Characterization of Carbon Nanotubes Utilizing Terahertz Electromagnetic Waves

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Since electronic devices and systems are becoming faster and more miniaturized, it is necessary to investigate the electrical characteristics of unidimensional materials. Among these materials, carbon nanotubes (CNTs) are eminent because they have various potential applications. Although CNTs have much merit for application, the difficulty of electrical property adjustments, which are dependent on chirality and diameter, constitutes one of the most important issues in current manufacturing processes. To solve this problem, alternative approaches are taken after growth through the gas vapor functionalization by chemisorptions [1]. The experiments detailed in this paper show the possibility of property modulation of CNTs after functionalization.

This paper investigates the characteristics of the CNTs and hydrogen-functionalized carbon nanotubes (H-CNTs) using terahertz time-domain spectroscopy (THz-TDS) in terms of frequency-dependent optical constants and electrical conductivities, and the results are fitted with the Maxwell-Garnett model (MG model) from the 0.2- to 1.5-THz frequency region [2-4]. THz-TDS has more advantages for the measurement of electrical and optical properties than do other techniques, such as FT-IR and SEM/EDX. For example, THz-TDS does not require complicated preprocesses because it offers noncontact measurement, making it possible to measure the same CNT film before and after hydrogen functionalization.

The CNTs were made through the traditional arc discharge technique, and were purified to remove the catalytic metal particles and carbon particles using an HNO_3 solution. To prevent bundling, the CNTs were sonicated in an isopropyl alcohol solution for 24 hours. The CNT films were then prepared on a flat quartz substrate with dimensions of 20 ㎜ × 10 ㎜ × 3 ㎜. Next, the films were heat-treated for 30 seconds in a vacuum, at a temperature of 1000ºC, through a rapid thermal process, for deoxidation. The hydrogen functionalization was also performed in a vacuum chamber by exposing the CNTs to atomic hydrogens produced by the thermal decomposition of H_2 gases using a hot tungsten (W) filament. During the exposure, the hydrogen pressure was maintained at 1 Torr, and the temperature of the tungsten filament was about 2200^{o}C. The hydrogenation of the CNTs was carried out for 10 minutes. The measured thickness of the CNT films was 21 ㎛.

The THz-TDS setup used typical photoconductive generation and detection techniques. The generation antenna was made of coplanar lines on the GaAs substrate. The detection antenna was made of a 5-㎛-gap dipole antenna on a low-temperature-grown GaAs. Both antennas were driven by 85-fs pulses

ISBN: 89-86522-79-9 94460©KEES

from a Ti:Sapphire laser with an average power of 5 mW. The generation antenna was biased with 100 volts. The signal-to-noise ratio of the THz wave was about 5000:1.

For the extraction of the optical constants, THz-TDS requires two transmitted signals, with and without a sample. The power absorption and refractive indices are calculated from the spectral amplitudes and phase differences acquired through fast Fourier transformation. The calculated data is [5-6]

$$Output\_S(\omega) = Input\_S(\omega)\exp(-\frac{d\alpha(\omega)}{2})\exp(i\frac{2\pi}{\lambda}n_1(\omega)d) \qquad (1)$$

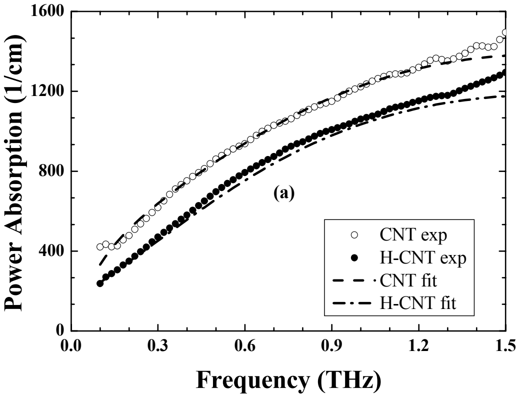
where $Input\_S(\omega)$ is the reference THz power signal while $Output\_S(\omega)$ is the signal passing through the sample after the fast Fourier transformation. $\alpha(\omega)$ is the power absorption, $n_1(\omega)$ is the real part of complex index of refraction $n(\omega) = n_1(\omega)+in_2(\omega)$, and d is the film thickness.

The dielectric constants and conductivities could be included since the imaginary index of refraction n_2 is given by $\alpha(\omega) = 4\pi n_2/\lambda_0$. The dielectric constants of the CNTs film is described by [5-6]

$$\varepsilon(\omega) = \varepsilon_{CNTs} + i\frac{\sigma}{\omega\varepsilon_0}, \qquad (2)$$

where ε_{CNTs} is the dielectric constant of the CNTs at the infinity, σ is the conductivity, and ε_0 is the free space permittivity.

The power absorption of the sample after hydrogen functionalization was smaller than that of the sample before hydrogen functionalization within all frequency ranges, as shown in Fig. 1(a). The indices of refraction decreased gradually, with the frequency increasing from 0.2 THz to 1.5 THz, as shown in Fig. 1(b). The magnitude difference between the two samples was reduced gradually with the frequency increment. Since the indices of refraction are dependent on phase retardation, the hydrogen ion bonding to carbon may further delay the phase in the low-frequency region. Fig. 1(c) shows the real conductivities. The magnitude difference of the real conductivities was reduced with the frequency increment. The steep decrease between 0.1 and 0.15 THz is assumed to be noise. Since the real conductivity is proportional to the multiplication of the power absorption and the real index of refraction ($\sigma(\omega) = c\alpha(\omega)n_1(\omega)\varepsilon_0$), the noise of power absorption is amplified by the steep decrease of the real index of refraction. This results in the steep decrease of the real conductivity from 0.1 to 0.15 THz.



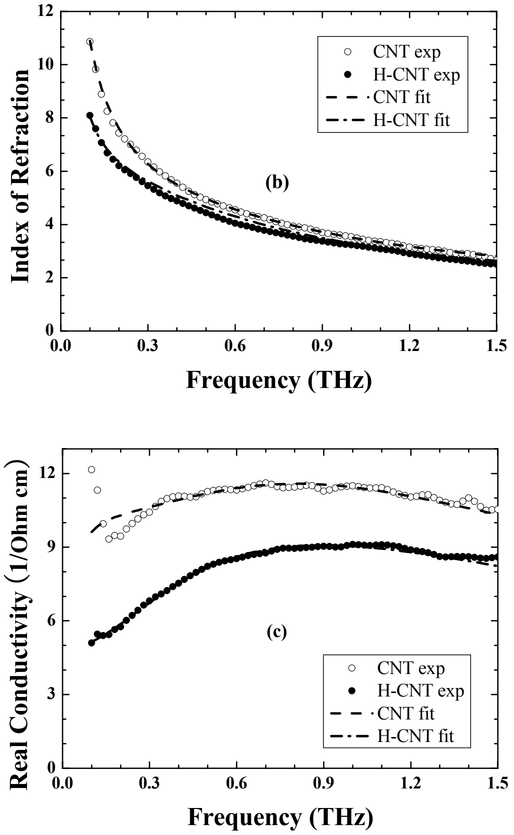


Fig. 1: (a) Power absorption of the CNT film (open circle), and of the H-CNT film (closed circle), which are fitted with the MG model; (b) indices of refraction; and (c) real conductivities.

In general, CNT films are composites consisting of CNTs, glassy carbons, etc. To understand these composite systems, an analytic approximation, like the Maxwell-Garnett model, is needed. The MG model assumes that the conducting particles are in the dielectric host materials. The effective dielectric constant $\varepsilon_{\mathrm{eff}}$ is given by

$$\varepsilon_{eff} = \varepsilon_i \frac{\{N_m + f(1-N_m)\}\varepsilon_m + (1-N_m)(1-f)\varepsilon_i}{N_m(1-f)\varepsilon_m + (fN_m + 1 - N_m)\varepsilon_i}, \qquad (3)$$

where ε_i is a dielectric constant of the insulator, ε_m is a dielectric constant of the conductor, N_m is a geometrical factor of the conductor, and f is a filling factor of the conductor.

To fit with this paper's experimental results, the dielectric host material was assumed to be a glassy carbon, and conducting particles to be CNTs. The geometrical factor value of CNTs sets to one-third since the CNTs can be regarded as randomly oriented long cylinders. Other fitting parameters are shown in Table 1. The plasma frequency of H-CNTs decreases to about two-thirds of that of CNTs, which suggests that hydrogen functionalization reduces the carrier density of H-CNTs.

Table 1: Fitting parameters of the Maxwell-Garnett model **(ε_∞ = 3.5, N=1/3)**

	$\omega_p/2\pi$	$\Gamma/2\pi$	$\omega_{p,j}/2\pi$	$\omega_j/2\pi$	$\Gamma_j/2\pi$	f
CNTs	7.2906	2.6418	2.7553	1.0429	1.9580	0.82
H-CNTs	4.6603	2.2606	4.8637	1.0343	2.7331	0.88

(N: geometrical factor of CNTs; f: filling factor; ε_∞: dielectric constant of infinity; ω_p: plasma frequency; Γ: damping rate; $\omega_{p,j}$: oscillation strength of Lorentz oscillator; ω_j: phonon frequency; Γ_j: spectral width)

In conclusion, the optical and electrical characteristics of the H-CNT and CNT films were measured for the range between 0.2 and 1.5 THz, using terahertz time-domain spectroscopy. The magnitude reduction of the refractive indices and electrical conductivities after hydrogen functionalization was observed. Using the MG model, the experimental results were fitted, and the important key parameters of the carrier transport were obtained.

References

1. K. S. Kim, D. J. Bae, J. R. Kim, K. A. Park, S. C. Lim, J-.J. Kim, W. B. Choi, C. Y. Park, Y. H. Lee, "Modification of electronic structures of a carbon nanotubes by hydrogen functionalization," Adv. Mater. Vol. **14**, No.24, 1818 (2002).
2. K. Tanaka, T. Yamabe, and K. Fukui *in The science and technology of carbon nanotubes*, Elsevier (1999).
3. J.-H. Son, T. B. Norris, and J. F. Whitaker, "Terahertz electromagnetic pulses as probes for transient velocity overshoot in GaAs and Si," J. Opt. Soc. Am. B **11**, 2519 (1994).
4. D. Grischkowcky, S. Keiding, M. van Exter, and Ch. Fattinger, "Far-Infrared Time-Domain Spectroscopy with TeraHz Beams of Dielectrics and Semiconductors", J. Opt. Soc. Am. B 7, 2006 (1990).
5. T.-I. Jeon, K.-J. Kim, C. Kang, S.-J. Oh, J.-H. Son, K. H. An, D. J. Bae, and Y. H. Lee, *Appl. Phy. Lett.*, vol. 80, 3403 (2002).
6. T.-I. Jeon, K.-J. Kim, C. Kang, I.-H. Maeng, J.-H. Son, K. H. An, D. J. Bae, and Y. H. Lee, *Jour. Appl. Phys.*, vol. 95, 5736 (2004).