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Synthesis of carbon films with controlled nanostructure by separation of neutral clusters in supersonic beams

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Abstract

Nanostructured carbon thin films have been grown by deposition of cluster beams produced in supersonic expansion. Due to separation effects consisting of an enrichment of heavy clusters in the central portion of the supersonic beam and of light clusters in the peripheral one, films with different nanostructures can be grown by simply intercepting with a substrate different regions of the cluster beam. Raman spectroscopy confirms that the films deposited with different beam portions have different nanostructures ranging from disordered graphitic (fullerene-like precursors) to amorphous, with the presence of sp coordination. © 1999 Elsevier Science B.V. All rights reserved.

The structural and functional properties of amorphous carbon films, assembled atom by atom, are largely determined by the kinetic energy of the ions impinging on the substrate during the film growth [1–3]. The use of carbon clusters, together with carbon atoms can open new possibilities for the synthesis of materials where the structural and functional properties are also determined by the hierarchical organization of units with dimensions ranging from mesoscopic to nanoscopic scale [4,5].

Carbon films with inclusions of fullerene-like structures and nanotube fragments have been produced with a filtered cathodic arc apparatus where the arc occurs in a localized high-pressure (10 torr) region. Due to the presence of the inert gas, condensation takes place and a beam of monomer ions and clusters is formed and deposited. The incorporation of three-dimensional networks, consisting of buckled planes with fullerene-like features, induces the formation of films with very high values of hardness and elasticity [6].

Although promising, these experiments suffered from the lack of characterization of the cluster formation processes and of cluster mass and kinetic energy distribution. In view of the use of clusters as building blocks of nanostructured thin films, intense and stable beams must be used and a good control on cluster mass and kinetic energies distribution must be achieved.

These characteristics can be obtained with the use of beams produced by supersonic expansions. A

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supersonic beam can be schematically described as a gas stream expanding very rapidly from a high-pressure region (source) to a low-pressure region. The characteristics of the beam are mainly determined by the size and shape of the nozzle orifice and by the pressure difference between the two regions [7]. Compared to effusive beams used in Molecular Beam Epitaxy, supersonic beams provide higher intensity, and directionality allowing the deposition of epitaxial films with very high growth rates [8,9].

Cluster beams can be used to grow nanostructured thin films where the original cluster structure is preserved after the deposition [10–13]. The use of supersonic expansions may improve the deposition rate and favour a better control on cluster mass distribution, thus making this technique competitive compared to other synthetic methods [13].

In this Letter we show that, by using pulsed supersonic cluster beams, carbon thin films can be grown at high deposition rates. Due to separation effects, typical of supersonic seeded beams, the cluster mass distribution can be varied to deposit films with controlled nanostructure.

Fig. 1 shows the principle of operation of the cluster beam apparatus used for the deposition. It consists of three differentially evacuated chambers

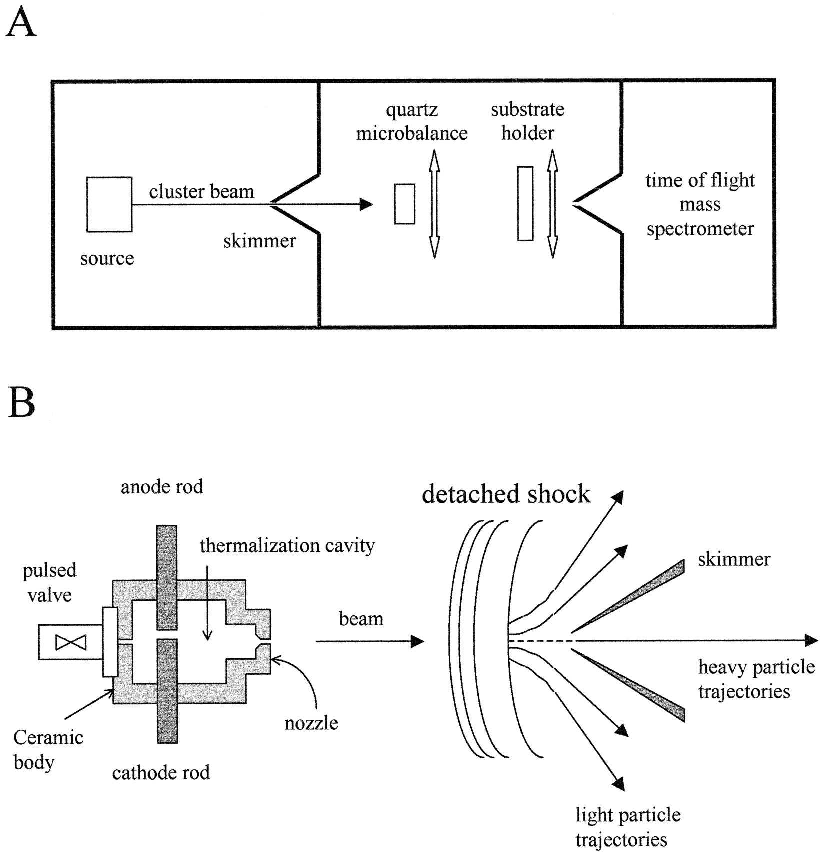

Fig. 1. (A) Schematic representation of the supersonic beam apparatus for the deposition of cluster beams. (B) Expanded view of the pulsed cluster source and of the region near the skimmer where a shock wave is formed. The trajectories of the heavy and light particles are schematically shown. Due to separation effects, films with different nanostructures can be deposited by placing a substrate to intercept different regions of the beam.

and operates in the high-vacuum regime. The first chamber hosts the cluster source and has a base pressure of typically 1.10^{-7} torr, during source operation the average pressure is maintained in the range of $1–3 \times 10^{-5}$ torr (see below). The supersonic cluster beam enters the second chamber through an electroformed skimmer of 2 mm of diameter [14]. The second chamber is equipped with a sample holder which can intersect the beam, a quartz microbalance for beam intensity monitoring, and can alternatively host a beam-chopper or a Fast Ionization Gauge for time of flight measurements of the velocity distribution of particles in the beam. During deposition the background pressure is typically 1×10^{-7} torr. The third chamber hosts a linear time-of-flight mass-spectrometer (TOF/MS) which is placed collinear to the beam axis in order to achieve the best transmission [15]. The detector of the TOF/MS, being sensitive to high-speed neutral clusters as well, can also be used for TOF characterization [15].

The cluster source is a modified version of the PACIS source [16] and it works on the same principle of vaporizing the material used for cluster production with a pulsed electric discharge. A schematic cross-section of the source is sketched in Fig. 1B. Two graphite electrodes are facing each other in a small cavity inside the ceramic body of the source. A pulsed valve injects He in the cavity so that an electric discharge can take place between the electrodes. The discharge, driven by high voltage (between 500 and 1500 V), is very intense (~ 1000 A), lasting a few tens of microseconds, and produces the ablation of the cathodic material. This is quenched by He and condenses in clusters which are carried out of the source in a seeded supersonic expansion through a nozzle of 2 mm of diameter and 8 mm length. During typical operation the average pressure inside the cavity is of several hundred torr and the source body reaches a temperature of ≈ 400 K. Stagnation temperature of the carrier gas is, however, a function of time, evolving very rapidly down to ≈ 100 K as expansion takes place and the source gets empty. The velocity of the carrier gas is thus about 2000 m/s at the time the first clusters come out of the nozzle, but slows down to ≈ 1000 m/s at the tail of the cluster pulse. A velocity slip of the clusters with respect to the carrier gas is also present but becomes of some relevance only for clusters exiting late from the source, when the stagnation pressure is reduced.

In analogy with the case of laser vaporization sources [17], the use of a cavity, where cluster aggregation occurs, is beneficial for several reasons. The erosion of the cathode does not affect significantly the dynamics of the gas during the expansion; moreover the presence of the cavity itself decouples the cathode sputtering from the cluster formation process. The stability of the source is substantially improved and electrode erosion affects mainly the intensity but not the mass distribution of the clusters.

With typical discharge conditions, we obtain a log-normal cluster mass distribution in the range of 0–1500 atoms/clusters, with a maximum peaked at around 400 atoms/cluster and an average size at about 950 atoms/cluster. The kinetic energy of the clusters is lower than 0.2 eV/atom, well below the binding energy of carbons in the cluster. At cluster impact on the surface there is thus no substantial fragmentation of the aggregates and deposited films may keep memory of the structure the clusters had in the gas phase [10–13].

Due to the long gas pulse exiting form the source (i.e. high duty cycle regime [18]), the source–skimmer distance D_{sk} and the background pressure strongly affect the expansion. Depending upon D_{sk}, a shock wave can be produced in front of the skimmer, causing mass separation effects and changing the final characteristics of the beam (see below) [7,18]. In the reported experiments, the nozzle–skimmer distance has been varied from 40 to 16 mm. With $D_{sk} = 40$ mm deposition rates of 60 nm/min are routinely obtained on a substrate placed at 300 mm from the source. Circular films with a radius of 1 cm and uniform thickness can be deposited in the second chamber of the apparatus. Intersecting the beam in the first chamber films with an area of several cm^2 can be prepared with a thickness which is uniform on a scale considerably larger than that of the experimental probes used for characterization. In Fig. 2A,B we report low-magnification SEM micrographs of the cluster-assembled films. An AFM picture (Fig. 2C) shows the granular structure based on clumps of spherical aggregates with typical diameter of few tens of nanometers.

Since the pioneering works on supersonic jets, it has been recognized that if species with different

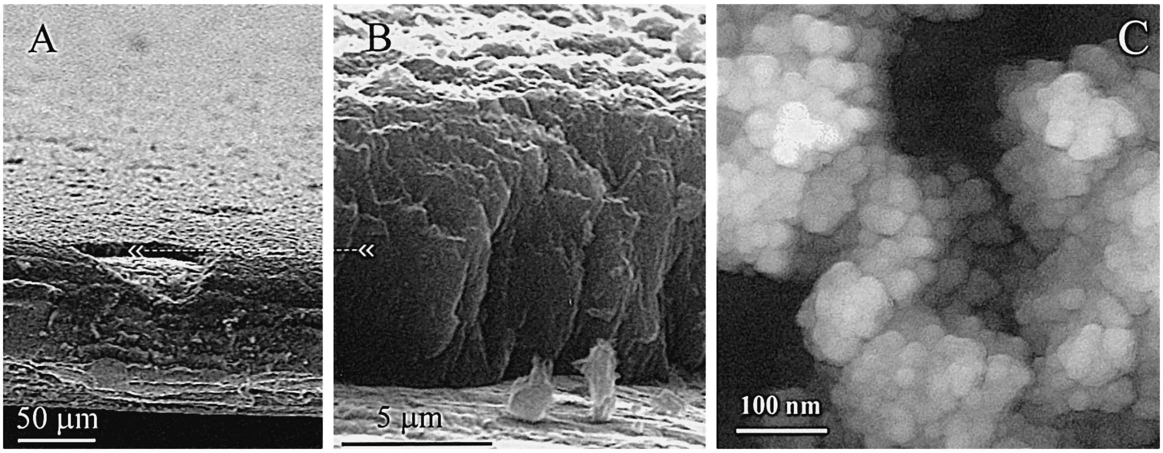

Fig. 2. (A,B). Scanning electron microscopy (SEM) micrographs taken with different magnifications of the surface and of the section of a cluster-assembled carbon film. (C) Atomic force microscopy (AFM) image of the topography of the film surface. This picture has been taken with a Digital Nanoscope IIIA operating in tapping mode.

weights are present in gas to be expanded, the heavier constituents concentrate along the core of the beam [19,20]. Different mechanisms have been proposed to account for this effects. Waterman and Stern have suggested that the flux of lighter species diverge radially more rapidly after the nozzle due to the greater thermal velocity components [21]. Reis and Fenn [19] have shown that mass separation can be obtained by exploiting the interaction of the beam with the shock wave detached from the skimmer. In particular, due to their different inertia, light species follow diverging streamlines after the shock front, while heavy species are not diverted and can follow straight trajectories through the skimmer (see Fig. 1B). Due to this effect large clusters are concentrated in the central portion of the beam, whereas the lighter ones are at the periphery.

In analogy with aerosols apparatus, where inertial effects are used for separation of particles [22], we have used separation effects to deposit thin films, with different cluster mass distributions, by intersecting different regions of the beam spot with a substrate. Since clusters maintain, at least partially, their original structure [12], the films should be reminiscent of the precursor clusters and present different coordinations and local order.

Experimental and theoretical investigations have shown that small carbon clusters (roughly below 40 atoms) have chain or ring structures [23] whereas larger clusters have the tendency to form three-dimensional cage-like structures characterized by sp^2

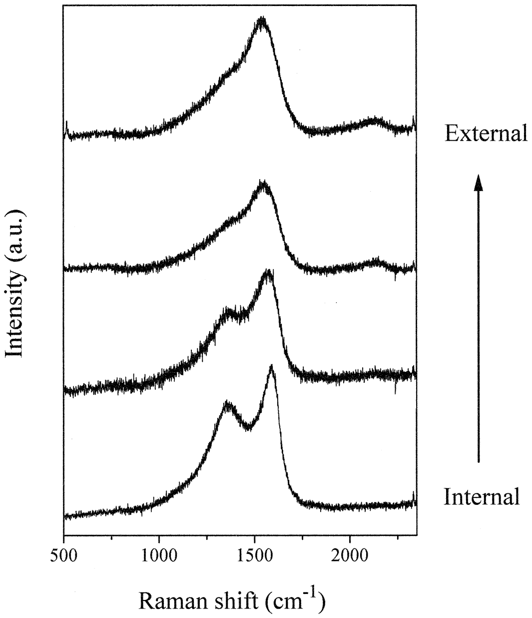

Fig. 3. First-order Raman spectra of films deposited with different portions of the cluster beam. Going from the bottom (internal part of the beam, i.e. large clusters) to the top spectrum (external part of the beam, i.e. small clusters) one can see the evolution from a disordered graphitic structure to an amorphous one. The peak around 2150 cm^{-1} is due to sp bonds.

coordination [24,25]. Separation effects in front of the skimmer should enrich the periphery of the beam of small chain-like clusters, leaving large fullerene-like clusters in the beam center. Films grown using the periphery of the beam are then expected to show a very disordered structure; on the other hand films grown with the central region of the beam should be characterized by a disordered graphitic structure reminiscent of the fullerene-like character of the clusters.

In order to characterize the nanostructure and the coordination of the films deposited with different portions of the supersonic beam, we have performed Raman spectroscopy, which is sensible to the film order on a nanometric scale (Fig. 3). The top spectrum is taken on a region rich in small clusters (periphery of the beam). The shape and the shift of the peak (G band) are typical of amorphous sp^2 carbon [26]. The D peak is present as a broad shoulder on the left of the G band. The peak at 2150 cm^{-1} is quite unusual for disordered carbon produced by depositing carbon atoms or ions and it can be attributed to the presence of carbon chains characterized by sp acetylenic bonding [27].

Going from the top to the bottom spectrum in Fig. 3, one can follow the evolution from an amorphous towards a disordered graphitic structure by shifting from the periphery of the beam towards the central region (large clusters). This evolution is confirmed by hardening of the G peak, the appearance of a well defined D band and by the narrowing of the two lines. All this parameters are in agreement with a graphitization of the sample [26].

In conclusion we have presented a new technique for the synthesis of cluster-assembled carbon thin films with supersonic cluster beams. Separation effects in the beam offer the possibility of producing films characterized by different nanostructures and coordination. This technique does not require the use of mechanical filters and it works with neutral particles.

We have deposited films with a structure ranging from disordered sp^2 graphitic phase to an amorphous phase where a large number of sp-coordinated sites is present. It is well known that gas-phase synthesis of carbon clusters can efficiently produce acetylenic species [28], our experiments suggest that they can be deposited and that they can survive without the use of stabilizing end-capping groups [28]. The control of carbon film nanostructure can open interesting perspectives for the application of these systems for field emission, catalysis, and gas adsorption.

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