

Formation of a Quenchable Dense Carbon Form by Compression of Double-Walled Carbon Nanotubes

Zhongwu Wang*

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Double-walled carbon nanotubes were pressurized to ~ 90 GPa by using a diamond anvil cell (DAC) at room temperature. High-resolution TEM and Raman spectroscopy on the recovered sample revealed that the carbon nanotubes collapse and result in the formation of a highly compressed carbon form. This carbon form has a *c*-layer interdistance of 0.21 nm, which is remarkably shorter than that of graphite (0.34 nm). The calculated density is 3.65 g/cm^3 , slightly greater than that of diamond (3.52 g/cm^3). It is suggested that this dense carbon form is a potential superhard material and is likely the significant precursor of the phase transformation of graphite to diamond.

Understanding the mechanism for the phase transformation of graphite or graphite-like material has been of considerable scientific interest due to great technological importance for optimizing the synthesis of diamond.¹ To make diamond, pressures above 10 GPa as well as high temperatures are generally needed. However, recent studies indicate that irradiating graphite by intense ionic beams results in the formation of carbon onion structures and the appearance of diamond in the core of the onion shell.^{2,3} In addition, the inter-shell spacing from the *c*-layer interdistance of graphite (0.34 nm) at the surface of the onions decreases to values around 0.22 nm in the center.^{2,3} It is thus suggested that the dense carbon with the *c*-layer spacing of 0.22 nm could be a stable and significant carbon form before the occurrence of the graphite-to-diamond phase transformation. So far, extensive studies have been performed to investigate the pressure-induced phase transformation of graphite.^{1,4–7} Within our knowledge, such a pressure-quenchable dense carbon has not been synthesized in high-pressure investigations. Although the hexagonal diamond has a shorter *c*-layer spacing relative to that of graphite, unfortunately, it is not preserved upon release of pressure to ambient conditions.^{4–7} As a result, it is essential to explore the possibility for the high-pressure synthesis of such a dense carbon that is stable at room conditions. On the basis of the *c*-axis linear compressibility of graphite, achievement of pressure as high as ~ 75 GPa could result in a decrease of the *c*-layer interdistance from 0.34 to 0.22 nm. In this study, we compressed the double-walled carbon nanotube (DWNT) bundles to 90 GPa and obtained a pressure-quenchable dense carbon form, which has the *c*-layer interdistance of 0.21 nm at room conditions. Raman spectroscopy excludes the possibility of the hexagonal diamond as well.

Double-walled carbon nanotubes (DWNT) used in this study were synthesized by a chemical vapor deposition (CVD) method. TEM image characterizes that the DWNT tubes have an average inner diameter of ~ 3.0 nm (inset of Figure 1). High-pressure compression was made at room temperature by using a gasket sealed high-pressure diamond anvil cell (DAC).⁸ The DWNT bundles without pressure medium were placed in a T301 steeliness gasket hole that is $50 \mu\text{m}$ in initial thickness and 70

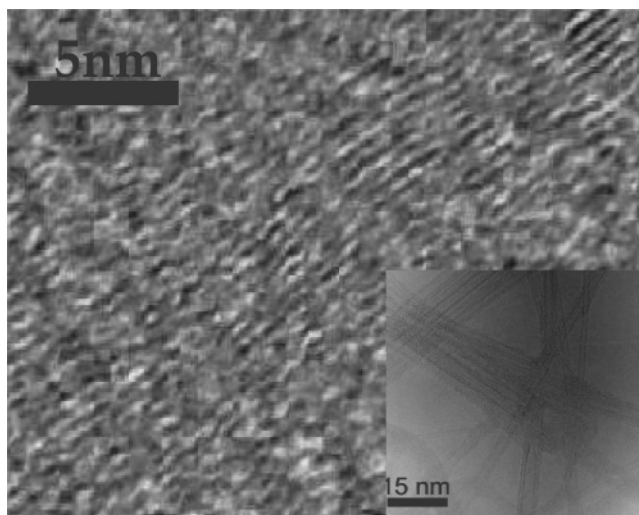


Figure 1. HRTEM image of the recovered sample from high pressure, which indicates the compact morphology of the recovered samples. The inset shows the HRTEM image of the starting double-walled carbon nanotube bundles.

μm in diameter. Such a loading method also allowed us to generate the large pressure gradient for better investigation of the strength of the DWNT samples. Three pieces of micron-sized ruby were loaded as well to act as a pressure marker. After achieving a pressure of ~ 90 GPa, the pressure was slowly released back to room conditions. The recovered sample was checked by Raman spectroscopy for structural characterization.⁸ In the Raman spectroscopic measurements, a Raman spectrometer in the backscattering configuration was used, and the Ti^{3+} : sapphire laser pumped by an argon ion laser was tuned at a near-infrared wavelength of 785 nm. Raman spectra were collected by using high-throughput holographic imaging spectrograph with volume transmission grating, a holographic notch filter, and a thermoelectrically cooled CCD detector with the resolution of 4 cm^{-1} . The sample was carefully removed from the gasket hole for further TEM observation.

Figure 1 shows the compact morphology of the recovered sample with comparison to that of the starting DWNT bundles. The DWNT bundles collapse after the pressure-induced orienta-

* To whom correspondence should be addressed. E-mail: z_wang@lanl.gov.

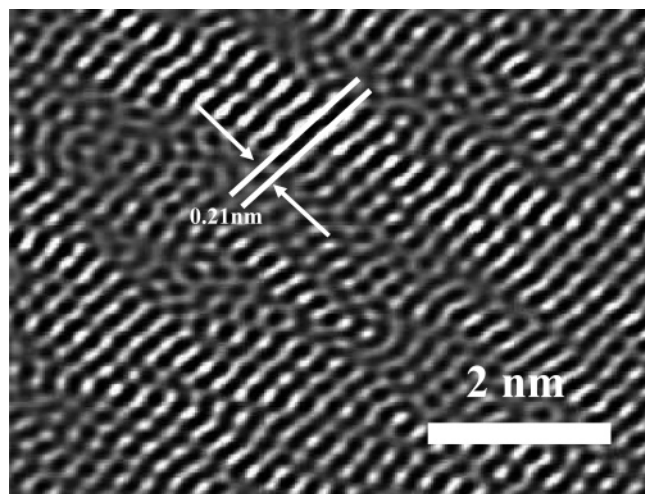


Figure 2. Filtered HRTEM image of the compressed carbon polymorph with highly imperfect fringes with the *c*-layer interdistance of 0.21 nm.

tion along the tube direction and thus compact together into a homogeneous phase. This is indicated by the multilayer structural characteristic, which is significantly different from the two-layer structure of the DWNT bundles (inset of Figure 1). The initial inner tube diameter (~ 3.0 nm) was apparently reduced to be the same as the interlayer spacing distance of the compressed carbon phase. The filter HRTEM image (Figure 2) indicates that the interlayer spacing distance is of ~ 0.21 nm. Moreover, this compressed carbon form displays highly imperfect fringes, implying the existence of a significant ratio of defects. It is well-known that graphite exhibits a large anisotropy of compressibility, in which the *c*-axis displays a linear bulk modulus of 36 GPa, and that the *a*-axis is much stiffer with an extremely high modulus of 1250 GPa.^{4,5} Thus, reduction of the cell volume of graphite typically results from the decrease of the *c*-layer interdistance. While the *c*-layer spacing is reduced to 0.21 nm as that observed from this dense carbon form, the density was calculated to be 3.65 g/cm^3 , which is slightly greater than that of diamond with the value of 3.52 g/cm^3 . Since this dense carbon form includes a significant ratio of defects, the density is relatively reduced, likely being compatible to that of diamond. Thus, it is highly possible that this dense carbon form is a potential super-hard material.

To date, extensive studies have been performed to investigate the pressure-induced phase transformation of graphite and graphitelike materials.^{1,4–7} Results indicate that graphite transforms to diamond at in situ high-temperature high-pressure conditions.¹ Under cold compression, a denser hexagonal diamond (or carbon) has been observed; however, such a phase is not quenchable upon release of pressure to room conditions.^{4–7} Moreover, hexagonal diamond displays a single Raman mode at $\sim 1310 \text{ cm}^{-1}$, which is significantly different from that of diamond (1333 cm^{-1}) and crystal graphite (1356 cm^{-1}) (Figure 3). However, the Raman spectrum of this compressed carbon exhibits two broad peaks centered at 1581 and 1355 cm^{-1} , which is actually similar to that of the laser-deposited glassy carbon⁴ rather than that of hexagonal diamond or the starting DWNT bundles.⁹ Previous studies indicate that the enhanced intensities of the D mode in the glassy and nanocrystalline carbon result from the existence of a significant ratio of sp^3 bonds relative to that of graphite.⁴ Since the dense carbon phase has similar size to nanocrystalline carbon and also the partial amorphization may exist at intergrain boundaries, therefore, it is reasonably suggested that such a compressed carbon form should also include a significant ratio of sp^3 bonds. However, the mechanism

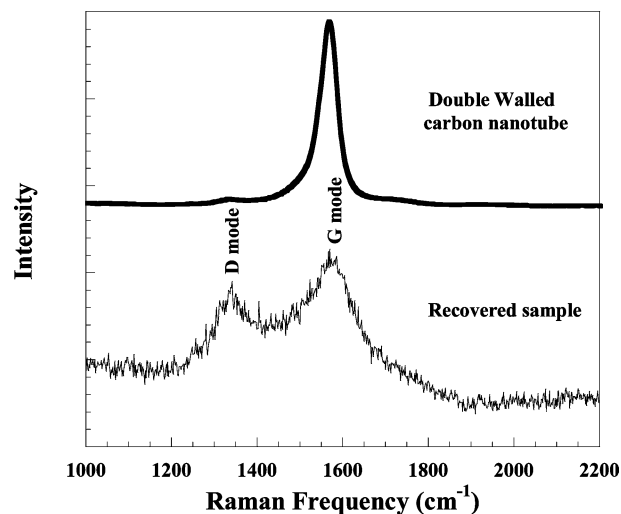


Figure 3. Raman spectra of the starting double-walled carbon nanotubes and the recovered samples from high pressure.

resulting in the formation of such a quenchable dense carbon still remains unclear. An alternative consideration may be the existence of a critical pressure. It is likely that, while the critical pressure is achieved, this dense carbon form may become stable and thus is enabled to be preserved upon decompression to ambient conditions. Correlating this dense carbon form to the formation of diamond from graphite, it is probable that this dense carbon form is the intermediate phase in the graphite-to-diamond phase transformation. Thermodynamically, the low-pressure polymorph generally is less dense than the high-pressure polymorph. The higher density of this carbon form than diamond implies the existence of a large energy barrier that inhibits the occurrence of the phase transformation from this carbon phase to diamond, so a slight heating could be required to stimulate the formation of diamond. Such a consideration is supported by previous high-pressure investigations and recent TEM studies on the irradiation-induced self-compression of carbon onions.^{1–3} In previous high-pressure experiments, the syntheses of diamond were successful only while an in situ heating was provided.¹ In recent TEM studies on carbon anion, it appears that the inner core with the *c*-layer interdistance of <0.22 nm transforms to diamond at heating above 600°C .^{2,3} This could be considered as the direct evidence, supporting the hypothesis that this dense carbon form with *c*-layer interdistance of 0.21 nm is the preliminary scenario for the formation of diamond from graphite. It is pointed out that this finding is also discovered by cold compression of the multiwalled carbon nanotubes to ~ 100 GPa.¹⁰ In addition, the high-resolution synchrotron X-ray diffraction study further confirmed that the dense carbon phase holds a hexagonal structure.¹⁰

In summary, we compressed double-walled carbon nanotubes (DWNT) to ~ 90 GPa and synthesized a quenchable and extremely dense carbon form that has the *c*-layer interdistance of 0.21 nm. This dense carbon form is well-preserved at 1 atm. The density was calculated to be 3.65 g/cm^3 , slightly greater than that of the cubic diamond. Such a highly compressed dense carbon form is likely a significant precursor for the phase transformation of graphite to diamond.

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