

Separation of the sp^3 and sp^2 components in the C 1s photoemission spectra of amorphous carbon films

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Two different types of amorphous carbon films were deposited on Si substrates, with film hardness of 22 GPa and 40 GPa, by pulsed laser evaporation of graphite targets. The x-ray photoemission spectra (XPS) of the C 1s core level in these films shown two components at 284.3 ± 0.1 eV and 285.2 ± 0.1 eV, which were identified with the sp^2 and sp^3 hybrids forms of carbon. The sp^3/sp^2 concentration ratio deduced from the area of the components had a value of 2/5 for the harder amorphous carbon film and 1/4 for the softer. Upon annealing the harder film at different temperatures, the sp^3/sp^2 ratio remained nearly constant up to about 900 K and then decreased until reaching a value of zero above 1100 K. The C 1s core level shifted 0.3 ± 0.1 eV toward lower binding energy in the films for annealing temperatures above 900 K. This shift was correlated with an increase in the asymmetry of the C 1s XPS spectra and of the density of states at the Fermi level, as observed by ultraviolet photoemission spectroscopy. There was no detectable π plasmon in the harder films below 900 K, despite the presence of sp^2 atoms and π bonds at those temperatures. [S0163-1829(96)07935-0]

I. INTRODUCTION

It is commonly assumed that carbon atoms in amorphous carbon films (*a*-C) hybridize their outermost *s* and *p* orbitals of carbon into sp^3 and sp^2 hybrids, with a negligible presence of *sp* hybrids,¹ to form π and σ bonds. π bonds are weaker than σ bonds and they govern the electronic properties of the *a*-C films such as their optical gap and electrical conductivity,² whereas σ bonds determine their mechanical properties such as hardness. π bonds form only between sp^2 hybrids, and it is expected that the tetrahedral disposition of σ bonds in sp^3 hybrids contribute to the hardness of the *a*-C films much more than the sp^2 hybrids.³ Therefore, a reliable and accurate measure of the sp^2 and sp^3 hybrid concentration in *a*-C films is desirable for understanding the properties of the films.

The existing methods to obtain the sp^3/sp^2 concentration ratio in *a*-C films consist of determining the density of states of π bonds with respect to σ bonds. Presently, near-edge x-ray absorption spectroscopy (NEXAFS) (Ref. 1) or high-energy electron loss spectroscopy (HEELS) (Refs. 5 and 6) are mostly used to measure sp^3/sp^2 concentration ratios in *a*-C films. The NEXAFS or HEELS spectra of carbon sharply differentiates the π states from the σ states. This method assumes that carbon atoms hybridize sp^3 and sp^2 in *a*-C as they do in graphite and diamond to determine the relative concentrations of sp^3 and sp^2 hybrids in *a*-C films. However, (*e*,2*e*) spectroscopy studies carried on *a*-C suggest that the *p* orbital in sp^2 hybrids has some *s* character.⁴ The decrease in the π^* resonance of a NEXAFS spectra of an *a*-C film would be then understood as a progressive rehybridization of the sp^2 hybrids to sp^3 . There are more reasons to think that the π bonding in *a*-C is different than in graphite. Specifically, it has been reported that HEELS spectra of *a*-C films exhibit additional resonances near the π^* peak, the origin of which is still unclear.⁵⁻⁸ Moreover, the core elec-

tron excitation in the NEXAFS experiments affects significantly the π^* resonance in the spectra of graphite.⁹ Therefore, a complete understanding of the structure and bonding in *a*-C is still lacking.

XPS has been used to deduce sp^3/sp^2 concentration ratios in *a*-C films^{10,11} by comparing their carbon Auger spectrum with that of graphite and diamond. However, to our knowledge, the decomposition of the C 1s photoemission spectra has never been done. Unlike all above-mentioned techniques, the ionization cross sections for the XPS core-level spectra are exclusively dependent on atomic factors and independent on the chemical state of the atoms when the energy of the x-ray photons is well above the absorption edge of the core level.³³ The intensity of the core-level peaks is then directly proportional to the density of atoms. If the C 1s core-level binding energies of the sp^3 and sp^2 hybrids in *a*-C are different, as they are in graphite^{9,10,12} and diamond,^{10,13} the C 1s photoemission spectra will be decomposed into two lines. Moreover, the determination of the sp^3 and sp^2 concentration will be straightforward with no need of reference samples, as is the case in NEXAFS or HEELS where the absolute measure of the sp^2 concentration in the *a*-C films requires a reference sample that has to be 100% sp^2 and isotropic in the orientation of its π bonds. We report in this work that, in free hydrogen amorphous carbon films, the C 1s core level is effectively decomposed into two components, which are identify with the sp^3 and sp^2 hybrids. The binding energy (BE) of the sp^3 hybrids is shifted with respect to the sp^2 hybridized carbon by 0.9 eV, similar to the value reported in Ref. 10 between diamond and graphite. This shift is 0.3 eV larger than the difference in binding energies between graphite^{9,12} and diamond¹³ reported in previous works. The parameters we used in the fitting procedure for the decomposition of the two components are consistent with the macroscopic properties of the films, the graphitization of the films upon annealing, and their UPS spectra.

TABLE I. Some physical properties of a -C thin films prepared in similar conditions than the a -C thin films analyzed by XPS and UPS.

Sample	Density (gr/cm ³)	Optical gap (eV)	Resistivity (k Ω cm)	Hardness (GPa)	Young modulus (GPa)
HP a -C	2.8	0.3	250	40–50	260
LP a -C	2.45	No gap		22	190

II. EXPERIMENT

The carbon was deposited on the native oxide of a previously degreased silicon wafer at room temperature and at a base pressure of $\leq 10^{-7}$ mbar. A pulsed Nd-YAG laser, with a wavelength of 532 nm and a pulse duration of 20 ns, evaporated the carbon from a graphite target. The frequency of the pulses was 10 Hz. The substrates were located in front of the target at 14 cm distance. The thickness of the a -C films, as monitored by a quartz balance, was 500 Å, which was large enough to avoid Si segregation to the surface during the annealing experiments. Two kinds of a -C films were grown with laser powers of 10^{10} W/cm² and $\sim 10^9$ W/cm² to deposit what we will designate as *high power* (HP) and *low power* (LP) films, respectively, with different physical properties (Table I).

XPS and ultraviolet photoemission spectroscopy (UPS) measurements were done in an UHV chamber at a base pressure of 5×10^{-11} mbar. Samples were inserted under vacuum from the preparation chamber with a load lock. Surface contamination was not noticeable as monitored by XPS and UPS. The sources of radiation were the MgK α line (1253.6 eV) for the x rays, and the He I (21.2 eV) and He II (40.8 eV) emission lines of a He lamp for the ultraviolet. The C 1s core level of a highly oriented pyrolytic graphite (HOPG), freshly cleaved and annealed at 1100 K, served as reference in energy in all XPS spectra, and we set it at 284.4 eV with respect to the Fermi level.^{9,12} The instrumental resolution in the XPS experiments was 0.8 eV as we determined by the fit of the C 1s XPS spectra of the HOPG. The Fermi level was obtained from the He I UPS spectra of a sputtered and annealed gold foil. A hemispherical electron analyzer measured the kinetic energy of the photoelectrons, and operated at a resolution of 0.4 eV, as determined from the Au Fermi edge. Charging effects were not observed in any of the analyzed samples. In the annealing experiments, samples were heated for 5 min at a given temperature by passing a dc current through the substrate. Spectra were recorded after turning off the dc current.

III. RESULTS

Table I presents some of the physical characteristics of films prepared in similar conditions to those analyzed by XPS and UPS. The density of the films was measured by x-ray reflectivity. The hardness and Young's modulus was obtained by nanoindentation in films thicker than 2000 Å. The hardness of the HP a -C film is comparable to or higher than that reported by others,⁷ despite its much smaller optical gap. Similar samples were studied also by Raman.¹⁴ The HP sample was semiconductor and harder than the LP sample, so the former should contain a larger concentration of sp^3 hybrids.

Figure 1 shows the C 1s core level XPS spectra of graphite, and of the HP and LP a -C films. The maximum of the spectral line shape of the graphite sample and the HP and LP a -C films coincide within 0.2 eV. The full width at half maximum (FWHM) of the spectra are 1.1 eV for HOPG, 1.9 eV for HP a -C, and 1.8 eV for LP a -C. The spectra of the HP a -C film become 1.4 eV wide and it shifts by 0.4 eV towards lower binding energy at 1200 K (Fig. 2).

We compare the plasmon loss features of the a -C films and graphite in Fig. 3. The π plasmon is at 6.4 eV from the C 1s peak maximum in graphite, and its position is at about the same energy in the LP a -C film. The π plasmon was detectable in the HP a -C film only for temperatures above 900 K.

The He II spectra of the a -C films, shown in Fig. 4, evolve from a smooth line shape at room temperature to spectra with better defined features at higher temperatures. Some of them can be identified with those measured in polycrystalline graphite.¹⁵ The increasing sharpness of the shoulder at 3-eV binding energy demonstrates π bonding formation with increasing annealing temperature, since this structure is exclusively related to the π band in graphite,¹⁵ and it is not present in diamond.¹⁶ The formation of π bonds or graphitization of the films during annealing is accompanied by a progressive population of states at the Fermi level, which stops at 900 K,

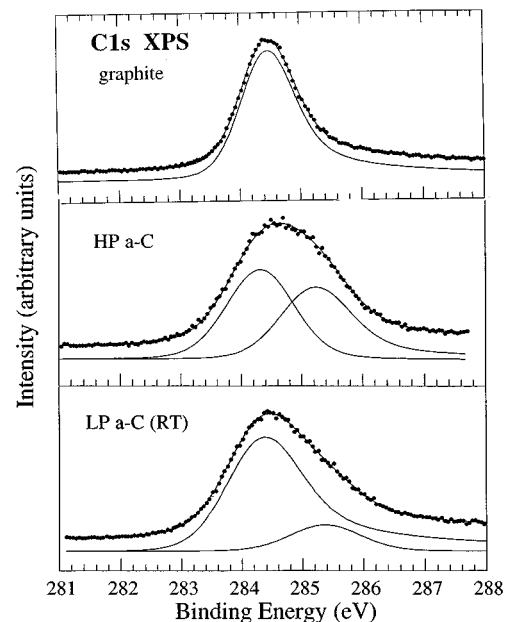


FIG. 1. Comparison between the C 1s XPS spectra of graphite and those of the amorphous carbon films HP and LP obtained at room temperature (RT). The solid lines are the components in which the spectra were decomposed. The resulting fit is superimposed to the data.

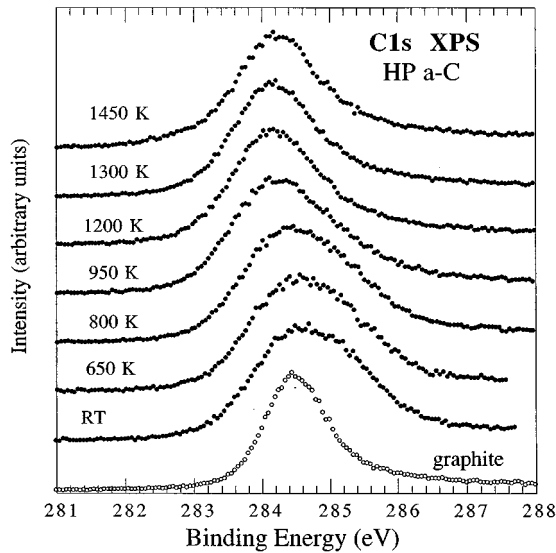


FIG. 2. C 1s XPS spectra of the HP *a*-C film annealed at different temperatures, compared with the spectra of graphite.

as it is more clearly shown in Fig. 5. This graphitization does not bring about a complete transformation of the *a*-C films to polycrystalline graphite, since not all the features present in the UPS spectrum of graphite appear in the spectra of the annealed *a*-C films.

IV. ANALYSIS OF THE DATA AND DISCUSSION

The best fits to the C 1s core-level spectra of our samples needed two components. We identified the component with the highest binding energy with the sp^3 hybrids, according to the higher binding energy of the C 1s core level in diamond¹⁴ than in graphite.^{9,13} Each of the components was the convolution of a Gaussian and a Lorentzian. The Gauss-

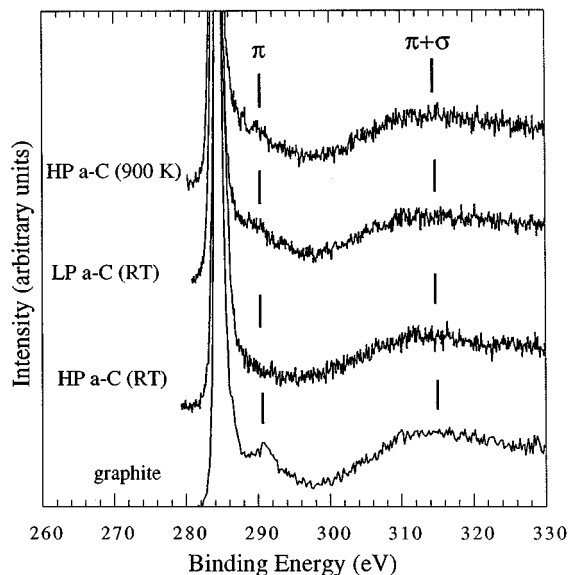


FIG. 3. C 1s shakeup spectra of the LP and HP *a*-C films obtained at room temperature (RT) and at 900 K, compared with that of graphite.

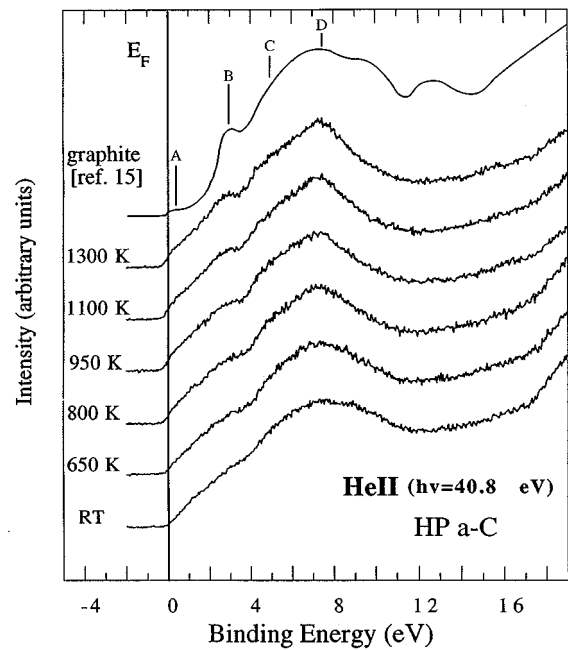


FIG. 4. UPS (He II) spectra of the HP *a*-C film obtained after annealing at different temperatures. The spectra are compared with the spectrum of polycrystalline graphite of Ref. 15 obtained at an excitation energy of 45 eV. Ticks are located at energies: A, 0.7 eV; B, 3 eV; C, 5.7 eV; D, 8 eV. All UPS spectra were normalized to their total intensity.

ian component accounted for the instrumental energy resolution together with the chemical disorder, and the Lorentzian for the lifetime of the photoionization process. The Lorentzian lifetime width for both components was fixed at 215 meV.¹² The Gaussian widths of spectra for *a*-C samples at room temperature were 1.25 eV for both components. When

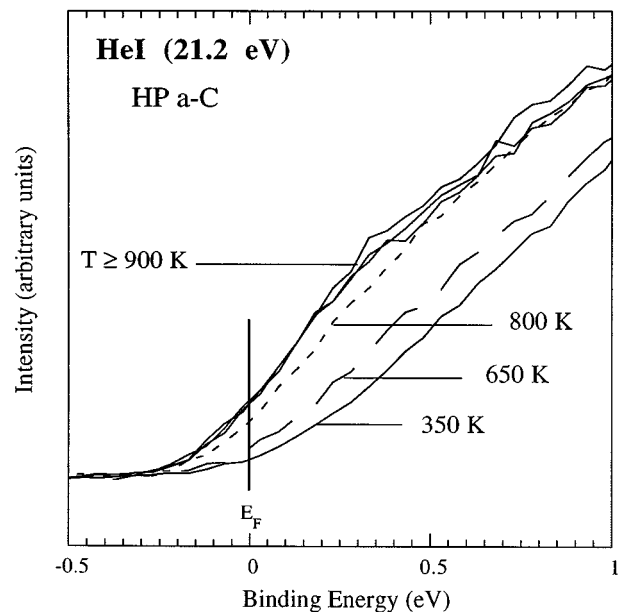


FIG. 5. UPS (He I) spectra of the HP *a*-C film at the Fermi level edge upon annealing at different temperatures.

the sample temperature was changed, the sp^2 component eventually narrowed to 1.2 eV at 1300 K and 1.1 eV at 1450 K, with the change in the width of the sp^3 component remained negligible. The disorder in the samples was still significantly higher at these temperatures since the widths were still larger than the intrinsic resolution of the spectra.

For the sp^2 component, a Doniac-Sunjic function was used.¹⁸ This function can be approximated as the convolution of the Lorentzian with a power function of the type:

$$1/E^{(1-\alpha)}, \quad (1)$$

where E is the binding energy and α is a parameter designated as singularity index. In metals, this function corresponds to the spectrum of electron-hole pair excitations created at the Fermi level to screen the core hole potential.¹⁷ The singularity index is related to the electron density of states at the Fermi level.¹⁹ The Doniac-Sunjic function is commonly used to fit the spectra of graphite^{12,20,21} and aromatic molecules and coals.^{22,23} We measured a singularity index in HOPG graphite of 0.14 which agrees with the value obtained in Refs. 20 and 23. This value of α is higher than the value of 0.075 measured by Chen *et al.*¹² at much higher photon energy resolution. The asymmetrical energy distribution of the Mn K_α x-ray emission,³⁴ that it was used by Refs. 20 and 23 and by us as an excitation source, is probably the cause of disagreement in the measured of the absolute value of α . To avoid such a discrepancy, our analysis will look only at the relative variations in α between spectra, since the energy asymmetry of the Mn K_α line is constant.

The C 1s spectra were fitted with five parameters: the Gaussian width and binding energy of each component, and the singularity index for the sp^2 component. Figure 1 displays the fits for HOPG, and for the HP and LP *a*-C films at room temperature (RT). The component attributed to the sp^2 hybrids in the *a*-C films is at a binding energy similar to that in graphite. The singularity index is 0.11 ± 0.01 for the HP film and 0.19 ± 0.01 for the LP film. The binding energy of the sp^3 component is 0.2 eV above that reported for diamond in Ref. 13. The binding energies of both components, the sp^3 concentration and the singularity index of the HP *a*-C film annealed at different temperatures, are depicted in Fig. 6. The assignation done at the beginning of the higher binding energy component to the sp^3 hybrids is correct since it decreases in intensity when the temperature increases, in agreement with the graphitization of the sample showed in the UPS spectra. The accuracy in the determination of the binding energy of the sp^3 component is not good at elevated temperature because its intensity was too low.

The fits show that there are 40% of sp^3 hybridized atoms in the HP *a*-C, almost twice than in the LP *a*-C (Fig. 6). This agrees qualitatively with expected since HP *a*-C is harder than LP *a*-C (see Table I) and this physical property is proportional to the sp^3 concentration.³

The difference in the binding energy of the sp^3 and sp^2 atoms is 0.9 eV, similar to the value reported by Mizokawa *et al.*¹⁰ between graphite and diamond, but 0.3 eV larger than the values given separately for graphite by Chen *et al.*¹² and for diamond by Morar *et al.*¹³ It is unclear how much the resolution of the spectra could affect the position of the peaks, but it can be asserted that the shift between the bind-

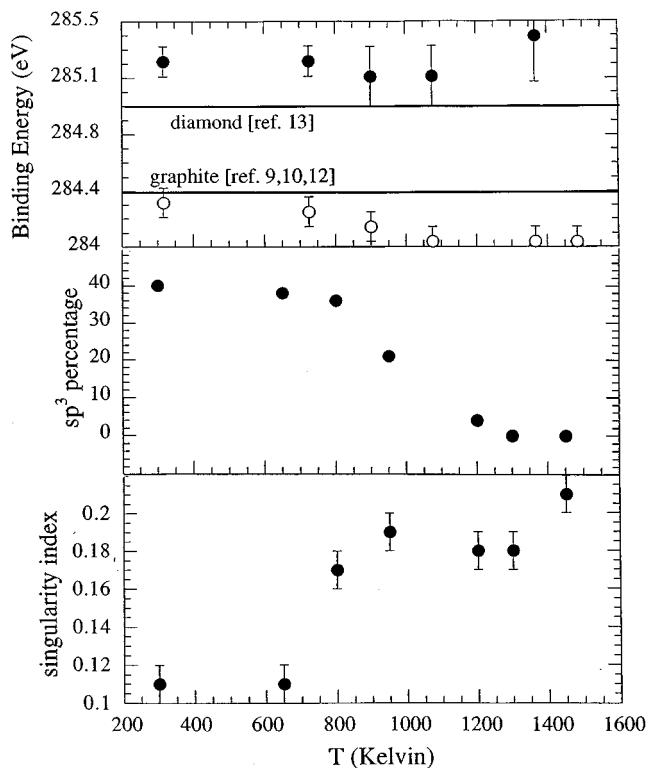


FIG. 6. Variation with the temperature of the C 1s XPS binding energies of the components related to the sp^2 and sp^3 hybridized carbon atoms, the concentration of sp^3 hybridized carbon atoms, and the singularity index α in the HP *a*-C film.

ing energies of the sp^3 and sp^2 hybridized carbon is definitively larger than the 0.2–0.3 eV claimed by other authors.^{24,25}

The sp^2 component in the C 1s core-level spectra shifted by 0.3 ± 0.1 eV toward lower binding energy with respect to its position at room temperature for temperatures above 1000 K (Fig. 6). Such a shift is not caused by charging effects since otherwise their UPS spectra should show a similar shift. Moreover, we measured the same shift in LP *a*-C films, which had no optical gap and were conducting. The negative shift of 0.3 eV is coupled with the density of states increase at the Fermi energy (Fig. 5), and the singularity index (Fig. 6). Such a correlation between the C 1s binding energy and the density of electrons at the Fermi level suggests as a possible cause for the C 1s binding energy shift is the change in the charge relaxation of the excited carbon atom.^{26,27}

The binding energy of the C 1s level in the annealed *a*-C film is also 0.3 eV lower than in graphite which would indicate that the density of states at the Fermi level is higher in the annealed *a*-C films than in graphite. There are two possible reasons to support this. If at high enough annealing temperatures the films are made of graphitic layers²⁸ there will be a reduction in the distance between layers, since the substitution of the sp^3 sites by sp^2 increases significantly the volume in the *a*-C films.²⁹ This causes an increase of the compressive stress of the film, since the film expansion is constrained in the directions along the substrate plane. Measuring the substrate bending by means of a profilometer, the *a*-C films exhibited a compressive stress that ranged from 2

to 5 GPa at room temperature, and risen up to 30 GPa after annealing at 1300 K. A 30 GPa compressive stress in microcrystalline graphite causes a reduction of more than 15% in the distance between planes,³⁰ which can produce an effective increase of the density of charge with respect to that in graphite. A second reason for the increase of the density of states at the Fermi level in the annealed *a*-C films is the bond disorder within the layers. The larger Gaussian width of the films annealed at 1300 K (1.2 eV) with respect to that of HOPG (0.8 eV) demonstrates that bond disorder is still present in the films. Defects within the layers as, for instance, the presence of five atoms rings instead of the benzene rings of graphite, may put states at the Fermi level.²

Finally, we call the attention to the absence of the π plasmon in the spectra of the HP *a*-C for temperatures below 900 K, despite the presence of sp^2 sites and π bonded electrons in these films, as proved by XPS and UPS. The reason might be the localization of the π electronic charge induced by disorder, which is consistent with the semiconductor character of these films and the relatively low value of their singularity index compared to graphite. However, the absence of the π plasmon in semiconductor *a*-C films seems not to be a general rule since hydrogenated *a*-C films, with larger optical gaps than the HP *a*-C film, exhibit the π plasmon in their spectra.^{31,32} The intensity and energy of the π plasmon in *a*-C films are perhaps related to the way *p* orbitals overlap to form the π bonds, and to the local disorder. Disorder may affect the π plasmon intensity for two reasons. First, because the overlap of the *p* orbitals is degraded compared to graph-

ite. Second, because the excited state has a shorter life time than in graphite and hence the feature broadens in the spectra.

V. CONCLUSIONS

We have demonstrated that the C 1s photoemission spectra of carbon in nonhydrogenated *a*-C films consist of two components arising from the sp^3 and sp^2 hybridized forms of carbon, which are chemically shifted 0.9 ± 0.1 eV from each other. Therefore, XPS provides a straightforward way to determine the relative concentrations of sp^3 and sp^2 hybrids in *a*-C films. From this analysis we found that samples with hardness of 40 GPa and 22 GPa had a concentration of sp^3 hybrids of 40% and 25%, respectively. The sp^3 concentration of the hard films remained constant for temperatures as high as 800 K, and decreased to zero for annealing temperatures above 1300 K.

It was demonstrated that the absence of the π plasmon in the C 1s photoemission spectra is not a direct proof of a negligible concentration of sp^2 hybrids in *a*-C films, since the π plasmon was not detected in films with concentrations of sp^2 hybrids as high as 60%.

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