Linköping University Post Print

**Interpretation of electron diffraction patterns
from amorphous and fullerene-like carbon
allotropes**

Zsolt Czigany and Lars Hultman

N.B.: When citing this work, cite the original article.

Original Publication:

Zsolt Czigany and Lars Hultman, Interpretation of electron diffraction patterns from amorphous and fullerene-like carbon allotropes, 2010, Ultramicroscopy, (110), 7, 815-819.

<http://dx.doi.org/10.1016/j.ultramic.2010.02.005>

Copyright: Elsevier Science B.V., Amsterdam.

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-58157>

Interpretation of electron diffraction patterns from amorphous and fullerene-like carbon allotropes

Zsolt Czigány

*Research Institute for Technical Physics and Materials Science of the Hungarian
Academy of Sciences P.O.Box 49. H-1525 Budapest. Hungary*

Lars Hultman

*Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM),
Linköping University, S-581 83 Linköping, Sweden*

Abstract

The short range order in amorphous and fullerene-like carbon compounds has been characterized by selected area electron diffraction patterns (SAED) and compared with simulations of model nanoclusters. Broad rings in SAED pattern from fullerene-like CN_x at ~ 1.2 Å, ~ 2 Å, and ~ 3.5 Å indicate a short-range order similar to graphite, but peak shifts indicate sheet curvature in agreement with high-resolution transmission electron microscopy images. Fullerene-like CP_x exhibits rings at ~ 1.6 Å and 2.6 Å that can be explained if it consists of fragments with short-range order and high curvature similar to that of C_{20} .

Keywords: electron diffraction, fullerene-like carbon, nanoclusters, simulation

1. Introduction

Amorphous carbon and carbon-based coatings show a broad variety of properties regarding mechanical hardness, elasticity as well as electronic and optical properties. The difference in properties is due to different chemical bonding and the consequent different atomic short range ordering.

The structure of fullerenes has been extensively studied by transmission electron microscopy (TEM) and modeling [1-3]. In contrast to fullerenes, an interesting group of carbon-based materials are the so called fullerene-like (FL) solid phases like CN_x ($x < 0.3$) and CP_x ($x \approx 0.1$) where the solid is composed of FL fragments and/or packages [4, 5]. Density functional theory (DFT) calculations [6-8] showed that incorporation of N or P makes it energetically favorable to form pentagonal [7,8] or tetragonal [6] defects, respectively, introducing curvature of graphene sheets. This made it possible to deposit such FL coatings at moderate temperatures in the range of 150-450°C [5,9]. The extreme mechanical resiliency of these phases attracted interest due to extension of in plane strength of sp^2 coordinated graphene network into three dimensions. For example the well-structured FL- CN_x proved to be interesting for applications as protective coating and as solid lubricant on the basis of resiliency, hardness and relatively low friction.

Multishell fullerene structures - so called nano-onions - were observed in $CN_{0.12}$ by high resolution transmission electron microscopy (HRTEM) [4]. In selected area electron diffractions (SAED) diffuse rings were observed at $\sim 1.2 \text{ \AA}$, $\sim 2 \text{ \AA}$ and at $\sim 3.5 \text{ \AA}$ [4,10]. The first two rings are typically observed for all amorphous carbon materials, the last one corresponds to the spacing of nano-onion shells. This spacing is close to that of basal planes in graphite indicating the presence of C layers similar to that in graphite.

CP_x has an amorphous appearance in HRTEM images [5]. The electron diffraction pattern, however, suggests structural differences between CN_x and CP_x FL phases and between CP_x and other amorphous carbon allotropes. In SAED of $CP_{0.1}$ diffuse rings were observed at $\sim 1.6 \text{ \AA}$, $\sim 2.6 \text{ \AA}$ and at $\sim 6 \text{ \AA}$. While these peaks are considered to be original in carbon phases indicating a new material with unique structure., the spacing of diffuse SAED rings of CP_x is not yet understood from structural point of view. The aim

of this work is to reveal diffraction properties of different C-based structures, setting up a library for different C structures altering their short-range order (SRO) from graphitic to DLC through FL and nanotube structures.

Here, we report the calculated electron scattering from different C allotropes, namely graphite, and diamond nanoclusters as well as fullerene molecules and fragments, as a function of the number of atoms in each characteristic structure. Amorphous phases are interpreted as structures composed from ultrafine random nanocrystalline or nanoclustered structures with characteristic cluster size of 10-30 atoms. It is shown that the SRO of each structure can be determined based on the relation between the calculated scattering of carbon nanoclusters and experimental selected area electron diffraction (SAED) patterns.

2 Models and calculation

The mathematical model for electron scattering of atom clusters is based on formulations established by Dove [11]. In this approach the atoms are treated as scattering centres. Each atom is a source of a plane wave having a scattering amplitude of $f(\mathbf{k})$. Atomic coordinates are $\mathbf{r}_h = \mathbf{r} + \mathbf{R}_h$ where $\mathbf{r}$ is the coordinate of an arbitrary atom of the cluster $\mathbf{R}_h$ are the relative coordinates of the atoms within the cluster.

The plane wave scattered from $\mathbf{k}_0$ to $\mathbf{k}$ by one atom is

$$\Psi_h(\mathbf{k}) = f(\mathbf{k}) \exp(2\pi i \mathbf{k} \mathbf{r}) \exp(2\pi i \mathbf{K} \mathbf{R}_h)$$

where $\mathbf{K}$ is the scattering vector, $\mathbf{R}_h$ is the position of atom h. The scattered intensity of one atom at $\mathbf{k}$ is $f^2(\mathbf{k})$. $\mathbf{K} = \mathbf{k} - \mathbf{k}_0$

The amplitude of the wave scattered by the whole cluster is the sum of the wave amplitudes of all the atoms in the cluster:

$$\Psi(\mathbf{K}) = \sum_h f_h(\mathbf{K}) \exp(2\pi i \mathbf{k} \mathbf{r}) \exp(2\pi i \mathbf{K} \mathbf{R}_h)$$

(It was used that $\mathbf{K} = \mathbf{k} - \mathbf{k}_0$, $f_h(\mathbf{K}) = f_h(\mathbf{K})$ where $K = |\mathbf{K}|$)

The scattered intensity of a group of atoms (cluster) can be calculated as $|\Psi(\mathbf{K})|^2$

$$\text{Int}(\underline{\mathbf{K}}) = \sum_{h,j} f_h(\mathbf{K}) f_j(\mathbf{K}) \exp [2\pi i \underline{\mathbf{K}}(\underline{\mathbf{R}}_h - \underline{\mathbf{R}}_j)]. \quad (\text{Eq. 1})$$

This formula involves the orientation of the cluster compared to the incident wave and scattering vector. Since in SAED scattering by several nanoclusters – situated in the selected area – is involved, we calculated the overall scattered intensity of several randomly oriented clusters. In this way, we ignore any texture in actual materials such as is commonly reported for FL- CNx [12].

$\text{Int}(\mathbf{K}) = \sum_{\text{orientation}} \text{Int}(\underline{\mathbf{K}}) / N_{\text{orientation}}$, where $N_{\text{orientation}}$ is the number of averaged orientations. This formula is suitable for description of aggregates of identical clusters.

Nanocrystalline materials were thus modelled as aggregates of nanocrystallites (nanoclusters) of different size, shape and orientation. Assuming that there is no correlation between the nanoclusters, the scattered intensity of their aggregates is the sum of scattered intensity of the individual clusters. Gaussian size distribution was applied with the parameters of the mean value of N_{average} and full width of half maximum of $\sigma = N_{\text{average}}/3$. The cluster shape was randomized using random elliptical shape and the orientation was randomized by rotation of the cluster with random angles.

Scattering of amorphous allotropes are modeled by approximating the material with aggregates of 10-30 Å large nanocrystallites. as small grain (cluster) size range/region of nanocrystalline material. At least 2000 nanocrystallites (nanoclusters) were involved in the scattered intensity calculation for assessing the statistic quality.

Atomic coordinates of nanoclusters were generated using perfect crystal lattice coordinates. After cutting the spherical or elliptical shape of cluster the coordinates were not optimized for energy minimum. Coordinates of fullerene cages were taken from Ref [13]. In the modeling of nanocrystals the size distribution was calculated for $n = 1$ to $n = 2 N_{\text{average}}$, for each n new random elliptical shape was generated. A random shift of the crystal lattice was also applied to randomize the center position of the ellipse compared to the crystal lattice. Random orientations were achieved by rotation of the cluster with random angles. Atomic scattering amplitudes from Ref [14] were fitted with the following formula: $f(\mathbf{K}) = a / (b + K^2)$

3 Experimental

FL CN_x and CP_x films were grown by magnetron sputtering of C target in Ar/N₂ mixture [4] and composite C-P target in Ar, respectively [5]. The HRTEM characterization was made in Philips CM20 UT and FEI Tecnai G2 transmission electron microscopes (TEM), both operated at 200 kV for a 1.9 Å resolution.

SAED patterns were recorded in a CM20 TEM operated at 200 kV on imaging plates utilizing the six orders of magnitude of linear dynamic range of imaging plates. The patterns were evaluated by calculating the scattered intensity distribution using Process Diffraction software [15].

4. Results and discussion

4.1 *Scattering by identical nanoclusters*

Figure 1 shows the calculated scattered intensity of randomly oriented spherical graphite nanoclusters as a function of the number of atoms in the cluster. The intensity shows peaks at the Bragg positions. We note that broad intensity maxima appear from very small clusters composed of 10-15 atoms. The Bragg peaks become distinct at size of 30 atoms. With increase of the cluster size towards 120 atoms, the Bragg peaks become more and more distinct and higher hkl peaks become recognisable.

In addition to Bragg peaks, peaks appear in the range of $K < 0.5 \text{ \AA}^{-1}$ due to finite size effect and shape factor of the clusters. Consequently, the positions of these maxima depend on the cluster size. The 3.5 Å peak becomes measurable at 45 atom size. Below 45 atoms the peak at 3.5 Å is mixed with shape/size oscillations.

Figure 1. Calculated electron scattering of spherical graphite clusters (centered on a lattice atom). The parameters of the curves are the number of atoms in the cluster.

Figure 2a) shows the calculated scattered intensity of a C_{60} fullerene. In the $1/K < 2\text{\AA}$ region intensity maxima appear at the same positions like in graphite ($\sim 1.2\text{\AA}$ and $\sim 2\text{\AA}$). Although the fullerene-related peaks do not correspond to any real space distances, we mark the peaks in $\text{\AA}$ and use this notation later on. The peaks at $\sim 1.2\text{\AA}$ and $\sim 2\text{\AA}$ can be observed in the scattered intensity of all fullerenes larger than C_{60} (not shown). The low angle region of $K < 0.5\text{\AA}^{-1}$ is dominated by finite size oscillations having several maxima and minima.

The scattered intensity of a random C_{60} molecule is also shown in Fig. 2a), where random C_{60} is an imaginary molecule of 60 carbon atoms randomly and evenly distributed on a sphere of C_{60} diameter. The scattered intensity of random C_{60} shows that randomization has minor effect on peak positions, the peaks appear in the same position like in C_{60} molecule, indicating that the curvature of the fullerene cage has a decisive influence on the peak positions. The sharp zero intensity minima of C_{60} are missing for random C_{60} in $K < 0.5\text{\AA}^{-1}$ region due to lack of symmetric nature of C_{60} .

Similar calculations are shown for C_{20} and random C_{20} in figure 2 b. Similar to C_{60} the peaks in the calculated scattered intensity of C_{20} and random C_{20} are at the same position (having the same curvature), but different position compared to C_{60} due to different cage curvature.

Figure 2. Calculated electron scattering of a) C_{60} and b) C_{20} molecule gas with perfect atom arrangement (blue curves) and randomly distributed C atoms on a sphere of the same radius (red curves), respectively.

4.2 Scattering by nanocrystals

Fig. 3 compares scattered intensities of nanocrystalline diamond (Fig 3 a and b), graphite (Fig 3 c), and graphene (Fig 3 d). Diamond is shown in two panels to provide a more detailed view for low n_{average} in panel b. In these scattered intensities of nanocrystalline structures there are no size oscillations observed at low scattering angles ($K < 0.5 \text{ \AA}^{-1}$). This is due to averaging for cluster size. For a varying cluster size, the finite size oscillations appear at different positions and will be averaged in the sum. This averaging is also enhanced by averaging for cluster shape.

Figure 3 Calculated electron scattering intensities for nanocrystalline diamond, graphite and graphene. The parameter of the curves is the average grain (cluster) size of the solid expressed in average number of atoms.

Important to note that broad intensity maxima appear from very small average cluster size composed of 10-15 atoms. The Bragg peaks become clear at size of n_{average} of 30

atoms. With increase of the average cluster size up to 60 and 120 atoms, the Bragg peaks become more and more clear and higher hkl peaks become recognisable.

The intensity distributions of the three phases show both similarities and differences between carbon allotropes. Similarities are observed in the peak positions: all the three carbon allotropes have peaks at $\sim 1.2\text{\AA}$ and $2\text{\AA}$. The three allotropes have Bragg peaks at slightly different positions, but it cannot be used for unambiguous distinction since the peak positions also depend on grain (cluster) size as shown below.

Graphite can be easily distinguished having an additional peak at $\sim 3.34\text{\AA}$. Graphene and diamond can be distinguished based on peak intensities: graphene has two peaks at $\sim 1.2\text{\AA}$ and $2\text{\AA}$ of similar intensities (like graphite), but diamond has a peak intensity ratio of $\sim 1/4$ for $\sim 1.2\text{\AA}$ and $\sim 2\text{\AA}$ peaks. Diamond also has additional peaks ($\langle 311 \rangle$ and $\langle 400 \rangle$) close to $1\text{\AA}$ which can be observed at larger average grain size ($n > 30$).

Figure 4 shows the peak position of graphite, graphene and fullerene cages as a function of cluster size. The intensity is calculated for fullerenes of different curvature and a shift in the $\sim 1.2\text{\AA}$ and $\sim 2\text{\AA}$ peak position is observed due to cage curvature. The highest values for peak positions are obtained for graphene (and graphite) $1.22\text{\AA}$ and $2.13\text{\AA}$ (for n average = 120). For C_{60} the values are slightly lower $1.19\text{\AA}$ and $2.00\text{\AA}$, but below the cage size of C_{60} more significant shift is observed. For the C_{20} molecule, the peaks shift to $1.08\text{\AA}$ and $1.72\text{\AA}$, respectively.

The peak positions show significant dependence on cluster size for planar structures. E.g., the peak of graphite and graphene at $\sim 2\text{\AA}$ shifts from $2.4\text{\AA}$ to $2.13\text{\AA}$ between cluster size of 15 and 120 atoms. C_{60} and smaller fullerene cages show minor cluster size dependence. The $3.34\text{\AA}$ peak of graphite is also shifted from $3.7\text{\AA}$ (n average = 20 atoms) to $3.34\text{\AA}$ (n average = 120 atoms) in the same cluster size range. These shifts can be utilized to evaluate the SAED and derive information on cluster size and plane curvature.

The diffraction pattern of multiwall carbon nanotubes has similar appearance to graphite [16]. The narrow peaks indicate a large coherence length in the graphitic short range order within the multiwall carbon nanotubes.

Figure 4 Size and curvature dependence of calculated diffraction peak positions for graphite, graphene and fullerene cages.

The SAED of FL-CN_x (Fig. 5) is also very similar to graphite indicating a similar short range order. However, peaks are shifted slightly towards lower values of 1.15Å and 2.04Å due to curved plane packages of onion like structures [4]. Therefore, the analysis of SAED confirms the presence of fullerene like structure established on the basis of high resolution TEM.

SAED of FL-CP_x have broad peaks at ~2.6Å and ~1.6Å (Fig. 6) which are close to those observed in calculated scattering of C₂₀ molecule and its fragments (Fig. 7) at ~3Å and ~1.7Å. This indicates that FL CP_x has a SRO similar to that of C₂₀ indicating that CP_x is predominantly composed of fragments with similar or even higher local curvature like C₂₀. Fullerene fragments of larger diameter would involve peaks at ~1.2Å and ~2Å, which would dominate the SAED.

Figure 5 HRTEM image, SAED pattern and its intensity distribution of FL-CN_x film [4]. The intensity distribution is similar to that of graphite indicating similar short range order of curved sheets.

This indicates that local curvature of sheets in CP_x is similar to that of C₂₀ or even higher. High curvature in CP_x is also confirmed by theoretical calculations [6] which showed that P additive makes the formation of square defects energetically favourable in graphene structure introducing high curvature.

The origin of the peak at 6 Å is presently unknown. Based on its position, it may be a sign of ordering between C₂₀ fragments, however, its shape is much sharper than the features at ~1.6 Å and ~2.6 Å. An alternative explanation is that it may be caused by intercalation of P atoms between curved sheets of CP_x [17]. Initial *ab initio* calculations shows that the inter sheet distance in the vicinity of P intercalation site can locally increase to 5.6-7.2 Å [18]. This is manifested in a peak at ~6 Å in the distribution of our SAED patterns.

Figure 6 HRTEM image, SAED pattern and its intensity distribution (background extracted) of FL-CPx film [5]. The broad peaks at 2.6 and 1.6 Å in the intensity distribution is similar to that calculated for C₂₀ indicating high local curvature in the structure.

5 Conclusions

A method is proposed to calculate electron diffraction of nanoclusters and nanocrystalline materials and evaluate the short range order in amorphous and fullerene-like allotropes of carbon. Nanocrystals are modeled as aggregates of crystalline clusters of different size, shape and orientation. Therefore, the scattered intensity is the sum of intensities from clusters of different size, shape and orientation. Amorphous materials are interpreted as nanocrystals of ultrafine grain (cluster) size composed of 10-30 atoms. Diffuse peaks in the distribution of scattered intensity appear for N_{average} of 10-15 atoms. Nanocrystalline character appears when $N_{\text{average}} > 60$. In graphitic and fullerene carbon allotropes the position of peaks at $\sim 1.2 \text{ Å}$ and $\sim 2 \text{ Å}$ depends on cage curvature. Significant dependence is calculated for cages of smaller diameter than C₆₀. High curvature induces peak shift to lower values of 1.08 Å and 1.72 Å , respectively, for curvature of C₂₀.

Based on calculations of scattered intensity the short range order of amorphous and fullerene-like carbon allotropes could be classified. The short range order of MWCN is graphitic. FL-CN_x has similar SRO, but peak shifts indicate sheet curvature in agreement with HRTEM. FL-CP_x has a SRO similar to that of C₂₀ indicating that FL-CP_x is predominantly composed of fragments with similar high curvature like C₂₀.

Figure 7. Calculated electron scattering of aggregates of C₂₀ molecule fragments. The parameter of the curves is the average number of atoms of the fragments. If the average fragment size larger than half C₂₀ molecule, the features are observable in the scattered intensity.

Acknowledgement

FOREMOST Project (EU 6th Framework Program) – NMP3-CT-2005-515840 is acknowledged for financial support. Prof. György Radnóczy, Dr. Andrej Furlan, and Docent G.K. Gueorguiev are acknowledged for discussions.

References

- [1] S. Iijima
Helical microtubules of graphitic carbon
Nature 354(1991)56
- [2] D.J.H. Cockayne, D.R. McKenzie, W. McBride, C Goringe, D. McCulloch
Characterization of amorphous materials by electron diffraction and atomistic modeling
Microscopy and Microanalysis 6 (2000) 329-334
- [3] C.A.Davis, D.R. McKenzie, D.J.H. Cockayne D.A. Muller A.M. Vassallo
The structure of the C70 molecule
Nature 355 (1992) 622-624
- [4] Zs. Czigány, I. Brunell, J. Neidhardt, K. Suenaga, and L. Hultman Growth of fullerene-Like Carbon Nitride Thin solid Films Consisting of Cross-Linked Nano-Onions Appl. Phys. Lett. 79 (2001) 2639-41
- [5] A. Furlan, G.K. Gueorguiev, Zs. Czigány, H. Högberg, S. Braun, S. Stafström, L. Hultman, Synthesis of Phospho Carbide Thin Films By Magnetron Sputtering. Rapid Research Letter in Physica Status Solidi 2 (2008) 191-193
- [6] G.K.Gueorguiev, A. Furlan, H. Högberg, S. Stafström and L. Hutman First-principles calculations on the structural evolution of solid fullerene-like CPx Chemical Physics Letters 426 (2006) 374-379
- [7] S. Stafström, L. Hultman, N. Hellgren Predicted stability of a new aza[60]fullerene molecule, C₄₈N₁₂ Chemical Physics letters 340 (2001) 227-231
- [8] S. Stafström Reactivity of curved Planar structures Appl. Phys. Lett. 77 (2000) 3941-3943
- [9] J. Neidhardt, Zs. Czigány, I.F.Brunell and L. Hultman Growth of fullerene like carbon nitride thin Solid films by reactive magnetron sputtering; role of low-energy ion irradiation in determining microstructure and mechanical properties. J. Appl. Phys. 93 (2003) 3002-3015

- [10] J. Neidhardt, L. Hultman and Zs. Czigány Correlated high resolution transmission electron microscopy and X-ray photoelectron spectroscopy studies of structured CN_x (0<x<0.25) thin solid films Carbon 42 (2004) 2729-2734
- [11] B.D.Dove: Electron diffraction analysis of the local atomic order in amorphous film, in Physics of Thin Films, Ed. G. Hass, M. h. Francombe, R.W.Hoffman, Academic Press, new York, London, 1973. Vol.7., pp 1-37
- [12] R. Gago, G. Abrasonis, A. Müncklich, W. Möller, Zs. Czigány, G. Radnóczy Fullerenelike arrangements in carbon nitride thin films grown by direct ion beam sputtering Appl. Phys. Lett 87 (2005) 071901
- [13] <http://www.cochem2.tutkie.tut.ac.jp/Fuller/fsl/fsl.html>
- [14] J.W. Eddington: Practical Electron Microscopy, Philips, 1974 Vol. 3. p 103
- [15] J.L.Lábár, Ultramicroscopy 103 (2005) 237-249
- [16] Cs. Balázs, Zs. Czigány, F. Wéber, Zs. Kövér, Z. Kónya, Z. Vértesy, L. P. Biró, I. Kiricsi, P. Arató, Carbon Nanotubes as Ceramic Matrix Reinforcements, Mat. Sci. Forum 537-538 (2007) 97-104
- [17] A. Furlan, PhD Thesis, No. 1247 Linköping Studies in Science And Technology, Linköping, Sweden 2009
- [18] G.K.Gueorguiev, A.Furlan, Zs. Czigány, L. Hultman, unpublished