Direct spectroscopic evidence of self-formed C_{60} inclusions in fullerenelike hydrogenated carbon films

J. G. Buijnsters,[1,a] M. Camero,[1] R. Gago,[1,2] A. R. Landa-Canovas,[1] C. Gómez-Aleixandre,[1] and I. Jiménez[1]

[1]*Instituto de Ciencia de Materiales de Madrid (CSIC), C\ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain*
[2]*Centro de Micro-Análisis de Materiales (CMAM) y Departamento de Física Aplicada, Universidad Autónoma de Madrid, 28049 Madrid, Spain*

The detection of self-formed C_{60} inclusions in hydrogenated carbon (C:H) with fullerenelike (FL) structure is reported. This material is synthesized by bias-enhanced electron cyclotron resonance chemical vapor deposition at low substrate temperatures (<120 °C). The FL structure is identified by high-resolution transmission electron microscopy whereas the presence of C_{60} inclusions is derived from spectral signatures in the $C(1s)$ x-ray absorption near edge structure. The formation of FL-C:H takes place for negative bias voltages higher than 100 V, in parallel with dehydrogenation and drastic improvement of the tribomechanical film properties. © 2008 American Institute of Physics. [DOI: 10.1063/1.2903502]

Amorphous carbon (a-C) is well known for exhibiting outstanding physical properties that have been traditionally assigned to the mixture of carbon atoms with sp^3 and sp^2 hybridizations.[1] However, a whole new family of carbon-based materials emerged in the last decade based on all-sp^2 three-dimensional (3D) networks, whose properties stem from the curvature and interconnection of the graphitic basal planes. Such a structure was first reported for graphitic carbon nitride (CN_x) (Ref. 2) and later for pure carbon films,[3] and has been named as fullerenelike (FL) structure due to the presence of highly curved graphitic structures as in C_{60} fullerenes. C and CN_x films with a FL structure present outstanding mechanical properties[4] that, unlike traditional diamondlike carbon, cannot be attributed to the presence of sp^3 hybrids with tetrahedral coordination but to the 3D sp^2-based FL structure. Regarding their synthesis, the FL-C(N) materials have been produced, hitherto, at temperatures around 400 °C by physical vapor deposition (PVD) techniques such as magnetron sputtering,[5] pulsed laser deposition,[6] arc deposition,[3] or ion beam assisted deposition,[7] that yield hydrogen-free materials. The FL structure in these materials can only be directly observed by high-resolution transmission electron microscopy (HRTEM),[7,8] although it can also be detected by specific spectroscopic signatures, indirectly derived.[9]

In contrast with the previously synthesized FL-C(N), here we report the formation of hydrogenated structures (FL-C:H) by chemical vapor deposition (CVD). Despite the presence of hydrogen, this material shows three advantages with respect to PVD coatings: (i) it is formed at room temperature, (ii) at higher deposition rates, and (iii) the CVD technique is more suitable for conformal growth due to its nondirectional character. In addition, the x-ray absorption near edge structure (XANES) shows the presence of typical signatures from C_{60}, indicating that these molecules are self-formed in the deposition chamber and incorporated as inclu-

sions in the coating. However, the reduced size of C_{60}, low Z number for carbon (which gives rise to very low contrast images), and its disordered distribution complicates their observation by HRTEM. Also, detection by infrared or micro-Raman spectroscopy is complicated by the small quantities of incorporated C_{60}. Nevertheless, the detection of fullerene C_{60} in CVD grown C:H films by photophysical and photochemical analysis,[10] as well as selected area electron diffraction[11] has, in fact, been reported before. However, in this work, we report on the direct spectroscopic detection of C_{60} inclusions in CVD grown C:H displaying a FL structure.

C:H films have been synthesized by electron cyclotron resonance CVD (ECR-CVD) in a two-zone deposition reactor[12] using methane and argon gas mixtures [15/35 SCCM (SCCM denotes cubic centimeter per minute at STP)] at an operating pressure of 1.1×10^{-2} Torr. A dc bias varying from +100 to −300 V was directly applied to the p-type silicon (100) substrates. The C:H films were grown for 1 h at a growth rate of 0.18–0.32 nm/s.[13] No intentional substrate heating was applied and, although the substrate temperature increased with the bias voltage due to the ion impingement, the deposition temperature did not exceed 120 °C over the entire range of applied substrate bias.

The elemental composition of the C:H films has been evaluated by the combination of Rutherford backscattering spectrometry and elastic recoil detection with a 2 MeV He$^+$ beam for the detection of C and H, respectively. HRTEM analysis of the carbon-based films was performed at a Phillips CM200 field emission gun microscope operated at 200 kV with spatial resolution of 0.235 nm. The specimens were prepared by film detaching and subsequent powdering. XANES measurements in the total electron yield mode were performed at the dipole beamline PM4 of the synchrotron facility BESSY-II in Berlin, Germany, using the SURICAT endstation. The tribomechanical properties of the C:H films were determined by pin-on-disk and nanoindentation experiments using a Microtest and a Nanotest system (MicroMaterials, Ltd.), respectively. A Dektak 3030 profilometer was used to compute the wear rate as the total volume loss during the tribotest, assuming a linear loss rate.

[a]Present address: Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands. Electronic addresses: j.buijnsters@science.ru.nl.
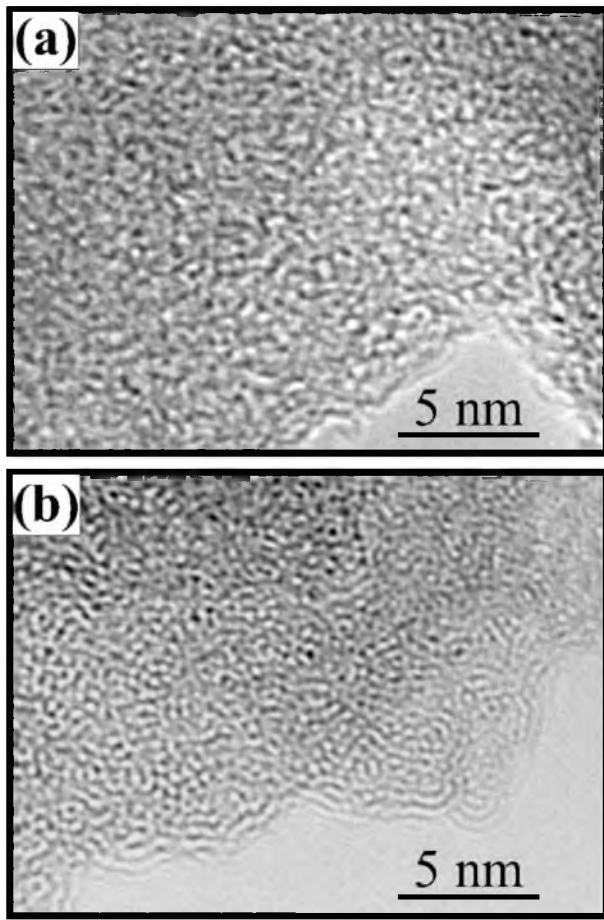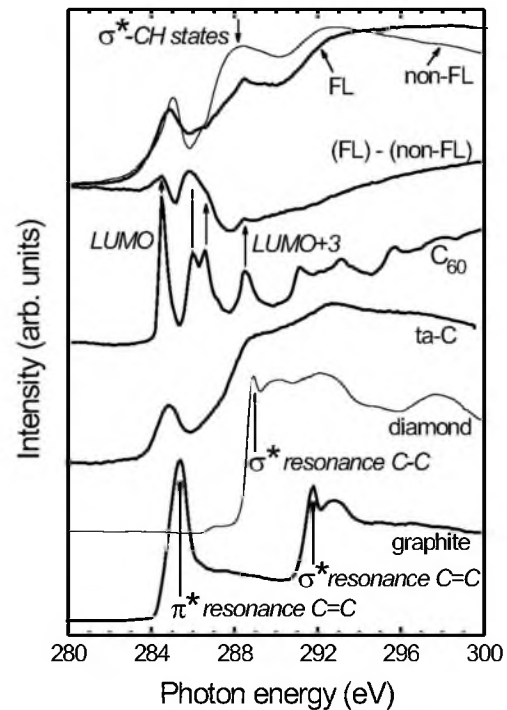
FIG. 2. XANES C(1s) spectra of the FL and non-FL-C:H films together with carbon reference materials. From bottom to top: XANES C(1s) spectra from graphite, diamond, ta-C, and C_{60} powder references, subtraction curve of FL and non-FL films, and the FL and non-FL-C:H films deposited at −250 and −85 V substrate bias, respectively. Indicated are the main spectral features of the various carbons.

FIG. 1. HRTEM images of the (a) non-FL-C:H film grown at zero bias and (b) FL-C:H film grown at a dc substrate bias of −200 V.

Detailed microstructural analysis of the C:H films was performed with HRTEM and XANES spectroscopy, which is very sensitive to the bonding structure of amorphous and nanostructured carbonaceous materials.[9,14] Clear differences in microstructure are observed between the C:H films grown at highly negative bias (few hundreds of volts), displaying a FL structure, and the non-FL-C:H films obtained at positive or small negative bias (several tens of volts). The presence of the FL structure is identified by HRTEM, appearing as a network of curved planes. Figure 1 shows the HRTEM images for a sample grown at zero bias (a) and at −200 V (b). The sample grown without bias [Fig. 1(a)] shows an amorphous character and, hence, lacks of the FL structure. On the contrary, the presence of curved planes in Fig. 1(b) is evident. Notice that the curved nature of the graphitic planes is only observed on the edge of the sample, where it is thinner, since in thicker areas the superposition of disordered FL nanostructures confuses the image and prevents the clear observation of curved graphitic planes.

XANES spectroscopy shows that the transition to the FL structure observed by HRTEM occurs at a negative bias of ~100 V. The typical XANES spectra of non-FL and FL-C:H are shown in Fig. 2, together with the reference spectra from graphite, diamond, tetrahedral a-C (ta-C) (sp^3 content ~80%), and C_{60}. The spectra of graphite and diamond are included as signatures of sp^2 and sp^3 hybridizations, respectively. Graphite displays two absorption edges around 285 and 292 eV related to $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions, whereas the absence of π bonding in diamond results in a single absorption edge (~289 eV). The XANES spectrum of ta-C is added as a reference of a hydrogen-free, disordered carbon material with dominant sp^3 character and reduced intensity in the π^* region.

Due to the novelty of hydrogenated FL structures, identification of XANES features with the evolution of FL arrangements has not been reported so far. Opposing, a correlation between the formation of such structures and XANES spectral features was recently reported in hydrogen-free FL-CN_x grown by reactive magnetron sputtering.[9] The spectrum of non-FL-C:H shows some similarities with that from ta-C, but with an increased intensity at 288.0 eV due to the contribution of σ^* C–H states.[15] Also, the π^* peak from the sp^2 hybrids in the non-FL-C:H spectrum is sharper than the corresponding peak in ta-C. Regarding the FL sample, there are three main apparent changes in its XANES line shape as compared to the non-FL films: (i) the π^* peak is broader in the FL curve, (ii) the CH peak is reduced, and (iii) there is a new peak appearing at 288.5 eV. These spectral changes are enhanced by subtracting the FL and non-FL signals (third uppermost curve). The subtracted curve evidences the presence of four sharp peaks that exactly appear at the position of the C_{60} molecular features: the lowest unoccupied molecular orbital (LUMO) at 284.5, the LUMO+1 at 286.0, the LUMO+2 at 286.6, and the LUMO+3 at 288.5 eV.[16] These sharp XANES signals are related to the growth conditions and not to any surface contamination, since all samples, both with and without FL structure, are similarly treated after deposition and, hence, should display a similar degree of contamination. However, only the samples with a FL structure observed by TEM exhibit the four sharp peaks corresponding to the four lowest unoccupied orbitals of C_{60}.
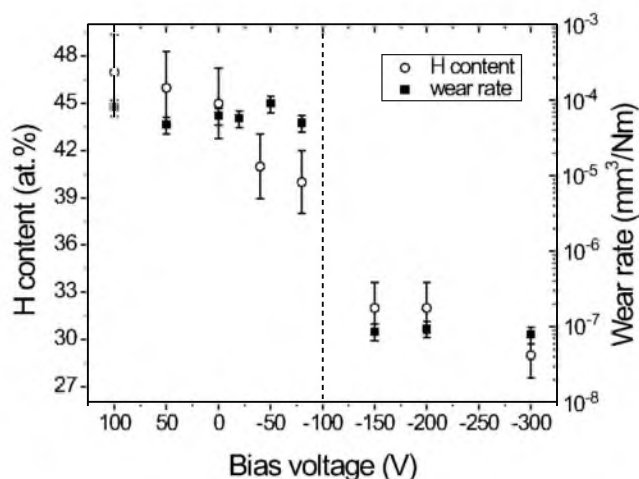
FIG. 3. Hydrogen content (○) and wear rate (■) of the ECR-CVD C:H films against substrate dc bias. The dashed line at −100 V indicates the sharp transition between the two regions for which the films display a FL and a non-FL structure.

Moreover, all the samples with FL structure show a similar intensity ratio of these four peaks. This is strong evidence for the formation of C_{60} inclusions in our FL-C:H films and represents the first direct observation of a spectral signature related to C_{60} molecules inside a carbon material with an extended FL structure. Since no intentional incorporation of C_{60} is performed, these molecules are self-formed during the growth process.

A prerequisite for the formation of the FL structure seems to be the bombardment of sufficiently energetic ions in order to promote plane curvature and H depletion of the intrinsically H-rich carbon films. Figure 3 (open symbols) summarizes the dependence of the elemental composition with the applied bias voltage. Indeed, the H content of the C:H films shows a drop at about −100 V from over 40 to about 30 at. %, which corresponds to the transition from non-FL to FL structures observed by XANES and HRTEM. This structural transition also reflects on the tribological properties, as derived from the wear resistance shown in Fig. 3 (black squares). The non-FL-C:H films obtained with positive bias or negative bias voltages up to −100 V show a low wear resistance of $\sim 10^{-4}$ mm³/N m. On the contrary, the FL-C:H films grown at higher negative bias voltages display a superior wear resistance of $\sim 10^{-7}$ mm³/N m. The radical change (three orders of magnitude), only displayed for the wear rate here, is also observed for the other tribomechanical properties including the coefficient of friction, Young's modulus and hardness.

In conclusion, we have shown a transition in the structure and properties of C:H films obtained by ECR-CVD at low substrate temperatures (<120 °C) when a negative dc bias voltage above 100 V is applied to the substrate. The abrupt change in the tribomechanical properties of the films above this bias threshold coincides with the detection of FL arrangements by HRTEM, a remarkable H loss within the film atomic matrix, and the detection of C_{60} inclusions by XANES. The achievement of FL coatings by CVD with respect to PVD methods is relevant for coating materials that do not withstand high growth temperatures (e.g., polymers), increasing the deposition rate, or improving conformal growth on patterned substrates.

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