Structure of multi-wall carbon nanotubes: AA stacked graphene helices
Jae-Kap Lee, Sohyung Lee, Yong-II Kim, Jin-Gyu Kim, Kyung-II Lee, Jae-Pyoung Ahn, Bong-Ki Min, Chung-Jong Yu, Keun Hwa Chae, and Phillip John

Citation: Applied Physics Letters 102, 161911 (2013); doi: 10.1063/1.4802881
View online: http://dx.doi.org/10.1063/1.4802881
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/102/16?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Controlled assembly of graphene sheets and nanotubes: Fabrication of suspended multi-element all-carbon vibrational structures

Correlation between site preference and magnetic characteristics of self assembled strontium ferrite dot array on functionalized multi-walled carbon nanotubes

First-principles study of hydrogenated carbon nanotubes: A promising route for bilayer graphene nanoribbons

Hydrogenation effects on the structure and morphology of graphene and single-walled carbon nanotubes

Electrochemical lithium insertion of heat treated and chemically modified multi-wall carbon nanotubes
AIP Conf. Proc. 590, 249 (2001); 10.1063/1.1420101
Structure of multi-wall carbon nanotubes: AA’ stacked graphene helices

Jae-Kap Lee,1,a) Sohyung Lee,1,2 Yong-II Kim,3 Jin-Gyu Kim,4 Kyung-II Lee,5 Jae-Pyong Ahn,6 Bong-Ki Min,7 Chung-Jong Yu,8 Keun Hwa Chae,6 and Phillip John9

1Surface Control Research Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea
2Department of Semiconductor Science, Dongguk University, Seoul 100-715, South Korea
3Division of Metrology for Quality of Life, Korea Research Institute of Standards and Science, Daejeon 305-600, South Korea
4Division of Electron Microscopic Research, Korea Basic Science Institute, Daejeon 305-340, South Korea
5Nano-Bio Division, Nuri Vista Co. Ltd., Incheon 406-840, South Korea
6Analysis Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea
7Instrumental Analysis Center, Yeungnam University, Daegu 712-749, South Korea
8Division of Science and Technology, Pohang University, Pohang 790-784, South Korea
9School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

(Received 25 January 2013; accepted 21 March 2013; published online 24 April 2013)

The structure of multi-wall carbon nanotubes has been attributed previously to disordered stacking of the graphene planes. Evidence is presented that the nanotubes analyzed in this paper occur with stacked graphene layers in the sequence of AA’, where alternate graphene planes are translated by half the hexagon width. We further present proof that the crystalline materials comprise graphene helices (~5 nm in width), rather than in the form of a perfect tube. We also show that the structural model proposed here may be a common structure for multi-wall carbon nanotubes. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4802881]

With their unique features and resulting diverse properties, multi-wall carbon nanotubes (MWNTs) are of worldwide interest, and numerous studies have been performed since the first report of their synthesis in 1991.1 Nevertheless, to date, the specific structure of MWNTs is still uncertain, and no single model is capable of addressing the various kinds of morphologies reported. There are two main types of structural models, concentrically nested tubes and a scroll of graphene sheets (or the coexistence of the two forms).2–6 Although the premise of the two models is the disordered stacking of graphene sheets, a few groups7–9 have suggested the existence of an intermediate state between crystalline AB graphite and the turbostratic stacking based on signals assigned to the hexagonal (100) and (110) planes together with the (002) plane in X-ray,7,10–15 electron,1,3,8,15–26 and neutron9,27 diffraction analysis. This feasible suggestion has not gained ground because a relevant structure could not be analytically proven whilst others attributed the appearance of the signals to regular chirality of the disordered graphene sheets or the structural diversity of graphitic materials.

Previously, we have shown that the AA’ stacking of graphene layers, in which alternate graphene planes are translated by a half width of the hexagon, appears together with AA stacked graphite on diamond (111) surfaces due to the symmetry of the unreconstructed diamond (111) plane.28 The theoretical spacing of the AA’ stacking was approximately 3.43 Å,28 which is very close to that normally measured from MWN Ts, i.e., about 3.44 Å.12,10–11 The total energy per atom for the AA’ stacking, ~40.44 eV/atom, lies between that of AB (lowest) and AA (highest) stacking, although the difference is small at ~10 meV per atom.28 This calculation suggests that AA’ graphite may be observed under conditions where the rate of formation is kinetically controlled. Nevertheless, the structure and the characteristic AA’ stacking have not been previously observed.

In this paper, we analyze the crystallographic structure of the AA’ stacking of graphene layers and show that the conventional MWNT samples characterized here29 are composed of AA’ stacked graphene helices. We also discuss that our structural model can explain the experimental data of MWNTs in the literature.

Figure 1 shows the crystal structure of AA’ graphite, assigned to an orthorhombic Fmmm (#69) space group, unlike AB29 or AA graphite which are assigned to a hexagonal group.30 The simulated X-ray diffraction (XRD) pattern of AA’ graphite is very similar to that of AB graphite (Fig. 2(a)), in which the allowed reflections, 002, 020, 111, 022, 004, 113, 024, 200, 131, 202, 133, 040, and 222 peaks are predicted. The key differences lie in the appearance of 131 and 133 peaks.

XRD patterns of vapor phase catalytic chemical vapor deposition (VCCVD)- and arc-MWNTs show the unique feature7,10–15 that two strong peaks at 2θ ≈ 42° (d-value = 2.13 Å) and 2θ ≈ 77° (d-value = 1.23 Å) appear, together with the dominant 002 (2θ ≈ 25.9°, d-value = 3.44 Å) and 004 peaks, as shown in Fig. 2(b). The 020 and 200 peaks of arc-MWNTs are very sharp, corresponding to those of crystalline graphite.10 Indeed, the XRD patterns well fit with the predicted pattern31 for (001) oriented AA’ graphite (the tubular material can be regarded as a thin graphite film (Fig. 3)) where 002 and 020 peaks become relatively stronger. The interplanar spacing, 3.44 Å, measured from each 002 peak of arc- and VCCVD-MWNTs, is close to the theoretical value of the AA’ stacking, 3.43 Å.28 The results indicate that the materials are crystalline comprising (100) oriented AA’ graphene layers.

The electron diffraction (ED) pattern measured from an arc-tubule, which was not tilted (i.e., the inclination...
angle,\textsuperscript{15,16} $\beta = 0$) on the horizontal line of the TEM grid, is identical to the expected pattern for the AA\textsuperscript{0} crystal in a zigzag structure, as shown in Fig. 4(b). The pattern is interpreted in terms of the orthorhombic AA\textsuperscript{0} unit cell although much weaker h100 and h110 spots, which are related with the hexagonal AB structure and 113 spots, appear. A clearer ED pattern obtained from different sample (Fig. 4(c)) shows evidence that the tubule was tilted by 3°. The spots of (020) and (200) planes, which are not parallel to the tubule axis, are split into two and appear as a pair of spots. From a tubule tilted by 10°, another pair of 020 and 200 spots appear on Ewald’s spheres (Fig. 4(d)). Also, the spots of the unique 131 plane of the AA\textsuperscript{0} crystal, which is oriented by 11° to the beam direction (Fig. 3(c)), (001), are evident. The data provide evidence that the arc-MWNTs adopt an AA\textsuperscript{0} zigzag configuration.

Many ED patterns that are similar to those shown in Figs. 4(b)–4(d) have been reported for MWNTs,\textsuperscript{1,3,15–26} including double-wall CNTs,\textsuperscript{17,18} mainly prepared by the arc discharge or the ACCVD (i.e., aligned catalytic CVD growth on a substrate) technique. Previous researchers have interpreted the ED patterns as the disordered stacking of graphene layers with uniform chirality. However, such ED patterns, where 020 and 200 spots coexist with 002 and 004 spots, cannot appear in the turbostratic stacking with any regularity.\textsuperscript{29} Particularly, the split ED signals, originating from the inclination tilts of the samples on the TEM grid which cannot be controlled,\textsuperscript{15} were interpreted as evidence of chirality.\textsuperscript{1,3,15–26} The ED pattern for the armchair structure has neither been reported in the literature nor observed in this study. The relatively larger angle to the tubule axis, leading to a steeper curvature of the graphene ribbons, makes the armchair structure energetically unfavorable; the calculated strain energy of graphene ribbons in the zigzag configuration is about one-third that of those of the
The armchair configuration. The results of ED analysis indicate that the AA' stacked zigzag configuration is a common structure of MWNTs.

The critical question is how the AA' stacking can be retained in the tubular material where the structure is commonly known as concentric graphene layers with different diameters. The helical growth of narrow but long graphene sheets provide a solution to the problem. The unique AA' stacking of armchair graphene ribbons can cause the helical growth when the (200) plane, which is the closest-packed plane, appears at an angle to tubule axis. Here, (200) becomes the preferential growth direction which drives the helical growth of the armchair graphene ribbons, resulting in the zigzag tubule where the angle of (200) with respect to the tubule axis is 30° (Fig. 3(b)).

Graphene helices, which appear as a stack, are detectable with high-resolution transmission electron microscopy (HRTEM) tilt experiments, as shown in Fig. 5. The VCCVD-tubule reveals the stacked graphene helices (the yellow arrows in Fig. 5(a)) in the curved part (such morphology prevails in the literature). With 40° tilt of the sample stage, the straight part of the VCCVD-tubule reveals the stacked graphene helices (the red arrows in Fig. 5(a')), and the angle of the helices to the tubule axis (the yellow arrows in Fig. 5(a')) becomes steep and is measured to be about 30°. The analysis indicates that the stacked graphene helices of the tubule lie at an angle of 30° to the tubule axis.

The profile of the graphene helices is evident in the AFM image obtained from a VCCVD-tubule (Figs. 6(a) and 6(b)) where the tubule with the diameter of 20 nm (Ref. 29) appears to be broadened (≈110 nm in width) due to the AFM tip effects. The angles of the helices to the tubule axis ranging 64°–72° in the distorted image span 21°–29° in the corrected image. The line scan data indicate that the heights between the graphene helices (plateaus in the line scan) are one or two atomic thicknesses (0.4–0.8 nm). The atomic height steps in AFM data are due to the incoherent scroll of the blocked graphene helices (Fig. 6(b)), resulting in the typical herring-bone morphology of VCCVD-MWNTs. The HRTEM and AFM analyses (Figs. 5 and 6) demonstrate that the tubular materials are composed of stacked graphene helices (with a thickness of 5 nm, corresponding to the thickness of the wall of the VCCVD tubule) subtending an angle

FIG. 4. ED pattern analysis of arc-MWNTs. (a) A HRTEM image of an arc-MWNT. (b)-(d) ED patterns measured from individual MWNT. The inset is a schematic diagram explaining the inclination angle (β) of the sample on the TEM stage.

FIG. 5. HRTEM images of a VCCVD-MWNT (a, a') and an arc-MWNT (b, b') with tilts. (c) A cross-section of an arc-MWNT revealing polygonized morphology. The yellow and red arrows indicate the stacked graphene helices.
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:137.195.59.30 On: Wed, 21 May 2014 15:05:20

...the unexpected 113 spots the relatively poor spatial resolution of AFM.

The current model also explains the cross-sectional image of an arc-MWNT (Fig. 5(c)). The polygonized (graphite-like) morphology is evident in can be seen as the bamboo or capped structures, respectively. The imaging mechanism of TEM, the tubules with locally are evidence of our graphene helices model. Due to the absence of 111, 022, 113, 024, and 202 signals in the typical XRD patterns for MWNTs the material crystallizes with heat-treatment at ~3000 °C, resulting in the dramatic change of the morphology from nanoparticles to polygonal graphic helices. Indeed, the XRD pattern of the polygonal graphic heliches is identical to those of MWNTs with the spacing of 3.44 Å (Fig. 4(c) of Ref. 46) are representative of imperfect turbostratic graphite. The material crystallizes with heat-treatment at ~3000 °C, resulting in the dramatic change of the morphology from nanoparticles to polygonal graphic helices. Indeed, the XRD pattern of the polygonal graphic heliches is identical to those of MWNTs with the spacing of 3.44 Å (Fig. 4(c) of Ref. 46) are representative of imperfect turbostratic graphite. The material crystallizes with heat-treatment at ~3000 °C, resulting in the dramatic change of the morphology from nanoparticles to polygonal graphic helices. Indeed, the XRD pattern of the polygonal graphic heliches is identical to those of MWNTs with the spacing of 3.44 Å (Fig. 4(c) of Ref. 46) are representative of imperfect turbostratic graphite. The material crystallizes with heat-treatment at ~3000 °C, resulting in the dramatic change of the morphology from nanoparticles to polygonal graphic helices. Indeed, the XRD pattern of the polygonal graphic heliches is identical to those of MWNTs with the spacing of 3.44 Å (Fig. 4(c) of Ref. 46) are representative of imperfect turbostratic graphite.
mechanical milling. The conventional interpretation of the structure as turbostratic since 1942 (Ref. 46) is challenged in the present paper.

We thank Wonyong Kim and Kil-joon Min for AFM work; Man-Ho Kim, Kwang-Ryeol Lee, Young-Man Kim, Seung-Cheol Lee, and Young-Su Lee for useful comments on the crystal of AA' graphite. This work was supported by KIST Future Resource Program (2V01900, 2V02120, and 2E24011).

29See supplementary material at http://dx.doi.org/10.1063/1.4802881 for methods and TEM images of commercial MWNTs prepared by the vapor phase catalytic chemical vapour deposition technique and an arc-discharge technique (Fig. S1); the crystal structure of AB graphite (Fig. S2); expected ED patterns of a turbostratic MWNT if it exists (Fig. S3); an expected ED pattern of an armchair MWNT if it exists (Fig. S4); and AFM analysis of a CVD-MWNT (Fig. S5).