

Mechanical and electrical properties of carbon films obtained from a C_{60}^+ fullerene ion beam

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INTRODUCTION

Many theoretical and experimental works have studied potential novel candidates for hard materials, such as hard carbon-based structures.

A wide variety of new hard carbon materials has been prepared from fullerenes under high pressures and temperatures inducing polymerization or amorphization. The polymerization of pristine C_{60} results in the formation of fullerene cage networks of various dimensionalities. Different electrical behaviors have been observed according to the structure obtained.

With the high-pressure/temperature methods applied to solid C_{60} it is not possible to obtain carbon films. We have replaced these methods by a dynamic process of deposition of fullerenes at different energies [1].

In this work, the structure of the obtained materials have been characterized by Raman spectroscopy as a function of the ion beam deposition energy. Besides, indentation hardness, elastic modulus, and electrical resistivity of the films have been measured.

EXPERIMENTAL

> Film Preparation

The method consists of sublimating fullerene powder (99.9% C_{60}) using a heater at ~ 600 °C. Then an electron discharge is established between the hot-filament and the anode, producing C_{60}^+ . The ions are extracted and accelerated from the discharge first to a negative electrode and then to a silicon wafer by a negative potential (from 200 to 2000 V) [2]. Carbon films of ~ 0.3 μm thickness were obtained at different energies.

> Film Characterization

Raman spectra were recorded using the 514.5 nm line of an Ar⁺ laser and a triple subtractive monochromator with a charge-coupled device.

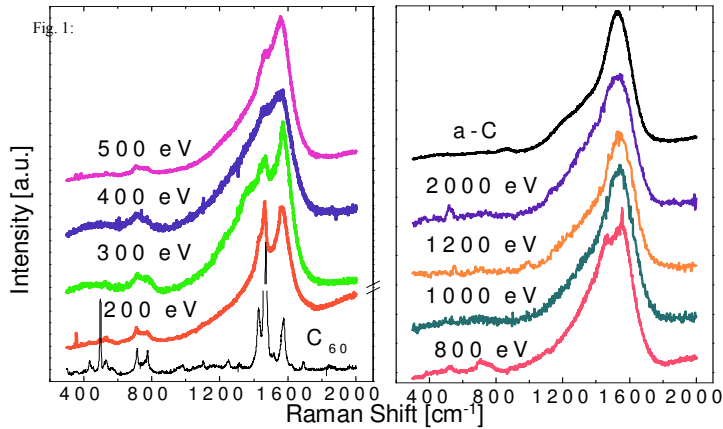
The **electrical resistivity** of the films was determined from I - V measurements. The thickness of the layers was large compared with the roughness of the substrate. The effect of the C-Si junction and the Si substrate was taken into account.

Microhardness and Young's modulus of the films were measured by the dynamical indentation technique using a commercially available apparatus. The resolutions are 1 nm in depth and 1 μN in load. The hardness and elastic modulus values were obtained from the analysis of the unloading branch of the load-penetration curve [3].

RESULTS

* RAMAN SPECTRA

Fig. 1 shows the Raman spectra of the samples as a function of the deposition energy. For the sake of comparison, the spectrum 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} presents 10 active $H_g + A_g$ modes, consistent with the I_h molecular symmetry; the spectra of a-C presents a broad band centered at about 1500-1520 cm^{-1} (G-peak) with a shoulder at 1350 cm^{-1} (D-peak).



For samples deposited at low energy, the spectra are similar to that of pristine C_{60} : the modes at 708 and 773 cm^{-1} are still present, but they are slightly broadened. The intensity of the A_g peaks at 496 (A_g radial breathing of the cage) and 1468 cm^{-1} (A_g pentagonal stretching) decreases while that of the peak at 1573 cm^{-1} (H_g hexagonal stretching) increases. The molecules preserve their identity and the bonding between neighboring molecules is still weak.

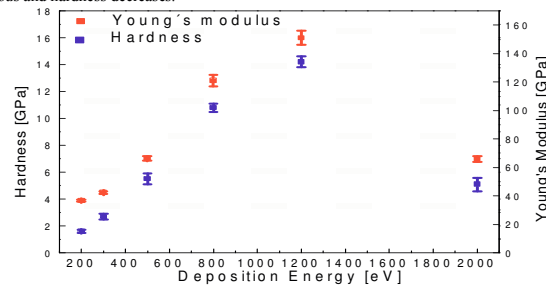
As deposition energy increases, the spectra are significantly broadened with respect to that of pristine and low energy deposited samples. The broadening of the Raman bands is due to the formation of covalent bonds between neighboring molecules. There is a group of peaks between 1400 and 1600 cm^{-1} and another group around 700 cm^{-1} while all bands below 600 cm^{-1} completely disappear. The intensity of the band at 1468 cm^{-1} further decreases and there is gradual inversion of the relative intensities of these two bands. The spectra become similar to that of amorphous carbon.

* ELECTRICAL RESISTIVITY

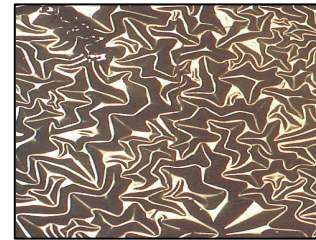
- > Pristine C_{60} has a high electrical resistivity of around 10^{10} $\Omega\cdot\text{cm}$.
- > For samples deposited up to 1000 eV, electrical resistivity decreases from 10^{10} to 10^9 $\Omega\cdot\text{cm}$. The materials are insulators.
- > For deposition energy around 1200 eV and higher ones, the electrical resistivity falls abruptly to the order of a few ohms-centimeter.

* HARDNESS

Fig. 2 shows measured hardness and Young's modulus of the films as a function of the deposition energy. It can be seen that the corresponding values increase with deposition energy up to 1200 eV, and then they decrease for samples grown at 2000 eV. This result suggests that as the polymerization process is in progress, as seen by Raman spectroscopy, films become harder due to the increasing number of covalent bonds between C_{60} molecules. At higher deposition energies the films become amorphous and hardness decreases.



However, for samples grown between 800 and 1000 eV, measured hardness widely varies (from 3 to 50 GPa) when taking different points in a same sample. For these deposition energies it is hard to obtain a good adherence of the films to the substrate. These films are very stressed and they tend to develop buckling and delamination, as can be seen under optical microscope (photograph).



CONCLUSIONS

Raman spectra show that the structure of the resulting material depends on the deposition energy. For low energies the fullerenes are deposited preserving the molecular identity, though some intermolecular covalent bonds begin to insulate. The amount of these covalent bonds increases with the deposition energy. The evidence suggests that at high energies the resulting material is completely amorphous. However, electrical resistivity measurements show that these samples have not the characteristics of standard amorphous carbon because their resistivity is very low.

Hardness and Young's modulus have a maximum value for a deposition energy of around 1200 eV. The films grown at 800-1000 eV are inhomogeneous and experimental evidence suggests that they could consist of nanocrystals of polymerized fullerene embedded in an amorphous matrix. So when the indenter tests amorphous regions, hardness is low, but in polymeric ones, it reaches values as high as 50 GPa. This is consistent with previous works that found extraordinary high hardness values for C_{60} fullerite obtained under high pressure, and with theoretical predictions of superhard structures for 3-D polymerized fullerenes.

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