Chemical and thermal stability of carbyne-like structures in cluster-assembled carbon films

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Nanostructured carbon films consisting of sp chains (polyynes and polycumulenes) embedded in an sp^2 matrix are grown using supersonic carbon cluster beam deposition in ultrahigh vacuum at room temperature. All the specimens have been analyzed by *in situ* Raman spectroscopy. The use of different excitation wavelengths (532 and 632.8 nm) confirms the presence of distinct carbynoid species. Chemical stability of the sp species has been studied by exposing the as-deposited films to 500 mbar of H_2, He, N_2, and dry air. Gas exposure produces an exponential decay of the carbynoid fraction slightly affecting the sp^2 component. Helium, hydrogen, and nitrogen do not chemically interact with the sp chains whereas oxygen reacts with the carbynoids species causing their fast and almost complete destruction. The films have been also thermally annealed at 20°, 100°, 150°, and 200 °C. The amount of carbynoid species is rapidly and strongly reduced at temperature larger than room temperature. The relevance for material science and interstellar chemistry of the production of a bulk form of carbon where sp and sp^2 hybridizations coexist is addressed.

I. INTRODUCTION

The combination of sp^3, sp^2, and sp hybridized atoms can give rise to a large number of carbon allotropic forms and phases, however only carbon solids based on all sp^3 (diamond) and sp^2 (graphite, fullerene) are well known and characterized.[1] In addition there are innumerable transitional forms of carbon where sp^2 and sp^3 hybridization bonds coexist in the same solid such as in amorphous carbon, carbon black, soot, cokes, glassy carbon, etc.[2-4]

Solids based on sp hybridization, although subject of intense experimental efforts, seem to be the most elusive of the different carbon families.[5] The existence of linear chains of carbon atoms linked by alternating single and triple bonds (polyyne) or double bonds (polycumulene) with stabilizing molecular complexes at the end of the chains, has been recognized in interstellar molecular clouds and can be artificially produced by different chemical routes.[6-8]

Polyyne and polycumulene are very fragile and reactive: exposure to oxygen and/or water completely destroys these species.[5,9] Isolated carbon chains have been extensively studied only in the gas phase[10-12] or by means of matrix isolation spectroscopy at very low temperature.[13-15] The high reactivity of unsaturated sp chains and their tendency to undergo chain–chain cross-linking reaction causing the evolution towards a sp^2 phase[7] generated a deep skepticism about the possibility of assembling sp carbon chains to form a solid.[5]

Despite their fragility, the existence of an elemental carbon solid formed solely by sp chains known as ''carbyne'' has been proposed by many authors and it has been subject of controversy.[16] Several results have been published mainly on the crystallographic characterization of this hypothetical material, however no compelling evidence of the existence of carbyne solid has been provided so far.[5]

sp chains synthetic routes are based on the high pressure and high temperature modification of carbon-based solids[17] or on chemical strategies aiming at the elimination of substituents from a linear organic molecule to end the naked linear carbon backbone.[7,18] This latter strategy includes catalytic dehydropolymerization of acetylene,[19] dehydrohalogenation of chlorinated polyacetylene,[19] air promoted coupling reaction of dicopper acetylide,[20] electrochemical reductive carbonization of poly(tetrafluoroethylene).[9]

The material obtained with the ''chemical'' approach is formed by carbon chains separated by reaction byproducts (for example alkali metal fluoride) preventing cross-linking reaction between adjacent carbynic chains and decomposition in a reactive environment.[9] These systems are conceptually similar to the matrix-isolated ones where polyyne of polycumulene species are kept isolated and protected form chain–chain and chain–moisture interaction.[21]

Recently we have shown the possibility of growing a pure carbon solid containing a significant amount of carbynoid structures by supersonic carbon cluster beam deposition (SCBD) at room temperature in an ultrahigh vacuum (UHV).[22] *In situ* Raman spectroscopy has confirmed the presence of polyynes and polycumulenes in a nanostructured sp^2 matrix. These sp hybridized linear carbon structures are metastable even in UHV at room temperature. When exposed to oxygen, the carbon network structure rapidly evolves towards a more common mainly sp^2 amorphous phase, with only a small residual amount of sp linear aggregates.[23] Polyyne chains appear to be more stable under oxygen exposure than polycumulenes.[22]

A deeper understanding of the stability of sp carbon structures and of their role in the nanostructured carbon network (abundance, stabilization mechanisms, interconnectivity) would provide a new insight in the physics and chemistry of linear carbon chains and it would address the long sought opportunity of combining carbon building blocks with differ-
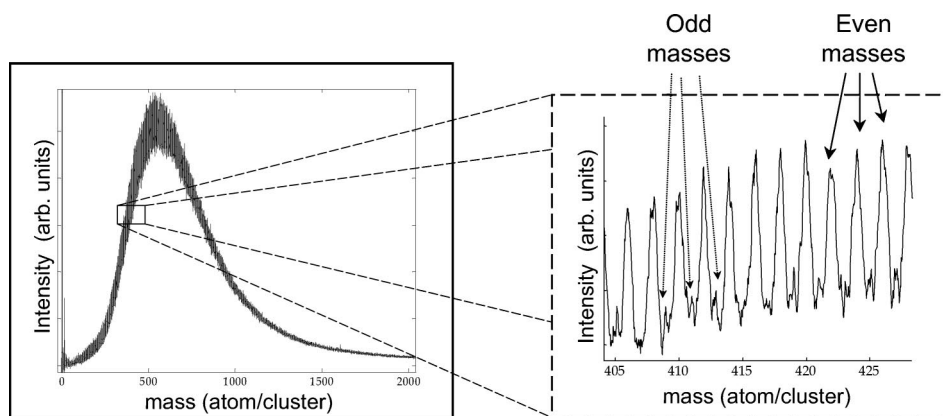
FIG. 1. Mass distribution of the cluster beam measured by a reflectron TOF/MS. The masses are expressed as number of carbon atoms per clusters. As shown in the enlarged windows clusters with both odd and even number of carbon atoms can be observed.

ent hybridization to produce new forms of carbon with tailored structural and functional properties.[1,24]

Here we present a Raman spectroscopy characterization of *sp* carbon chains embedded in a nanostructured carbon thin film deposited by SCBD. The evolution of *sp* carbon chains when exposed to different inert or reactive atmospheres (He, N_2, H_2, and dry air), or when annealed in vacuum at various temperatures up to 200 °C has been followed by monitoring the variation of the Raman peaks associated to polyynes and polycumulenes in order to achieve detailed information about the chemical and thermodynamical stability of these species.

II. EXPERIMENTAL SETUP

Nanostructured carbon thin films containing carbynoid species were grown in UHV conditions by the deposition apparatus CLARA (Cluster Assembling Roaming Apparatus) described in detail in Ref. 25. CLARA consists of three differentially pumped vacuum chambers equipped with a pulsed microplasma cluster source (PMCS) (Refs. 26,27) and a linear time-of-flight mass spectrometer (TOF-MS).

The PMCS produces a pulsed beam of carbon clusters seeded in helium with a mass distribution with an approximately log-normal shape peaked around 600 atoms/cluster and extending up to several thousands atoms (Fig. 1). The kinetic energy of the clusters is roughly 0.3 eV/atom. High resolution TOF/MS characterization and *in situ* x-ray photoemission spectroscopy indicates that no contaminants (oxygen, nitrogen, hydrogen) are present in the beam and on the deposited films.[28]

Cluster-assembled films were prepared and characterized by Raman spectroscopy in a small UHV chamber connected to CLARA, where a substrate on a holder intercepts the cluster beam. Clusters have been deposited on a silicon substrate kept at room temperature up to a thickness of 200 nm, estimated by means of a quartz microbalance rate measurement. The deposition rate was typically 4 nm/min. The excitation light was the 532 nm line of a frequency-doubled Nd-Yag or the 632.8 nm line of a He–Ne laser. Backscattered light was analyzed by a Jobin-Yvon T64000 spectrometer in triple grating configuration and detected by a liquid nitrogen cooled CCD camera. Spectral resolution is below 3 cm^{-1}.

The substrate temperature has been varied after the film deposition up to 350 °C by means of a tungsten heater

mounted on the sample holder. The final temperature can be reached in a few minutes and it can be kept constant within ±2 °C by means of an electronic controller.

The deposition chamber was also equipped with a precision leak-valve and a capacitance manometer in order to allow the introduction of pure gases after the deposition and a careful control of their pressure.

III. EXPERIMENTAL RESULTS

A. Raman characterization of the as-deposited films

Raman spectra of cluster-assembled carbon films grown in ambient conditions are characterized by the presence of the so-called *G* and *D* bands in the 1300–1600 cm^{-1} spectral region.[29] Their position and shape can be related to the degree of structural disorder of the film and to the distribution of bond lengths and angle distortions.[30] A weak feature in the 2000–2200 cm^{-1} spectral region is also present.[23] This feature can be interpreted *a posteriori* as due to *sp* chains protected from oxidation by the sp^2 carbon matrix (see Fig. 2).

A peak at 2100 cm^{-1} dramatically increases in intensity in the *in situ* spectrum (we will refer to it as ''*C*'' peak), as
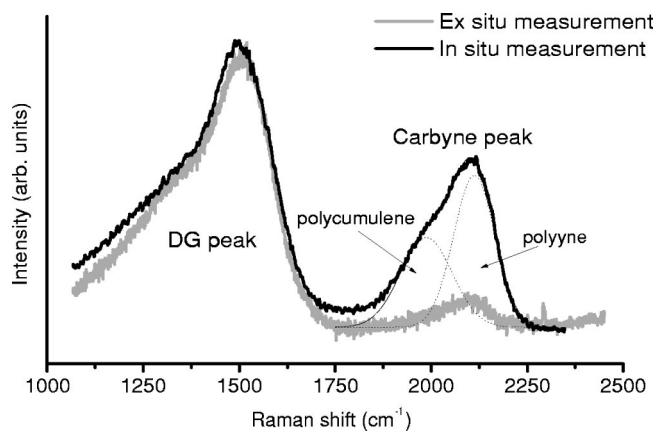

FIG. 2. Raman spectra of cluster-assembled carbon films grown at room temperature. The two spectra were collected *ex situ* (gray) and *in situ* in UHV conditions (black). For the *in situ* spectra we show the two fitting curves of the carbyne peak, identifying the polycumulene (left) and polyyne (right) contributions.
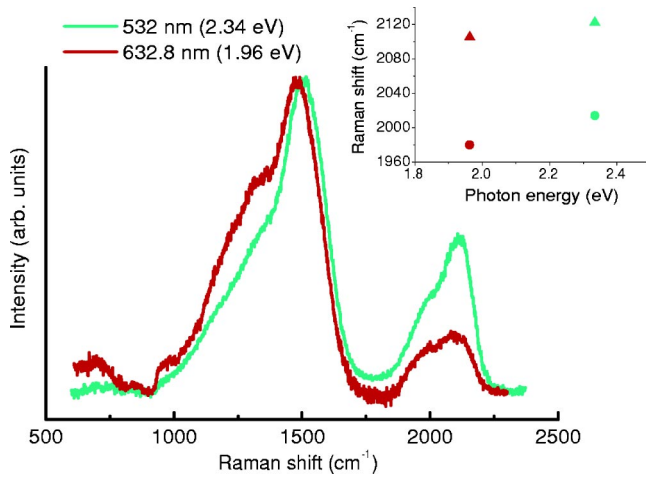
FIG. 3. (Color online) *In situ* Raman spectra of cluster assembled carbon films obtained with different excitation wavelengths: a frequency-doubled Nd-Yag (532 nm) and a HeNe (632.8 nm). In the inset: dispersion of polycumulene peak (solid circles) and polyyne peak (solid triangles).

shown in Fig. 2, whereas G and D bands undergo small changes from *ex situ* to *in situ* deposition.

The C peak has a remarkably strong intensity and appears to be structured and composed of a main broad peak at about 2100 cm^{-1} and a weaker shoulder centered around 1980 cm^{-1}, as evidenced by a two-Gaussian fit (see Fig. 2). The peaks at 2100 and 1980 cm^{-1} can be assigned to the vibrational frequencies of the C–C bond in both polyyine and polycumulene chains respectively.[5,9,31] The relative C peak intensity of the as-deposited carbon, expressed by the ratio between its integrated intensity and the D–G band integrated intensity ($I_C^{rel} = I_C/I_{D,G}$) is roughly 45%.

An accurate quantitative determination of the sp content with respect to sp^2 is not possible by Raman spectroscopy,[30] since the actual Raman cross section of linear chains and rings embedded in the carbon amorphous network is not known. Nevertheless, the integrated intensity of the carbyne peak I_C^{rel} is directly related to the carbyne amount in the network and was thus chosen as the main parameter relating to their evolution. Owing to the amorphous character of the material, Gaussian fitting functions have been chosen for the analysis of Raman peaks.

In Fig. 3 we report the Raman spectra of the cluster-assembled material immediately after deposition in UHV conditions, obtained with different excitation wavelengths (532 nm and 632.8 nm). Using an excitation wavelength of 632.8 nm we observe a G peak shift towards a lower frequency (roughly 30 cm^{-1}) and an I_D/I_G increase with respect to the case in which a 532 nm wavelength is used. This reflects the typical dispersion behavior for G and D features in mainly sp^2 amorphous carbon.[32] I_C^{rel} is smaller at 632.8 nm in agreement with the observation on polymeric carbon reported in Ref. 9. By varying the laser excitation energy also the relative polycumulene/polyyne intensity ratio varies and it is larger at 632.8 nm than at 532 nm.
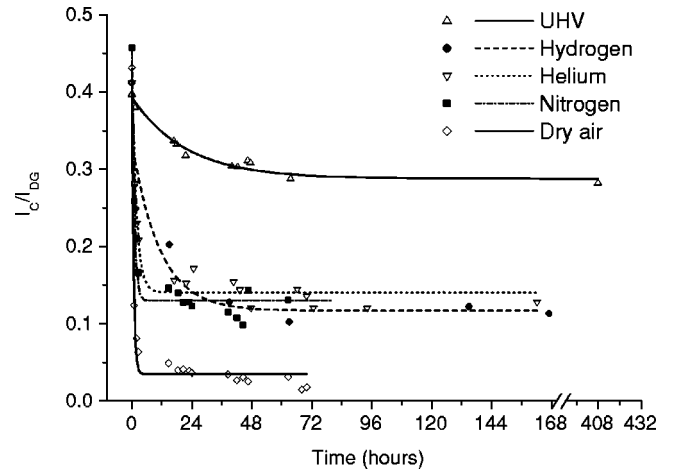

FIG. 4. Decay behavior of the relative C peak intensity as a function of UHV residence time and different gases exposure times.

B. Gas exposure

The sp chains are metastable and have the tendency to undergo cross-linking reactions to form the sp^2 phase.[7] In order to characterize the sp metastable decay we have monitored the sp chain stability through the evolution of the C peak intensity, either keeping the sample under UHV for several days (at a pressure of about $2 \cdot 10^{-9}$ Torr) or exposing it to different atmospheres (H$_2$, He, N$_2$, and dry air). In the case of UHV conditions, we have observed a slow decrease of the intensity of both the two components of the C peak and small changes in the shape of the G and D bands. The temporal evolution of I_C^{rel} is well described by an exponential decay plus a constant: $I_C^{rel} = R_0 + R_1 e^{-t/\tau}$ (see Fig. 4). This provides an estimate of the characteristic decay time constant and of the residual nonreacted fraction of carbynoid structures. A characteristic decay time of the order of 22 h, resulting in a reduction of I_C^{rel} to a 29% of the as-deposited value has been observed (see Table I). It is worth noting that this residual intensity is almost one order of magnitude greater than the intensity measured in *ex situ* samples, and that it remains stable even after 18 days from the deposition.

In order to characterize the effect of gas exposure on polyynes and polycumulenes, we have monitored the evolution of I_C^{rel} in films exposed to the different gases at the pressure of 500 mbar. Figure 5 shows the temporal evolution of the Raman spectrum of a film exposed to N$_2$. Similar spectra have been obtained for helium and hydrogen expo-

TABLE I. Fitting parameters for the exponential plus a constant decay of the relative C peak intensities under exposure of different gases.

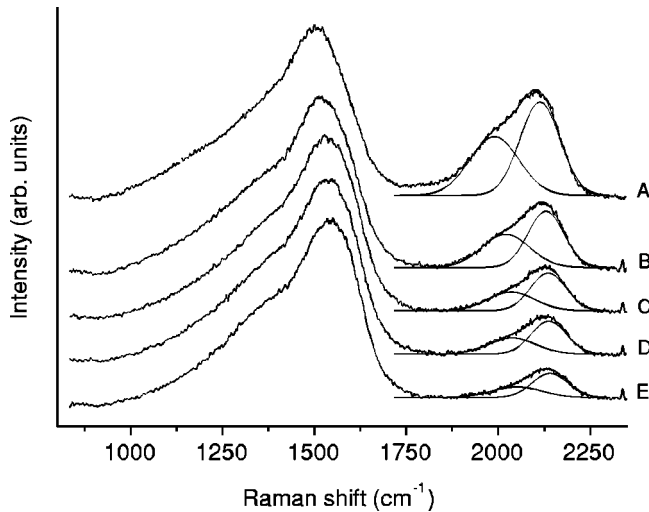|	R_0	τ (h)
UHV	28.8±0.5%	22±3
H$_2$	12.0±0.8%	11±3
He	14.1±0.3%	2.0±0.1
N$_2$	13.0±0.2%	1.0±0.1
dry air	3.6±0.2%	0.58±0.03

FIG. 5. Raman spectra of a 200 nm thick sample exposed to 500 mbar of molecular nitrogen after different exposure times: as deposited (A), after 50 min (B), 2.5 h (C), 18.5 h (D), and 44.5 h (E). Gaussian fit of the two components of the carbyne peak is also reported.
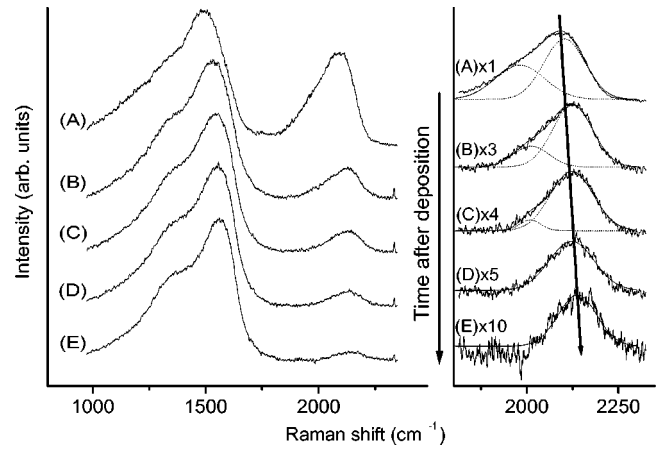

FIG. 6. Left panel: Raman spectra of a 200 nm thick sample exposed to dry air at different time; as deposited (A), after 50 min (B), 2.5 h (C), 15 h (D), and 70 h (E). Right panel: evolution of the corresponding carbyne peak and Gaussian fit of its two components. The arrow underlines the blueshift of the carbyne peak occurring during its decay.

sure indicating that the evolution of the polyyne and polycumulene peaks is substantially similar for all these gases. Dry air induces a different behavior that will be discussed later.

The intensity of the C peak decreases readily following an exponential law and reaching an asymptotic value after a few hours from gas injection (Fig. 4). Table I presents the results of the analysis of the evolution of I_C^{rel}, fitted with an exponential decay: the time constants τ and the percentage R_0 of the nonreacted fraction of sp chains for the different gas exposures are shown, together with the parameters of the metastable decay in UHV as discussed above.

The gas exposure slightly affects the sp^2 component of the carbon network. Since these changes are not relevant as for the C band, I_C^{rel} can be considered a reliable parameter when following the sp component evolution.

Qualitatively the same behavior is observed for exposure to helium and molecular hydrogen, the analysis of the decay time constants and the R_0 for hydrogen, helium, and nitrogen shows that the values of R_0 varies from 12% to 14% for the three gases, while τ is substantially different ($\tau_{N_2} = 1$ h, $\tau_{He} = 2$ h, $\tau_{H_2} = 11$ h). The relative intensity of the polyyne and the polycumulene components remains substantially unchanged during the peak evolution and only a small blueshift is observed for both peaks.

This indicates that exposure to a different atmosphere, at the same pressure, mainly affects the kinetics of the decay, while the fraction of sp chains surviving the gas exposure is independent of the specific gas. τ values are found to decrease with increasing mass of the gas molecule: the higher the mass, the faster the decay. The τ trend does not seem to be directly related to the gas molecule size.

A different interaction mechanism is expected and it is observed when the cluster-assembled films are exposed to dry air, since oxygen is known to readily react chemically with carbon chains.[7] Figure 6 shows the evolution of the

Raman spectrum during exposure to dry air. As reported in Table I, the C peak decay is faster for dry air than for the other gas ($t_{\mathrm{air}} \cong 0.6$ h, with a partial pressure of oxygen of 100 mbar), and the corresponding asymptotic I_C^{rel} value is significantly smaller ($R_0 \cong 3\% - 4\%$) and comparable to what observed in *ex situ* measurements.

The relative intensity of the polyyne and polycumulene contributions to the C peak is not constant during dry air exposure. In the right panel of Fig. 6 the C peak evolution is shown in detail: the polycumulene peak decreases much more rapidly, and roughly 15 h after air injection there is no remaining detectable signal from polycumulenic chains.

C. Thermal stability

In order to investigate the thermal stability of linear carbon chains, we have characterized *in situ* the C peak evolution in Raman spectra of thermally annealed films at different temperatures (up to 200 °C) under UHV conditions. For each temperature, starting from RT we have taken a series of Raman spectra at fixed time intervals for a period of several days.

In Fig. 7 we report the I_C^{rel} evolution as a function of time at RT, 100 °C, 150 °C, and 200 °C. This evolution cannot be fitted by a simple exponential decay; a better description can be obtained by using a sum of two exponential decays with different time constants: $I_C^{\mathrm{rel}} = R_0 + R_1 e^{-t/\tau_1} + R_2 e^{-t/\tau_2}$. The first time constant is of the order of tens of minutes, while the second is of the order of hours. The values of the two decay constants τ_1 and τ_2 and the asymptotic value R_0 are reported in Table II.

We observe threshold effects at different temperatures both for the slow decay constants τ_2 and in the fraction of surviving carbynes after the thermal treatment R_0. This has a value of roughly 29% after the metastable decay at RT, it drops at 15% at 100 °C remaining constant up to 150 °C. We observe another drop to 8% at 200 °C. This suggest the pres-
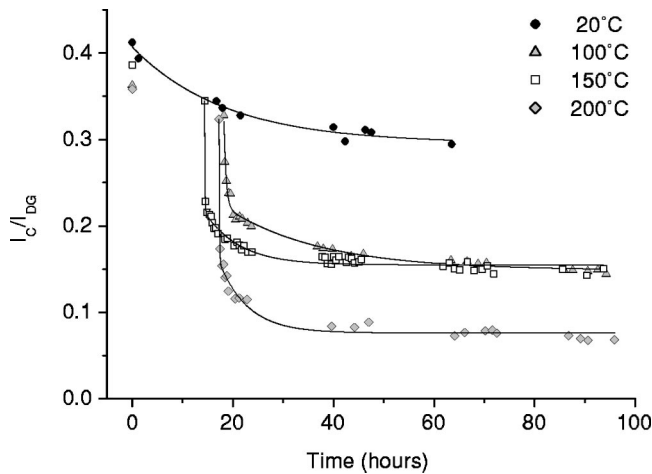
FIG. 7. Decay behavior of the relative C peak intensity during temperature treatment of the sample.

ence of two activated processes with energy barriers situated between 25 and 40 meV.

On the other hand, τ_2 abruptly decreases when passing from 100 to 150 °C annealing, while only a small decrease is observed at 200 °C, when a new energy barrier is presumably being overcome. In the range 100–150 °C, instead, a τ_2 decrease suggests that the temperature only affects the decay kinetics.

IV. DISCUSSION

Up to now it was widely accepted that polyyne chains can be stabilized in structures where a large interchain distance is maintained by interdispersing foreign materials.[7] Moreover polycumulene structure have been predicted to be so fragile that the synthesis of a material containing this type of sp chains has been considered extremely difficult if not impossible.[5]

Our experiments provide several novel aspects to the scenario of sp chains production and assembling. In cluster-assembled films polyynes and polycumulenes can survive in an sp^2 carbon matrix at room temperature if oxygen is absent, moreover they can survive a landing process where the kinetic energy per atom is of several fraction of an eV.[22]

The presence of the different carbon sp species is confirmed also by the behavior of Raman peaks at different excitation wavelength. So far, the only reported studies of the carbynoid peak dispersion behavior were performed by Kastner et al.[9] for carbynoid chains obtained by carbonization of PTFE by alkali metals, and by Akagi et al.[33] Kastner et al.

TABLE II. Asymptotic value and exponential decay times obtained by double exponential plus constant fit of the relative C peak intensities for different thermal annealing of the sample.

	R_0	τ_1 (min)	τ_2 (h)
20 °C	29.0±0.9%	⋯	21±5
100 °C	14.9±0.5%	27.0±2.1	18.3±2.2
150 °C	15.5±0.3%	16±4	6.5±0.9
200 °C	7.6±0.3%	12±3	6.1±1.2

observed a shift of the C–C peak (attributed to polyyine chains) from 1960 to 2080 cm^{-1} when the excitation energy changes from 1.9 to 3.1 eV. This dispersion effect in conjugated systems is explained in terms of a correlation between conjugation length and electronic structure and attributed to a photoselective resonance process.[34] Akagi et al. report a dispersion of the polyyinic peak (observed at higher frequencies, roughly 2100–2150 cm^{-1}) of 60 cm^{-1}/eV. We were able to observe a similar dispersion behavior for both spectral contributions (70–80 cm^{-1}/eV for the polycumulene peak, 60 cm^{-1}/eV for the polyyne peak as shown in the inset in Fig. 3). Moreover, both Akagi et al. and Kastner et al. observed an enhancement of the C peak intensity, relatively to the $G+D$ intensity, of an order of magnitude or more, when changing the excitation source in the same interval. We also observe an enhancement of the overall C peak, but with a larger increase of the polyyne peak with respect to the polycumulene peak. This represents a further indication of the different electronic structure of the two components of the carbynoid peak.

The interaction with H_2, N_2, and He causes a decrease of the carbynoid species. Since the decay times are related to the mass of the gas molecules or atoms, we suggest that the gas action is simply mechanic and that the gas species hit the sp chains causing the rearrangement of the metastable species.

Cluster-assembled carbon film are very porous with a pore diameter peaked at 3–4 nm, as shown by adsorption/desorption isotherm analysis.[35] The gases used in our experiments have a molecular or atomic size much smaller than the average pore size, so it is reasonable to assume that they equally diffuse in the mesoporous film network and interact with the same amount of linear carbon structures. This explains the similar R_0 value observed for the three gases. The time required to reach the asymptotic value of I_C^{rel} is affected by the momentum transferred from the molecule to the film network during collisions, hence by the mass of the gas molecule. We note that H_2 does not seem to chemically interact with sp chains.

A different behavior is observed for the interaction with oxygen where a chemical reaction takes place. In this case we observe a much faster decay and a stronger shortening of the sp chains, as shown by a higher blueshift of the carbynic Raman peaks, indicating that a sort of chain cleavage is taking place causing the shortening of polyynes and polycumulenes (see Fig. 8). Both theoretical[36] and experimental observations[33] suggest that the vibrational frequency of carbon chains should increase with decreasing length. Moreover, we also observe that the cumulenic fraction is completely destroyed by oxygen exposure, whereas some polyyne chains survive. This confirms the theoretical predictions[31] that cumulenic chains are less stable with respect to oxygen, and also explains why their contribution in previous ex situ Raman spectroscopy studies was not observed.

During exposure to all the gases, a blueshift (up to 60 cm^{-1}) and narrowing of the G peak, and an increase in the I_D/I_G relative intensity were detected. These changes (stronger in the case of oxygen), although not dramatic, seem
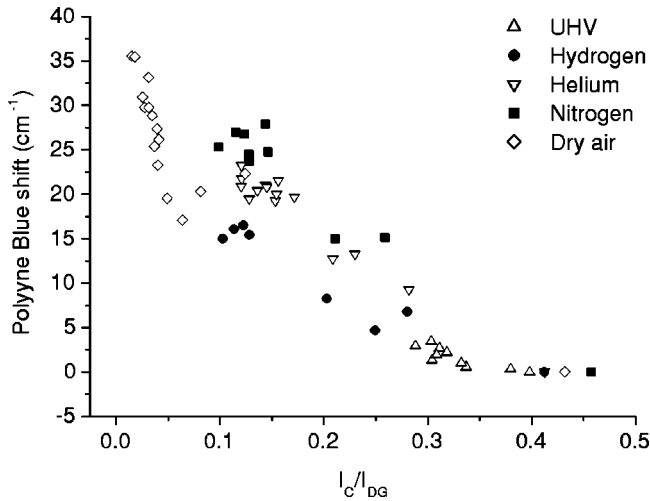
FIG. 8. Blueshift of the polyyne peak for different gas exposure.

to indicate a small trend towards ordering of the sp^2 phase.[30] An increase of the D component and a blueshift and narrowing of the G band are also visible in the evolution of the Raman spectra as a consequence of thermal treatments. While sp^2 phase changes during heating are certainly also related to the onset of an ordering (graphitization) process due to annealing, similar changes need an explanation in the case of exposure to oxygen and other gases.

In Fig. 9 we show the correlation between G peak position and I_C^{rel}. It can be observed that the decreasing of the I_C^{rel} corresponds to a shift of the G peak towards higher frequencies indicating a slight ordering of the sp^2 network. This indicates that a crosslinking mechanism,[5,18] proposed for the breaking of both polyynic and polycumulenic chains, is taking place leading to the formation of ordered hexagonal sp^2 graphitic domains.

Carbynoid systems obtained from perfluorinated hydrocarbons have shown to decay faster when heated although a systematic characterization of the effect of thermal annealing has not been provided.[9] We observe that moderate thermal heating in UHV conditions strongly affects the decay behav-
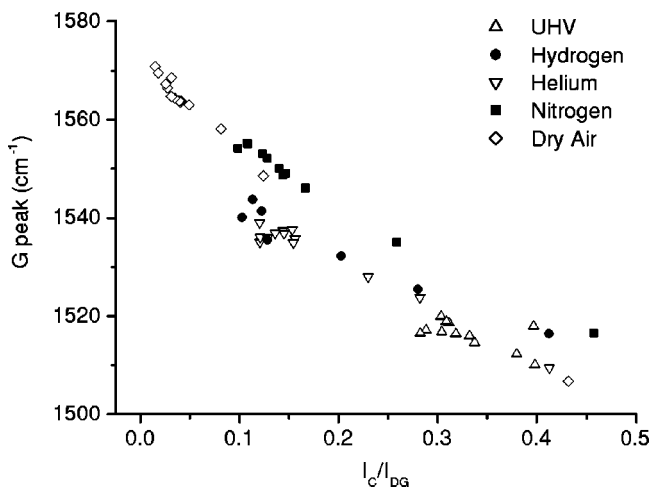

FIG. 9. Blueshift of the G peak versus I_C^{rel} for different gas exposure.

ior of the sp chains in nanostructured carbon. The sp phase seems to be very sensitive to temperature variations even in a small range. The presence of two very different decay times may suggest that the faster one is related to structural rearrangements induced by temperature gradients. The slower one should be related to accelerated cross-linking processes. Two different activation energies should correspond to these two regimes.

Considering the formation and deposition process of carbon clusters by PMCS, it is reasonable to assume that the carbynoid species are formed in the cluster source prior to deposition. The picture coming out from our observations is characterized by relatively fragile sp chains that are quite surprisingly able to survive deposition at kinetic energies per atom well above the thermal energy measured to induce the sp rearrangement and sp^2 formation.

One possible mechanism for the stabilization of sp chains in the carbon matrix may be the formation of joints between the chain ends and sp^2 island adatoms. Jarrold and coworkers have reported the observation of ball-and-chain dimers formed by fullerenes linked by sp chains obtained by laser desorption of fullerene films.[37] The same type of connections could be formed in our films, rich of fullerenelike fragments,[38] thus allowing the stabilization of the carbynoid species. Different type of stabilization sites could be present in our films since we observe a metastable decay of the carbynoid population.

The landing process and the heating process are taking place over two very different time scales. The landing process takes place on a short time scale and the kinetic energy can be efficiently dissipated among a huge amount of degrees of freedom of the substrate and of the cluster itself, especially for large clusters.[39] On the other hand the thermal heating is a process where vibrational modes are statistically populated: the time scale of the process is such that the modes leading to rearrangement can be efficiently populated.

Our results address also another relevant aspect of carbon clusters that is the shape and the hybridization of the precursor aggregates. As we have shown, we are depositing particles in a mass range where fullerenelike shape and sp^2 hybridization should be predominant.[40,41] However an accurate analysis of the mass spectra shows that the contribution of odd clusters is not negligible (Fig. 1). This suggests that nonfullerene-type of clusters could be more abundant than expected even for relatively large clusters. Another possibility, supported by the studies of Jarrold and co-workers[37] is that fullerene like clusters can form complexes with the presence of sp chains.

In any case the survival ability of polyyne and polycumulenes upon landing indicates that they are somehow protected by the aggregate where they have been formed, like a kind of "cushion" capable of absorbing and dissipating the deposition energy and to prevent the cross-linking reactions.

V. SUMMARY AND CONCLUSIONS

Our experiments show unambiguously that a pure carbon film rich of sp linear chains can be formed by assembling carbon clusters at room temperature under ultrahigh vacuum.

Polyyne and polycumulene species are present and stabilized in all-carbon metastable structures without the need of heteroatom terminal groups. Under He, N_2, and H_2 exposure the amount of sp species reduces with an exponential decay with time constants depending upon the mass of the gas. For the investigated gases no chemical interactions have been observed.

Oxygen chemically reacts with polyynes and polycumulenes causing an almost complete degradation of these species. Thermal treatments at moderate temperatures also cause a substantial reduction of the sp contents favoring cross-linking reactions. Threshold effects are observed at different temperatures suggesting the presence of activated rearrangement processes.

The existence of a form of solid carbon where carbynoid species can coexist with sp^2 hybridization has important implications for the achievement of a deeper understanding of the processes leading to the formation of carbon clusters,[40]

for the synthesis of novel carbon allotropic forms and nanomaterials,[1] for the chemistry of the interstellar medium.[12]

The production of a solid consisting of sp^2 and sp hybridized atoms support the theoretical prediction by Baughman *et al.*[24] about the existence of a layered carbon phase containing sp^2 and sp atoms dubbed graphyne.

Carbyne-containing carbon clusters may also be the vehicle for providing sp chains to different reactions taking place in the interstellar medium even for conditions considered, up to now, unfavorable for the survival of naked sp chains.[8]

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