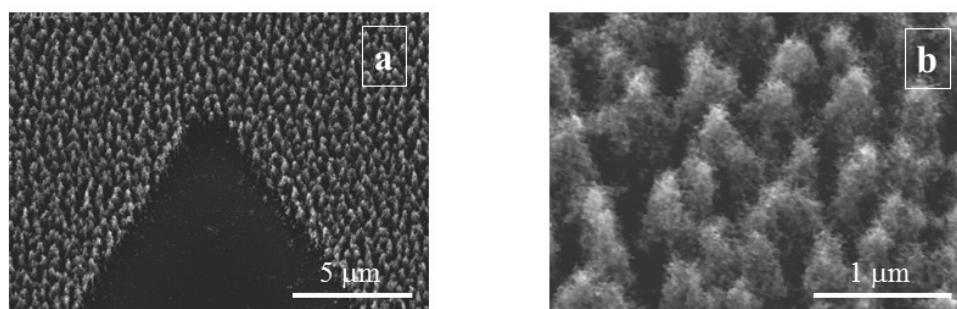


Fig. 3. – SEM image of Si nanocones covered by CNT bundles (a) and a detail of the deposit in (b).

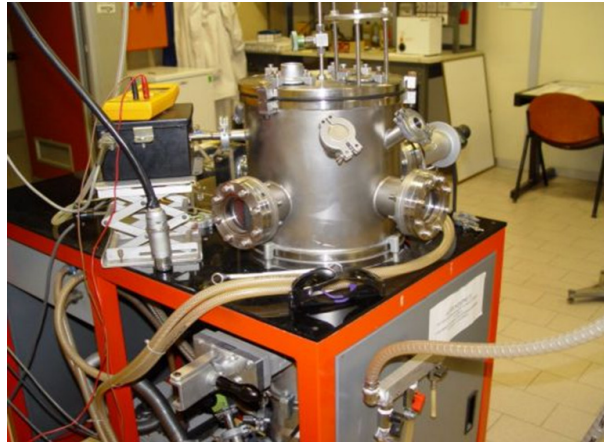


Fig. 4. – Scheme of HF-CVD apparatus.

The peculiarity of the chamber consists in a powder-flowing system, specially designed for powder storage and delivering, that enables the combined use of gases and powders as reactants and the controlled doping of the growing structures.

As reported in [6-12], this reactor has been used to produce continuous or patterned deposits of oriented CNT bundles (both SWCNT and MWCNT), nanodiamond films and coatings (also characterized by pre-determined metal-like or semiconductive charge transport properties), interesting deposits of nanodiamond on nanotube arrays, carbon nanofibers, tree-like and onion-like carbons. The conductive or semiconductive diamond films are obtained by inserting metal and semiconductor powders (W, Nd, Si) or organometallic compounds driven by inert gas carriers during the growing of the diamond phase. The nanodiamond-coated nanotubes are produced using as reactants H_2 (flow rate: 200 sccm) and carbon nanopowders (mean diameter 40 nm) carried by Ar flowing at 30 sccm. For the growth of CNTs and onion-like carbons the feeding gas is CH_4 , the different forms of $C-sp^2$ are generated by selecting pressure values (in the range 20–80 Torr) and modulating the temperature ramps (see figs. 5 and 6).

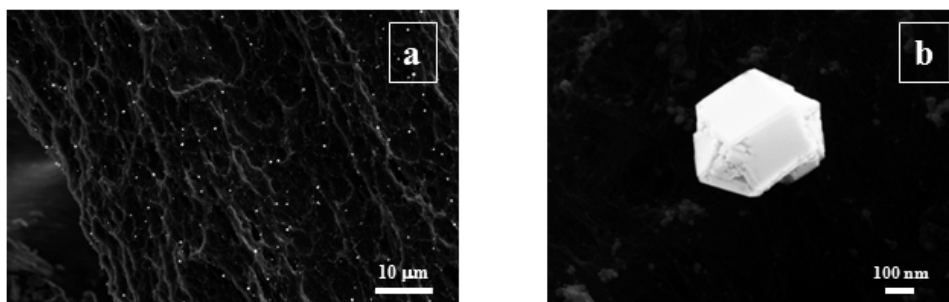


Fig. 5. – SEM images of a SWCNT macroscopic fiber covered by nanodiamond crystals (a); a detail of the nanodiamond crystal is depicted in (b).

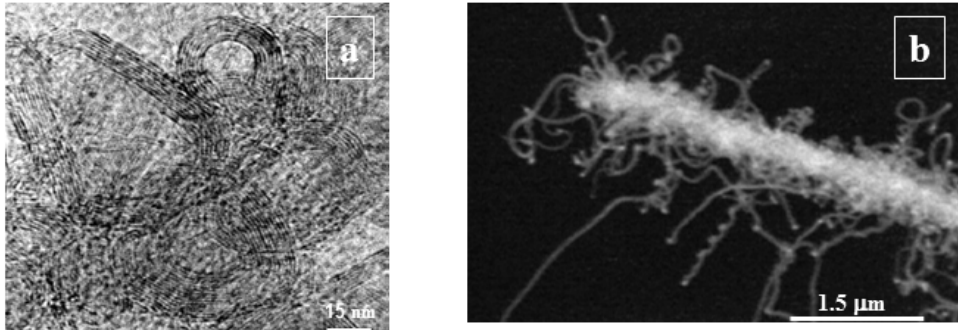


Fig. 6. – TEM image of an onion-like structure (a) and a tree-like one in (b).

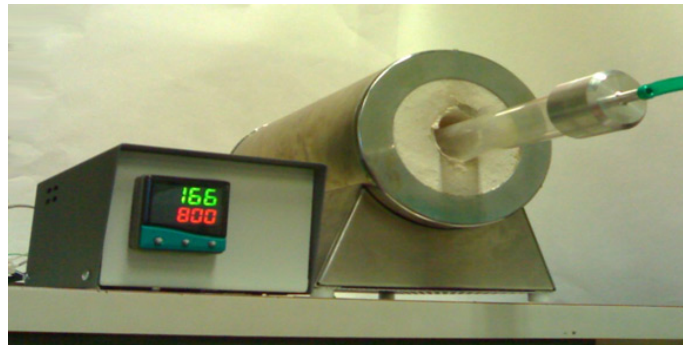


Fig. 7. – Scheme of T-CVD apparatus.

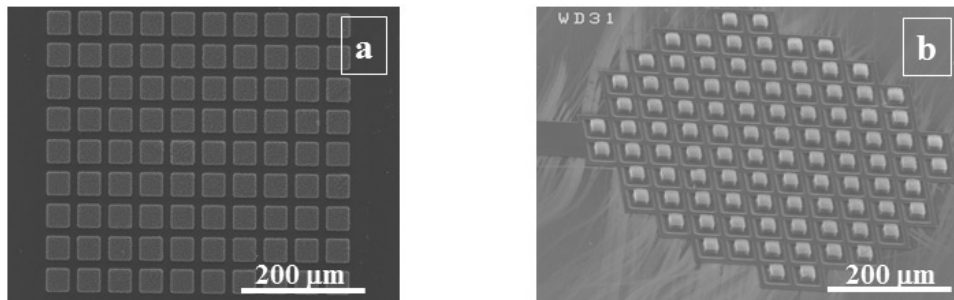


Fig. 8. – SEM images of CNT bundles grown onto differently patterned Si substrates.

2.3. T-CVD. – The T-CVD (fig. 7) system uses a flow reactor quartz tube inserted in a furnace. The reactor is kept under atmospheric pressure, the operating temperature is in the range 200–1100 °C. The apparatus is connected to a gas inlet and mass flow controller, and is equipped with a system for separated injection of gases and liquids, that are subsequently vaporized.

This technique demonstrated the ability to grow highly homogeneous deposits of oriented nanotubes on rather large areas. The structural order of the CNT arrays makes them good candidates for the building of more complex architectures. Moreover the nanomaterials are produced in absence of atomic hydrogen, and this makes it possible the direct integration of CNT also inside series of electronic components (see fig. 8).

3. – Conclusions

Activation of carbon-containing chemical species and reactions with atomic hydrogen using various CVD apparatuses and diversifying the methodologies allowed us to generate a large number of nanocrystalline carbon materials in a tailored and controlled way. The CVD apparatuses are suitable for the production of carbon nanotubes and curled nanofilaments, onions-like and cages, tree-like and dendritic carbons, nanodiamond films and nanocones.

An exciting new class of materials is represented by the hybrid systems, such as nanotubes ensembles on elongated 1D Si structures, or nanodiamonds supported on nanotube bundles. The obtained microstructures depend upon the kinetics, in which the balance between the relative rates of competing mechanisms drives the reactions along specific chemical routes.

In such kinetically controlled processes the selective production of a variety of $C-sp^2$ and $C-sp^3$ crystalline nanostructures is promoted by the different reaction pathways that open up under conditions far from thermodynamic equilibrium. Moreover, we would also like to outline the feasibility to use the same CVD apparatuses for post-synthesis treatments of other carbon nanomaterials. An example is the use of the MW/RF-CVD apparatus for the etching of diamond films produced by HF-CVD or of deposits obtained by self-assembling of detonation nanodiamonds [13,19]. In these last cases packed arrays of diamond nanowhiskers can be fabricated.

The possibility of shaping in a predefined way low-dimensional structures either by direct synthesis or by post-synthesis treatments opens new scenarios in the preparation of diamond-based systems for electronic and optoelectronic applications. A deep investigation of the processes occurring in different CVD systems is being carried out in our laboratories in order to define the methodologies for the production of selected carbon forms under conditions far from the thermodynamic equilibrium. The know-how acquired during the research stage represents a boost for the scaling of processes and the industrial production of innovative crystalline carbon nanomaterials.

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