t-SWCNTs as shown in Fig. 2(d). Only a little or no *t*-SWCNTs were observed in other sites **2**, **3** and **5**. Although metal impurity, black dots in Fig. 2(b) and (c), was also accompanied, the *t*-SWCNTs were successfully separated from fabricated texture of SWCNTs by ultrasonic atomization. It is worth noting that wreath-shaped aggregates of SWCNTs were observed in **2** and **5** (Fig. 3), when much shorter SWCNTs (HiPco) cut oxidatively with piranha solution were used [13].

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sp/sp^2 bonding ratio in sp rich amorphous carbon thin films

L. D'Urso, G. Compagnini *, O. Puglisi

Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria 6, Catania 95125, Italy

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The possible existence of a linear sp-allotropic form of carbon has been discussed in the literature since the beginning of the 1960's [1]. Nowadays carbynoids are considered very attractive systems for their possible technological applications and for fundamental reasons involving several fields. A crucial aspect in polyyne chemistry is the stabilization of the produced carbynoid structures. In fact adjacent carbon chains are highly reactive and hence transform to higher dimensional materials [2,3]. Either in studying stability or in the evaluation of the yield of the synthesis method, the evaluation of the amount of the sp hybridized carbons is of central importance. Since that Raman spectroscopy is considered as one of the most powerful tools to characterise pure carbon species, the aim of this letter is to show that this technique is suitable to be used for an easy determination of the sp/sp^2 bonding ratio in cluster assembled carbon films and for a general evaluation of the sp/sp^2 Raman scattering cross section.

In order to have sp rich carbon thin films with a wide variety of carbynoid concentrations, we started by depositing carbon cluster beams generated by using a pulsed laser vaporisation source (Nd:YAG laser operating at 532 nm) and seeded in a flow of helium buffer gas (5 bar). The ablated target was a high purity (99.9999%) graphite rod. The properties of such clusters have been widely

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* Corresponding author. Tel.: +39 095 7385077; fax: +39 095 580138.
E-mail address: gcompagnini@unict.it (G. Compagnini).

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investigated in the past [4]. For instance TOF mass spectra have shown the presence of alternated even-odd signals related to the formation of carbynoid structures. Immediately after the deposition, the samples (100–300 nm thick films deposited onto a silicon substrate) were positioned in front of a fused silica window for an "in situ" Raman analysis. Raman scattering was excited either by a 514.5 nm radiation (Ar laser) or by a 632.8 nm one (He–Ne laser). The backscattered light was collected and analysed by a confocal system, a Jobin Yvon single monochromator equipped with a notch filter and a CCD detector (3 cm^{-1} spectral resolution).

Since sp chains embedded in carbon thin films easily degrade as a consequence of their interaction with atmospheric gases, we have progressively reduced the amount of sp-hybridized carbons in our samples by allowing dry air to enter into the chamber. Fig. 1 shows the effect of such degradation on the first order Raman spectrum. Each spectrum is composed by a prominent wide band located between 1000 and 1700 cm^{-1} which is generally decomposed into a high frequency component (*G* line) at around 1550 cm^{-1} and a low frequency one (*D* line) at around 1360 cm^{-1}. Both *D* and *G* features are typical of highly disordered graphite-like structures. Their positions, widths and relative intensities depend on the deposition method and the experimental condition used [5]. In order to separate them, a two-peak-gaussian fitting procedure has been used (see inset in Fig. 1), considering that this is widely deemed suitable in disordered materials [5]. In addition to the expected *G* and *D* peaks, a strong asymmetric and broad signal between 1900 and 2200 cm^{-1} is evident. According to previous Raman spectroscopic studies on carbynoid samples this signal is related to the presence of a mixture of polyynes and polycumulenes [1,2]. Since these isomers have very similar Raman spectra, a distinction between them is not straightforward at this stage.

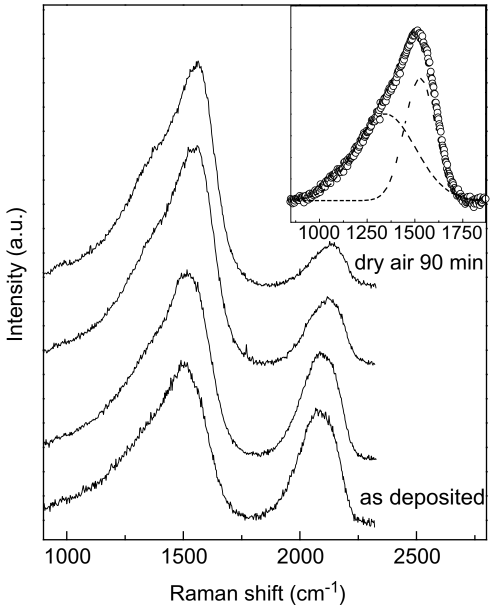

Fig. 1. Raman spectra for sp-rich amorphous carbon thin films with different carbynoid concentrations. The inset shows a typical deconvolution into D and G features.

When the as deposited sample is progressively exposed to dry air a number of changes are evident in the two Raman regions:

- The graphite-like band increases in intensity and the *G* component, initially at ~1512 cm^{-1}, is shifted toward higher frequencies.
- The sp signal progressively decreases in intensity and blue-shifts too. After 90 min in air, only a narrower band between 2000 and 2250 cm^{-1} is detected.

Then, there is an evident correlation between the increase of the sp^2 Raman signal and the decrease of the sp correlated one in agreement with other studies [3,6]. Regarding the *G* line blue shift, Casari [2] has already observed that this indicates a trend towards ordering of the sp^2 phase.

Now we consider, in the Raman scattering volume, the number fraction (x_{sp}) of sp-hybridized carbon atoms that constitute carbon chains of a variety of lengths. The rest should be composed by a graphite-like mixture where sp^3 hybridized carbon atoms are absent. In any case, even in the presence of a consistent fraction of tetrahedral carbons, their contribution to the overall signal can be neglected because the Raman cross section for sp^2 bonded species is much greater (50–200 times) than that for a sp^3 bonded one, at least using visible laser excitations [7]. In this way it is always possible to state that $x_{sp} + x_{sp^2} = 1$, where x_{sp^2} is the fraction of sp^2-hybridized bonded carbons.

We now introduce one of the most cited relations correlating the sp^2 average cluster size L (or the in-plane correlation length) with the integrated intensity ratio I_D/I_G: $\frac{I_D}{I_G} = \alpha L^2$; as proposed by Ferrari et al. [5]. In this formula α is a constant which only depends on the excitation wavelength (5.5×10^{-3} Å^{-2} for 514.5 nm excitation).

Naming ρ_D the density of sp^2 domains (assumed as a constant during the degradation process) in the scattering volume V, ρ_{sp^2} the density of sp^2 bonded carbons in a (planar) graphite-like domain and N the total number of carbon atoms embedded in V:

$$x_{sp^2} = \frac{1}{N}\rho_D \rho_{sp^2} V \left[\pi\left(\frac{L}{2}\right)^2\right] = \frac{1}{N}\rho_D \rho_{sp^2} V \frac{\pi}{4}\frac{1}{\alpha}\left(\frac{I_D}{I_G}\right) \tag{1}$$

Here we have assumed that graphite-like domains are present as fused sixfold rings rather than rows of rings. This condition has been found to be the most stable in amorphous carbons [8]. For this reason the sp^2 domains are assumed circular.

On the other hand, the integrated intensity ratio of the carbynoid signal (I_{sp}) with respect to the graphite-like one (including both *G* and *D* lines, I_{sp^2}) can be written as: