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# Microstructural analysis of carbon films obtained from C<sub>60</sub> fullerene ion beams

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## Abstract

Carbon films have been produced by accelerating C<sub>60</sub><sup>+</sup> ions on silicon substrates with energies between 100 and 800 eV. Furthermore some samples have been vacuum-annealed at 600 °C. The samples have been characterized by Raman and positron annihilation spectroscopies (RS–PAS). The measurements for the as-deposited material show that there is a coexistence of polymerized fullerenes and amorphous-carbon islands and that the structure depends on the energy of the incident ions. At low energies, fullerenes are deposited preserving the molecular identity and some intermolecular covalent bonds begin to insinuate; at higher energies, the amount of these covalent bonds increases and the amorphous islands predominate. After the annealing process, the amorphous phase organizes in graphitic clusters and the unbroken C<sub>60</sub> cages are transformed back to pristine and slightly polymerized C<sub>60</sub>.

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## 1. Introduction

Many theoretical and experimental works have investigated potential novel candidates for hard materials. In particular, the development of hard carbon-based materials has been extensively studied. The amazing

high value predicted for the bulk modulus of C<sub>60</sub> molecules and high-pressure crystals has prompted researches about these materials [1].

A wide variety of new hard carbon structures has been prepared from fullerenes under high-pressures and -temperatures inducing polymerization or amorphization [2–5]. At ambient conditions, C<sub>60</sub> forms nearly ideal molecular crystals with the molecules bound together by Van der Waals interactions. The polymerization of pristine C<sub>60</sub> results in the formation

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of fullerene cage networks of various dimensionalities: linear chains of polymerized fullerene molecules (1D  $C_{60}$ ), covalently bonded molecular planes (2D  $C_{60}$ ) and three dimensional fullerene crystals (3D  $C_{60}$ ) [6–9].

Although hard carbon structures have been produced from high-pressure and -temperature methods applied to solid  $C_{60}$ , these processes do not allow to obtain carbon films. We have replaced the high-pressure and -temperature methods by a dynamic process of deposition of fullerenes at different energies; it has been concluded that the characteristics of the obtained material depends on the deposition energy [10,11].

In this work, the materials obtained at different ion beam energies, are studied by Raman spectroscopy (RS) and positron annihilation spectroscopy (PAS) techniques, in order to get a picture of its microstructure. PAS and RS give complementary and valuable information on the structure of carbon films [12,13]: PAS is used to detect the distribution of the open volume (structural) defects while RS provides bulk information about the bonding character of the atoms (coordination and bond-angle disorder).

## 2. Experimental

Carbon films were deposited on silicon wafers by means of a fullerene ion beam at different energies [11]. Initially, fullerene powder (99.9%  $C_{60}$ ) is degassed during several hours at 200 °C until the pressure reaches a value below  $1 \times 10^{-6}$  mbar. Then,  $C_{60}$  is sublimated using a heater that carries the temperature of the powder to about 600 °C. An electron discharge is established between a hot filament and the anode, producing  $C_{60}^+$  into the discharge chamber. These ions are extracted from the discharge and accelerated first to a negative electrode and then to the substrate by a negative potential (from 100 to 800 V). The potential in the grid was maintained low during the discharge in order to avoid multiple ionization and fragmentation of the fullerenes [14]. The resulting samples were cleaned with toluene to dissolve the superficial molecular  $C_{60}$  that could have remained without bonding. On most of the samples, vacuum-annealing at 600 °C for 1 h was carried out. The as-grown and annealed samples were characterized by Raman and positron annihilation spectroscopies.

Raman spectra were recorded using a triple subtractive Jobin-Yvon T64000 monochromator equipped with a charge-coupled device. The 514.5 nm line of an  $Ar^+$  laser was used as a probe beam and the power was adjusted to minimize the temperature rise at the illuminated spot.

Positron measurements were carried out with an electrostatic slow positron beam using the Doppler-broadening technique. Positrons injected in a solid reach the thermal equilibrium in a few picoseconds then, after a diffusion path annihilate with an electron of the medium. In PAS with the Doppler-broadening technique, the 511 keV annihilation line is recorded by a High Purity Germanium Detector (resolution 1.2 keV at 511 keV), and its shape is characterized by the so-called  $S$  parameter. The  $S$  parameter is calculated as the ratio of the counts in the central area of the peak ( $|511 - E_\gamma| \leq 0.85$  keV, where  $E_\gamma$  is the energy of the Doppler shifted gamma ray) and the total area of the peak ( $|511 - E_\gamma| \leq 4.25$  keV). The Doppler-broadening of the 511 keV annihilation line  $\Delta E_\gamma = |511 - E_\gamma|$  is related to the electron-positron annihilating pair momentum component  $p_z$ , in the detector direction, by the relation  $\Delta E_\gamma = p_z c/2$ . The  $S$  parameter reflects the fraction of positrons annihilating with low-momentum electrons. An increase of the  $S$  parameter values with respect to a non-defected sample is an indication of the positron annihilation in open volume defects. In condition of trapping saturation, the higher the  $S$  value, the larger the open volume defects (i.e. vacancy, divacancy, voids) in which positrons annihilate. Details about the apparatus and the measurements can be found in Refs. [15,16] and in the references therein. The  $S$  parameter was measured as a function of the positron implantation energy in the 0.15–20 keV energy range. In the fullerene films, this range corresponds to a mean positron implantation depth ranging from 1 to 2500 nm. For each positron implantation energy,  $3 \times 10^5$  counts in the 511 keV annihilation line were accumulated. It corresponds to a statistical error of 0.1% on the measured  $S$  parameter.

## 3. Results

Samples of about 0.5  $\mu\text{m}$  thickness, obtained by the deposition of ionized fullerenes, were analyzed.

Raman and positron annihilation spectra of the as-deposited and vacuum-annealed samples were recorded as a function of the deposition energy.

### 3.1. Raman spectroscopy

Fig. 1 shows the Raman spectra of the as-deposited samples. For the sake of completeness, the spectra of pristine  $C_{60}$  evaporated on a silicon substrate and of amorphous-carbon (a-C) are also shown. The Raman spectrum of pristine  $C_{60}$  contains two  $A_g$  and eight  $H_g$  active modes, consistent with the  $I_h$  molecular symmetry; the spectra of a-C presents a broad band centered at about  $1500\text{--}1520\text{ cm}^{-1}$  (G-peak) with a shoulder at  $1350\text{ cm}^{-1}$  (D-peak).

From RS measurements (Fig. 1), different behaviors can be distinguished. The spectra of samples deposited up to 200 eV are similar to that of pristine  $C_{60}$ : the modes at 708 and  $773\text{ cm}^{-1}$  are still present, but they are slightly broadened. It can be observed that the intensity of the  $A_g$  peaks at 496 and  $1468\text{ cm}^{-1}$  decreases while

that of the peak at  $1573\text{ cm}^{-1}$  increases: there is a gradual inversion of the relative intensities of the last two bands. The spectrum of the sample deposited at 300 eV shows three bands between 1400 and  $1600\text{ cm}^{-1}$  and another group around  $700\text{ cm}^{-1}$  while all bands below  $600\text{ cm}^{-1}$  completely disappear. The bands at  $1400\text{--}1600\text{ cm}^{-1}$  are significantly broadened with respect to that of pristine and low energy deposited samples. For the samples deposited at energies from 400 to 800 eV the bands between 1400 and  $1600\text{ cm}^{-1}$  are even broader.

Fig. 2 shows the Raman spectra of the annealed samples. These spectra present a broad band at about  $1350\text{ cm}^{-1}$  and the group around  $700\text{ cm}^{-1}$ , together with the bands around 1426, 1468 and  $1573\text{ cm}^{-1}$ . It is to be stressed that as the deposition voltage increases, the intensity of the  $1350\text{ cm}^{-1}$  band increases and the peak at  $1573\text{ cm}^{-1}$  shifts to higher frequencies approaching to the  $1580\text{ cm}^{-1}$  graphite mode; on the other hand, the intensity of the fullerene bands around of 1450 and  $700\text{ cm}^{-1}$  gradually decreases.

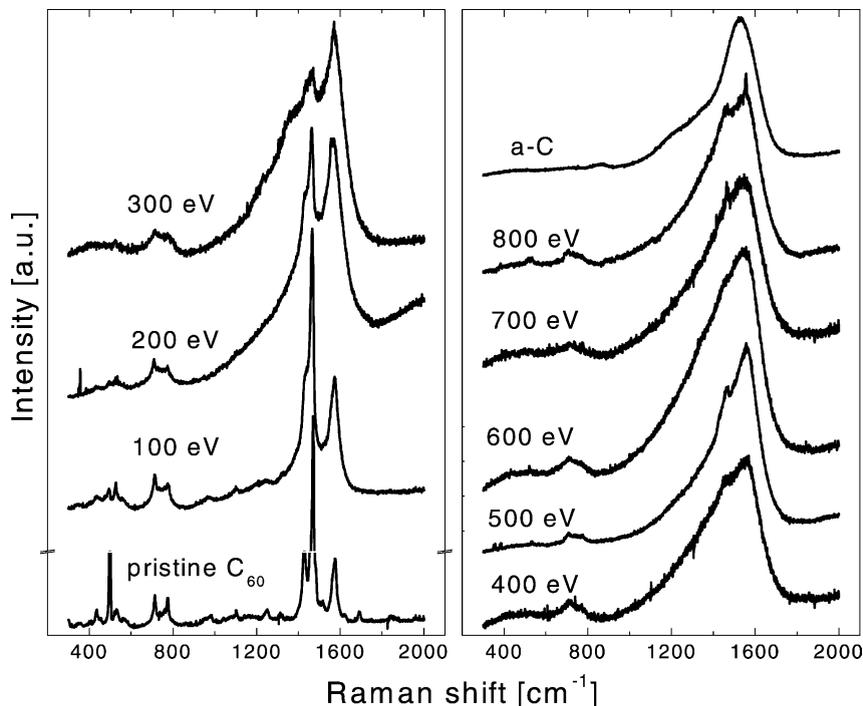


Fig. 1. Raman spectra of the as-deposited samples as a function of the deposition energy, pristine  $C_{60}$  evaporated on a silicon substrate and a-C sample.

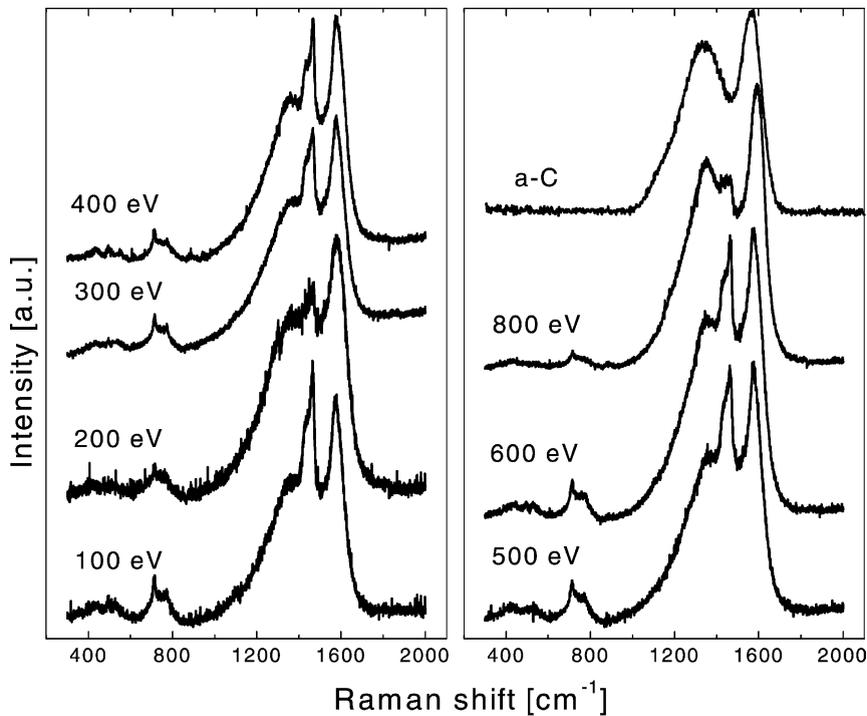


Fig. 2. Raman spectra of the vacuum-annealed samples at 600 °C, as a function of the deposition energy. For the sake of completeness, the spectrum of an annealed a-C sample is also shown.

### 3.2. Positron annihilation spectroscopy

Figs. 3 and 4 show the  $S$  values obtained from the positron annihilation measurements. The  $S$  parameter, normalized to the silicon  $S$  bulk value, is reported as a function of the mean positron stopping depth:

$$\bar{z} = \frac{AE^n}{\rho} \quad (1)$$

where  $A = 4.0 (\mu\text{g}^{-1} \text{cm}^{-2} (\text{keV})^{-n})$ ,  $\rho$  is the density ( $\rho = 2.1\text{--}2.2 \text{ g cm}^{-3}$ , in our samples) and  $n = 1.6$ ; the positron implantation energy ( $E$ ) is expressed in keV [17].

The  $S$  curves obtained from the measurements in hard amorphous-carbon (a-C) and in commercial microcrystalline graphite (m-graphite) have been included in Fig. 3. The a-C curve shows a  $S$  parameter that starts from a surface value ( $S = 0.917$ ), and then rapidly increases to reach the bulk value typical of the as-grown film ( $S = 0.948$ ). This value remains constant up to the interface with silicon, showing that the open volume defects have a homogeneous distribution

through the film. The curve obtained from m-graphite is almost constant ( $S = 0.92$ ). In this material, positrons are efficiently trapped in the small open volumes distributed among the microcrystallites and the positron lifetime ( $\tau_p$ ) is about 370 ps [12,18]. For  $\text{C}_{60}$ ,  $\tau_p \sim 370\text{--}400$  ps [19–21], this parameter is directly related to the electronic density at the positron annihilation site, therefore, the very close values for both materials show that the open volumes have approximately the same characteristics as probed by positrons. Furthermore, PAS in  $\text{C}_{60}$  is well known: experimental and theoretical studies agree in the conclusions that positrons test the interstitial regions in fullerenes [19–21].

From PAS measurements, shown in Fig. 3, different behaviors can be distinguished. For the samples deposited up to 200 eV, the  $S$  value is about 0.920 and remains constant up to the interface with silicon. For deposition energies close to 250 eV, the  $S$  parameter increases in the bulk (from 20 nm to the interface). For the samples deposited at higher energies, the  $S$  parameter starts from the same surface  $S$  value

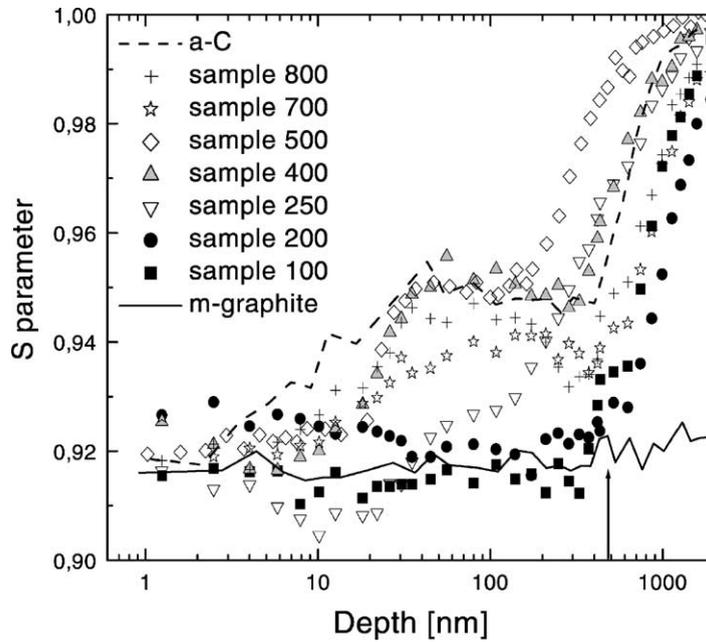


Fig. 3. Positron annihilation measurements:  $S$  parameter (normalized to the  $S$  bulk value of silicon) as a function of the mean positron implantation depth for the samples deposited at different energies. Positron annihilation measurements in amorphous-carbon (a-C, dashed line) and in microcrystalline graphite (m-graphite, solid line) are also shown. The arrow indicates the carbon-silicon interface position.

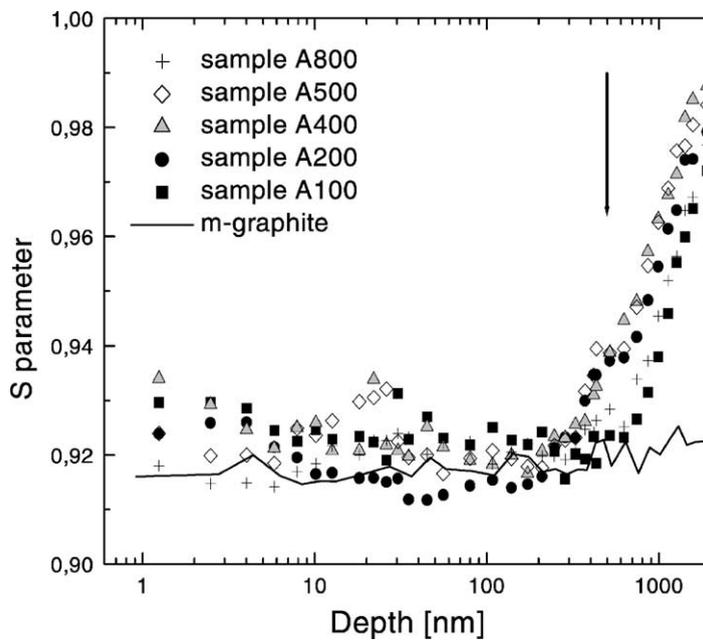


Fig. 4. Positron annihilation measurements:  $S$  parameter (normalized to the  $S$  bulk value of silicon) as a function of the mean positron implantation depth for the vacuum-annealed samples at 600 °C. Positron annihilation measurements in microcrystalline graphite (m-graphite, solid line) are also shown. The arrow indicates the carbon-silicon interface position.

( $\sim 0.92$ ) and quickly increases to reach a higher  $S$  value in the bulk. This  $S$  value is around 0.95 for the samples deposited at 400–500 eV and slightly lower ( $\sim 0.94$ ) for deposition energies of 700–800 eV.

Fig. 4 shows the positron annihilation spectra of the annealed samples. It can be observed that the  $S$  parameter has almost the same value for all the cases. However, for low-energy depositions,  $S$  value is similar for annealed and for as-deposited samples, while for higher deposition energies we observe a sharp decrease in the  $S$  value of the annealed samples with respect to the as-grown ones (from 0.948 to 0.922): the  $S$  value in the bulk reaches the one in the surface. At this annealing temperature, the films are homogeneous in all their thickness but with a lower  $S$  value.

#### 4. Discussion

The analysis of experimental data shows that the microstructure of the obtained material is highly dependent on the deposition energy.

For the samples obtained at 100 and 200 eV (Fig. 3), PAS measurements show that the  $S$  parameter is similar to that corresponding to microcrystalline graphite and pristine  $C_{60}$ . Positrons, as was mentioned above, annihilate with the same characteristics in the open volumes of the two carbon materials, and this is also confirmed by the similar  $S$  values. The Raman spectra are also similar to that of pristine  $C_{60}$ . However, there is a remarkable modification in the peaks corresponding to the  $A_g$  modes: the one at  $493\text{ cm}^{-1}$  (radial breathing of the cage) almost disappears while the intensity of the peak at  $1468\text{ cm}^{-1}$  (pentagonal stretching) significantly decreases. These results suggest that in these films the  $C_{60}$  molecules maintain their structure but some intermolecular covalent bonds begin to insinuate.

For deposition energies close to 250–300 eV, a noticeable change is observed by PAS and RS. The  $S$  value, from Fig. 3, is higher than the corresponding to 100–200 eV samples. The Raman spectrum (Fig. 1) shows that the bands are broadened with respect to that of pristine and low energy deposited samples. This broadening suggests that the covalent bonds between neighboring molecules are stronger.

As the deposition energy increases, Raman spectra become similar to that of amorphous carbon.

Nevertheless, a gaussian fitting shows that the  $C_{60}$  bands at  $1426$ ,  $1468$  and  $1573\text{ cm}^{-1}$  are still present. PAS results show that  $S$  value is similar to the corresponding to a-C. These results suggest that quite a lot of fullerene molecules have lost their identity. However, a slight difference between samples deposited at 400–500 eV and 700–800 eV can be observed in Fig. 3: the  $S$  parameter is lower for the later group, indicating that the material deposited at higher energies is more compact.

After annealing at  $600\text{ }^\circ\text{C}$  the behavior of a-C is well known: the carbon atoms organize themselves in graphitic clusters. The Raman spectrum (characterized by two peaks centered at  $1350$  and  $1580\text{ cm}^{-1}$ ) and the  $S$  value ( $\sim 0.91$ ) are similar to those corresponding to microcrystalline graphite [12]. The behavior of our samples after annealing is quite different, at least from the RS's point of view. All the spectra of the annealed samples present the aforementioned bands from graphitic clusters together with some peaks characteristic of fullerene molecules ( $1426$ ,  $1468\text{ cm}^{-1}$  and group around  $700\text{ cm}^{-1}$ ). These peaks suggests the presence of depolymerized fullerenes. From PAS measurement, the  $S$  value for all the samples reaches the one corresponding to microcrystalline graphite and pristine  $C_{60}$ , indicating an homogeneous distribution of small open volumes. These results show that the as-deposited material is a mixture of both amorphous-carbon and polymerized fullerene; after thermal annealing the amorphous islands organize in graphitic clusters and the unbroken  $C_{60}$  cages are transformed back to pristine and slightly polymerized  $C_{60}$ .

#### 5. Conclusions

Carbon films, deposited from ionized fullerenes accelerated to different energies, have been characterized by RS and PAS. It has been shown that the structure of the resulting material depends on the deposition energy; below 300 eV fullerenes are deposited preserving the molecular identity, though some intermolecular covalent bonds begin to insinuate. The amount of these covalent bonds increases with the deposition energy up to 800 eV.

The results from the annealed samples suggest that these materials consist of polymerized fullerenes

mixed with amorphous-carbon islands. The ratio between polymerized-fullerenes and a-C depends on the energy of the incident ions: for lower energies the fullerene-phase predominates while for higher energies the presence of a-C becomes more significant. It should be emphasized that not only the amount of polymerized fullerene changes but also the degree of polymerization.

As it has been shown, PAS and RS give valuable information on the structure of these films. The analysis of the microstructural properties is an important previous stage to study the mechanical behavior of this kind of novel carbon-materials.

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