

## Growth of Nanostructured Carbon Films by Cluster Assembly

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The structural properties of nanostructured films obtained by deposition of supersonic beams of carbon clusters are investigated by classical molecular dynamics simulations and compared to experiments. Simulations are shown to predict how the structural properties of the deposited film depend on the actual growth protocol. In particular, it is shown that the assembly of small linear clusters can lead to the formation of random schwarzite structures.

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Supersonic cluster beam deposition (SCBD) has recently emerged as a powerful technique for the growth of nanostructured carbon thin films [1–3]. When the incident energy of clusters accelerated in a supersonic expansion is small enough to prevent massive fragmentation, films are obtained in a large, albeit controllable variety of morphologies. Such films, as it appears from various experimental characterizations [4,5], are shown to retain a memory of the precursor clusters and to display a disordered graphitelike character with a prevalent threefold coordination. Transmission electron microscopy (TEM) shows a porous structure with a density of  $\sim 1 \text{ g/cm}^3$ , consisting of closed graphitic particles and curved graphene foils embedded in an amorphous matrix (see Fig. 1). The inhomogeneity is observed at different length scales up to the macroscopic one and appears to be self-affine [3]. This makes these systems appealing for possible applications, e.g., in gas sensing and gettering [3,6–8]. Moreover, carbon cluster assembling has been suggested as a possible route to the formation of negatively curved graphitic carbon (random schwarzites) [9,10]. Unlike fullerenes, tubulenes, and graphite, whose tridimensional solids are partially bound by van der Waals forces, schwarzites are entirely  $sp^2$  covalent tridimensional structures [11,12]. As such they would constitute a further fundamental allotropic form of carbon, combining a high porosity with a robust crystalline structure.

A key feature of SCBD is the relationship between the structure and size (of a few up to several hundred atoms) of the clusters in the beam and the resulting structural and functional properties of the film. Because of the large variety (as regards size, isomerization, and reactivity) of clusters, the effects of cluster-cluster interaction on the substrate and the extent of rebonding during the film growth are hard to predict and control. Thus the cluster assembling during the beam deposition and the structure of the resulting films at the nano- and mesoscale is still a matter of discussion [5,13,14].

Despite the above unclear scenario, a number of facts and key parameters governing the SCBD film growth have been identified: (i) experimental results based on ion-drift

measurements [15] have shown that small carbon clusters (roughly below 40 atoms) have chain or ring structures, whereas larger clusters tend to form fullerenic cages; (ii) the actual mass distribution and deposition energy deeply affect the final atomic-scale structure, notably the density and the porosity of the sample; (iii) the vibrational temperature of the impinging clusters, the geometrical parameters of the beam-substrate interaction (e.g., incidence angle), as well as the energy distribution within the beam can vary in a wide range.

In this Letter we present a computer study, tailored on SCBD experiments and based on classical molecular dynamics (MD) simulations, aimed at improving our basic understanding of the SCBD growth phenomena. Although the real length and time scales of experiments fall in the mesoscopic range and are presently out of reach of MD simulations, the latter are nevertheless *scalable to the mesoscopic domain thanks to self-affinity* [3] and are suggestive of the growth mechanisms leading to a nanostructured film. Moreover, the present MD simulations, besides providing a full atomic-scale characterization of these new materials, enable us to establish a rational link between the physical properties of the grown films and the beam features. In particular, MD simulations

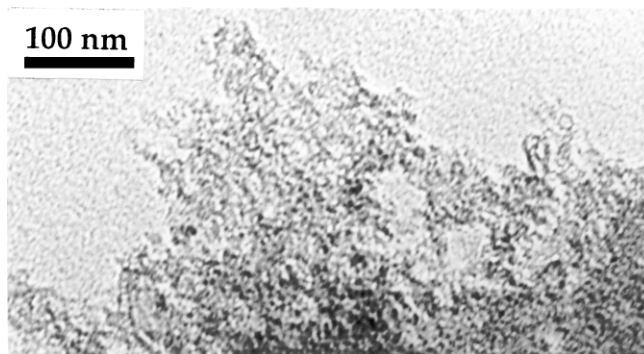


FIG. 1. TEM micrograph of a cluster assembled film showing large pores and fullerene-like particles embedded in an amorphous matrix. The film has been deposited with a cluster mass distribution described in the text and a deposition energy of 0.1 eV/atom.

of the SCBD process with small ( $<10$  atoms) low-energy clusters yield the first clear evidence that random schwarzites are formed.

The present computer-intensive investigation has been carried out by classical MD simulations based on the many-body Tersoff interaction potential [16]. We made use of an improved version of this potential which better models the effects of the local environment on the atom-atom interactions [17]. The reliability of Tersoff potential (although not including dispersion forces, similar to more refined tight-binding or first principles interaction models) for the investigation of structural properties of carbon-based materials has been well established.

The deposition of clusters was performed with a normal incidence and a uniform in-plane distribution on a (001)-oriented periodically repeated diamond substrate. The substrate temperature was fixed at 300 K by velocity rescaling, while the dynamics of the free surface was left unperturbed (i.e., no rescaling was operated for the outmost atoms) in order to avoid artifacts during the early stages of beam-substrate (then beam-film) interaction. All computer experiments discussed here were performed with monoenergetic cluster beams with a vibrational temperature of  $T_v = 500$  K. The deposition energy  $E_d$  was tuned in the interval  $0.1 < E_d < 1.0$  eV/atom. The values of  $T_v$  and  $E_d$  have been chosen according to the typical source conditions of a supersonic cluster beam produced by a pulsed plasma source [1–3,5]. By using a time step  $\delta t$  of 0.5 fs, we deposited up to  $\sim 10^4$  atoms (corresponding to a thickness of the deposited film of  $\sim 50$  Å). These parameters correspond to a very high deposition rate, varying in the range  $10^{24}$ – $10^{25}$  (atoms/s)/cm<sup>2</sup>. This is to be compared to the typical experimental values of  $10^{17}$ – $10^{18}$  (atoms/s)/cm<sup>2</sup>. Despite this difference, the theoretical deposition rate is low enough to warrant that the next cluster impact occurs after a full relaxation of the previous one. Special care has been taken in selecting the configuration of carbon clusters in the beam. The precursors for the film growth have been shaped according to experimental ion-drift measurements [15]: while clusters with more than 40 atoms have been arranged in fullerene-like cages, smaller clusters (containing up to 23 atoms) have been shaped as either linear chains (odd number of carbon atoms) or closed rings (even number of carbon atoms). No clusters with intermediate size (from 24 to 45 atoms) have been inserted in the beams, according to Ref. [18].

We first consider the role played by the mass distribution in the beam. To this aim we performed two different simulations where a bimodal distribution was assumed. In both cases we selected a beam consisting of clusters of size 1–23 atoms and 46–120 atoms with a relative intensity of 5:1 and 1:10, respectively. The respective snapshots of the grown samples are reported for samples (a) and (b) in Fig. 2. In these simulations the substrate was quite extended (deposition area of  $53$  Å  $\times$   $53$  Å),

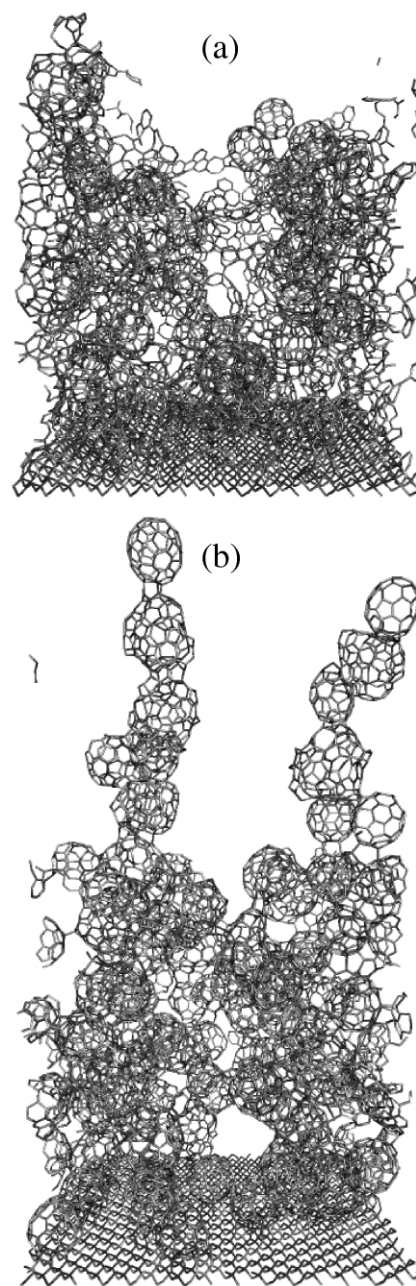


FIG. 2. Atomic structure of amorphous film obtained by deposition of beams with bimodal mass distribution in the range 1–23 atoms and 46–120 atoms with relative weight 5:1 [sample (a)] and 1:10 [sample (b)], respectively.

as requested by the relatively large dimensions of the deposited precursors. We selected  $E_d = 0.1$  eV/atom. Sample (a) resulted to have a density of  $0.85$  g/cm<sup>3</sup> and an  $sp^2/sp^3$  ratio of  $\sim 11$ , in substantial good agreement with real SCBD films [4] where the density was found to be  $\sim 0.9$ – $1.2$  g/cm<sup>3</sup> and the bond network is dominated by graphitic-like coordination. Furthermore, sample (a) is homogeneous showing only very small density fluctuations in the bulk region when measured along the growth axis. The fullerene structures, still detectable in the film,

are connected by an amorphous matrix characterized by threefold coordination and hexagonal bond rings. The overall structure is far dominated by threefold coordination, in agreement with the experiments [4,5].

By reversing the relative occurrence of small and big precursors we obtained a different kind of film. Indeed, sample (b) shows intriguing structural properties. While the overall disorder in the bond network is apparent, the presence of nearly unaffected fullerene cages is easily recognized. The random stacking of fullerene precursors gives rise to a locally structured, stress-free, porous film with a low density ( $0.79 \text{ g/cm}^3$ ). Sample (b), unlike the former case, is no longer homogeneous. Rather it displays density fluctuations of about 20%, which we attributed to a local gettering effect of fullerenes over smaller clusters. Again, the atomic coordination is definitely graphite-like with 87% of atoms showing threefold coordination. We also collected the ring statistics following the shortest-path criterion by Franzblau [19]. Although the hexagonal rings dominate, we computed twice as many pentagonal rings as heptagonal ones. The resulting film is therefore characterized by fullerene-like closed structures, rather than graphitelike foils, most connections occurring through a few four-coordinated atoms.

The above simulations proved that fullerene cages are nearly unaffected by the deposition process, since nearly no fragmentation was observed. Therefore, we decided to study the role played by smaller and more fragile clusters. In particular, we considered the role played by  $E_d$ . We simulated a cluster beam deposition with a unimodal mass distribution containing small clusters of two to ten atoms, with average cluster size equal to six (Fig. 3). Single carbon atoms were included in the beam as well. The simulation cell area of the substrate was in this case of  $25 \text{ \AA} \times 25 \text{ \AA}$ . Three snapshots of the grown films corresponding to  $E_d = 0.1 \text{ eV/atom}$  [sample (c)],  $E_d = 0.5 \text{ eV/atom}$  [sample (d)], and  $E_d = 1.0 \text{ eV/atom}$  [sample (e)] are shown in Fig. 3. It is apparent that sample (c), obtained with the lowest deposition energy, is highly porous, while a much denser sample is obtained at higher deposition energy. The fraction of occupied volume [20] ranges from 22% for sample (c), to 32% for sample (d), to 34% of sample (e). The corresponding surface specific area is  $\sim 1.5 \times 10^3 \text{ m}^2/\text{g}$ , remarkably larger than in carbon foams systems [21]. The corresponding mass density is 0.92, 1.45, and  $1.56 \text{ g/cm}^2$ , respectively. The grown samples are dominated by threefold coordination, with a fraction of  $sp^2$  network sites of about 70% in all cases. This is consistent with the graphitelike character observed experimentally [2,3]. Samples (c) and (d) also display a sizable percentage (about 25%) of twofold coordinated atoms, mainly located at the surface of the internal cavities. The presence of such linear structures has been recently found by Raman measurements in SCBD films [5]. With regard to the ring statistics, we found a majority of hexagonal (18%–33%) and heptagonal (14%–18%) rings, while

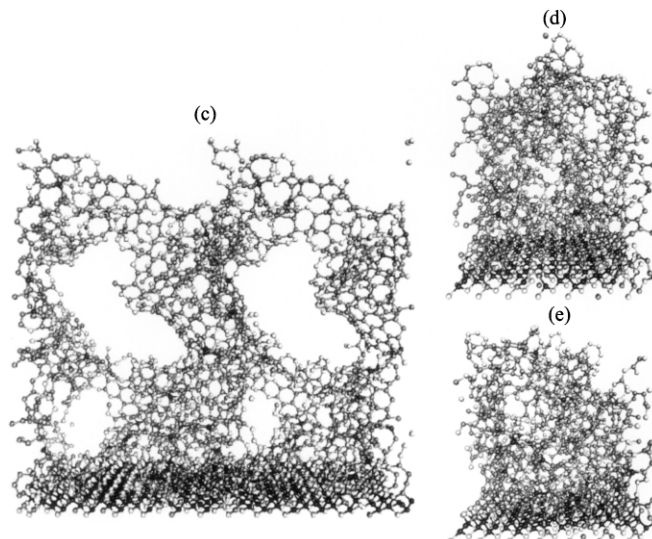


FIG. 3. Atomic structure of amorphous film obtained by deposition of beams with unimodal mass distribution ranging from 1 to 9 atoms/cluster. The deposition energy was  $E_d = 0.1 \text{ eV/atom}$  [sample (c)],  $E_d = 0.5 \text{ eV/atom}$  [sample (d)], and  $E_d = 1.0 \text{ eV/atom}$  [sample (e)].

at variance with samples (a) and (b) pentagonal rings are nearly absent. This statistics indicates that open structures (e.g., graphene sheets with a negative curvature) are preferred, as actually seen in Fig. 3. In particular, sample (c) clearly exhibits a random pore structure typical of random schwarzites [9,10]. Despite their porosity, the structures are rather stable with a binding energy  $\sim 0.8 \text{ eV/atom}$  smaller than that of diamond. Robust thermal annealing operated up to 2000 K on the as-grown samples did not significantly affect the overall atomic architecture. After annealing, the macroscopic elastic stress parallel to the growth direction of samples (c) and (d) was found to be slightly compressive ( $\sim 0.5 \text{ GPa}$ ) and mainly located at the film/substrate interface. All samples are stress-free along the growth direction. The absence of stress is in good agreement with experiments proving that SCBD films as thick as  $30 \mu\text{m}$  can be grown without delamination [3].

In summary, classical MD simulations tailored on real experiments have been used to characterize and to predict the growth of carbon thin films by supersonic cluster beam deposition. From this study SCBD is argued to open new routes to the synthesis of exotic carbon forms, e.g., schwarzites, which incorporate the peculiar properties of fullerenes and tubulenes into an easy-to-grow solid tridimensional structure.

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