X-ray absorption spectroscopy study of pulsed-laser-evaporated amorphous carbon films

A. Gutiérrez1,*, J. Díaz2, M. F. López1,*

1 Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin, Germany
2 E.S.R.F., B.P. 220, F-38043 Grenoble, France

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Abstract. Amorphous carbon (a-C) films obtained by pulsed-laser ablation of graphite have been investigated by X-ray Absorption Spectroscopy (XAS). The onset of $1s \rightarrow \sigma^*$ transitions in the films lies in the gap between the $\pi^*$ and $\sigma^*$ bands in graphite and very close to the absorption edge of diamond, indicating a high content of $sp^3$ hybridization. A sharp feature at this onset is observed and assigned to a core excitation in $sp^3$-hybridized disordered C atoms. Its shift of 0.5 eV with respect to the core excitation in diamond is probably due to a higher localization of the excited electron induced by disorder. A small peak coming from C–H bonds at the surface is observed and its intensity increases with the amount of $sp^3$-hybridized atoms in the sample. This can be easily explained by associating a higher amount of dangling bonds at the surface to a higher $sp^3$ content. Polarization-dependent XAS measurements show that the angular distribution of these C–H bonds has a mean value close to the normal to the surface.

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Amorphous carbon films (a-C) with a high content of $sp^3$ hybridization, also called “diamond-like” films, are technologically very important due to their similar properties to diamond, like hardness, chemical inertness, very low electrical conductivity and wide band gap [1, 2], having, in addition, the possibility to easily accept impurity donors, like nitrogen [3] or phosphorus [4]. Preparation of these a–C films usually involves atomic or ionic beams with moderate energies produced by a variety of methods like cathodic carbon arcs [5], rf sputtering [6] or rf-assisted plasma deposition [7, 8]. The possibility to prepare very thin films of these materials makes them very interesting for applications in microelectronics, where integration of small-sized elements is playing a crucial role. Recently, epitaxially grown ultrathin diamond-like films have been obtained by laser ablation of graphite [9]. Laser-assisted evaporation of graphite produces high quality a–C films with a very low hydrogen content [10, 11]. The quality of the films is given by the ratio of $sp^3$ to $sp^2$ hybridization, and depends on a variety of parameters, like laser power, laser wavelength, angle between target and sample, thickness of the films, etc. [12, 13]. XAS is a standard technique to investigate chemical and electronic properties of materials [14]. Its site and symmetry selectivity can also give information about bonding lengths and angles. In the case of carbon-containing species, the ratio of $sp^3$ to $sp^2$ hybridization can be easily determined because $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions in $sp^2$-coordinated atoms are well separated in energy from $1s \rightarrow \sigma^*$ transition in atoms with $sp^3$ hybridization. This makes XAS a very good tool to characterize a–C films.

In this paper, we report on a XAS study of a–C films prepared by pulsed-laser evaporation of graphite. Samples were prepared under high-vacuum conditions using a Nd:YAG laser beam focused onto a graphite target. This produces a high-energy carbon beam, or plume, consisting of a mixture of neutral and charged atoms and clusters. We used a laser power of $10^{10}$ W/cm$^2$, with 20 ns pulses carrying an energy density of 250 mJ/cm$^2$. A Si(100) crystal was used as substrate. These parameters have already proved to give films with good quality and high $sp^3$/$sp^2$ ratio, as demonstrated by previous Raman, Auger, EELS, and STM studies [9, 12, 13]. The density of neutral and charged particles and their mean kinetic energy depend on the angle of the substrate with respect to the normal to the target $\phi$, being maximum for $\phi = 0^o$ [13]. Four samples were prepared with substrates placed at angles $\phi = 0, 20, 45$ and $70^o$, respectively. Another sample at $\phi = 0^o$ was grown using a neutral C beam produced by removing the plasma content of the plume by means of an electric field normal to the beam trajectory. The thickness of the films ranged between 1000 Å for $\phi = 70^o$ and 2500 Å for $\phi = 0^o$. XAS measurements were performed at the SX700/II monochromator of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) in Total Electron Yield mode (TEY). The resolution was set to $\approx 150$ meV at the C-1s absorption edge. Additionally to the a–C films, a Highly Oriented Pyrolitic Graphite sample (HOPG) and a diamond film grown by Chemical Vapour Deposition (CVD) were measured as references.

Figure 1 shows XAS spectra of the HOPG sample (a), the CVD-diamond sample (b), as well as four a–C films grown at...
different angles with respect to the graphite target (c–f). The angle between the electric vector of the incident light and the normal to the surface was 90° and secondary electrons leaving the surface at 45° from the normal were collected. Spectra (a) and (b) show well-defined features similar to other spectra previously reported [15, 16]. In graphite, the onset of $1s \rightarrow \pi^*$ transitions lies at $\approx 285$ eV while $1s \rightarrow \sigma^*$ transitions start at $\approx 291$ eV. In diamond, the onset of $\sigma^*$ states lies in the gap between $\pi^*$ and $\sigma^*$ states in graphite, i.e., at $\approx 289$ eV. CVD-diamond films usually consist of small diamond crystallites embedded in an amorphous or graphitic carbon matrix made of $sp^2$-hybridized atoms. The first broad peak at 284.6 eV in spectrum (b) seems to originate from $1s \rightarrow \pi^*$ transitions in the $sp^2$-hybridized atoms of this amorphous matrix. Note the asymmetry of this peak and its shift of $\approx 0.7$ eV to lower energies with respect to graphite, typical of amorphous $sp^2$ carbon. Another feature observed in spectrum (b) and not present in pure diamond is the shoulder at $\approx 288$ eV, just below the $\sigma^*$ edge. Other authors have interpreted similar features in the XAS spectrum of CVD diamond and a-C films to C–H bonds [17], an interpretation which is further justified by the existence of C–H resonances at the same energy position in different hydrocarbons like benzene and cyclohexane [7]. The presence of these C–H bonds in the CVD diamond can be easily explained taking into account that this kind of sample is grown from hydrocarbons, so one can expect a certain amount of hydrogen in it. The shoulder at $\approx 288$ eV in spectrum (b) is thus originated from C–H bonds in the CVD sample. The sharp peak observed at 289.2 eV has been assigned to a $C$$1s$ core exciton [18], though its theoretical description in the equivalent-core approximation [19, 20] or in the effective-mass approximation [18, 21], is still not clear. The rest of the spectrum consists of the same structures observed in pure diamond, including the second absolute gap at $\approx 302$ eV [18]. Spectrum (c) corresponds to an a-C sample grown at $\varphi = 0^\circ$. The first peak at 284.6 eV is assigned to $\pi^*$ states from $sp^2$-hybridized atoms in an amorphous matrix, and has the same shape and energy position as that observed in spectrum (b). The rest is almost featureless, except for a sharp weak peak at 288.7 eV and two broad bands centered at 293 and 302 eV. At higher angles (spectra d–f), the peak at 288.7 eV gradually decreases and the high-energy band splits into a double structure. A similar double band at around 300 eV has been assigned to graphitization of an amorphous sample at high temperatures [7]. A previous Raman study on a similar set of samples gave a higher crystallinity and a lower $sp^3$ content for samples grown at higher angles [13]. According to these previous results, the sample grown at $\varphi = 70^\circ$ probably consists of small graphitic nanocrystals embedded in the amorphous matrix. The most striking feature observed in Fig. 1 is, however, the sharp peak at 288.7 eV, especially visible in spectrum (c). Since C–H resonances are much broader and lie at lower energies, we can exclude that this peak comes from C–H bonds. On the other hand, its similar lineshape and proximity to the diamond core exciton suggest that this peak can be originated by an excitonic process in amorphous, $sp^2$-hybridized atoms. Its observed shift of 0.5 eV with respect to the diamond exciton may be due to either a shift of the band edge position in the a-C with respect to the CVD sample, or a change in the excitonic binding energy. A similar increase in the binding energy is indeed expected in amorphous with respect to crystalline samples due to a higher localization of the excited state induced by disorder [22, 23].

There is a direct correlation between the intensity of the peak at 288.7 eV and the $sp^3$ content of the sample (Fig. 2). The strong intensity fall of this peak observed between spectrum (c) and spectrum (d) in Fig. 1 indicates that already for angles as small as 20° the $sp^3$ content of the samples is much lower than for the central sample. The intensity of this peak gradually decreases from spectrum (d) to spectrum,
(f), which is the one with less sp\(^3\) content, but not negligible. This can also be seen from the small peak at \(\approx 318\) eV, whose position is different in graphite as in the rest of the samples. At this energy the EXAFS region starts, and for a complete detailed analysis a much broader energy range is needed. However, since scattering amplitudes and phases are only element dependent, and in all cases we have the same elements, i.e., carbon, the differences between graphite and the rest of the samples in this region may originate from differences in the bond length. If this is the case, the fact that for all a-C samples the position of this peak is the same as in spectrum (b) suggests that all of them have sp\(^3\)-coordinated atoms, even that grown at \(\varphi = 70^\circ\).

To make a more detailed quantitative analysis, we performed a least-squares fit of the data for the energy range close to the absorption edge. In Fig. 2, we show the result of such an analysis for the samples grown at \(\varphi = 0^\circ\) (solid line across the data points) and \(\varphi = 45^\circ\) (dashed line). To reproduce all spectral features we used two arc-tangents, centered at 285 and 288.9 eV, for the \(\pi\) and \(\sigma\) edges, respectively, and three Lorentzians, shown at the bottom of Fig. 2. The first arc-tangent describes the transitions from the 1s core level to the continuum states above the \(\pi\) edge in sp\(^2\)-hybridized atoms, while the second one accounts for transitions to continuum \(\sigma^*\) states of atoms with sp\(^3\) hybridization. Transitions to \(\sigma^*\) states in sp\(^2\)-hybridized atoms would be described by an arc-tangent at 292.5 eV, as indicated by a similar least-squares fit of the graphite spectrum (not shown). In the case of the CVD-diamond sample, the same energy positions of the arc-tangents as in a-C samples describe quite well the experimental data. Additionally to the arc-tangents, three Lorentzian lines were needed to fit the data. The first one, at 284.5 eV (labelled A in Fig. 2) accounts for the \(\pi^*\) resonance in the sp\(^2\) atoms. The peak at 288.7 eV is described by the Lorentz line labelled C in Fig. 2. An extra peak at 288 eV, labelled C, has to be included in the fit in order to describe well the data points. The small intensity of this peak may induce to think that it is only an artifact of the fitting procedure. However, as it will be shown below (Fig. 4), the peak is clearly visible when another polariza-

![Fig. 3. Evolution of the intensity of peaks B (empty circles, right scale), and C (full squares, left scale) of Fig. 2, relative to the intensity of peak A, with respect to the angle between the normal to the target and the substrate \(\varphi\).](image)

![Fig. 4. Polarization dependent XAS spectra of an a-C film grown using a neutral plume, i.e., removing the plasma. \(\theta\) is the angle between the electric field of the incident X-ray beam and the normal to the sample surface. The vertical lines show transitions to states assigned to C–H bonds (288 eV) and to an excitonic peak from sp\(^3\)-hybridized atoms (288.7), respectively.](image)
hybridized carbon form two-dimensional structures, whereas in \( sp^3 \)-hybridized carbon they are three-dimensional, and, consequently, the probability to form dangling bonds at the surface is higher in this last case.

To exclude the possibility that peak C, related to the \( sp^3 \) content in our amorphous samples, has the same origin as peak B, i.e., that it comes from the hydrogen content of the surface, we show in Fig. 4 a polarization-dependent XAS spectrum of an a-C sample grown without ions. For this sample, the mean kinetic energy of the particles in the plume is the same as that for the sample with ions and \( \varphi = 0^\circ \).

However, since the main parameter determining the quality of the samples is the plasma content of the plume [25], the peak at 288.7 eV in Fig. 4 has a lower intensity, similar to the sample with \( \varphi = 45^\circ \). In a polarization-dependent XAS experiment the relative angle between the electric field vector of the X-ray beam E and the surface is varied. Since the transition probability depends upon the scalar product between E and the symmetry axis of the bonding, dipolar transitions from bonds arranged parallel to the electric field have a higher probability as those with other angles, while for E perpendicular to the symmetry axis of the bond the intensity becomes zero. This makes XAS a good tool to study the geometrical properties of materials at an atomic scale. In Fig. 4, \( \theta \) is the angle between the electric field vector and the normal to the surface. For \( \theta = 90^\circ \), the electric field is parallel to the surface, and intensity from bonds normal to the surface is zero. For \( \theta = 45^\circ \), normal and parallel to the surface make a contribution to the XAS signal. As is shown in Fig. 4, the peak at 288 eV shows a strong polarization dependence, while the peak at 288.7 eV does not change when \( \theta \) is varied, indicating no preferred orientation in the last case, and, consequently, a different origin as that of the peak at 288 eV, assigned to C-H bonds. The increase in intensity of peak B when \( \theta \) decreases involves that the C-H bonds align close to the normal to the surface, but not completely normal since in that case the intensity of this peak for \( \theta = 90^\circ \) would be zero. This arrangement of the C-H bonds can be easily understood assuming that the dangling bonds at the surface are more likely aligned away from the sample surface, since bonds parallel to the surface have other C atoms around to become saturated. Assuming an angle distribution of the C-H bonds around a mean value, a quantitative estimation of this value base on the observed intensity variation of the peak, at 288 eV can be made, giving \( 20^\circ \) with respect to the normal to the surface.

In summary, we have presented an X-ray absorption study of several amorphous "diamond-like" films prepared by pulsed-laser evaporation of a graphite target. The quality of the samples can be estimated by looking at the intensity of the 1s \( \rightarrow \sigma^* \) transitions. The \( sp^3 \) content of the samples changes with the angle between substrate and graphite target during deposition, strongly decreasing for angles apart from the normal, where the ionic content of the plume is lower. C-H bonds are found at the surface as a consequence of the presence of dangling bonds. Since samples with higher content of \( sp^3 \)-hybridized atoms have a higher degree of dislocations, and, consequently, a higher amount of dangling bonds, they have more hydrogen content at the surface than samples with lower quality. The polarization dependence of the C-H resonance gives an angle distribution of the C-H bonds with a mean value of \( 20^\circ \) with respect to the normal to the surface.

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References


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