Structure and property changes of single-walled carbon nanotubes under pressure

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Abstract

Single-walled carbon nanotubes form raft-like bundles when they are produced by laser evaporation of graphite targets. When hydrostatic pressure is applied to the pristine carbon nanotubes, we found that the nanotubes can be compressed easily with a high volume compressibility of 0.024 GPa -1. Though polygonization must have occurred under the present circumstances, there was no significant change such as a phase transformation from semiconducting to metallic was observed with electrical resistivity measurements within the pressure range (up to 2 GPa) we employed.

Keywords: X-ray diffraction, graphite and related compounds, fullerenes and derivatives

1. Introduction

Carbon nanotubes have been extensively studied after they were first discovered about ten years ago [1] due to their extraordinary properties and their promising potential for nanotechnology applications. Because of the finite lateral dimension and its perfection in atomic structure, carbon nanotubes are expected to exhibit physical behaviors that can be fundamentally different from that of graphite. Electronically, for example, a carbon nanotube can be either a semiconductor or a metal, depending on its diameter and helicity, and the electronic band structure is sensitive to the cross-sectional geometry of the nanotube.

We have applied hydrostatic pressure to the single-walled carbon nanotubes produced by laser evaporation and here we report the results on the structural and transport property changes derived from in situ synchrotron X-ray diffraction analysis and four-probe measurements of the electrical resistivity conducted at various pressures.

2. Experimental

Carbon nanotubes were produced by laser evaporation of a graphite target at 1200 °C using Ni/Co as catalyst [2-3]. The thus produced carbon nanotubes often form raft-like bundles in which the nanotubes are stacked together forming a hexagonal closed-packing structure with a trigonal lattice [3]. The trigonal lattice diffracts X-rays with detectable Bragg reflection intensities and therefore allows us to monitor the structural changes under various pressures.

High pressure was generated with a diamond anvil cell (DAC) with a liquid medium in order to obtain hydrostatic pressure. In situ synchrotron X-ray diffraction intensity data were collected using an imaging plate to assure high resolution. The electrical resistivity measurement was carried out using the four-probe method under various pressures generated by a piston apparatus and the resistivity measurement was performed at temperatures from 2 K up to room temperature (300 K).

3. Results and Discussion

Single-walled carbon nanotubes were found to follow a linear change of volume under pressure up to 2 GPa. Figure 1 shows the dependence of the lattice constant of the nanotube lattice on the applied hydrostatic pressure up to 2 GPa, beyond which the characteristic nanotube lattice reflection becomes too weak to be identifiable. As can be
seen from the figure, the deformation of the nanotube lattice exhibited a linear behavior. Neglecting the very small change in the C-C bonding length, from Figure 1, the volume compressibility, defined by \( \kappa = -\frac{\partial \ln V}{\partial P} \) where \( V \) and \( P \) are the sample volume and the applied pressure, respectively, was obtained to be 0.024 GPa\(^{-1}\).

The circular cross-section of carbon nanotubes is polygonized when nanotubes are subject to pressure. The polygonization of the constituting nanotubes can be specified by the ratio \( \eta = r_S/r_L \), where \( r_S \) and \( r_L \) are the short and the long radial dimensions of the polygonized cross-section, respectively. The inter-tubular separation between neighboring nanotubes in the raft-like bundle is obtained from energetics calculations [4]. It was found that when the nanotubes are brought together, slight polygonization takes place even at zero pressure (\( \eta = 0.991 \)) due to the van der Waals forces between neighboring nanotubes. At 1.5 GPa pressure, the polygonization factor was found to be \( \eta = 0.982 \).

![Graph](image)

Fig. 1. Linear dependence of the trigonal nanotube lattice constant on the applied hydrostatic pressure. The volume compressibility of 0.024 GPa\(^{-1}\) was obtained for nanotubes of 14 Å diameter.

It has been shown theoretically that semiconducting nanotubes will become metallic when their cross-sections are polygonized from circular to polygonal [5]. In particular, it was suggested that when a semiconducting nanotube is polygonized, its electronic band gap will be reduced due to the facetting that induces \( \sigma^* - \pi^* \) hybridization and lowers the symmetry of the otherwise cylindrical tubules.

Figure 2 shows the experimental data of the measured electrical resistance of the single-walled carbon nanotube material as a function of temperature at various pressures up to 2 GPa. When the pressure increases, the electrical resistance decreases monotonically, and no change in the sign of \( dR/dP \) was observed in contrast to the results of Gaal et al [6]. Under all the pressures employed in the present experiment, the samples showed \( dR/dT < 0 \) and a semiconducting behavior. The logarithmic relationship between the electrical resistance and \( T^{-1/4} \) at low temperature, shown in Fig. 2, implies that the Mott variable range hopping conduction plays a very important role in the nanotube material. It suggests that the transport was limited by the tube-tube contact region.

![Graph](image)

Fig. 2. Electrical resistivity vs. temperature of single-walled carbon nanotubes under various hydrostatic pressures. Semiconducting behavior was apparent as shown in the curves. Plots show \( \ln R \) as a function of \( T^{-1/4} \) to reveal the hopping-like conduction.

4. Conclusions

The volume compressibility of single-walled carbon nanotubes of 14 Å diameter has been measured to be 0.024 GPa\(^{-1}\). Combining with the results from numerical computations, it was found that the nanotubes must have been polygonized under the hydrostatic pressure employed in the present experiment. However, no drastic change in transport properties was observed, implying that the polygonization is not yet sufficiently large to induce significant changes like the metallization of the nanotubes as predicted theoretically due to the morphological modifications.

References