JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 12, December 2008, p. 3257 - 3260

Studies of carbon nanostructures by TEM procedures

I. M. OANCEA-STĂNESCU*, V. CIUPINĂ, G. PRODAN, I. MORJAN[a], I. VOICU[a], F. DUMITRACHE[a], E. VASILE[b], R. TRUŞCĂ[b], M. PRODAN
Universitatea "Ovidius", Mamaia Avenue No. 124, Constanta,900527, Romania
[a]*INCDFLPR, Atomistilor Street, No. 409, Magurele-Bucharest 077125, Romania*
[b]*S.C. Metav CD, C.A. Rosetti Street No. 31, Bucharest, 020011, Romania*

The paper performs studies on carbon nanostructures based on electron microscopy data. These data are collected from amorphous carbon, graphite, carbon nanotubes, and onion like carbon. Techniques used to acquire information were BF-TEM (Bright Field Transmission Electron Microscopy), DF-TEM (Dark Field Transmission Electron Microscopy), HR-TEM (High Resolution Transmission Electron Microscopy) and SAED (Selected Area Electron Diffraction). The structural properties of carbon were verified using a theoretical model consisted in small crystalline region with value less than 2-3 nm.

(Received October 21, 2008; accepted November 27, 2008)

Keywords: Graphene, Carbon, BSU, HRTEM, SAED

1. Introduction

Carbon materials are intensively studied for large application in many domains that include chemistry, engineering, medicine, and material science. The carbon nanostructures have advantage that can be very easily obtained with a large number of forms. We mention here the very well know form of carbon: graphite, diamond and amorphous carbon. Starting from graphite we can model and obtain onion like carbon and carbon nanotubes by means of modifying deposition parameters in case of CVD/PVD (**C**hemical **V**apor **D**eposition/ **P**hysical **V**apor **D**eposition) method or by changing the laser parameters in case of pyrolysis method [1-10]. The structure can be a start point to understand physical properties and physical phenomena that occurs in these materials.

The concept of basic structural unit (BSU) was introduced by Franklin in 1950 [11-16] based on X-Ray and TEM (**T**ransmission **E**lectron **M**icroscopy) studies. The Franklin idea was to divide the carbon structures in small bricks, with graphite structure that has determined orientation that form studied structure. The onion carbon can be build by arranging the bricks to form a sphere. A nanotube is build of same bricks using a cylindrical arrangement. Also, nanotubes can be described by means of two vectors $\mathbf{C_h}$ and $\mathbf{T}$, whose rectangle define the unit cell. $\mathbf{C_h}$ is the vector that defines the circumference on the surface of the tube connecting two equivalent carbon atoms, $\mathbf{C}_h = n\hat{\mathbf{a}}_1 + m\hat{\mathbf{a}}_2$, where $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ are the two basis vectors of graphite and n and m are integers. *n* and *m* are also called indexes and determine the chiral angle give by

$$\theta = \tan^{-1}\left(\sqrt{3}\frac{n}{2m+n}\right)$$

The chiral angle is used to separate carbon nanotubes into three classes differentiated by their electronic properties: armchair ($n = m$, $\theta = 30°$), zig-zag ($m = 0$, $n > 0$, $\theta = 0°$), and chiral ($0 < |m| < n$, $0 < \theta < 30°$). Zig-zag and chiral nanotubes can be semimetals with a finite band gap if $n - m/3 = i$ (*i* being an integer and $m \neq n$) or semiconductors in all other cases. The band gap for the semimetallic and semiconductor nanotubes scales approximately with the inverse of the tube diameter, giving each nanotube a unique electronic behavior.

Size of BSU are determined from HRTEM images and from diffraction data, using Scherrer relation, applied to XRD (**X**-**R**ay **D**iffraction) and electron diffraction data. The minimum value was 1 nm, and maximum tends to 5 nm. To identify more easily the BSU, we applied a filter to HRTEM images that convert 8 bit image in black and white image.

2. Experimental

Samples are obtained by dispersion in alcohol ~10% vol. Formvar coated cooper grid designed for TEM investigation are used as support for all samples. Electron micrographs are obtained using a Philips CM120ST transmission electron microscope working at 100kV. Digital micrographs are capture using a Gatan 673 CCD wide angle camera. Microscope is connected with PC using Analysis software that performs image acquisition and processing algorithm.

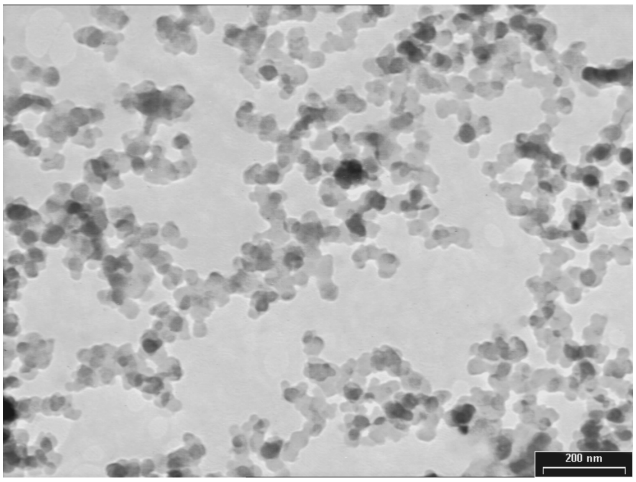
Samples were obtained by laser pyrolysis. The laser parameters and flow of precursors gas was modified to controls size of final nanostructures: sphere or tubes. The carbon nanotubes were growth on Si substrate seeded with carbon encapsulated iron nanoparticles.

The application software developed for testing ideal carbon nanostructure is based on graphite crystal design. In this case of nanocarbon the model consists in large sphere formed by small bricks.

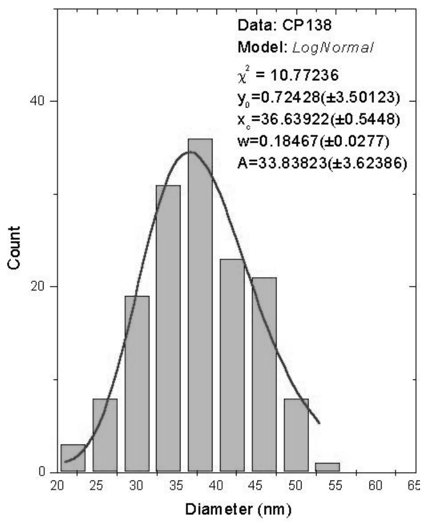
3. Results and discussion

The BFTEM micrographs were used to estimate the size of nanocrystalline materials. We assume that dimensions measured on electron micrograph are lognormal distributed, so experimental data are fitted with lognormal function as show in following lines. The electron diffraction contains data about structural information.

In Fig. 1 is studied sample CP (**C**arbon nanoonions-**P**yrolysis) and in figure 2 is studied CNT (**C**arbon **N**ano**T**ubes). As result of this study we found 36 nm mean diameters for CP sample and 17 nm on CNT sample, quite large compared with dimension of BSU estimate to be around 1 nm value.

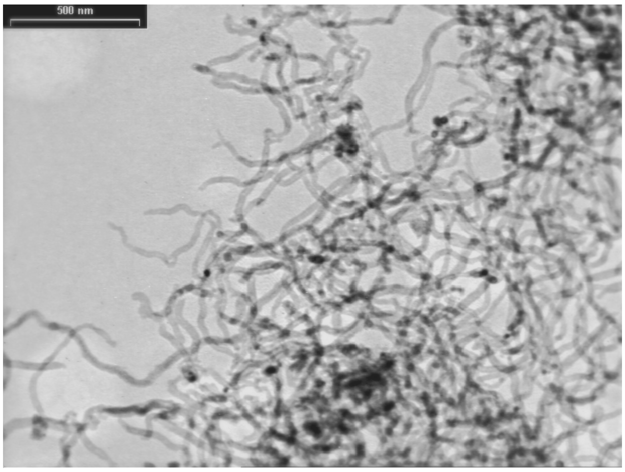


(a)

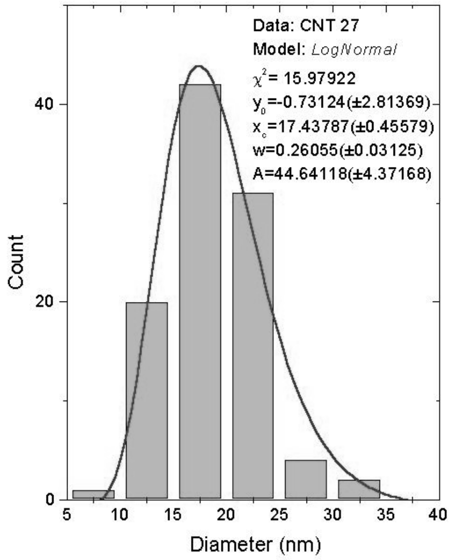


(b)

Fig. 1. BFTEM electron micrograph and diameters histogram for sample CP138 obtained by laser pyrolysis.



(a)



(b)

Fig. 2. BFTEM electron micrograph and diameters histogram for sample CNT27 obtained by laser pyrolysis.

The morphological information is important to estimate crystalline area so we know if sample are suitable for high resolution works. In case of large crystalline area is very difficult to obtain usable information at high magnification, due to reflection and diffraction effects. In our case we calculate contrast transfer function (CTF) for CM120 microscope when accelerated tension is set to 100kV and Scherzer defocus (~ -89 nm). As we can see in the CTF plot (figure.3), for graphitic carbon structures it is possible to obtain condition for high resolution. First, plane family 002 has a distance plane about 0.34 nm that is close to negative maxima of CTF. This means that atomic plane will be black on high resolution images. These can be modified by changing the objective lens settings, or focus values. The next family, 100 with d = 0.212 nm, it's difficult to identify on high resolution images due to low intensity in CTF graphics corresponding to 0.212nm.

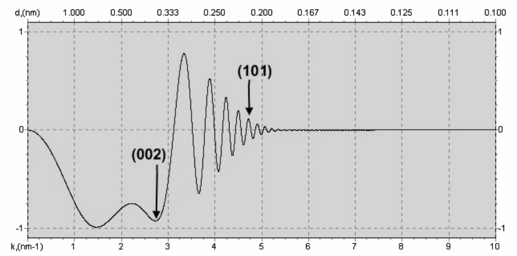
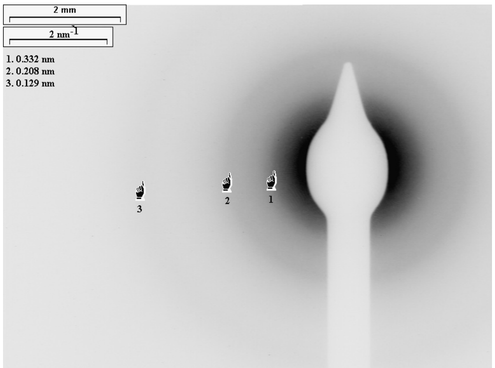
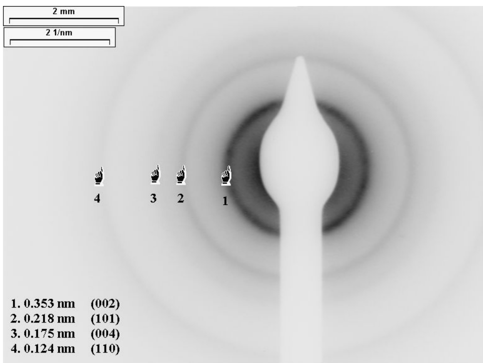


Fig. 3. CTF for CM120ST microscope working at 100kV and setup to Scherzer defocus (-89 nm).

The SAED and HRTEM image are used to determine crystalline structure. The graphitic structure of carbon was used for indexing electron diffraction pattern as shown in images (Fig. 4).



(a)

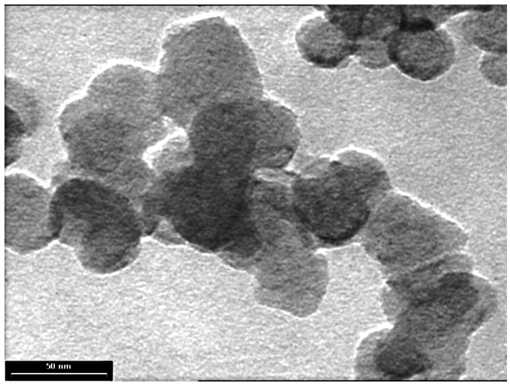


(b)

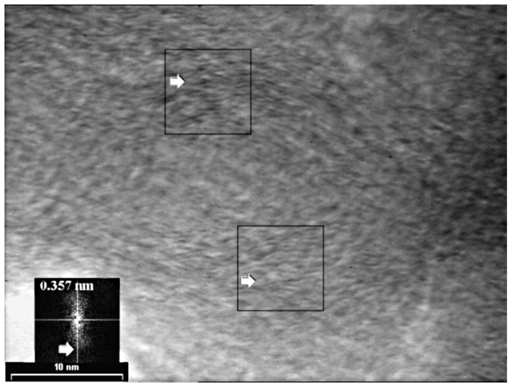
Fig. 4. (a) Electron diffraction pattern for nanoonions; (b) nanotubes.

Samples was indexed using hexagonal structure with lattice parameters a = 0.245 nm and c = 0.696 nm.

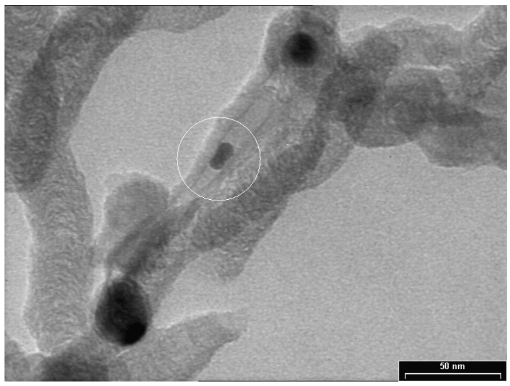
Diffraction data and HRTEM images provide information about carbon structure. In first case we can determine the structure of material and dimension of crystalline region by means of Scherrer relation. Determined dimensions from diffraction data could be compared with those evaluated from electron micrographs (Fig. 5). Reading such information we can further develop models of structure that can be applied to calculate other physical or chemical properties of material.



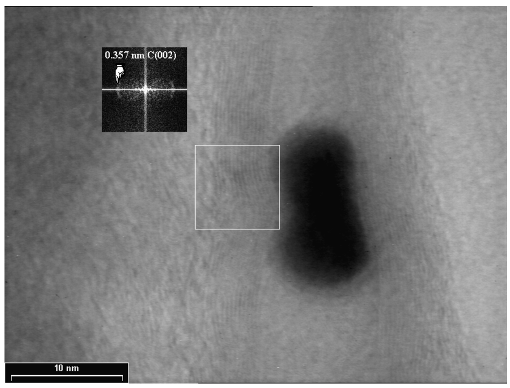
(a)



(b)



(c)



(d)

Fig. 5. TEM micrograph and high resolution images.Inset present FFT (Fast Fourier Transformation) representation of selected rectangle from image.

4. Conclusions

Laser pyrolysis is a common method to obtain nanoparticles. High energy of laser beam is capable to decompose gas precursor in component that are used to build a new structures, in our case carbon onion and tubes.

Morphology of sample studied by means of electron micrograph reveals nanostructured materials with dimension under 50 nm. In case of nano-onions we found a mean value around 36 nm. Carbon nanotubes diameters were found to be dispersed around 17 nm. In both case the experimental data histograms was assumed to follow a lognormal distribution.

The electron diffraction patterns were used to confirm the crystalline structure of carbon nanostructures. We found that both samples can be described using graphite hexagonal structure with lattice parameters a = 0.256 nm and c = 0.696 nm.

High resolution transmission electron microscopy reveals interference fringes associated with (002) planes family. Also, in high resolution micrograph we can identify and measure BSU.

Acknowledgements

This work was supported by Romanian Ministry of Education and Research, under project CEEX 106/2006.

References

[1] A. Galveza, N. Herlin-Boimeb, C. Reynaud, C. Clinard, J.N. Rouzau, Carbon **40**, 2775 (2002).
[2] J. M. Bonard, M. Croci, C. Klinke, R. Kurt, O. Noury, N. Weiss, Carbon **40**, 1715 (2002).
[3] J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, C. Dekker, Nature **391** (1998).
[4] A. T. Johnson, 1999 IEEE International Solid-State Circuits Conference
[5] A. V. Eletskii, B. M Smirnov, Physics –Uspekhi **38**(9), 935 (1995).
[6] M. Terrones, A. Jorio, M. Endo, A. M. Rao, Y. A. Kim, T. Hayashi, H. Terrones, J.-C. Charlier, G. Dresselhaus, M. S. Dresselhaus, Mat. Today, Oct. 2004.
[7] C. J. Lee, J. Park, Carbon **39,** 1891 (2001).
[8] V. Z. Mordkovich, A. G. Umnov, T. Inoshita, Int. J. of Inorg. Mat. **2,** 347 (2000).
[9] C. J. Lee, D. W. Kim, T. J. Lee, Y. C. Choi, Y. S. Park, Y. H. Lee, W. B. Choi, N. S. Lee, G. S. Park, J. M. Kim, Chem. Phys. Lett. **312,** 461 (1999).
[10] I. Morjan, I. Soare, R. Alexandrescu, L. Gavrila-Florescu, R.-E. Morjan, G. Prodan, C. Fleaca, I. Sandu, I. Voicu, F. Dumitrache, E. Popovici, Physica E **37**(1-2), 26 (2007).
[11] D. S. Novikov, Phys. Rev. B **76,** 245435 (2007).
[12] G. P. Mikitik, Y. V. Sharlai, Phys. Rev. B **77**, 113407 (2008).
[13] L. Benfatto, S. G. Sharapov, J. P. Carbotte, Phys. Rev. B **77,** 125422 (2008).
[14] R. E. Franklin, Proc R Soc **209**, 196 (1950).
[15] H. O. Pierson, Handbook of carbon, graphite, diamond, and fullerenes : properties, processing, and applications , Noyes Publications, New Jersey, 2 (1993).
[16] I. Morjan, I. Voicu, R. Alexandrescu, I. Sandu, F. Dumitrache, I. Soare, T. C. Fleaca, M. Ploscaru, V. Ciupina, Carbon **42**, 1269 (2004).

*Corresponding author: istanescu@univ-ovidius.ro