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


1Department Electrical and Electronic Engineering, University of Liverpool, Liverpool, L69 3GJ, United Kingdom
2Department of Engineering, Materials Science and Engineering, University of Liverpool, Liverpool, L69 3BX, United Kingdom
3School of Electronic Engineering, University of Surrey, Guildford, Surrey, GU2 5XH, United Kingdom
4Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ, United Kingdom

(Received 9 April 1999; revised manuscript received 6 March 2000)

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, 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:

$$f_{\pi^*} = \frac{I_{\pi^*} \Delta E}{I_{\pi^*} \Delta E_s}, \tag{1}$$

where $f_{\pi^*}$ is the ratio between the two $\pi^*$ peaks, $I_{\pi^*}$ is the integral of the $1s \rightarrow \pi^*$ transition, and $\Delta E$ 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 $\pi^*$ 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 quantification$^1$ 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.

The computer fitting of a Gaussian or Lorentzian 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 \( \pi \) 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 \( \sigma \) bonding character compared to that of a graphite sheet structure. However, it does not influence the nature of the \( \pi \) 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 \( \sigma \) bonding within the amorphous carbon film too would be three-dimensional (instead of planar as in graphite), and therefore a similar change in ‘s’s’ like nature of the \( \sigma \) bonding would be expected. Therefore, we believe that the error in the EELS analysis due to any additional influence of the \( 1s-\pi^* \) energy loss peak on the \( 1s-\pi^* \) due to pentagon-
same as that of graphite, but with random orientation, for this molecule in which the character of the p

NEXAFS

perfluorobutadiene9–11 have shown that all these molecules spectroscopy of cyclic hydrocarbons, fluoroethenes, and 1,3 to fit the spectrum obtained from rises to the 287 eV peak. The 287 eV feature is also required the angular effect however, is not enough to cause the shoulder seen in the C 60 fullerite spectrum should be considered until the onset of the 1s → σ* transition at 289 eV. Further calculations by Pickard and Payne8 on the NES of diamond shows that the 1s → σ* transition is also made up from a large number of such peaks. Therefore, the size and shape of the 1s → σ* edge will influence the size and shape of the 1s → π* peak if there is some residual overlap between them. The 1s → π* 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 → π* 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 I,3 perfluorobutadiene10–11 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 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 → π* peak (but in their case the 1s → π* peak is at −284 eV). We believe the peak we observe on our C 60 sample at 287 eV on the STEM-EEELS 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 fσπ = 0.99 and fπ = 0.86 are obtained for a-C. This indicates that while the a-C analyzed is almost entirely sp2 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 sp2 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. They were prepared for EELS by releasing thin electron transparent films from a Si substrate using an HF etching procedure. The $s^p$ bonding fraction determined without taking into account films from a Si substrate using an HF etching procedure. The prepared for EELS by releasing thin electron transparent phitic in character, clusters with molecularlike properties be-

The presence of small graphitic domains in material. These results show clearly the importance of considering the 287 eV peak when analyzing amorphous carbon films with high $s^p$ bonds bonding fraction. We propose the use of the 287 eV peak to measure the relative fraction of molecular structure of $a$-C. It has been shown that the $s$-$\pi^*$ (285 eV), the molecular crystalline (287 eV), and the $s$-$\sigma^*$ (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 $s^p$ bonding content within a carbon film. $C_{60}$ fullerite has been shown to be a more suitable standard than HOPG for obtaining the $s^p$ bonding fraction. We propose the use of the 287 eV peak to measure the relative fraction of molecular nature within carbon films.

ACKNOWLEDGMENTS

The authors acknowledge EPSRC for financial support.