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THE RAMAN SCATTERING OF CARBON NANOTUBES PRODUCED IN DIFFERENT INERT GASES AND THEIR PRESSURES BY ARC DISCHARGE*

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First- and second-order Raman spectra of carbon nanotubes produced in helium and argon atmospheres at a pressure ranging from 11 to 92 kPa by arc discharge have been measured and compared with each other. The position and bandwidth of the spectral lines depend on the kind of inert gases and their pressure. The Raman spectra of the nanotubes produced in argon gas atmosphere are much more similar to that of polycrystalline graphite than those of the nanotubes produced in helium gas atmosphere. The position and bandwidth of nanotube Raman peaks change with gas pressure in arc discharge because different diameter distribution of nanotubes is produced at different inert gas pressure. The Raman spectra of nanotubes produced at high pressure is much more like that of graphite than those produced in lower pressure

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I. INTRODUCTION

Raman scattering is a useful tool to characterize carbon materials, such as graphite and diamond, since it offers the amount of ordering and degree of sp^2 and sp^3 bonding of carbon materials. The Raman spectra of carbon nanotubes have been studied[1−5], and the results show that carbon nanotubes have the physical dimensions of both large fullerenes (several nanometers in diameter) and solid graphite (several micrometers in length), so it should have their own vibrational properties. The basic structure of nanotubes consists of one or usually more graphitic sheets with a hollow core. Due to its curved nature of the graphitc sheet in the tubes, the tubes contain fewer dangling bonds than graphite crystallites where open bonds are at the large edges, and different vibrational properties can be expected.

On the other hand, theoretical calculations have shown that, depending on the nanotube diameters, carbon nanotubes can be metallic or semiconducting.[6,7] The thermal oxidation properties of carbon nanotubes have shown that they also relate to the diameter of nanotubes[8], so the properties of nanotubes of different diameters and their controlling growth are important for the research and application of nanotubes. As is known, the diameters of multiwall nanotubes produced in arc discharge depend mainly on the preparation atmosphere and its pressure.[9,10] We report here the influence of the inert atmosphere used and its pressure in carbon arc method on the Raman vibrational modes of nanotubes.

Ⅱ. EXPERIMENTAL

The carbon nanotubes in this study were made by carbon arc method. Briefly, a dc arc plasma was formed between two graphitic rods of 99.99% purity in the inert atmosphere of helium or argon. The cathode deposits containing carbon nanotubes were produced by varying inert atmosphere pressures ranging from 11 to 92 kPa. The inner soft black parts of deposits, being a mixture of tubes, nanoparticles, and amorphous carbon, were purified by oxidation, and then measured with transmission electron microscope (TEM). We obtained the samples of purity approximately 90% nanotubes in purified samples, the nanotubes exhibited a different distribution in diameter for different pressures. Due to the high tube concentration it can be assumed that the spectral lines from the tubes dominate the Raman spectra of the samples.

All Raman spectra were recorded using Renishaw 1000 machine spectrometer.Raman excitation

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was performed by 514.5nm laser light with an incident laser power of 5mW. Line positions and widths were obtained from a numerical fit using Lorentzian line shapes.

We measured the Raman spectra of the nanotubes produced under different pressures ranging from 11 to 92 kPa at Ar gas, and took Raman spectra of graphite and the nanotubes samples produced in He gas for comparison.

Ⅲ. RESULTS AND DISCUSSION

The first-order and second -order Raman spectra of carbon nanotubes (CNTs) have been studied and assigned.[1−5] Raman bands have been observed and compared in the ranges from 100 to 1800cm^{-1} and from 2300 to 3400cm^{-1} for our nanotubes produced in argon or helium atmosphere as shown in Table 1.

Table 1. The first-order and second- order Raman spectra modes of CNTs produced in Ar atmosphere (Ar gas CNTs) and those produced in He atmosphere (He gas CNTs) compared with polycrystalline graphite, as excited with 514.5nm laser.

Raman modes	D	G	E_{2g}	$G+A_{2u}$	D^*	$D+G$	$2G$	$2E_{2g}$
Frequency/cm $^{-1}$ (He gas CNTs)	1354	1579	1618	2450	2701	2943	3175	3244
Frequency/cm $^{-1}$ (Ar gas CNTs)	1352	1584	1620	2455	2707	2945	3178	3247
Frequency/cm $^{-1}$ (graphite)	1351	1584	1622	2444	2731	–	–	3251

Figure 1 shows the difference of first-order Raman spectra of the nanotubes produced in Ar atmosphere (Ar gas CNTs) and those produced in He atmosphere (He gas CNTs) compared with polycrystalline graphite. No Raman bands were observed in the range 100–1300cm^{-1}. In the first-order spectrum of Ar gas CNTs, a strong Raman band located at 1584cm^{-1} resembles that of polycrystalline graphite, while the same Raman band of He gas CNTs is slightly downshifted to 1579cm^{-1}. The bandwidth (BW) around 1584cm^{-1} of Ar gas CNTs(24cm^{-1}) is wider than that of polycrystalline graphite(19cm^{-1}), while this bandwidth of He gas CNTs(32cm^{-1}) is wider than that of

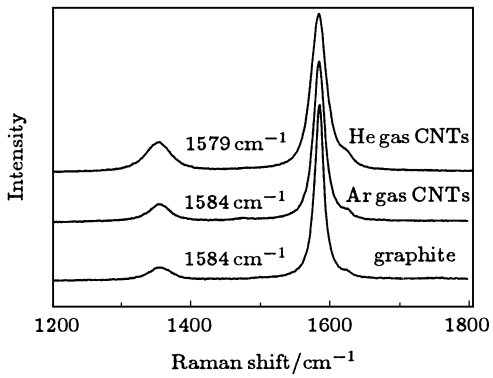


Fig.1. First-order Raman spectra of the carbon nanotubes produced in He atmosphere (He gas CNTs), the carbon nanotubes produced in Ar atmosphere (Ar gas CNTs), and polycrystalline graphite.

Ar gas CNTs (24cm^{-1}). The strong Raman band at 1584cm^{-1} belongs to G modes, which have been assigned to the vibrational mode corresponding to the movement in opposite directions of two neighboring carbon atoms in a graphite sheet.[10] This shows that the structures of Ar gas CNTs is more similar to that of graphite than He gas CNTs, which has a more perfect crystalline graphitic structure in the graphite sheet of tubes.

In polycrystalline graphite, an additional line appears at 1351cm^{-1} that is usually called the D line. The intensity of D line of He gas CNTs or Ar gas CNTs is higher than that of polycrystalline graphite. This means there are more disorder states (carbon nanopartides and finite size crystallite of nanometer order) in nanotubes than in polycrystalline graphite. The D line of He gas CNTs located at 1354cm^{-1} is shifted slightly as compared with Ar gas CNTs(1352cm^{-1}) and polycrystalline graphite (1351cm^{-1}). These all indicate the first-order Raman spectrum of Ar gas CNTs or He gas CNTs resembles that of polycrystalline graphite, especially that of Ar gas CNTs.

The second-order Raman spectra for all the three materials studied are shown in Fig.2 (The nanotubes are all produced at a pressure of 60 kPa). It is dominated by a strong line D^* at around 2700cm^{-1} which is the second-order of the D line 1350cm^{-1}. No Raman bands were observed in the range 1800–2350cm^{-1} for these carbon solids. In the polycrystalline graphite spectrum, a strong D^* Raman band located at 2731cm^{-1} with a shoulder at 2689cm^{-1} is

observed, while the Raman spectrum D^* line of carbon nanotubes produced in Ar atmosphere or He atmosphere is remarkably different from that of polycrystalline graphite, there is only one strong peak at around 2701cm^{-1} (He gas CNTs) or 2707cm^{-1} (Ar gas CNTs). This shows that 2701cm^{-1} or 2707cm^{-1} band is unique to multiwall nanotubes. Furthermore, this band (2701cm^{-1} or 2707cm^{-1}) shows a large downshift in frequency with respect to the 2731cm^{-1} band of graphite.

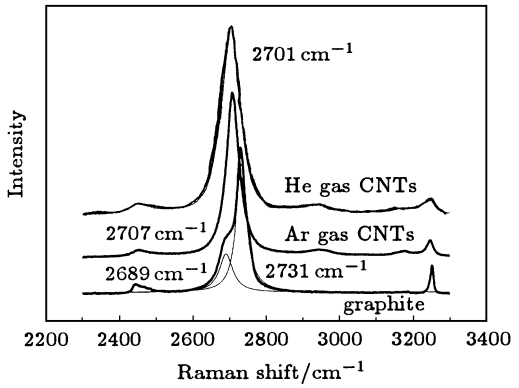


Fig.2. Second-order Raman spectra of the carbon nanotubes produced in He atmosphere (He gas CNTs), the carbon nanotubes produced in Ar atmosphere (Ar gas CNTs), and polycrystalline graphite.

The difference of second-order Raman spectra between He gas CNTs and Ar gas CNTs is more clear than that of first-order Raman spectra. The D^* line is much broader for He gas CNTs(BW$\sim$ 79cm^{-1}) and downshifted ($v = 2701$cm^{-1}) as compared with Ar gas CNTs (BW$\sim$50cm^{-1} and $v = 2707$cm^{-1}).

Except the strong D^* band, two additional weak bands (these peaks are not observed in graphite) are observed. One is at 2945cm^{-1} (Ar gas CNTs) or 2943cm^{-1} (He gas CNTs) which is thought to arise from a combination of the Raman modes at 1351 and 1584cm^{-1}. The other is at 3178cm^{-1} (Ar gas CNTs) or 3175cm^{-1} (He gas CNTs) which is assigned to $2G$ mode. Furthermore, a weak band around 2455cm^{-1} (Ar gas CNTs) or 2450cm^{-1} (He gas CNTs) can be recognized which is assigned to $G + A_{2u}$ modes. Another weak band around 3247cm^{-1} (Ar gas CNTs) or 3244cm^{-1} (He gas CNTs) also can be recognized which is assigned to $2E_{2g}$modes as shown in Table 1. We can also find that the Raman spectra of Ar gas CNTs looks much more like the Raman spectra of polycrystalline graphite than that of He gas CNTs.

The Raman data have been analyzed in terms of CNTs produced at different Ar gas pressures. The second-order Raman scattering of CNTs prepared in the same inert atmosphere at different pressures also revealed some difference as shown in Fig.3. Figure 3 shows the Raman spectrum of CNTs prepared in Ar atmosphere, at pressures ranging from 11 to 92 kPa. The Raman band around 2700cm^{-1} is up shifted from 2703 (11 kPa) to 2709cm^{-1} (92 kPa). The bandwidth of CNTs Raman spectrum decreases with increasing Ar gas pressure from 11 (BW$\sim$ 60cm^{-1}) to 92 kPa (BW$\sim$ 40cm^{-1}). These results may be related to different diameter distributions of the nanotubes produced at different pressures by arc discharge. In the previous study[8,9], the diameter distribution of nanotubes varies with inert gas pressure in arc discharge.

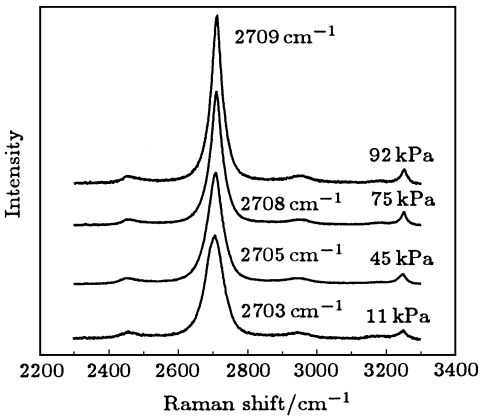


Fig.3. Second-order Raman spectra of the carbon nanotubes produced in Ar atmosphere at pressures ranging from 11 to 92 kPa.

The higher the pressure, the larger the average diameter of nanotubes. In CNTs samples of the present study, TEM observation has also shown this point as in Fig. 4. Figure 4 (a) shows the diameter of nanotubes produced at a pressure of 11 kPa ranges from 3 to 30 nm, while the diameter of nanotubes produced at a pressure of 92 kPa varies from 12 to 80nm [Fig. 4(b)]. While Raman shifts of nanotubes produced at Ar gas pressure (see Fig.3) indicate tubes of different diameters with different mode frequencies. Furthermore, the Raman spectra of the nanotubes produced at a higher pressure is much more like that of graphite than those of nanotubes produced at a lower pressure. This result is in agreement with the result of CNTs thermal properties.[8] For a tube diameter large enough, the character of electronic states should be essentially independent of tube diameter, and should therefore closely resemble that of a graphite sheet.[4]

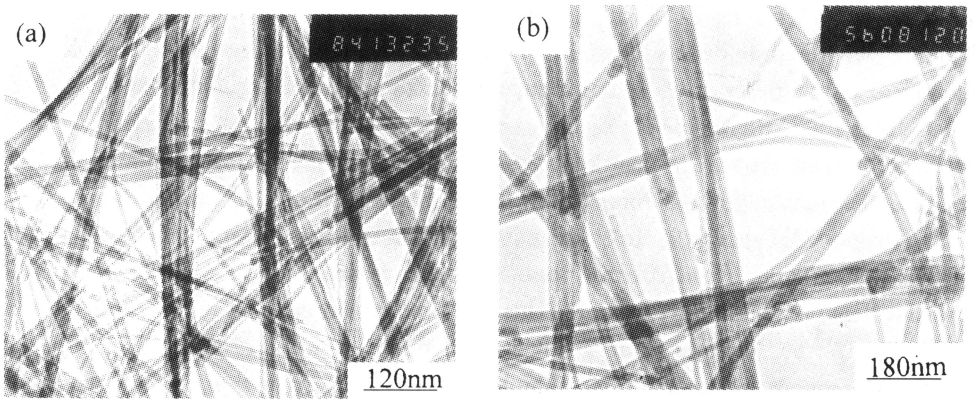


Fig.4. TEM image of (a) the nanotubes produced at a pressure of 11 kPa and (b) the nanotubes produced at a pressure of 92 kPa.

The effect of inert atmosphere and pressure used in preparation by means of carbon arc method on the Raman vibrational modes of nanotubes shows that the energy band gap and carbon—carbon bond length of nanotubes may vary with the preparation conditions (atmosphere and pressure). We can obtain the carbon nanotubes of given Raman modes by controlling the kinds of inert gas and its pressure.

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