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P doped random C₂₀ fullerite - model structure for fullerene-like CP_x

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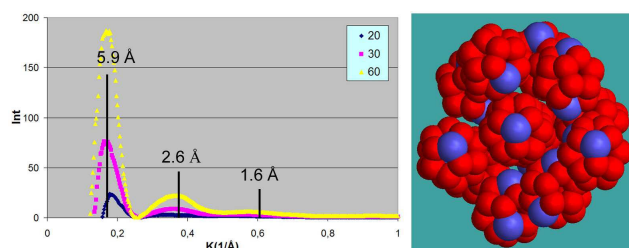
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Carbon based amorphous and fullerene-like (FL) thin films have a great potential due to their mechanical resiliency. TEM investigation and interpretation of results from fullerene like structures embedded in bulk phases is not straightforward. Here a model is presented for description of the structure of FL-CP_{0.1} thin films and to describe all the rings in the electron diffraction pattern in a self consistent way. The model structure consists of random close packed and P doped C₂₀ clusters resembling a kind of amorphous fullerite (crystals of fullerene cages). The 10% P doping was implemented by creating C₁₈P₂ cages by replacing two C atoms by P in the C₂₀ cage. The simulated electron scattering is in agreement with experimental electron diffraction pattern and reproduces all the observed diffuse diffraction rings of FL-CP_{0.1} at ~1.6 Å, ~2.6 Å and ~5.9 Å. Simulation of HRTEM images confirmed the amorphous appearance of this nanostructured material



A cluster of P doped random close packed C₂₀ fullerite (right) and its calculated electron diffraction (left) for different average cluster size (expressed in number of atoms).

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1 Introduction Carbon based amorphous and fullerene-like (FL) materials have a great potential for applications due to their mechanical resiliency [1-3]. Bulk FL structures can be realized by high temperature and high pressure treatment of C₆₀ fullerite [1-3]. These procedures cause amorphization of the original fullerite and provide a hard and elastic [1,2] or ultrahard [3] material. Diffraction techniques are widely used to determine the structural changes during such transformations [2-5]. Luminescence properties of C₆₀ fullerene films are also studied for using them in novel electron and optoelectronic devices [6].

Heterofullerenes are an extended group of the family of the fullerene materials with several type of doping elements like B, O, Si, S, Fe, Pt, Nb [7] including N [7,8] and P [7,9-11]. Excellent photoabsorption of P doped carbon (n-C) and p-type Si (p-Si) heterojunctions was also demonstrated for solar cell application [12].

Formation of fullerene-like allotropes of carbon in form of thin films can be realized by energetic deposition conditions in arc evaporation of graphite [13]. These pure carbon films contain onion-like fragments that were formed in the discharge [13]. These films also exhibit high hardness and elasticity [13]. Similar encapsulated polyhedra in onion-like carbon was previously known for high-energy electron irradiated carbon material [14]. However, in the presence of N or P dopants [8,11], the corresponding formation of nano-onions in carbon-based films during vapour phase deposition requires much less of thermal activation. Deposition of thin films of fullerene-like (FL) allotropes of carbon based compounds has been reported for carbon-nitride (CN_x; x≈0.1) [15] and phosphorus-carbide (CP_x; x≈0.1) [16]. In both cases the incorporation of N and P reduces the energy barrier to form pentagonal [8] and tetragonal [11] defects, respectively, thus inducing curva-

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ture of the hexagonal graphitic carbon network [8,11,15]. The addition of both N and P also promotes the cross-linking between C atoms in neighbouring fullerene domains [8,11,15] to support fullerene-like features in a solid matrix of the same elements and provides new, inherently nanostructured materials.

Based on the diffuse rings in their selected area electron diffraction (SAED) pattern, both CN_x and CP_x are very similar to amorphous materials. The unique fullerene like short range ordering is difficult to detect by high resolution transmission electron microscopy (HRTEM) due to superposition of overlapping nano-features within the specimen [17]. In FL- CN_x ($x \approx 0.1$) films (deposited in 3mTorr Ar at 450°C and -25V bias in 16% N_2 /Ar mixture) ~ 5 nm sized multishell features – so called nano-onions – were observed by HRTEM on very thin specimens [17]. Based on selected area electron diffraction, the atomic short range order is similar to that of graphite [18]. The interpretation of the TEM results of CP_x is even more complicated. HRTEM images show an appearance similar to amorphous structures for all deposition parameters [16]. Although the presence of any onion-like FL features, similar to those in FL- CN_x , cannot be ruled out from such HRTEM images due to the possible superposition of nano-scale features [17], formation of extended fullerene shells is not expected for CP_x since calculations show a strong tendency for P-induced interlinking between the shells [11] which breaks the continuity of the curved FL sheets. Though CP_x films seemed to be essentially amorphous by HRTEM [16], their unique atomic short-range ordering of curved fullerene-like features could be evidenced by SAED [16]. The FL- CP_x ($x \approx 0.1$) film (deposited in 3mTorr Ar at 300°C and -25V bias) has broad rings at ~ 1.6 Å, ~ 2.6 Å and ~ 5.9 Å in the SAED pattern [16]. These rings differ from those of other C allotropes [18], as well as from FL structures like FL- CN_x . The unusual diffraction pattern indicated the creation of a novel film structure which was interpreted based on scattering calculations of fullerene carbon cages [18]. The scattering pattern of C_{20} molecule is very similar to that of $CP_{0.1}$ indicating that local curvature of sheets in $CP_{0.1}$ is similar to that of C_{20} . The similarity is based on the position and shape of intensity maxima in the range of ~ 1.6 Å and ~ 2.6 Å but the ring at ~ 5.9 Å was interpreted from a point of a different approach of P intercalation between FL sheets [19]. The P intercalation would require extended sheets which is not consistent with the high curvature of the FL fragments and also not consistent with the SAED pattern which would be dominated in that case by rings at ~ 2 Å and 1.2 Å originated from extended sheets [18].

In this paper a model is proposed for FL- $CP_{0.1}$ to describe all the rings in the electron diffraction pattern, originated from a CP_x compound with structurally incorporated P, in a self consistent way. The model structure consists of random close packed and P doped C_{20} clusters resembling a kind of amorphous fullerite (crystals of fullerene cages). The 10% P doping was implemented by creating $C_{18}P_2$

cages by replacing two C atoms by P in the C_{20} cage. The calculated electron diffraction and the simulated HRTEM image of the model structure are suitable to explain the experimental SAED and the amorphous appearance of the material.

2 Model system and calculations

2.1 Model system This model is based on calculation of the diffraction pattern of FL- $CP_{0.1}$ [18], which showed that the measured pattern can be explained by high local curvature of sheets in CP_x similar to that of C_{20} molecule [18]. This statement is in agreement with theoretical predictions by synthetic growth concept [11] for the energetic feasibility of tetragon defects in FL- CP_x , which induce strong curvature. According to the prediction of frequent interlinkage of the curved fullerene like fragments [11] the C-C covalent bond distance of ~ 1.5 Å was used between the cages when the coordinates of a random close packed aggregate of C_{20} shaped molecules were assembled. The atomic coordinates of C_{20} fullerene cages were taken from Yoshida's fullerene database [20]. The P doping was implemented by transforming C_{20} cages into $C_{18}P_2$ cages by replacing two C atoms by P atoms. The two P atoms within the $C_{18}P_2$ cage were separated by 3, 4 and 5 chemical bonds. Thus the two P atoms in each $C_{18}P_2$ cages were separated by at least 3 inter-atomic bonds. By applying this restriction, the accommodation of two P atoms in the same ring was avoided [11] and low P-doping (~ 10 at%) was also fulfilled [10,11]. On this basis 3 isomers of $C_{18}P_2$ cages were defined (Figure 1).

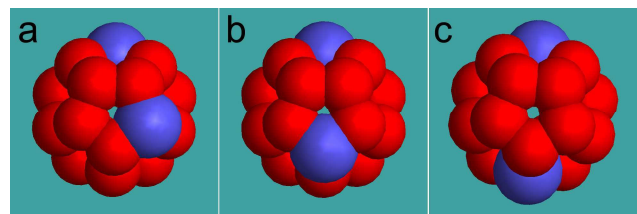


Figure 1 Building blocks of the model structure for FL- $CP_{0.1}$ [16]. Three types of isomers of $C_{18}P_2$ cages, where the two P atoms are separated by 3 (a), 4 (b) and 5 (c) chemical bonds.

For random arrangement of the cages the centres of the nearest neighbour $C_{18}P_2$ isomer cages were defined randomly on a sphere of 5.5 Å radius (~ 4 Å diameter of C_{20} + ~ 1.5 Å cage distance). If the randomly defined new cage was too close (closer than 5.5 Å) to any of the already defined cages, the cage coordinates were neglected. Due to high probability of unsuccessful trials, 10000 trials were attempted to fit neighbours to a cage, then the procedure continued on the next cage position according to the order of the agglomerate formation. In addition the orientation of the $C_{18}P_2$ isomer cages was randomised within the aggregate. An example of the defined clusters is shown in the inset of Figure 2a.

2.2 Calculations of SAED and HRTEM image The intensity distribution of the SAED pattern was calculated using the model of [18]. The model based on calculation of electron scattering of clusters of different size, orientation and shape, cut out from the above defined aggregate. Gaussian size distribution was applied for the number of atoms in the cluster with the parameters of the mean value of N_{average} and the width of the distribution was fixed with $\sigma = N_{\text{average}}/3$. The cluster shape was randomized using random elliptical shape and the orientation was randomized by rotation of the cluster with random angles. The intensity distribution of the SAED pattern can be calculated as a function of N_{average} which represents the extension of the short range order in an amorphous or nanostructured material.

The HRTEM image simulations were made by the JEMS program (by P. Stadelmann) using the multislice method. The microscope parameters were adjusted to the parameters of FEI Tecnai G² TEM, applied in the experimental investigations of FL-CP_x films [16]. The FEI Tecnai G² TEM was equipped with Philips CM20 ultrawin lens and Schottky field emission gun (FEG). Therefore, the following lens parameters were applied: acceleration voltage $V_{\text{acc}}=200\text{kV}$; chromatic aberration $C_c=1\text{mm}$; spherical aberration $C_s=0.5\text{mm}$, half convergence beam angle = 1 mrad and beam energy spread (E_s) of 0.7eV. The above parameters allowed for 1.9Å point resolution.

3 Results and discussion The calculated intensity distribution is shown in figure 2. The parameter of the curves in figure 2 is the average number of atoms in the clusters representing a kind of average extension of the short range structure in this material with amorphous character. The square root of intensity is plotted in figure 2a to make visible the low intensity maxima on the background. Similar low intensity maxima were observed on a strong background in the experimental SAED of FL-CP_x, therefore, only a background extracted SEAD intensity profile is reported in [16]. For comparison and better visibility of the position of maxima, the pattern is shown after a background extraction in figure 2b. The intensity maxima show a good coincidence with the experimentally observed intensity maxima of FL-CP_{0.1} indicated by the markers. The agreement with the experimental SAED indicates that the random close packed aggregate of C₁₈P₂ isomer cages provides an adequate model capable of approximating the short range structure of FL-CP_{0.1}. Previous model calculations of the scattering of C₂₀ cages [18] correctly explained the intensity maxima in the range of ~1.6 Å and ~2.6 Å which can be attributed to the intramolecular short range ordering within the C₂₀ fullerene cage.

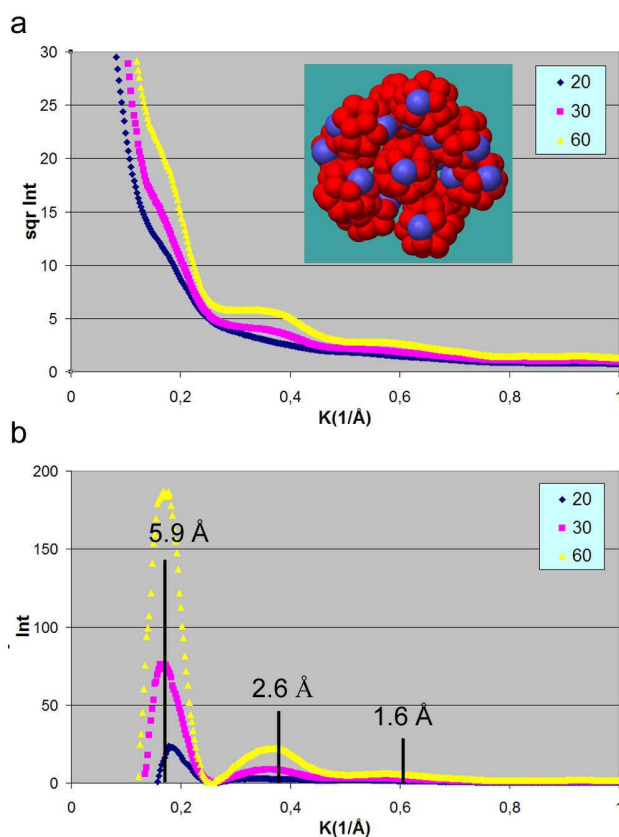


Figure 2 Calculated electron diffraction intensity distribution for a model structure of random close packed C₁₈P₂ isomer cages (illustrated in the inset: C atoms are red, P atoms are larger and blue). The square root of intensity (a) and background extracted intensity (b) are displayed. The diffraction intensity profile was calculated based on the model of [18] derived from electron scattering of clusters of different size, orientation and shape. The parameter of the curves is the average number of atoms in the clusters. The intensity maxima show a good coincidence with the experimentally observed intensity maxima of FL-CP_{0.1} [16], as indicated by the markers.

The ring at ~5.9Å was interpreted by sheet distance increase induced by P intercalation between FL sheets [19]. The latter approach supposes the presence of extended FL sheets, which would not be capable of explaining the intensity maxima at ~1.6 Å and ~2.6 Å which are the consequences of high curvature. The model structure, presented in this paper, is self-consistent: the P atoms are incorporated into C₂₀ sized cages and the proposed structure consists of random close packed C₁₈P₂ cages. The model is developed on the basis of [18] and [11] and it describes all the rings in the electron diffraction pattern of FL-CP_{0.1} [16]. In this model structure the intensity maxima at ~1.6 Å and ~2.6 Å reflects the intramolecular atomic short range ordering within the C₁₈P₂ cages, while the appearance of the additional ring at ~5.9Å is the consequence of the intermolecular short range ordering of C₁₈P₂ cages. The phenom-

ena is analogous with the short range ordering in C_{60} fullerene powder and films detected by XRD [5]. Taking into account that formation of complete $C_{18}P_2$ cages is not probable in the sputter deposition process of CP_x , the model of random close packed $C_{18}P_2$ cages involves some idealization. The real structure is most probably more similar to high pressure treated C_{60} fullerenes where the C_{60} cages are at least partially crushed and incomplete. That structure was described as a combination of interlinked curved fragments of C_{60} molecules and nanographite nuclei [2]. The analogy between the structure of random close packed $C_{18}P_2$ cages and high pressure treated C_{60} fullerenes is also supported by the observed high hardness and high elastic recovery in both materials [2, 16]. In case of high pressure treated C_{60} fullerenes Bhrashkin et al. [2] applied HRTEM to detect interlinked curved FL fragments. The detection of similar curved FL fragments by HRTEM in case of CP_x was not detected [16] due to overlapping effects of nanometer sized features within the specimen as described in [17].

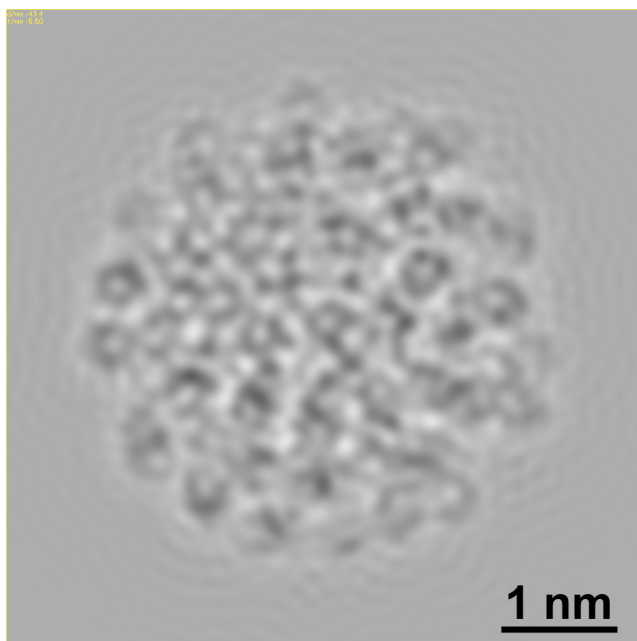


Figure 1 Simulated HRTEM image of a random close packed cluster of $C_{18}P_2$ of ~ 5 nm in diameter calculated for FEI Tecnai G^2 microscope at Scherzer defocus (-43 nm). The image has a uniform amorphous-like appearance in agreement with the experimental observations on FL- $CP_{0.1}$ [16].

The simulated HRTEM image of a random close packed cluster of $C_{18}P_2$ of ~ 5 nm in diameter is shown in figure 3. The HRTEM images were calculated for FEI Tecnai G^2 microscope at Scherzer defocus (-43 nm). Due to multiple overlap of the ~ 0.4 nm sized $C_{18}P_2$ cages, the cages cannot be distinguished even at 5 nm specimen thickness and the simulated HRTEM image has a uniform

amorphous-like appearance in agreement with the experimental observations on FL- $CP_{0.1}$ [16].

4 Summary A model structure of random close packed $C_{18}P_2$ cages describes all the diffuse diffraction rings of FL- $CP_{0.1}$ at ~ 1.6 Å, ~ 2.6 Å and ~ 5.9 Å in a self consistent way. The model reproduces the unusual SAED pattern by unifying the intramolecular and intermolecular short range ordering of $C_{18}P_2$ cages. The applicability of the model structure indicates that FL- $CP_{0.1}$ consists of highly curved interlinked FL fragments as predicted by first principle calculations and suggested based on calculations of the electron scattering of C_{20} cages. Analogy can be realized between the short range structure of FL- $CP_{0.1}$ and high pressure treated C_{60} fullerenes, which is confirmed by similar mechanical properties, i.e. high hardness and elastic recovery in both materials. The simulated HRTEM image of the model structure is also in agreement with the experimental observation providing a general indication, that quite complex nanostructured materials may have amorphous-like appearance in real TEM observations.

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