Structural and Electronic Property Changes of Single-Walled Carbon Nanotubes under Pressure

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Abstract. The mechanical and electronic properties of single-walled carbon nanotubes have been studied under hydrostatic pressure up to 2 GPa. A high volume compressibility of 0.024 GPa\(^{-1}\) was obtained. The carbon nanotubes are polygonized slightly when they form bundles of hexagonal close-packed structure and the inter-tubular gap is smaller by 0.25 Å than the equilibrium spacing of graphite (002). Under high pressure, further polygonization occurs to accommodate the extra amount of volume reduction. Accompanying the polygonization, the band gap of the nanotubes increases with increasing pressure. A discontinuous change in electrical resistivity was observed at 1.5 GPa pressure, suggesting a phase transition had occurred when the polygonized nanotubes became elliptical in cross-section.

INTRODUCTION

Carbon nanotubes have been extensively studied since they were first discovered about ten years ago [1] due to their extraordinary properties and their promising potential for nanotechnology applications. While the multiwalled carbon nanotubes show greatest values of axial Young's modulus of about 2 TPa [2], approaching to the theoretical value of graphene, carbon nanotubes appear very soft in the radial directions. The van der Waals forces between neighboring carbon nanotubes can induce flattening of the otherwise circular tubules and the softness of carbon nanotubes in the radial directions has been observed experimentally [3-4]. On the other hand, single-walled carbon nanotubes are even softer than multiwalled nanotubes [5]. Molecular dynamics simulations have demonstrated that large radial compressions could be induced by a small force impact without C-C bond breakage [6]. However, there is still no quantitative measurement of the radial elasticity of carbon nanotubes reported in literature.

Hydrostatic high pressure provides an ideal condition to studying the radial elasticity of carbon nanotubes. Since the C-C bond is very strong, the axial deformation under moderate pressure is still negligible while substantial radial deformation is already induced, as indicated by the very small Poisson ratio of graphite (=0.012) [7].

The electronic structure of carbon nanotubes is very sensitive to the morphological change when their cross-sections are polygonized from the circular shape [8]. In
particular, it has been suggested that the electronic band gap of a semiconducting carbon nanotube would be changed due to the faceting that should induce a $\sigma^*\pi^*$ hybridization and lowers the symmetry of the otherwise cylindrical tubules when the polygonization took place.

We applied hydrostatic pressure to single-walled carbon nanotubes and employed X-ray diffraction to monitor the structural changes. Four-probe measurements of the electrical resistance were conducted at various temperatures under pressure to correlate the transport properties with the structural deformation. Energetics calculations have also been carried out to establish the equilibrium inter-tubular gap and to simulate the morphological evolution under increased pressure in connection with the experimentally measured compressibility.

**EXPERIMENTAL**

Single-walled carbon nanotubes were produced by single-beam laser evaporation of graphite powders catalyzed by Ni/Co fine particles. The pristine carbon nanotubes often aggregated to form raft-like bundles [9]. Loosely tangled nanotube bundles were put into a gasketed diamond anvil cell and hydrostatic pressure was applied to the nanotubes via a pressure medium made of ethanol-methanol. The applied pressure was measured using the R-line emission from the ruby crystals embedded in the pressure medium. Synchrotron X-ray diffraction data were collected utilizing imaging plates with an intensity sensitivity of 10,000 scales at the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan using a selected wavelength of 0.8000 Å to ensure that the Bragg lattice reflections from the nanotube bundles were well preserved. Electrical resistance measurements were carried out using the four-probe method under various pressures generated by a piston apparatus. The resistivity measurements were performed at temperatures from 2 K up to the room temperature.

**RESULTS AND DISCUSSION**

Figure 1 shows the dependence of the lattice constant of the nanotube crystals under pressure up to 2 GPa, beyond which the characteristic Bragg reflection from the nanotube lattice becomes too weak to be identifiable. The deformation of the nanotube lattice followed a linear behavior and the volume compressibility, defined by $K = -(1/V) dV/dP$, where $V$ and $P$ are the sample volume and the applied pressure, respectively, was obtained to be 0.024 GPa$^{-1}$.

The inter-tubular separation between the neighboring nanotubes in the raft-like bundles is obtained from energetics calculations [10]. It was also found that the equilibrium value of the inter-tubular gap is smaller than the graphite (002) spacing by 0.25 Å, though they reduce at almost the same rate under increasing pressure [10]. These results explain successfully the pressure dependence of the lattice constant as shown in Fig. 1.
Figure 1 Linear dependence of the nanotube lattice constant on applied hydrostatic pressure. The volume compressibility of 0.024 GPa$^{-1}$ was obtained for nanotubes of 14 Å diameter. The solid line is the calculated lattice constant as a function of pressure.

(a) Figure 2 (a) Electrical resistance vs. temperature (plotted in $T^{1/4}$) of single-walled carbon nanotube material under various pressures. A semiconducting behavior was observed as shown in the curves. (b) Pressure dependence of the band gap obtained from the electrical resistance measured at various temperatures above 200 K. Inserted shapes illustrate the morphological evolution of the cross-section of nanotubes with increasing pressure.

Figure 2(a) shows a set of experimental data on the electrical resistance of the single-walled carbon nanotube material, measured under various pressures up to 2 GPa, plotted as a function of $T^{1/4}$. The relationship between the electrical resistivity and temperature of the nanotube material indicates that, under all the pressures employed in the present experiment, the nanotube material showed a semiconducting behavior [11]. The band gap deduced from the experimental data is given in Fig. 2(b). When the pressure is below 1.5 GPa, the band gap exhibited a monotonic increase with increasing pressure. This phenomenon is attributed to the fact that, as the pressure increased, the band gap of the semiconducting nanotubes increases as a result of polygonization. However, at 1.5 GPa pressure, the band gap showed a sudden drop in value and this phenomenon suggests that a structural phase transition should have occurred, in which the polygonized nanotubes become elliptical in cross-section. This feature is consistent with a similar model proposed basing on Raman spectroscopic
data [12]. The morphological evolution of the nanotubes with increasing pressure is schematically illustrated with the inserted geometric shapes, from circular to hexagonal to elliptical, in Fig. 2(b). On the other hand, it should be noted that the ellipticity is still very small at this pressure range to be sufficient to accommodate the resulted volume reduction and that, as has been discussed theoretically [13], the band gap of the semiconducting nanotubes would increase only slightly as the ellipticity increased further.

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 obtained from numerical computations, it was found that the nanotubes must have been polygonized under the hydrostatic pressure employed in the present experiment. Measurement of the transport properties showed that the nanotubes exhibited a semiconducting behavior with a narrow band gap. The polygonization due to the applied external pressure enlarged the band gap and a phase transition from trigonal to a new structure of lower symmetry, where the polygonal cross-section becomes elliptical, is proposed to account for the abrupt drop of band gap observed experimentally at 1.5 GPa pressure.

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