Research Article

Large Area C₆₀ Film Obtained by Microwave Oven Irradiation from an Organic Resin

J. Martínez-Reyes,¹ L. G. Díaz Barriga-Arceo,² L. Rendón-Vazquez,³ R. Martínez-Guerrero,⁴ N. Romero-Parada,⁴ E. Palacios-González,⁵ V. Garibay-Febles,⁵ and J. Ortiz-López¹

¹ ESFM-UPALM, IPN, Apartado Postal 118-395, 07051 México, DF, Mexico

² ESQIE-UPALM, IPN Apartado Postal 118-395, 07051 México, DF, Mexico

³ Facultad de Ciencias, Universidad 3000 Circuito Exterior S/N, Ciudad Universitaria, 04510 México, DF, Mexico

⁴ ROMFER Industries Inc., Mexico

⁵ Molecular Engineering Program, IMP Lázaro Cárdenas 152, 07730 México, DF, Mexico

Correspondence should be addressed to J. Martínez-Reyes; jacobomartinezreyes@gmail.com

Received 21 March 2013; Accepted 20 May 2013

Academic Editors: A. M. Ali, A. Kajbafvala, and C. Wang

Copyright © 2013 J. Martínez-Reyes et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the present work the synthesis of fullerene thin film produced in a conventional microwave oven from the decomposition of terpenoid is reported. The polycrystalline structure of the sample was determined by X-ray diffraction (XRD); the sample showed several phases, and the main phase corresponds to fullerene ordered in a face-centered cubic structure (FCC), with a lattice parameter $a = 14.16 \text{ \AA}$, with two more structures: one is orthorhombic system with lattice parameters $a = 9.53 \text{ \AA}$, $b = 8.87 \text{ \AA}$, and $c = 8.354 \text{ \AA}$, and the other is the monoclinic system with lattice parameters $a = 10.24 \text{ \AA}$, $b = 7.80 \text{ \AA}$, $c = 9.49 \text{ \AA}$, and $\beta = 92.4^\circ$ coexisting also with graphite 2H phase with lattice parameters $a = 2.46 \text{ \AA}$, $c = 6.71 \text{ \AA}$. It was observed in a scanning electron microscopy (SEM) that the sample formed thin films of stacked carbon. The film thickness was measured by a SEM, and it was 140.8 to 523 nm and the macroscopic area of 12 cm^2 , whereas a high-resolution transmission electron microscopy (HRTEM) revealed that the main phase of the material is C₆₀ ordered in a face-centered cubic structure (FCC). In the sample surface by atomic force microscopy (AFM), islands deposited crystals were observed having symmetry $\bar{4}3m$ crystal habit associated with the tetrahedron.

1. Introduction

Carbon thin films are important for the development of applications in semiconductors, nano electronics, and aerospace industry due to the physical properties of their crystal structure. These properties are high electric conductivity or semiconductivity, photo conductivity, and optical non-linearity [1]. Several methods are currently used for the preparation of carbon films [2–5]. In these methods the films are obtained in temperature conditions at ranges of 950–1250°C [6] with different energies from 100 to 1000 eV [7] at pressure from 1 to 5×10^{-7} Torr [8–10] using inert atmospheres or carbon gases as control atmospheres with flowing in a continuous way to obtain small area films with thicknesses from 500 nm to 10 000 nm with a crystalline or

amorphous structure [11], making this synthesis expensive. Comparing the carbon film precursors at present, the use of organic resins such as terpenoids has proven to be efficient in obtaining carbon films by using techniques such as CVD [12–17]. Comparing the chemical precursors used in the synthesis of carbon films, it was observed that organic resins present more advantages than the inorganic precursors because some of these resins are environment friendly [18]. It is important to mention that camphor resin has been successfully used in carbon nanomaterials synthesis and also in carbon films, graphene, carbon nanotubes, and other carbon allotropes [19, 20]. However it must be mentioned that the sample amount obtained in these experiments is very small. Based on the previous information it is necessary to look for new synthesis methods which must be not only more effective but also

cheaper [21, 22]. Therefore the microwave assisted synthesis (MAOS) [23] is a cost-effective alternative technology which reduces the impact on the environment by saving energy, being able to produce materials and microstructures that cannot be performed by other methods [24]. The synthesis of carbon films using camphor has already some history with not very clear results about the crystal structure of the same and the method of synthesis [20, 25–28], and we believe that it is still a very attractive study and control method variety. The aim of this work was to find the synthesis and microstructural characterization of the carbon films by microwave radiation using the techniques such as X-ray diffraction, scanning electron microscope, high-resolution transmission electron microscopy, and atomic force microscopy.

2. Experimental Details

2.1. Microwave Oven Preparation. The plate was removed from the microwave oven, and the samples were placed in a position where the microwave radiation reaches the maximum. Determinations of maximum and minimum points were done as reported in the literature [24, 29–33]. Resin sample was located in one of the points where microwave radiation has one maximum.

2.2. Sample Preparation. For this work 250 mg of camphor Sigma-Aldrich was placed in a Florence flask because it was observed that this glass's result better than of Pyrex glass under the same radiation condition. The flask volume was 250 mL, and the glass container with camphor was located inside a commercial SANYO microwave oven with a frequency of 2450 MHz. The sample was heat-treated to the maximum power (1480 Watts) for five minutes, until a carbon film was observed through the microwave oven windows. During the heat treatment, the temperature was measured by using an Infrared Thermometer Cole Palmer Mod. 800-323-4340 with LCD display, with a temperature range from –18 to 900°C.

2.3. Sample Characterization. The film sample was characterized by X-ray diffraction in a Siemens D-500 diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$). The sample was observed with two instruments a scanning electron microscope SEM/FIB NOVA 200 (with point resolution of 1.7 Å) and high-resolution transmission electron microscopy FEI Tecnai G-20 to 200 kV with resolution of 1.9 Å. The micrographs were analyzed using Digital Micrograph Software version 3.7 for GMS 1.2 Gatan Company. Topography was also measured with AFM (JEOL 5200) using a standard scanner (10 × 10 microns in “XY” and 3 microns “Z”) with a 20 nm platinum-iridium coated silicon tip (Veeco SCM-PIT) with 5 N/m spring constant and 20 nm tip diameter.

3. Results and Discussion

3.1. XRD Patterns. The diffraction pattern of carbon thin film is shown in Figure 1. In this pattern many phases were observed and they were identified using a reference database

FIGURE 1: XRD pattern carbon thin film.

cards ICDD PDF-2 Release 2003. It was observed that the well-defined peaks in this pattern correspond to the highly ordered crystalline structures. In this pattern those peaks are thin and correspond to main phase of the sample which is C_{60} fullerene molecule ordered in a face-centered cubic structure which is the phase of higher symmetry. In this pattern a broad peak, in the range between 20 and 26 degrees, can be observed, and this peak is crowned by other well-defined low intensity peaks, corresponding to lower symmetry phases C_{60} ordered in orthorhombic and monoclinic structures. Another phase observed was the hexagonal 2H graphite phase. It can be noticed that the presence of these phases may be caused by the difference in temperature in the container and between the sample and glass substrate. A summary of the observed phases is shown in Table 1.

3.2. Scanning Electron Microscope. In Figure 2(a) the SEM electron micrograph of fullerene film is shown. Since graphite tape may cause confusion with the carbon film, which is commonly used to hold samples, the carbon film was supported on a copper tape.

In Figure 2(b) it was observed that fullerene film consists of a series of stacked monolayers. The film thickness was measured using FEI Nova Nanolab analysis and imaging software. The film thickness varies from 140.8 to 523.3 nm. A qualitative chemical composition was performed (Figure 2(c)) by electron dispersive spectroscopy (EDS). The sample is mainly composed by carbon (93.88% at) and oxygen (6.12% at).

3.3. High-Resolution Transmission Electron Microscopy. In Figure 3, bright field electron transmission micrograph of sample is observed. From this figure, it is easy to observe the crystalline behavior of cubic phase. Two interplanar distances were measured, using the Digital Micrograph program (D.M). The direction indices associated with those d spacings

TABLE 1: Phases of the diffraction pattern of carbon film.

Name	Crystalline structure	Lattice parameter (Å)	Space group	Percentage of phase (%)
C_{60}	Face-centered cubic	$a = 14.16$	$Fm\bar{3}m$	82.7
C_{60}	Orthorhombic	$a = 9.56$ $b = 8.87$ $c = 8.34$	—	4.1
C_{60}	Monoclinic	$a = 10.27$ $b = 7.80$ $c = 9.49$ $\beta = 92.4$	—	2.5
Graphite 2H	Hexagonal	$a = 2.464$ $c = 6.711$	$P6_3/mmc$	4.1
Amorphous carbon	—	—	—	6.6

FIGURE 2: (a) SEM micrographs of the fullerene film. (b) Thickness of fullerene film. (c) EDS-fullerene film.

FIGURE 3: Bright field electron HRTEM fullerene films.

were $[400]$ y $[333]$ and zone axis from plane $(0\bar{1}1)$. The buckyball molecule diameter was also measured using the D.M, It was found that molecule diameter value was 6.83 Å and corresponds to C_{60} molecule diameter.

3.4. Atomic Force Microscopy. On the surface of the carbon thin film, spiral-shaped tetrahedron single crystals were

shown with ~ 535.03 to 345.32 nm and an angle of counter-clockwise rotation of the spiral from 103.7 to -16.8° (Figures 4(a)-4(b)). The surface topography of the sample mounds was observed with an average height from 40.3 to 71.6 nm (Figure 4(c)). In the sample surface, islands deposited crystals found in stages are observed (Figure 5(a)), having a corresponding symmetry $\bar{4}3m$ crystal habit associated with the tetrahedron (Figure 5(b)), comprising deriving four faces of the octahedron in class $4/m\bar{3}2/m$. And observing a height of the mounds of crystals in the range from 18 to 120.8 nm (Figure 5(c)).

4. Conclusions

- (i) In this work, it was possible to obtain a carbon thin film from the pyrolysis of camphor in a conventional microwave oven. The film is polycrystalline and consists of fullerenes arranged in different crystal structures, graphite 2H and amorphous carbon. This indicates that the the sample is formed within the furnace in a gradient of temperatures around 800°C working with maximum power of the oven. The main phase corresponds to fullerene ordered in

FIGURE 4: (a) Height 2D AFM spiral with 10×10 microns. (b) Spiral tetrahedral single crystal. (c) 3D image of the surface topography of the fullerene film.

FIGURE 5: (a) Islands tetrahedron crystal. (b) Crystals with symmetry $\bar{4}3m$. (c) 3D image of AFM topography of the surface of the fullerene film with scanning of 10×10 microns.

a face-centered cubic structure and other phases such as C_{60} orthorhombic, C_{60} monoclinic.

- (ii) The surface of the film consists of several monolayers of carbon molecules stacked carbon, even leading material of varying thickness from 140.8 to 523.3 nm, and the sample shows oxidation with 6.12% at.
- (iii) The space group of the main phase is $Fm\bar{3}m$. In this phase a crystalline tetrahedral habit was observed having $\bar{4}3m$ symmetry. The carbon thin film shows spiral-shaped tetrahedron single crystals of 535.03 to 345.32 nm and an angle of counterclockwise rotation ranging from 103.7° to -16.8° .

Acknowledgments

The authors wish to express their gratitude to Ing. Joaquín Ibarra, Laboratory of X-ray diffraction of the ESFM-IPN, and Florentino Leyte of IMP Molecular Laboratory for their technical assistance in scanning microscopy.

References

- [1] S. Mohammed Mominuzzaman, M. Rusop, T. Soa, T. Jimbo, and M. Umeno, "Rearrangements of hybridized bonds in nitrogen incorporated camphoric carbon thin films deposited by pulsed laser ablation," in *The International Conference on Mechanical Engineering (ICME '03)*, pp. 1–4, 2003.

- [2] C. Chen and Z. Lou, "Formation of C_{60} by reduction of CO_2 ," *Journal of Supercritical Fluids*, vol. 50, no. 1, pp. 42–45, 2009.
- [3] A. D. V. Turina, M. V. Nolan, J. A. Zygodlo, and M. A. Perillo, "Natural terpenes: self-assembly and membrane partitioning," *Biophysical Chemistry*, vol. 122, no. 2, pp. 101–113, 2006.
- [4] D. M. P. Mingos, *Chem. Ind.*, pp. 596–599, 1994.
- [5] A. H. Jayatissa, T. Gupta, and A. D. Pandya, "Heating effect on C_{60} films during microfabrication: structure and electrical properties," *Carbon*, vol. 42, no. 5–6, pp. 1143–1146, 2004.
- [6] T. D. Burchell, *Carbon Materials For Advanced Technologies*, Pergamon, 1999.
- [7] A. G. Dall'Asén, M. Verdier, H. Huck, E. B. Halac, and M. Reinoso, "Nanoindentation on carbon thin films obtained from a C_{60} ion beam," *Applied Surface Science*, vol. 252, no. 22, pp. 8005–8009, 2006.
- [8] R.-F. Xiao, "Growth of large fullerene C_{60} crystals and highly oriented thin films by physical vapor transport," *Journal of Crystal Growth*, vol. 174, no. 1–4, pp. 821–827, 1997.
- [9] P. Milani, M. Ferretti, P. Piseri et al., "Synthesis and characterization of cluster-assembled carbon thin films," *Journal of Applied Physics*, vol. 82, no. 11, pp. 5793–5798, 1997.
- [10] M. Rusop, X. M. Tian, T. Kinugawa, T. Soga, T. Jimbo, and M. Umeno, "Preparation and characterization of boron-incorporated amorphous carbon films from a natural source of camphoric carbon as a precursor material," *Applied Surface Science*, vol. 252, no. 5, pp. 1693–1703, 2005.
- [11] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Elsevier, New York, NY, USA, 1996.
- [12] X. Y. Zhang and S. K. Manohar, "Microwave synthesis of nanocarbons from conducting polymers," *Chemical Communications*, no. 23, pp. 2477–2479, 2006.
- [13] K. Chen, C. Wang, D. Ma, W. Huang, and X. Bao, "Graphitic carbon nanostructures via a facile microwave-induced solid-state process," *Chemical Communications*, no. 24, pp. 2765–2767, 2008.
- [14] S. Yim and T. S. Jones, "Growth dynamics of C_{60} thin films: effect of molecular structure," *Applied Physics Letters*, vol. 94, no. 2, Article ID 021911, 3 pages, 2009.
- [15] B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina, and L. T. Scott, "Aromatic π -systems more curved than C_{60} . The complete family of all indenocorannulenes synthesized by iterative microwave-assisted intramolecular arylations," *Journal of the American Chemical Society*, vol. 131, no. 30, pp. 10537–10545, 2009.
- [16] A. Lew, P. O. Krutzik, M. E. Hart, and A. R. Chamberlin, "Increasing rates of reaction: microwave-assisted organic synthesis for combinatorial chemistry," *Journal of Combinatorial Chemistry*, vol. 4, no. 2, pp. 95–105, 2002.
- [17] S. M. Mominuzzaman, T. Soga, T. Jimbo, and M. Umeno, "Camphoric carbon soot: a new target for deposition of diamond-like carbon films by pulsed laser ablation," *Thin Solid Films*, vol. 376, no. 1–2, pp. 1–4, 2000.
- [18] A. I. Oreshkin, R. Z. Bakhtizin, J. T. Sadowski, and T. Sakurai, "Epitaxial growth of C_{60} thin films on the Bi(0001)/Si(111) surface," *Bulletin of the Russian Academy of Sciences*, vol. 73, no. 7, pp. 883–885, 2009.
- [19] M. Rusop, T. Kinugawa, T. Soga, and T. Jimbo, "Preparation and microstructure properties of tetrahedral amorphous carbon films by pulsed laser deposition using camphoric carbon target," *Diamond and Related Materials*, vol. 13, no. 11–12, pp. 2174–2179, 2004.
- [20] D. Pradhan and M. Sharon, "Electrochemical behavior of amorphous carbon obtained from camphor," *Electrochimica Acta*, vol. 50, no. 14, pp. 2905–2910, 2005.
- [21] P. R. Somani, S. P. Somani, and M. Umeno, "Planar nanographenes from camphor by CVD," *Chemical Physics Letters*, vol. 430, no. 1–3, pp. 56–59, 2006.
- [22] S. M. Mominuzzaman, M. Rusop, T. Soga, T. Jimbo, and M. Umeno, "Nitrogen doping in camphoric carbon films and its application to photovoltaic cell," *Solar Energy Materials and Solar Cells*, vol. 90, no. 18–19, pp. 3238–3243, 2006.
- [23] C. O. Kappe and D. Dallinger, "Controlled microwave heating in modern organic synthesis: highlights from the 2004–2008 literature," *Molecular Diversity*, vol. 13, no. 2, pp. 71–193, 2009.
- [24] *Microwave Processing of Materials: An Emerging Industrial Technology*, National Academy Press, Washington, DC, USA, 1994, Publication NMAB-473.
- [25] M. Rusop, S. M. Mominuzzaman, T. Soga, and T. Jimbo, "Properties of a-C:H films grown in inert gas ambient with camphoric carbon precursor of pulsed laser deposition," *Diamond and Related Materials*, vol. 13, no. 11–12, pp. 2180–2186, 2004.
- [26] D. Pradhan and M. Sharon, "Opto-electrical properties of amorphous carbon thin film deposited from natural precursor camphor," *Applied Surface Science*, vol. 253, no. 17, pp. 7004–7010, 2007.
- [27] S. Adhikari, H. R. Aryal, D. C. Ghimire, G. Kalita, and M. Umeno, "Optical band gap of nitrogenated amorphous carbon thin films synthesized by microwave surface wave plasma CVD," *Diamond and Related Materials*, vol. 17, no. 7–10, pp. 1666–1668, 2008.
- [28] K. Kohli, H. Chaudhary, P. Rathee, S. Rathee, and V. Kumar, "Fullerenes: new contour to carbon chemistry," *Pharma Times*, vol. 41, no. 2, pp. 9–12, 2009.
- [29] T. Koryu Ishii, *Hanbook of Microwave Technology: Applications*, vol. 2, 1995.
- [30] A. T. Johns and D. F. Warne, *Engineers' Hanbook of Industrial Microwave Heating*, vol. 25 of IEE Power Series, 1998.
- [31] D. Bogdal, *Microwave-Assisted Organic Synthesis: One Hundred Reaction Procedures*, Elsevier, New York, NY, USA, 2005.
- [32] A. Stadler, B. H. Yousefi, D. Dallinger et al., "Scalability of microwave-assisted organic synthesis. From single-mode to multimode parallel batch reactors," *Organic Process Research and Development*, vol. 7, no. 5, pp. 707–716, 2003.
- [33] R. Martínez-Palou, "Microwave-assisted synthesis using ionic liquids," *Molecular Diversity*, vol. 14, pp. 3–25, 2010.