# X-ray absorption and Auger electron spectroscopy studies of the quality of diamond thin films grown by the oxy-acetylene flame method

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Diamond thin films grown by the oxy-acetylene flame method have been investigated by x-ray absorption and Auger electron spectroscopies. The quality of the films, defined as the ratio of diamond to non-diamond carbon, has been determined by using both techniques, giving values as high as 95% for the sample grown with the highest $C_2H_2/O_2$ molar ratio (0.97). Values obtained by Auger electron spectroscopy are slightly lower due to the smaller probe depth of this technique as compared with x-ray absorption spectroscopy (5 Å in the first case against 50 Å in the latter), and to the higher non-diamond carbon content of the surface, as it is expected from the mechanisms of diamond growth by this method. © *1997 American Vacuum Society.* [S0734-2101(97)00902-0]

## I. INTRODUCTION

Diamond thin films have attracted much interest due to their possible technological applications. Several techniques to obtain diamond or diamond-like films have been developed in the last years.[1–3] The quality of the obtained films is given by the ratio of diamond to non-diamond carbon, and it determines most of the properties of the diamond film, like electrical conductivity, hardness, or band gap. The most commonly used technique to estimate diamond films quality is Raman spectroscopy.[4–6] However, due to the big differences in Raman cross section between $sp^3$ carbon and $sp^2$ carbon (almost two orders of magnitude)[7] the information given by this technique can only be qualitative. An alternative method to estimate diamond quality is x-ray absorption spectroscopy (XAS). Its main advantage is that the absorption coefficient only depends on the atomic number $Z$, and, consequently, no differences originated by cross section effects exist between $sp^2$ and $sp^3$ carbon. Additionally, the diamond absorption edge (290 eV) lies between $1s\rightarrow\pi^*$ and $1s\rightarrow\sigma^*$ transitions in $sp^2$ carbon (285 and 292 eV, respectively), making it possible to easily distinguish between both types of carbon with a very simple analysis.[8–11] A different method to characterize diamond films is Auger electron spectroscopy (AES). The differences in spectral line shape between $sp^2$ and $sp^3$ carbon make it possible to estimate the quality of the sample.[12–14] Additionally, as is discussed below, a further analysis, based on the width of the main carbon peak in the derivative spectrum, can be used to make a quantitative estimation of the $sp^2/sp^3$ ratio.[15,16]

In this work we have investigated several diamond thin films grown by the oxy-acetylene flame method in order to determine the ratio of $sp^3$ to $sp^2$ carbon, i.e., their quality. Several samples, prepared with different $O_2/C_2H_2$ molar ratios, were studied by XAS and AES. XAS results confirm the very high quality of diamond films grown by this method and give quantitative high values of the $sp^3/sp^2$ ratio. The slightly lower values obtained by AES are explained in terms of the higher $sp^2$-carbon content of the surface as compared to the bulk.

## II. EXPERIMENTAL DETAILS

Diamond thin films, approximately 5 $\mu$m thick, were deposited on molybdenum substrates using different $O_2/C_2H_2$ molar ratios, R, according to the experimental procedure described in Ref. 17. Films grown at molar ratios lower than 0.9 produced microcrystalline graphite, as is seen below. The deposition rate was 15 $\mu$m/h for the film grown at $R=0.97$ and 20 $\mu$m/h for that at $R=0.93$. A continuous diamond film started to grow after $\approx 1–2$ min. Substrate temperature during diamond growth is a very important factor for the final quality of the films, and was controlled with an optical-infrared pyrometer focused at the center of the substrate surface. In all cases the temperature was set to $1025\pm25$ °C, which is the optimal for diamond growth using our experimental setup.[17] Quenching the samples to room temperature produces delamination of the diamond films due to the different thermal coefficients of diamond and molybdenum. Diamond films detached from the substrate were fixed with a conductive glue onto the sample holder.

XAS measurements were performed at the TGM5 monochromator of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY), using undulator light, in total electron yield mode (TEY). All spectra were normalized by the absorption spectrum of a clean gold foil to avoid effects originated by carbon contamination of the optical elements of the beam line. A highly oriented pyrolitic graphite (HOPG) sample was used as a reference and to calibrate photon energy. No cleaning procedure was done on the samples since both heating and ion-sputtering produced amorphization of the sample surface (not graphitization). Nevertheless, all samples showed a high chemical inertness, reflected by their very low, almost negligible, oxygen content. AES spectra were obtained in a standard surface-analysis ultrahigh vacuum (UHV) chamber equipped with a

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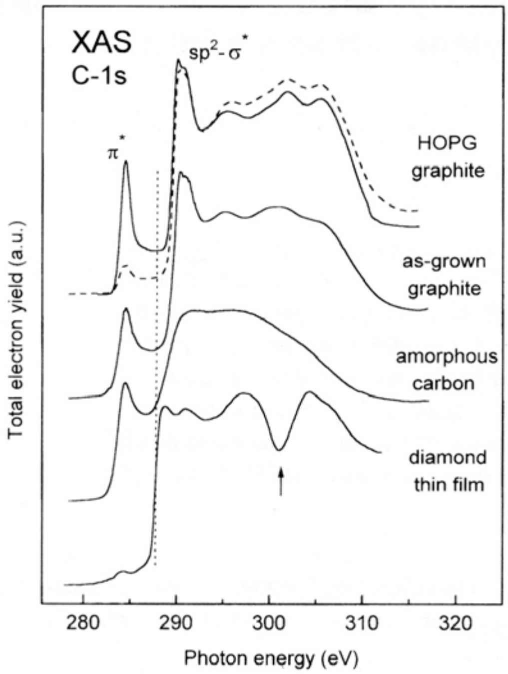

FIG. 1. XAS spectra of a HOPG graphite sample, a graphite film grown with an $O_2/C_2H_2$ molar ratio R of 0.9, an amorphous carbon film, and a diamond thin film obtained with R=0.97.

VG-CLAM hemispherical electron energy analyzer, using 3 keV electrons.

## III. EXPERIMENTAL RESULTS

In Fig. 1 XAS spectra of the graphite reference sample, a thin CVD graphitic layer on molybdenum, an amorphous carbon film, and a diamond film are shown. The HOPG sample (top spectrum) was measured at two different angles between the polarization vector of the incident light and the *c* axis perpendicular to the graphite atomic planes. The solid line corresponds to an angle of 60°, and the dashed line to an angle close to 90°. Both spectra show all features of other graphite spectra reported in the literature.[10] The spectrum labeled ''as-grown graphite'' corresponds to a thin graphite film grown on molybdenum by acetylene combustion with an $O_2/C_2H_2$ molar ratio lower than 0.9 (R=0.75). This value separates conditions for diamond growth (higher values) from non-diamond growth (lower values). It is interesting to note that this non-diamond film grows as graphite, and not as amorphous carbon. The spectrum shows all features of the HOPG spectrum, except the broad peaks at ≈302 eV and ≈306 eV, with a slight shift similar to that observed in microcrystalline graphite.[18] The height of the peak corresponding to the onset of $1s \rightarrow \pi^*$ transitions (≈284 eV) has an intermediate value between the two spectra of the HOPG sample, indicating a random distribution of the orientations of graphite microcrystals in the sample.

The third spectrum of Fig. 1, labeled ''amorphous carbon,'' was obtained from a diamond sample after 5 min sputtering with 3 keV $Ar^+$ ions. It is similar to other spectra of amorphous carbon reported in the literature.[8,9] The thickness of the amorphous layer after this sputtering treatment is larger than 50 Å, which is the probe depth of XAS in TEY mode,[19] indicating that the effect of ion bombardment is not limited to the surface, but to a thicker region of several atomic layers. Finally, the spectrum labeled ''diamond thin film'' corresponds to a diamond film grown on Mo at an $O_2/C_2H_2$ ratio of 0.97. All typical features of diamond are present in the spectrum, including the second absolute gap at ≈302 eV, indicated in the figure by a vertical arrow.[8,9] The energy resolution employed in the measurements does not allow us to resolve the C-1*s* exciton at the onset of $1s \rightarrow \sigma^*$ transitions (≈288 eV).[11,20] This figure evidences the suitability of XAS to distinguish between diamond and non-diamond carbon, since the absorption edge of diamond lies at the gap between $\pi^*$ and $\sigma^*$ states in non-diamond carbon, as is indicated by the vertical dotted line. According to this, the diamond sample has a small non-diamond component visible as the small peak at ≈284 eV. This non-diamond signal originates from amorphous or graphitic carbon present in the sample. The intensity of this feature as compared to that of the leading peak of the diamond signal is a direct indication of the amount of non-diamond carbon in the sample.

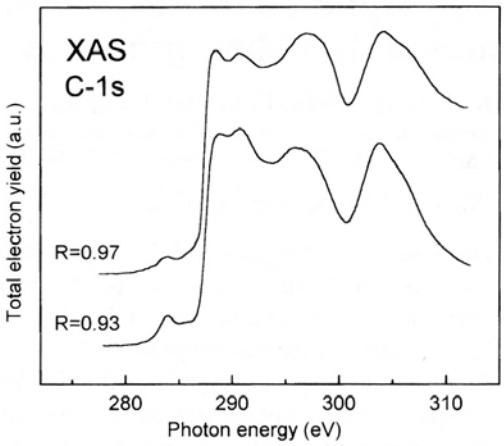

FIG. 2. XAS spectra of two diamond thin films grown by the oxy-acetylene flame method with $O_2/C_2H_2$ molar ratios of 0.97 and 0.93, respectively.

In Fig. 2 we show XAS spectra of two diamond films grown with different $O_2/C_2H_2$ ratios, R=0.97 and R=0.93, respectively. Both spectra have all features of diamond absorption spectra plus the additional peak at ≈284 eV, assigned to $sp^2$ carbon. At first sight it is evident that the sample with R=0.93 has a higher content of $sp^2$ carbon, i.e., a lower quality. In order to subtract the $sp^2$ contribution from the spectra of Fig. 2, we can first assume that all non-diamond carbon present in both samples is amorphous carbon, and not graphitic carbon. We can then use the amorphous carbon spectrum of Fig. 1, previously normalized to the intensity of the peak at 284 eV in both spectra, to extract the $sp^2$-carbon contribution from the diamond spectra. We show below that this assumption is not completely right, because there is some contribution from graphitic carbon to the $sp^2$ signal. Nevertheless, this approach to extract the $sp^2$

contribution from the diamond spectra remains valid, since the obtained numerical values are the same in this case as using the opposite assumption, i.e., that all $sp^2$ carbon in spectra of Fig. 2 comes from graphitic carbon. By comparing the intensities of the leading diamond peak after subtracting the amorphous carbon contribution, and the peak at 284 eV of the normalized amorphous carbon spectrum, we can obtain the relative amount of $sp^2$ and $sp^3$ carbon. Proceeding in this way we obtain for R=0.97 5% of $sp^2$ carbon, and for R=0.93 15%. It must be noted that these values are bulk values extending over approximately 50 Å. The better quality of the sample with R=0.97 agrees with previous results obtained by different techniques on similar samples,[17] but in this case we can give quantitative estimations of the $sp^2$ content of the diamond films and, consequently, of their quality.

Some small differences between both diamond spectra can be observed in Fig. 2. In particular, the first two peaks after the diamond absorption edge have opposite intensity behavior, being the peak situated at ≈291 eV higher for the sample with R=0.93. This can be explained assuming that the $sp^2$ signal for this sample has two contributions: amorphous carbon and graphitic carbon. In the case of graphitic carbon, $\sigma^*$ states produce an intense peak at approximately 291 eV, as can be seen in the graphite spectrum of Fig. 1, which overlaps with the second diamond peak. A simple analysis assuming 30% graphitic carbon in the $sp^2$-carbon signal for the sample with R=0.93 describes well the observed differences in spectral line shape between both samples. Note that for R values lower than 0.9 pure graphite films are obtained, so one can expect that the lower the R value of the diamond film, the higher the graphite/amorphous-carbon ratio of its $sp^2$ component.

An alternative method to make quantitative estimations on diamond film quality, although more surface sensitive, is Auger electron spectroscopy. In Fig. 3 we show AES derivative spectra of a diamond sample, a ''low-quality'' diamond film with a high content of $sp^2$-hybridized carbon, and graphite. Features a, b, and c, are usually employed to qualitatively assign AES spectra to either diamond or graphite. Feature b is observed only for diamond, and peak c has a lower kinetic energy position for diamond than for graphite. Feature a is the self-convolution of occupied $\pi$ states in the valence band of $sp^2$ atoms and, consequently, is absent in the diamond spectrum, as can be observed in the figure. The presence of feature a induces a broadening of the Auger main peak, which will increase with the $sp^2$ content of the sample. The width of the main peak constitutes thus a fingerprint of the amount of $\pi$ bonding present in the sample, i.e., of the amount of $sp^2$ carbon. A linear interpolation between the width of a pure diamond sample and that of a graphite sample can lead to a quantitative estimation of the $sp^2$ carbon content in diamond thin films. Following such a procedure we find for the sample with R=0.97 14% of $sp^2$ carbon, and for the sample with R=0.93 20%. It must be taken into account that a linear interpolation in the C Auger mainline width slightly overestimates the real values, since the width is expected to increase at a slower rate for low $sp^2$ contents. Nevertheless, the deviation should be small, and the obtained values constitute a fairly good approximation.

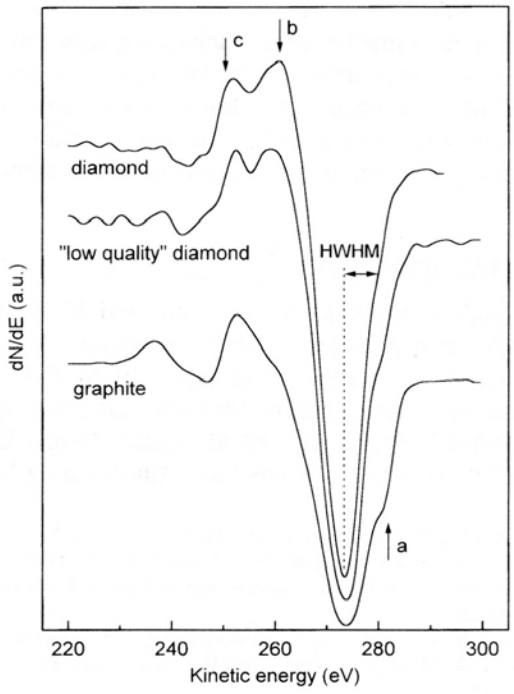

FIG. 3. Carbon *KLL* Auger spectra in derivative mode of a diamond sample, a low quality diamond sample, with high $sp^2$ content, and a graphite sample.

The higher values obtained by AES as compared to XAS can be explained by taking into account the different probe depth of both techniques, as well as the mechanisms of diamond growth. The mean free path of C 1*s* Auger electrons is ⩽10 Å, whereas in XAS measured in total electron yield mode, the probe depth is ≈50 Å. The process of diamond growth by the oxy-acetylene flame method occurs in several stages. First, C atoms of either $sp^2$ or $sp^3$ symmetry are deposited onto the surface. In a subsequent stage, some etching radicals present in the flame remove some of the deposited C atoms. The rate at which $sp^2$ atoms are removed is much faster than that of the more tightly bound $sp^3$ atoms, leading to a net diamond growth.[12] This growth mechanism involves that the surface has a higher amount of $sp^2$ carbon than the bulk, explaining the higher values obtained by AES as compared with those obtained by XAS.

## IV. CONCLUSIONS

In summary, we have investigated diamond films grown by the oxy-acetylene flame method by x-ray absorption spectroscopy and Auger electron spectroscopy. In the first case, the quality of the films, defined as the ratio of $sp^3/sp^2$ hybridizations, is determined by measuring the intensity of $1s\rightarrow\pi^*$ transitions in $sp^2$-hybridized carbon and that of $1s\rightarrow\sigma^*$ transitions in diamond. Samples grown at an $O_2/C_2H_2$ molar rate of 0.97 have a lower $sp^2$ content than those grown at lower molar rates (5.5% for R=0.97 and 14.8% for

R=0.93). In the case of AES, an interpolation of the width of the carbon main line between graphite and diamond is used to obtain the same information. The lower quality of the diamond films obtained in this last case with respect to the XAS results can be explained by the higher surface sensitivity of this technique, and to the higher $sp^2$ content of the surface.

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[1] J. M. Albella, C. Gómez-Aleixandre, O. Sánchez Garrido, L. Vázquez, and J. M. Martínez Duart, Surf. Coat. Technol. **70**, 163 (1995).

[2] S. Matsumoto, Y. Sato, M. Tsutsumi, and N. Setaka, J. Mater. Sci. **17**, 3106 (1982).

[3] Y. Hirose, S. Amanuma, and K. Komaki, J. Appl. Phys. **68**, 6401 (1990).

[4] J. Díaz, J. A. M. Gago, S. Ferrer, and F. Comin, Diam. Relat. Mater. **1**, 824 (1992).

[5] S. C. Sharma, M. Green, R. C. Hyer, T. D. Black, A. R. Chourasia, D. R. Chopra, and K. K. Mishra, J. Mater. Res. **5**, 2424 (1990).

[6] R. J. Nemanich, J. T. Glass, G. Lucovsky, and R. E. Shroder, J. Vac. Sci. Technol. A **6**, 1783 (1988).

[7] N. Wada and S. A. Solin, Phys. B **105**, 353 (1981).

[8] M. Jaouen, G. Tourillon, J. Delafond, N. Junqua, and G. Hug, Diam. Relat. Mater. **4**, 200 (1995).

[9] A. Gutiérrez, J. Díaz, and M. F. López, Appl. Phys. A **61**, 111 (1995).

[10] P. E. Batson, Phys. Rev. B **48**, 2608 (1993).

[11] J. F. Morar, F. J. Himpsel, G. Hollinger, J. L. Jordon, G. Hughes, and F. R. McFeely, Phys. Rev. B **33**, 1346 (1986).

[12] I. García, A. Gutiérrez, and A. Vázquez, Surf. Coat. Technol. (to be published).

[13] Q. S. Chia, C. M. Younes, P. G. Partridge, G. C. Allen, P. W. May, and C. A. Rego, J. Mater. Sci. **29**, 6397 (1994).

[14] C. R. Lee, J. Y. Leem, and B. S. Chun, J. Mater. Sci. Lett. **14**, 361 (1995).

[15] J. A. Martín-Gago, J. Fraxedas, S. Ferrer, and F. Comin, Surf. Sci. **260**, L17 (1992).

[16] J. A. Martín, L. Vázquez, P. Bernard, F. Comin, and S. Ferrer, Appl. Phys. Lett. **57**, 1742 (1990).

[17] I. García and A. Vázquez, Rev. Metal. (Madrid) **30**, 352 (1994).

[18] G. Comelli, J. Stöhr, C. J. Robinson, and W. Jark, Phys. Rev. B **38**, 7511 (1988).

[19] M. Abbate, J. B. Goedkoop, F. M. F. de Groot, M. Grioni, J. C. Fuggle, S. Hofmann, H. Petersen, and M. Sacchi, Surf. Interface Anal. **18**, 65 (1992).

[20] P. E. Batson, Phys. Rev. Lett. **70**, 1822 (1993).