Electron-energy-loss spectroscopy characterization of the sp^2 bonding fraction within carbon thin films

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When using electron-energy-loss spectroscopy (EELS) to quantify the sp^2/sp^3 bonding fraction in thin film carbon, the spectrum taken from the film must be compared to that of a suitable known standard. In contrast to the work of Berger [S. D. Berger and D. R. McKenzie, *Philos. Mag. Lett.* **57**, 285 (1988)], C_{60} fullerite is used in this work as the standard since highly oriented pyrolytic graphite (HOPG) is highly anisotropic, and can therefore lead to preferential orientation effects in EELS. It was found that C_{60} had a shoulder on the high-energy side of the $1s \rightarrow \pi^*$ peak, which was centered at 287 eV. In theory, many Gaussian peaks can be fitted to the near edge structure (NES) of the energy-loss spectrum. In practice, we show that only three, centered at energies of 285, 287, and 293 eV, are necessary for semiquantitative analysis. The 285 eV peak is indicative of the sp^2 bonding fraction; the second peak at 287 eV is attributed to molecular structure within the sample; the third at 293 eV is determined by sp^3 bonding contributions in the sample. We show that by fitting these three peaks to C_{60} fullerite and evaporated amorphous carbon (a -C), that the a -C has a 0.99 sp^2 bonding fraction compared with the C_{60} fullerite standard. The importance of considering the 287 eV peak in highly sp^2 bonded amorphous carbon is further illustrated by analysis of a -C:H:N thin films.

INTRODUCTION

Amorphous carbon films often comprise a combination of two types of bonding: namely, sp^2 and sp^3 type hybridizations. The bonding can be analyzed by studying the K ionization edge in an electron-energy-loss spectrum (EELS). A method for quantifying the sp^2 bonding fraction in an amorphous carbon film is described by Berger and McKenzie,¹ where the area of the $1s \rightarrow \pi^*$ peak of the film is compared to that of graphite. The mathematical principle of quantifying the edge is to obtain a ratio of the two areas, one of which is the standard as shown in the following formula:

$$f_{\pi^*} = \frac{I_{\pi^*}^u \Delta E^s}{I_{\pi^*}^s \Delta E^u}, \quad (1)$$

where f_{π^*} is the ratio between the two π^* peaks, I_{π^*} is the integral of the $1s \rightarrow \pi^*$ transition, and ΔE is the integrated counts for the normalizing energy window. The superscripts s and u denote the standard and unknown spectra, respectively.

Unfortunately, there are two ambiguities in the Berger method. First, what form of carbon should be used as the standard? Secondly, what sort of fit can be applied to the π^* peak (i.e., Gaussian, Lorentzian, or a mixture of the two)? In this paper, we address both of these issues.

EXPERIMENTAL DETAILS

All the carbon samples in this study were analyzed on a VG HB601UX FEGSTEM operating at 100 keV, with a 3.4

Å diameter probe. A 70 μm objective aperture having a convergence angle of 21.3 mrad and a 500 μm collector aperture having a collection angle of 3.4 mrad were used in the microscope alignment. The FEGSTEM was equipped with the Gatan model 666 parallel EELS spectrometer, with the photodiode array operating at 0.3 eV/channel for the collection of K ionization edge spectra. This gives a spectral energy resolution of 0.7–0.8 eV when considering the spread in the data of the zero loss peak. Data processing was carried out using Gatan EL/P 3.0 software, where each spectrum had the background and plural scattering removed, and then the energy resolution was enhanced by a zero loss peak deconvolution routine. The HOPG and C_{60} fullerite samples were prepared for EELS analysis by ultrasonic vibration in pure ethanol for ten minutes. A drop of the graphite flake suspension was then placed on a lacey carbon grid and the ethanol allowed to evaporate. This TEM specimen preparation method produced 10 nm thick flakes of HOPG in random orientations, thus allowing the HOPG to be analyzed both perpendicular and parallel to the basal plane. The C_{60} suspension was also placed on a lacey carbon grid, allowing the analysis to be performed on C_{60} fullerite crystals that were overhanging a void. The lacey carbon film on the grid was analyzed as an example of a highly sp^2 bonded a -C sample (as it is obtained from evaporation of graphite).

RESULTS AND DISCUSSION

The method of quantification¹ of the near edge structure (NES) requires a standard, as it is based on using the ratio of the normalized $1s \rightarrow \pi^*$ to $1s \rightarrow \sigma^*$ peak integral of the

FIG. 1. The C K -ionization edge spectra of HOPG, (a) normal and (b) parallel to the c axis.

sample to that of the standard. Therefore, the standard should usually be 100% sp^2 bonded. There are only two realistic contenders which satisfy this criteria. Namely, highly oriented pyrolytic graphite (HOPG) or C_{60} fullerite. Figure 1 shows the orientation effects of HOPG of the EELS spectrum. It can be seen in Fig. 1(a) which is an EELS spectrum obtained parallel to the graphite layers, that there is a significant amount of peak overlap with the two Gaussians that are fitted to the π^* and σ^* peaks at 285 and 292 eV, respectively. This overlap does not occur when the sample orientation is such that the c axis of HOPG is parallel to the electron beam, as shown in Fig. 1(b). This is due to the much sharper features in the spectrum and a much reduced π^* peak. These effects make HOPG less than ideal for use as a standard for K -edge EELS characterization of amorphous carbon.

C_{60} fullerite, on the other hand, does not suffer from these preferential orientation effects and is close to 100% sp^2 bonded due to its nearly pure π character.² C_{60} is not exactly 100% sp^2 due to the bowing introduced into its structure by the pentagonal carbon rings, which changes the σ bonding character compared to that of a graphite sheet structure. However, it does not influence the nature of the π bonding in the C_{60} compared to that of graphite, as confirmed by Martins, Troullier, and Weaver.² In the case of amorphous carbon films we believe this to have minimal effect on the calculated sp^2 fractions calculated by analysis of the $1s-\pi^*$ energy loss feature taking C_{60} as the standard. This is because the σ bonding within the amorphous carbon film too would be three-dimensional (instead of planar as in graphite), and therefore a similar change in “ s ” like nature of the σ bonding would be expected. Therefore, we believe that the error in the EELS analysis due to any additional influence of the $1s-\sigma^*$ energy loss peak on the $1s-\pi^*$ due to pentago-

nal rings in the C_{60} standard compared to that of a -C, with close to 100% randomly oriented sp^2 bonds is minimal. It is perhaps worth noting again that it is the relative intensities and areas of the π peaks which are important in calculating the sp^2 fraction using Eq. (1).

Model calculations³ of the bond hybridization in C_{60} confirm that the π bonds remain largely unaffected by their directional “randomization” in the sphere geometry. There is only a very small amount of s -character introduced into the π bonds. The σ bonds however, were found on average to be $sp^{2.5}$ hybridized in C_{60} compared to the sp^2 hybridization in graphite. In the EELS measurements this difference in the hybridization of sigma bonds will not be evident in the relative intensity of the $1s-\sigma^*$ peak compared to that of the $1s-\pi^*$ peak. The fractions of σ bonding per carbon atom and pi bonding per carbon atom remain the same in C_{60} as in a “randomized” graphitic structure. The position of the $1s-\sigma^*$ on the energy axis may of course be shifted in C_{60} compared to that of graphite due to the differences in hybridization. But, the important parameter in our use of C_{60} for calibration of the relative fraction of π bonding per carbon atom in amorphous carbon is the relative intensity of the two peaks.

The computer fitting of a Gaussian or Lorentzian or a mixture of the two to energy loss spectra (see for instance, Wan and Egerton⁴) can be carried out according to a standard procedure. The Gaussian peak fitted to the π^* peak of HOPG in Fig. 1(b) shows that there is no overlap between the π^* and σ^* peaks, i.e., the π^* peak has no contribution from the σ^* peak. HOPG can therefore be a very good base for a sp^2 bonded carbon system with a Gaussian fitted to the π^* peak centered at 285 eV. However, this is only strictly applicable when there is an orientation effect within the carbon, which is the same as that of the HOPG standard film being analyzed.⁵ Figure 2(a) is the K edge spectrum of C_{60} fullerite. A Gaussian or Lorentzian peak fitted at 285 eV will not model correctly the shape of the edge due to a shoulder on the high-energy side of the π^* peak. This problem is not new since Silva *et al.*⁶ reported that the peak fitting to the spectra from a -C:H films could be improved if a third Gaussian peak was introduced at 287 eV. The physical origin of this third Gaussian peak was thought to be associated with the shift of the $1s \rightarrow \pi^*$ peak due to hydrogen bonding to sp^2 carbon.⁶ By adding a third peak at 287 eV, a good fit to the C_{60} spectrum edge [shown in Fig. 2(a)] can also be obtained. The problem here is that C_{60} , in common with HOPG, is purely sp^2 bonded carbon without any bonded H. Also, HOPG does not require a third peak [Fig. 1(b)], therefore, an explanation as to why C_{60} should need a third peak at 287 eV is required. Figure 2(b) shows the K edge spectrum of hydrogen free evaporated a -C, which also requires a third peak to be fitted at 287 eV. Unlike Silva,⁶ who attributed this peak to hydrogen bonding within the film, in our case it occurs in pure sp^2 carbon films, which have no orientation effects. It is plausible to postulate that this third peak at 287 eV may be due to indirect transition from the $1s$ to π^* state. The work of Pickard *et al.*⁷ on *ab initio* calculations of the near edge structure (NES) for the graphite K edge suggests that as the angle of incidence of the fast electron changes in relation with the graphite c axis, the $1s$

FIG. 2. The C K -ionization edge spectra obtained from (a) C_{60} fullerite and (b) a -C, showing the fit obtained when using three Gaussian peaks centered at 285, 287, and 293 eV.

$\rightarrow\pi^*$ peak decreases in size and simultaneously gains a shoulder on the high-energy side of the peak. Pickard proposed that a family of peaks should be considered until the onset of the $1s \rightarrow \sigma^*$ transition at 289 eV. Further calculations by Pickard and Payne⁸ on the NES of diamond shows that the $1s \rightarrow \sigma^*$ transition is also made up from a large number of such peaks. Therefore, the size and shape of the $1s \rightarrow \sigma^*$ edge will influence the size and shape of the $1s \rightarrow \pi^*$ peak if there is some residual overlap between them. The $1s \rightarrow \pi^*$ peak will also change with the angle of the π bonds in relationship to the incident direction of the fast electron. It is therefore clear that the NES of the carbon ionization edge is determined by a number of factors, and to model the NES satisfactorily a number of Gaussian peaks have to be considered. Figure 1(a) shows that the $1s \rightarrow \pi^*$ peak has a slight shoulder on the high-energy side. This shoulder is due to the angle of the incident electron beam. The angular effect however, is not enough to cause the shoulder seen in the C_{60} fullerite spectrum [Fig. 2(a)]. C_{60} is a molecule in which the character of the π bonding is the same as that of graphite, but with random orientation, for this reason we can discount mixing of the π and σ states giving rise to the 287 eV peak. The 287 eV feature is also required to fit the spectrum obtained from a -C. Electron energy loss spectroscopy of cyclic hydrocarbons, fluoroethenes, and 1,3 perfluorobutadiene^{9–11} have shown that all these molecules have a peak with varying strengths at around 287 eV. It was concluded that this peak was due to a molecular transition, which varied in intensity, depending upon the intramolecular bond length.

There is much work reported in the literature on the NES of C_{60} based on x-ray absorption spectroscopy (XAS, NEXAFS) and dedicated high resolution EELS without any

FIG. 3. The variation of the sp^2 bond fraction in nitrogenated a -C:H thin films deposited on the driven electrode; (a) for sp^2 hybridizations using a simple two peak fit with only the 285 and 293 eV peaks, (b) for sp^2 hybridizations using a fit that includes an additional peak centered at 287 eV, and (c) the variation of the integrated area under the 287 eV peak; as a function of nitrogen flow into the chamber in standard cubic centimeters per minute (sccm). Curve (c) appears to indicate that the “molecular content” of the a -C:H:N films stays approximately constant over the nitrogen range.

capability of having spatial resolution for imaging.^{12–14} The fine structure obtained with these techniques that have a resolution better than 0.2 eV clearly shows the need for 4–5 Gaussians to map the data accurately. Interestingly, they too report the observation of a peak approximately 2 eV above their $1s \rightarrow \pi^*$ peak (but in their case the $1s \rightarrow \pi^*$ peak is at ~ 284 eV). We believe the peak we observe on our C_{60} sample at 287 eV on the STEM-EELS with its superior nanometer scale spatial resolution, which allows for chemical mapping, is a “smudged” reproduction of the fine structure reported in these papers.

Additionally, Treacy and Gibson¹⁵ has shown that paracrystalline domains exist in group IV amorphous materials. It is therefore possible that within the a -C film there are small paracrystalline domains which give it some heterogeneous properties. These small domains in turn could be viewed as being pseudomolecules within an amorphous matrix. If this were the case, then we could expect that the 287 eV peak would be higher for C_{60} than for a -C, as C_{60} fullerite is a truly molecular crystal, whereas a -C is only paracrystalline.

Using Eq. (1) with C_{60} as the standard, and defining the peaks at 285 and 287 eV as shown in Fig. 2, values of $f_{\pi^*} = 0.99$ and $f_{287} = 0.86$ are obtained for a -C. This indicates that while the a -C analyzed is almost entirely sp^2 bonded, the relative influence of transitions to molecular-like states ascribed to the 287 eV feature is significantly reduced. The association of the 287 eV peak being with a molecular transition is further reinforced by the fact that it is not present in the EELS K -edge NES of diamond or graphite.

Further evidence of the importance of properly accounting for the influence of the 287 eV peak when determining the sp^2 bonding fraction, was seen in the EELS analysis of hydrogenated and nitrogenated amorphous carbon (a -C:H:N) films. These films were obtained using the capacitively coupled radiofrequency plasma enhanced chemical vapor

deposition method. Details of the particular deposition parameters used can be found in the literature.¹⁶ They were prepared for EELS by releasing thin electron transparent films from a Si substrate using an HF etching procedure. The sp^2 bonding fraction determined without taking into account the 287 eV peak is plotted as a function of nitrogen (N) flow in Fig. 3. The sp^2 bonding fraction appears to start at a fraction close to 100% for films with a low nitrogen content, and then monotonically reduces to around 60% as the N content increases. This is clearly in error, as it is known that with increasing N content a -C:H:N films graphitize, and thereby increase the proportion of sp^2 bonding within the films.¹⁷ The results obtained by also taking into account the relative influence of the 287 eV peak from the same EELS data is shown in Fig. 3. It is now observed that the sp^2 bonded fraction starts at 70% for low N content, and then rises to a maximum of 94% for high N content. This is much more in keeping with data obtained from this class of material.¹⁸ These results show clearly the importance of considering the 287 eV peak when analyzing amorphous carbon films with high sp^2 bonding fractions using EELS K -edge NES.

The relative strength of the 287 eV peak in these films, compared to that of C_{60} fullerite, shows a distinct drop at higher N contents (Fig. 3). On the basis of the molecular transition origin of the 287 eV peak, this would be expected. The presence of small graphitic domains in a -C is predicted from the sp^2 cluster model developed from tight-binding calculations by Robertson.¹⁹ As the films become more graphitic in character, clusters with molecularlike properties be-

come much less prevalent since the clusters will tend to merge to give a more fine-grained polycrystalline type structure. The loss in intensity of the 287 eV peak at high N contents would then be in keeping with this model for the structure of a -C.

CONCLUSIONS

It is generally not possible to fit just one Gaussian or Lorentzian peak to the $1s \rightarrow \pi^*$ transition in the NES of the carbon K ionization edge electron energy loss spectrum. The exception to this is for HOPG and CVD diamond forms of carbon. When considering C_{60} fullerite and amorphous forms of carbon, a peak centred on 287 eV must be included to take into account the molecular crystalline nature of C_{60} and paracrystalline nature of a -C films. It has been shown that the $1s \rightarrow \pi^*$ (285 eV), the molecular crystalline (287 eV), and the $1s \rightarrow \sigma^*$ (293 eV) transitions all contribute to the edge shape. Therefore, all three transitions have to be fitted with Gaussian peaks for the determination of the sp^2 bonding content within a carbon film. C_{60} fullerite has been shown to be a more suitable standard than HOPG for obtaining the sp^2 bonding fraction. We propose the use of the 287 eV peak to measure the relative fraction of molecular nature within carbon films.

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