

## **Study of different forms of carbon by analytical electron microscopy**

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### **Abstract**

Polycrystalline diamond films grown on non-scratched Si substrates by the Hot Filament-Chemical Vapor Deposition (HF-CVD) were studied by Parallel EELS (PEELS) and Extended Electron Energy Loss Fine Structure Spectroscopy (EXEELFS) techniques. PEELS spectra of diamond films were compared with those obtained for natural diamond. These spectra show that the plasmon and carbon K-edge main features are almost indistinguishable (in position and shapes) in both, natural and our HF-CVD diamond films. The radial distribution function around the carbon atoms was obtained through the Fourier transform of the extended fine structure located in a 300 eV range beyond the carbon K-edge in the energy loss spectra. The values obtained for the C–C distances are very close (within 0.003 nm) to those of the natural cubic diamond structure. These results were accomplished by analyzing the respective X-Ray diffraction pattern (XRD) of the diamond films. This study confirms the good quality of the diamond films produced by our experimental technique.

Keywords: Carbon; PEELS; EXEELFS; AEM

### **Introduction**

With the application of synchrotron radiation sources to materials science investigation, a powerful technique has evolved for the study of the local structure of a wide variety of

materials. This technique focuses on the fine structure found in the vicinity of sharp X-ray absorption edges and is known as Extended X-ray Absorption Fine Structure (EXAFS) [1]. A similar process occurs when electrons interact with the surface of a given material. The incident particle may lose a discrete amount of energy by the ionization of a core level corresponding to atoms near the surface. In the vicinity of the ionization threshold, fine structure has been found to have the same physical significance as that found in EXAFS. In this case, the technique is called Extended Electron Energy Loss Fine Structure Spectroscopy (EXEELFS) in both transmission and reflection modes. This technique has been applied to the study of local structure of crystalline surfaces, [2–5] polycrystalline systems [6] and because of the strong electron solid interaction, EXEELFS has been used to study adsorbates [7–10], clusters [11] and thin films [12]. In the reflection mode, these experiments have been performed in commercial surface spectroscopy systems equipped with an electron spectrometer, typically a cylindrical mirror analyzer CMA. In most of these experiments, the incident electron energy used is between 500 and 3000 eV.

The aim of this article is to show the good quality of diamond films obtained by Hot Filament-Chemical Vapor Deposition (HF-CVD) through an Electron Energy Loss study. This is accomplished by analyzing their respective radial distribution functions (RDF), or  $F(r)$  obtained by applying the Fourier transform to experimental data around the carbon K-edge, known as fine structure.

Thus, one may select the EXEELFS technique depending on the instrumentation available and the material to be analyzed. Also, we intend to show that EXEELFS is a reliable and accurate technique for structural studies of surfaces and thin films.

## **Experimental**

High quality microcrystalline silicon carbide (*McSiC*) buffer films of different thickness were deposited onto crystalline silicon (c-Si) wafers by an ECR-CVD technique, as previously described [13]. The diamond films were grown on these SiC/Si substrates by using a heated tungsten filament and a CH<sub>4</sub>/CH<sub>2</sub> gas mixture in a CVD cell. TEM cross section samples were prepared by gluing two samples together, face-to-face (this is done to protect the area of interest and at the same time to increase the number density of crystals in the thinned area), cutting a 3 mm disk and thinning by standard micropolishing and ion milling methods. The natural diamond particles with a nominal size of 1 *mm* were taken from commercial diamond powder.

The EXEELFS and PEELS experiments were done in a PHILIPS-CM200 TEM with a GATAN- 766 PEELS attachment. A primary energy of 200 KeV and a spot size of 440 nm with an average acquisition time of 5 min was used. The extended fine structure (EFS) energy range was 300 eV. In order to obtain the local structure, the standard procedure developed for EXAFS [14–17] was applied here. In order to obtain a good structural characterization, we compared the PEELS spectra of amorphous carbon and highly oriented pyrolytic graphite (HOPG) with the corresponding diamond spectra. In order to obtain the RDF, the experimental raw data

which contains information about the spacing among nearest neighbours (fine structure), can be written as follows.

$$\chi(E) \propto \left| \langle \psi_j | \hat{\epsilon}_q \cdot \vec{r}_c | \psi_i \rangle \right|^2 \int_{q_{\min}}^{q_{\max}} \frac{dq}{q}, \quad (1)$$

Where:  $\psi_i$  and  $\psi_j$  are the initial and final states of the electron participant in the process  $\hat{\epsilon}_q$  is the unitary vector of the transferred momentum  $\vec{r}_c$  is the distance between nearest neighbours and  $q$  is the magnitude of the transferred momentum. In this expression, the matrix element is very similar to the matrix element of the EXAFS process [12] where the term  $\hat{\epsilon}_q$  is replaced by the polarization vector of the X-ray.

This is then conventionally transformed into  $X(k)$  where  $k$ , the corresponding wave vector, is associated with  $k = \sqrt{0.263(E_0 - E)}$ . Here,  $E$  is the energy loss,  $E_0$  in our case is chosen at the inflection point of the carbon K-edge and  $E_0 - E$  is their respective energy loss. Finally, structural information about each carbon atom can be obtained from  $X(k)$  via the optical Fourier transform

$$F(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} \chi(k) k^\mu \omega(k) e^{-2ikr_c} dk. \quad (2)$$

Here,  $X(k)$  is the experimental raw data transformed through the relation for  $K$ ,  $\mu$  is a weight factor and  $\omega(k)$  is a window function, usually a Gaussian function to avoid truncation effects on  $\chi(k)$ . As we can see, the standard EXAFS procedure was used and the EXAFS phase shifts were not applied here. Finally the XRD pattern was obtained

with a General Electric X-Ray Diffraction (GE-XRD)-6 X-Ray Diffractometer. In order to excite the Cu K $\alpha$  line ( $\lambda=50.15418$  nm) a potential energy of 40 KeV and a current of 20 mA were used.

## Results and discussion

Fig. 1 shows the PEELS spectra in the low loss region for (a) amorphous carbon, (b) HOPG (c) natural diamond particle and (d) diamond thin film (cross section). As can be seen, the most prominent plasmon loss peaks characterizing the diamond film are located at the same energy loss for natural diamond (33 eV), certainly at higher energies than graphite (26 eV) or amorphous carbon (23 eV). Further, in the natural diamond and diamond film, a small shoulder appears around the 23 eV. This agrees well with measurements in diamond films where bulk plasmon losses are observed at 23 eV and 33 eV [18, 19]. The origin of the loss peak located at 23 eV in the deposited films and in natural diamond is interpreted as caused by the presence of a surface plasmon.

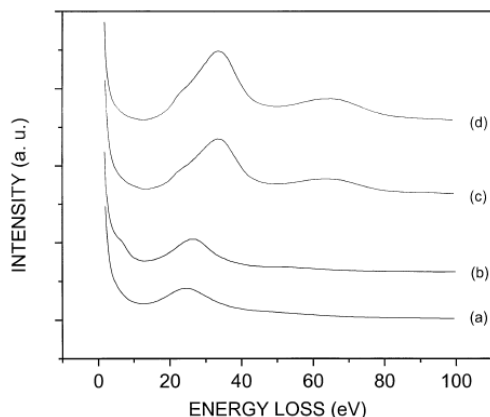


Fig. 1. EELS spectra at the plasmon region for (a) amorphous carbon, (b) highly oriented pyrolytic graphite, (c) natural diamond and (d) polycrystalline diamond thin film. Plasmon ( $\pi + \sigma$ ) energies for the three structures are 23, 26 and 33 eV, respectively.

Fig. 2 shows the energy loss spectra around the ionization carbon K-edge corrected for background and multiple scattering processes. Again, the near edge structure is almost indistinguishable between both diamond samples. In this figure the difference in the  $\pi^*$  and  $\sigma^*$  transitions among the three different structures of carbon can be observed.

Amorphous carbon and HOPG have basically the same edge shapes, the similarities can be explained in terms of the similarities in their bonding. In particular for the diamond samples the lack of the  $\pi^*$  transition (284 eV) indicates no graphitic layers was formed in these films. Thus, through a careful comparison among these spectra one can distinguish among the different structures formed by carbon atoms. These spectra are considered as a *finger print* of the structure. Similar results have been reported by M. De Crescenzi [12] and in [20].

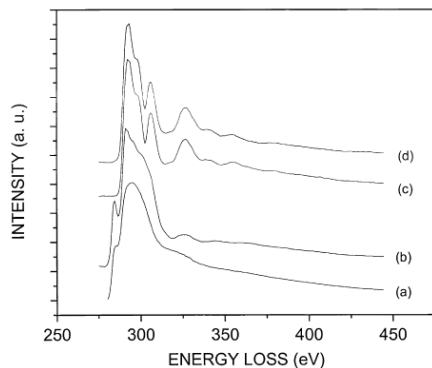


Fig. 2. Extended Fine Structure above the carbon K-edge for (a) amorphous carbon, (b) highly oriented pyrolytic graphite, (c) natural diamond and (d) polycrystalline diamond thin film.

Some experiments have been reported by other authors using low primary energies and their results have been in good agreement with the properties of each system analyzed. In this sense, we also obtained spectra of graphite and diamond film with a primary energy of 500 eV in a standard CMA and a lock-in amplifier for collecting data. Data taken in this way are very important because of the possible overlap in the CVV Auger transition and the K-edge of carbon. The CVV Auger transition and the K-edge of carbon. This is shown in Fig. 3 for the case of fraphite, where the CVV Auger transition, displayed in the first derivative, is taken together to the ionization edge of carbon. As can be seen, the main features in addition to the Auger excitation are the  $\pi^*$  and  $\sigma$  transitions. Similar results appears for the diamond film in Fig. 4, where the lack of the  $\pi^*$  transition in notable. There were some problems of data acquisition, such as beam instability for large acquisition time. However, Fig. 5a,b show the extended fine structure and the radial distribution function for the diamond film sample.

Fig. 6 shows the radial distribution functions obtained by applying the Fourier transform to the energy loss spectra of Fig. 2. The values obtained for the nearest neighbours in the two diamond samples are in good agreement with the known crystallographic values [21] of 0.154 nm for the first nearest neighbours and 0.251 nm for there second nearest neighbors of cubic diamond. With respect to the third main peak, the apparently disagreement between the two diamond structures, is well known and is attributed to the fact that EXEELFS process is a short range order. Numerical values for the nearest neighbour positions are presented in Table 1. We note that the difference among the values obtained here and the known crystallographic positions is 0.002 nm and 0.003 nm for the first and second nearest neighbors in the diamond film and 0.002 nm and 0.002 nm for the first and second nearest neighbours in the natural diamond sample. The estimated difference between our results and the known crystallographic values is around 0.003 nm (3%). Numerical results for the other carbon structures were published for the authors elsewhere [22]. For comparison, Table 2 shows numerical values for the different forms of carbon obtained applying the Fourier transform to spectra shown in Fig. 2.



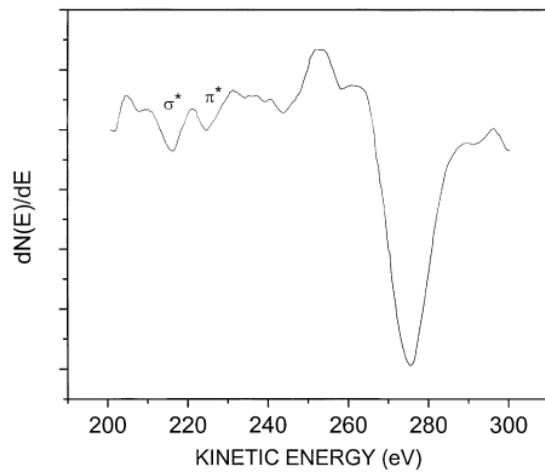


Fig. 3. CVV Auger transition of graphite together with the ionization carbon K-edge. Note the main electronic transitions around the near edge.

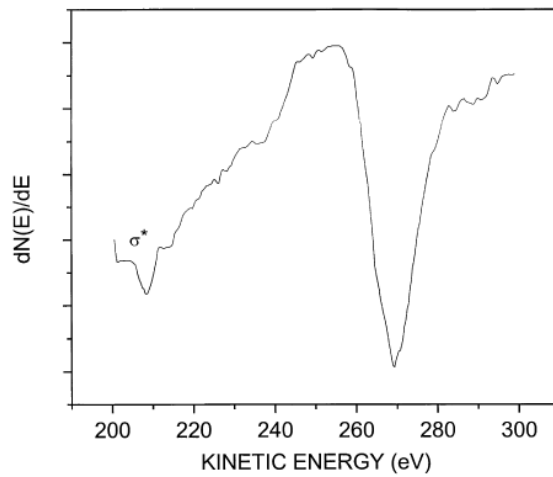


Fig. 4. CVV Auger transition of diamond film together with the ionization K-edge. Note the lack of the  $\pi^*$  transition.

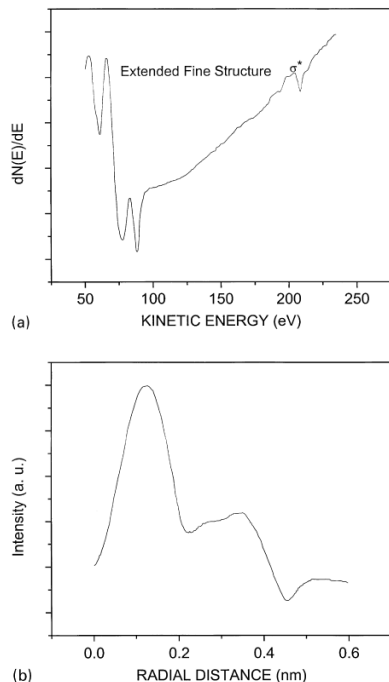


Fig. 5. (a) Extended fine structure of diamond film, excited by electrons with a primary beam energy of 500 eV. (b) radial distribution function obtained by applying the Fourier transform to the fine structure.

The same diamond thin films studied by EELS, were also characterized by XRD. Fig. 7. Shows an XRD spectrum of a diamond film grown on  $\mu\text{cSiC} : \text{H} / \text{x-Si}$ . This spectrum shows three main peaks located at  $2\theta = 43.9^\circ, 75.3^\circ$  and  $91.4^\circ$  corresponding to the contributions of three crystallographic planes; (111), (220) and (311) respectively. These results are in good agreement with those reported in the ASTM card 6-0675. Finally one peak centered around  $2\theta = 69^\circ$  represents the Si substrate in direction [100].

Table 1

Numerical results for the two diamond samples showing the values obtained in this work and the known crystallographic values from [22].

Sample	First nearest neighbors (nm)	Second nearest neighbors (nm)
Natural Diamond	$0.152 \pm 0.002$	$0.255 \pm 0.002$
Diamond Film	$0.156 \pm 0.002$	$0.251 \pm 0.002$
Known crystallographic values	$0.1544 \pm 0.002$	$0.251 \pm 0.002$

Table 2

Numerical results for the two main atomic positions of different structures formed by carbon atoms, including diamond structures.

Sample	Nearest neighbors (nm)	Known crystallographic values (nm)
Amorphous carbon	$0.148 \pm 0.002$	0.144
	$0.248 \pm 0.002$	0.256
Graphite (HOPG)	$0.157 \pm 0.002$	0.142
	$0.244 \pm 0.002$	0.246
Natural diamond	$0.152 \pm 0.002$	0.154
	$0.255 \pm 0.002$	0.251
Diamond film	$0.156 \pm 0.002$	0.154
	$0.253 \pm 0.002$	0.251

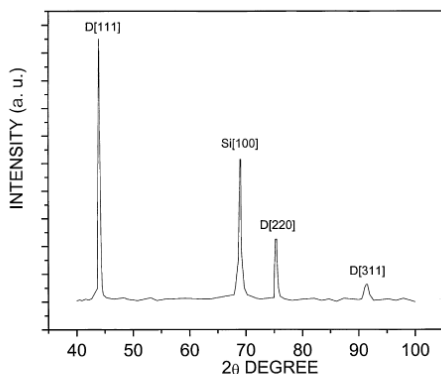


Fig. 7. XRD spectra of diamond film grown on  $\mu\text{c-SiC:H/x-Si}$ . Note the prominent peak located at  $2\theta = 43.9^\circ$  corresponding to the diamond [111] direction.

## Conclusions

We have demonstrated that good quality diamond films can be obtained using HF-CVD technique on non-scratched Si substrates. The energy loss spectra (Figs. 1 and 2) resembles closely those of pure diamond. We have calculated the radial distribution function, showing the possibility of assessing the quality of diamond films obtained with

the HF-CVD technique. In this case, the third main peak is not reliable because of the short range process of EXEELFS. We have done experiments with low primary electron beam energies showing the possibility of obtaining the same structural information. Finally we conclude that the values obtained for nearest neighbour distances for the different forms of carbon, in particular for the diamond samples studied here, are in good agreement with respective known crystallographic values.

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