

Diamondlike Carbon Films Obtained by Low Energy Cluster Beam Deposition: Evidence of a Memory Effect of the Properties of Free Carbon Clusters

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Free carbon clusters with various selected sizes (C_{20}, C_{60}, C_{900}) have been deposited on different substrates to obtain continuous thin films (thickness ~ 100 nm). The characterization of nanostructures and electronic structures of the films have been performed using various complementary techniques (atomic force microscopy, transmission electron microscopy, electron energy loss spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy). A memory effect of the free carbon cluster properties permits the synthesis of amorphous diamond or graphite films depending on the deposited incident species (C_{20} or C_{900} , respectively).

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Free clusters of various elements have been extensively studied for several years because they represent an intermediate state between atoms or molecules and bulk solid phases. New concepts have to be introduced to understand their physical and chemical properties. Furthermore, they can play an important role in various fields such as astrophysics, catalysis, new material formation, etc.

The recent development of cluster generators and particularly of laser vaporization sources [1] allows the production of cluster beams in a wide range of sizes, with practically any kind of material, even the most refractory or complex systems (bimetallic clusters, oxides, etc.). In this context, studies of deposited clusters have been initiated with some promising results. For example, Yamada [2] obtained epitaxial coatings of Al/Si despite a 25% misfit, using high energy ionized cluster beam deposition (ICBD) of Al on a Si(111) substrate at room temperature. In this case, the energetic Al_{500} clusters fragmented upon impact on the surface of the substrate, enhancing the formation of nucleation sites and adatom diffusion. In a different way, previous works on antimony thin film growth performed by Melinon *et al.* [3] showed that low energy cluster beam deposition (LECBD), compared to molecular beam deposition, leads to a nearly random substrate "pavement" when the mean cluster size is high enough (> 5 nm) to limit their diffusion. In this technique, the cluster size is a key parameter which controls the nucleation and growth processes of the films. Our experimental challenge using this LE CBD technique is to synthesize thin films which conserve the specific properties of the incident free clusters (atomic and electronic structures) in order to produce new materials.

For this purpose, carbon clusters and more generally covalent clusters seem interesting. The covalent nature allows *ab initio* calculations [4,5], even for large clusters, which are impossible for metallic clusters because of their compact structure. In this last case, for particles of more

than ten atoms, the number of degrees of freedom dramatically increases and leads to very complex calculations to obtain information on the electronic structure, closely connected to coordination and bond length in clusters. Furthermore, since the discovery of fullerenes [6], many theoretical and experimental studies have been performed to propose geometrical arrangements of carbon atoms in free clusters as a function of their size. It is well established that the smallest clusters ($N < 10$ atoms) prefer an arrangement in cumulated or acetylenic chains corresponding to sp^2 or sp^1 hybridization of atoms, respectively. In the C_{10} - C_{20} range of sizes, some monocyclic rings add to these chains. Beyond the critical size $N=20$, it has been reported that all even numbered clusters can take at least one form of a closed hollow cage known as fullerene [7-9]. Euler's relation gives the number of pentagons (equal to 12) to obtain spherical fullerenes [10]. Finally, the electronic structure of these fullerenes is directly related to their geometrical structure taking into account that the aromaticity of hexagons is responsible of the sp^2 bonding character while pentagons introduce a sp^3 bonding character. Consequently, the first fullerene C_{20} having the form of a dodecahedron with one dangling bond per atom and a σ bond angle of 110° is close to diamond (pure sp^3 with a σ bond angle of 109.17°) [11]. As the number of hexagons increases, the electronic structure of fullerenes tends towards pure graphite (pure sp^2). The well known C_{60} corresponds to an intermediate state with a mean hybridization equal to $sp^{2.3}$ [12]. The aromaticity allows the closure of electronic shells by satisfying the atom valences but only a few fullerenes without dangling bonds, namely, C_{60} and C_{70+2N} , are stable.

In this paper, we show the correlation between the properties of free clusters and the properties of thin films obtained by deposition of selected size distributions. Three characteristic distributions, corresponding to different electronic states, have been chosen: the distribu-

tion centered around C_{20} for its nearly pure sp^3 hybridization, C_{60} for its mixed state, and C_{900} , which could be compared to a disordered graphite nanoparticle, for its quasipure sp^2 bonding character. The structure and properties of the films were characterized using various complementary techniques as mentioned below.

We used the laser vaporization technique developed by Smalley [1] to produce carbon clusters. Our source was similar to the one described by de Heer and Milani [13] and was convenient to produce pure carbon clusters over wide ranges of sizes. Many parameters can be adjusted to vary the mean size of a distribution: laser fluence, helium flow (pressure and opening time of the pulsed nozzle), and residence time of clusters in the source. Cluster mass distributions were analyzed in a time of flight mass spectrometer. We initially checked that size distributions of photoionized neutral clusters and ion clusters naturally generated in the source were very similar. In agreement with other authors [14], we observed only even numbered photoionized clusters and both odd and even numbered nascent ion clusters in the fullerene regime, with enhanced stability for even numbered ones. Therefore in our experiments, for reasons of convenience, the nascent cluster ions were used to adjust the size distributions before depositions.

Deposition experiments were performed on various substrates (optical grade polished sapphire, Corning glass, silicon, beryllium, etc.) at room temperature in a vacuum of 10^{-7} Torr. During deposition, ion clusters were systematically deflected in order to prevent any charge effect on the substrate, and only neutral clusters reached the substrate. In fact, in this preliminary work, we were mainly interested in size effect characterization. Deposition rates were measured using a quartz balance and checked after deposition by Rutherford backscattering spectrometry (RBS) of 2 MeV alpha particles, using the samples deposited on beryllium substrates. *In situ* electrical conductivity measurements of the films during deposition allowed the following of the film growth process, from isolated supported clusters up to the percolation threshold and the formation of a continuous film. Structural characterization of carbon films were performed using atomic force microscopy (AFM), electron diffraction, and Raman spectroscopy. Electronic structures were studied from UV/visible optical spectroscopy, electrical measurements, and electron energy loss spectroscopy (EELS). Fourier transform infrared spectroscopy (FTIR) and Auger electron spectroscopy (AES) were used to determine the chemical composition of the films (i.e., hydrogen and oxygen contents).

Three size distributions centered around C_{20} , C_{60} , and C_{900} have been deposited (Fig. 1). The size distributions were nearly Gaussian for C_{20} and C_{60} and exhibited a log-normal law for C_{900} [15,16]. This last observation is an indication of coalescence effects during the nucleation of clusters in the source [Fig. 1(c)]. According to *in situ* electrical measurements, the growth process of the films

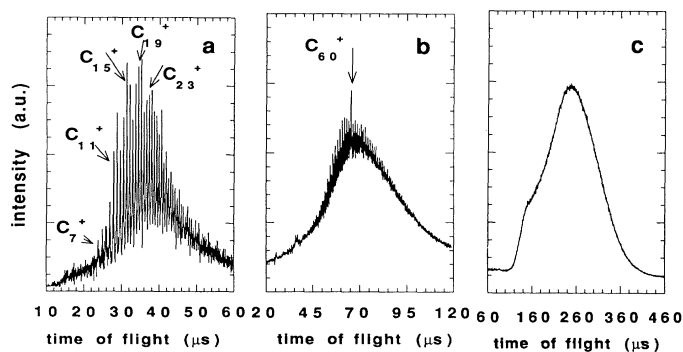


FIG. 1. Size distributions of carbon clusters centered around C_{20} (a), C_{60} (b), and C_{900} (c), used for deposition experiments.

corresponds rather well to a random "pavement" of the substrate surface as generally observed with various types of elements deposited by the LECBD technique [3]. No significant oxygen peak has been detected by AES measurements but the presence of hydrogen in the films has been revealed from FTIR spectra, obtained from 100 nm thick films on sapphire substrates. The most representative lines at 2952, 2926, 2868, and 2855 cm^{-1} in the infrared spectra presented in Fig. 2 are assigned to sp^2 CH_2 ($C_{2v}:A_1$ symmetry), sp^3 CH_2 ($C_{2v}:B_1$ symmetry), sp^3 CH_3 ($C_{3v}:A_1$ symmetry), and sp^3 CH_2 ($C_{2v}:A_1$ symmetry), respectively [17]. Note that carbon atoms bonded to one or more hydrogen atoms are almost entirely sp^3 hybridized. The hydrogen content in our films decreases as the mean size of free clusters deposited increases. This result is in good agreement with the larger hydrogen avidity of the smallest fullerenes. In addition, a weak signal located near 2180 cm^{-1} in the IR spectra of C_{20} films could be attributed to $\text{C}\equiv\text{C}$ bonds, which is a signature of acetylenic rings or chains in very small carbon clusters.

In Fig. 3 are reported the typical Raman spectra obtained with 100 nm thick films on sapphire substrates. These spectra are composed of three broad bands; the broadening effect being characteristic of the presence of disorder and the loss of long range order. They can be analyzed on the basis of graphite and diamond phase mixing. From a disorder-induced breakdown of the selection rules, Shuker and Gammon [18] showed that bands in Raman spectra of amorphous covalent materials quantitatively represent the vibrational density of states in the corresponding crystals. Using their formalism, the *G* band (centered on the pure graphite E_{2g} line at 1580 cm^{-1}) and the *D* band (1350 cm^{-1}) observed in the spectra of Fig. 3 can be assigned to graphitic islands. In particular, the *D* band corresponds to the breakdown of the wave-vector selection rule resulting from finite crystal size effects [19]. Consequently, a graphite cluster size lower than the shortest coherence length of the modes ($\cong 2.5$ nm) gives a signal close to an amorphous sample. Increasing the cluster size, the selection rule is not entirely broken (the localized modes are the modes with a

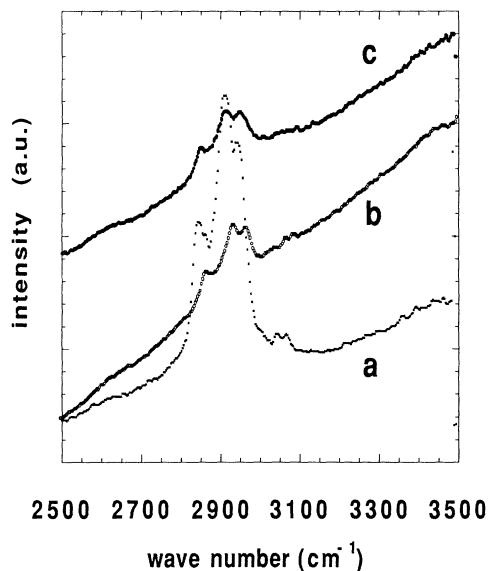


FIG. 2. Infrared spectra obtained with C₂₀ film (a), C₆₀ film (b), and C₉₀₀ film (c).

small wave vector) and the *D*-peak intensity decreases. These results are in good agreement with the incident mean cluster size. Some authors obtained empirical rules between the intensity ratio I_D/I_G and the percentage of sp^3 hybridization [20]. In this model, the increase of the I_D/I_G ratio (from C₉₀₀ to C₂₀, respectively) should correspond to an enlargement of sp^3 hybridization.

Another band, visible in the Raman spectra near 1150 cm^{-1} , may have an origin related to the hypothetical amorphous diamond density of states. This amorphous or disordered diamond has been unambiguously detected from the Raman scattering analysis [21]. Some authors [22,23] assume that this band is a signature of pure nanocrystalline diamond. We agree with this last interpretation since amorphous or pure nanocrystalline diamond with a smaller size than the coherence length gives the same Raman signal. Finally, the C₂₀ films could be formed by small amorphous graphitic particles embedded in an amorphous diamond matrix. Notice that the Raman spectra of the C₉₀₀ films does not exhibit this amorphous diamond signature but a unique amorphous graphitic character. In the C₆₀ films, an intermediate state between C₂₀ and C₉₀₀ films is observed.

The presence of the amorphous phases discussed above in our samples is corroborated by electron diffraction results. Using optical densitometry, we have measured the diffuse rings and compared them with references. The observed halos in C₂₀ films ($d=0.207$ nm and $d=0.124$ nm) correspond to the main diamond diffraction peaks [(111) and (220)], while those of C₉₀₀ and C₆₀ films correspond to the (101) and (112) graphite peaks. As usual for very disordered systems, the most intense graphite peaks [(002), (004), etc.] are not observed [24].

The electronic structure of the phases present in our

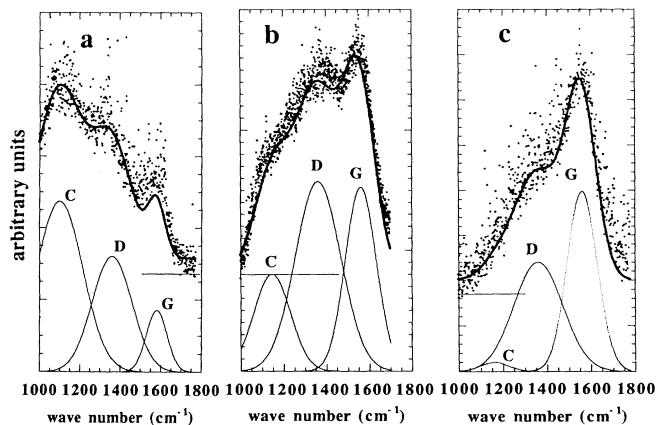


FIG. 3. First order Raman scattering spectra of C₂₀ film (a), C₆₀ film (b), and C₉₀₀ film (c). The thick solid line represents the best fit obtained from the superposition of three individual Gaussian bands C, D, G. The horizontal slash indicates the background level.

films have been investigated by EELS measurements. The spectra obtained for C₂₀, C₆₀, and C₉₀₀ films are plotted in Fig. 4 as well as the spectrum of pure graphite for comparison. A thin top layer of amorphous carbon, due to the sample contamination during the transfer in the microprobe, is observed when the primary electron energy (1 keV) is too low to probe deeply under the surface. Measurements performed with primary electrons of 2 keV energy allow a better minimization of the amorphous

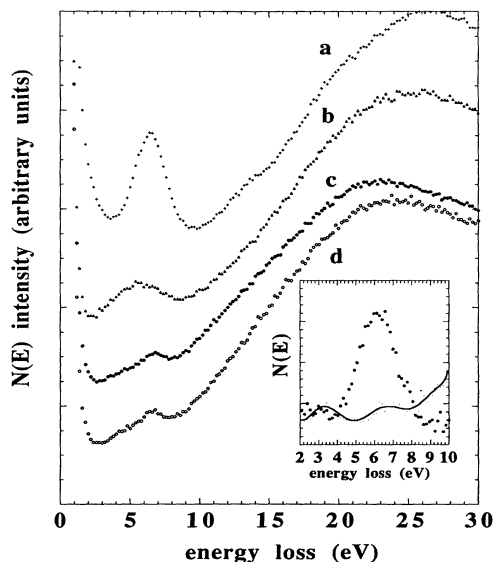


FIG. 4. Energy loss spectra measured with 1 keV electrons and a resolution of 1 eV for HOPG graphite (reference sample) (a), C₉₀₀ film (b), C₆₀ film (c), and C₂₀ film (d). Energy loss spectra obtained with 2 keV electrons and a 0.5 eV energy resolution, for HOPG sample (dotted line) and C₂₀ film (solid line), are presented in the inset.

carbon surface contribution (see inset in Fig. 4). Higher electron energies graphitize the samples. The most intense plasma peak is due to collective excitations of electrons participating to σ and π transitions. This peak position is dependent on the material density. It is observed at 33 eV in diamond and 27 eV in graphite. As in various diamondlike carbon films which have a lower density than graphite, we observe a slight peak shift towards lower energies for our samples. Such an effect can be explained by the granular structure of our films deduced from AFM and scanning electron microscopy observations. The second peak located near 6.3 eV in the spectrum, corresponding to the HOPG (high oriented pyrolytic graphite) sample given for reference, is due to π - π^* transitions of delocalized electrons. This plasmon band disappears in the spectrum of the C₂₀ film in benefit of a peak near 3.4 ± 0.5 eV, which can be attributed to π - π^* transitions of localized electrons. Such a peak is systematically observed in the spectra of pure C₆₀ powders [25]. The presence of these localized π electrons (confirmed by optical measurements [21]) once more suggests that the C₂₀ films are constituted by small isolated graphitic grains embedded in a sp^3 hybridized random network. The low conductivity of the C₂₀ films (10^{-7} Scm⁻¹), compared to the C₉₀₀ film conductivity (10^{-2} Scm⁻¹), confirms the loss of the semimetallic character by small cluster deposition.

In conclusion, we show for the first time that the LECBD technique allows the growth of thin films in which the particular electronic structure of the free clusters is conserved. Moreover, our results confirm the proposed cage model for smaller fullerenes than C₆₀ (namely, C₂₀), up to now only observed in mass spectrometry experiments or predicted by calculations. The attractive field of applications of this technique concerns the possibility of realizing diamondlike thin films with controlled hybridization and particle sizes. The use of a size distribution containing various species with different hybridizations can explain the mixing of graphitic and diamond phases in our films. However, from the large exploration of cluster sizes (from C₂₀ to C₉₀₀), it has been possible to establish clearly the correlations between the nature of free clusters and corresponding films. In future experiments with mass selection of a unique type of cluster, we could expect to produce films with a pure hybridization. Mechanical and optical specific property studies of our films are in progress. Potential extensions of such studies to other covalent materials (e.g., silicon) as well as to metals seem promising.

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