Frequency-dependent optical constants and conductivities of hydrogen-functionalized single-walled carbon nanotubes

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The frequency-dependent optical constants and electrical conductivities of hydrogen-functionalized single-walled carbon nanotubes (SWNTs) have been measured from the 0.2 to 1.5 THz region using a terahertz time domain spectroscopy. The indices of refraction and electrical conductivities of the sample after hydrogen functionalization were smaller than those of the sample before hydrogen functionalization. The experimental results were fitted using the Maxwell–Garnett model, and a reduction of plasma frequency was observed. This can be attributed to the fact that the hydrogen functionalization has reduced the number of free carriers with the bonding change from sp² to sp³.

Since electronic devices and systems are becoming faster and more miniaturized, it is essential to investigate the electrical characteristics of one-dimensional materials. Among these materials, carbon nanotubes are eminent because they have various potential applications. The electrical characteristics of carbon nanotubes, in particular, need to be understood for miniaturized electronic applications.\(^1\) In the last few years, many researchers have explored the possibility of creating electronic devices using various kinds of carbon nanotubes. Examples of these are diodes, transistors, and random access memories, as well as applications in field-emission displays using the emission characteristics of carbon nanotube tips.\(^2\)–\(^3\)

Although carbon nanotubes have much merit for application, much research must also be done regarding these. The electrical property adjustments of carbon nanotubes, which are dependent on chirality and diameter, constitute one of the most important issues in the present manufacturing process. It is very difficult to control the electrical properties of carbon nanotubes during their growth. To solve this problem, alternative approaches are taken after growth, including the insertion of metal particles in carbon nanotubes and gas vapor functionalization by chemisorptions.\(^2\)–\(^3\) The band gap opening of single-walled carbon nanotubes has been observed with the gas vapor functionalization process through dc-field measurements and simulations in recent research.\(^4\)–\(^7\) The possibility of property control of carbon nanotubes in large volumes is a significant advantage of these approaches.

The electrical properties of carbon nanotubes are typically measured using the four-probe technique, Fourier-transform infrared (FTIR), and the microwave measurement technique, among other techniques. In this study, terahertz time domain spectroscopy (THz-TDS), which measures the characteristics in a region between microwave and infrared, was utilized.\(^8\) This technique provides essential electrical and optical properties of nanomaterials when they are applied to devices in the high-frequency region.

A typical THz-TDS system consists of a femtosecond laser, a source transmitter, and a detection receiver. Terahertz pulses are most commonly generated by photoconductive switching or optical rectification, and are detected by photoconductive sampling or electro-optic sampling techniques.\(^8\)–\(^12\) The THz-TDS system has advantages over other spectroscopic techniques. FTIR spectroscopy, for example, requires complicated numerical transformation processing of Kramer–Kronig relations for the acquisition of optical constants and conductivities. It also has many complicated preprocesses, such as temperature cooling, in order to acquire data in the low-frequency region. Similarly, the four-probe measurement, a typical measurement technique of electrical characteristics, also needs many preprocesses, such as probe-line fabrications. THz-TDS, however, does not require such complicated preprocesses because it is a noncontact measurement. It also has a good signal-to-noise ratio compared with other techniques. The general FTIR spectroscopy typically has a signal-to-noise ratio (SNR) of 100:1 while THz spectroscopy has over 10 000:1.\(^8\) In this measurement, the SNR ratio is over 5000:1.

This paper investigates the characteristics of frequency-dependent optical constants and electrical conductivities of the hydrogen-functionalized SWNTs from the 0.2 to 1.5 THz frequency region, utilizing a THz-TDS experimental setup.\(^11\)

The THz electromagnetic pulses were generated using the photoconductive switching method, and were detected using the photoconductive sampling techniques. The generation antenna was made of coplanar lines on the GaAs substrate. The detection antenna was made of 5 \(\mu\)m gap dipole antenna on a low-temperature-grown GaAs. Both antennas were driven by 85 fs pulses from a Ti:Sapphire laser with an average power of 5 mW. The generation antenna was biased with 100 V. For the detection of THz signals, the travel lengths of pump and probe laser pulses should be the
The signal was acquired using a lock-in amplifier with 400 Hz mechanical chopping. The sample was located in the focal position between 2 in. focal paraboloidal mirrors. It was held in a 4 mm pinhole. The focal diameter of the THz beam was 2 mm.

For the extraction of frequency-dependent optical constants and conductivities, THz-TDS requires two transmitted signals, one with and one without a sample. Since the power absorption and other optical constants are included in the transmitted wave forms in the time domain, fast Fourier transformation was used to obtain the spectral amplitude and phase signal in the frequency domain.\textsuperscript{8,10,11}

The same SWNTs film was measured before and after hydrogen functionalization. The SWNTs film was made through the traditional arc discharge technique. The SWNTs were purified to remove the catalytic metal particles and any carbon particles using an HNO\textsubscript{3} solution. To prevent bundling, the SWNTs were sonicated in an isopropyl alcohol solution for 24 h. The SWNTs film was then prepared on a flat quartz substrate with dimensions of 20 mm × 10 mm × 3 mm. Next, it was heat treated for deoxidation through a rapid thermal process at a temperature of 1000 °C for 30 s in a vacuum. The hydrogen functionalization was also performed in a vacuum chamber by exposing the SWNTs to atomic hydrogen atoms that were produced by a thermal decomposition of H\textsubscript{2} gas using a hot tungsten (W) filament. During the exposure, the hydrogen pressure was maintained at 1 Torr, and the temperature of the W filament was about 2200 °C. The hydrogenation of SWNTs was carried out for 10 min. The measured thickness of the SWNTs film was 21 \(\mu\)m. Scanning electron microscopy photos of the samples were taken before and after hydrogenation, but no significant change could be found on the surface. The Raman scattering measurement was also performed to see whether there was any structural change after the functionalization. As shown in Fig. 1, the peaks at the \(D\) band (1380 cm\(^{-1}\)) and \(D+G\) band (2700 cm\(^{-1}\)) were found to have increased after hydrogenation due to the increase of \(sp^3\) bonding.

The time-domain data were obtained for the sample before and after hydrogen functionalization as well as the reference wave form. They are the current signals acquired by a lock-in amplifier which are proportional to the THz beam power at the detection receiver. Magnitude reduction and phase delay in the time domain waveforms, transmitting through samples with respect to reference waveform, could be observed. The acquired time-domain waveforms were transformed into spectral amplitudes and phase retardations in the frequency domain, using a fast Fourier transformation.

A difference in the spectral amplitudes of the samples before and after hydrogen functionalization was observed due to differences in absorption and transmission rates through the samples.
Because the complex index of refraction and power absorption were included in the transformed THz electromagnetic waves, the experimental results could be easily acquired to compare signals with the reference waveform. The output data is

\[
\text{Output}_S(\omega) = \text{Input}_S(\omega) \exp \left( -\frac{d\alpha(\omega)}{2} \right) \times \exp \left[ \frac{2\pi}{\lambda} n_1(\omega)d \right],
\]

where \( \text{Input}_S(\omega) \) is the reference THz power signal, while \( \text{Output}_S(\omega) \) 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 \( n_2(\omega) \) is given by \( \alpha(\omega) = 4\pi n_2(\omega)/\lambda_0 \). The dielectric constants of the SWNTs film is described by Refs. 10 and 11

\[
\epsilon(\omega) = \epsilon_{\text{SWNT}} + \frac{i}{\omega\epsilon_0},
\]

where \( \epsilon_{\text{SWNT}} \) is the dielectric constant of the SWNTs at the infinity, \( \sigma \) is the conductivity, and \( \epsilon_0 \) 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. 2(a).

The indices of refraction decreased gradually, as the frequency increases from 0.2 THz to 1.5 THz, as shown in Fig. 2(b). The magnitude of the difference between the two samples decreased gradually with the frequency increase. Since the indices of refraction are dependent on phase retardation, the hydrogen ion bonding to carbon may further affect the phase in the low-frequency region.

Figure 2(c) shows the real conductivities. The magnitude difference of the real conductivities was reduced with increasing frequency. The steep decrease between 0.1 and 0.15 THz is assumed to be noise. Since real conductivity is proportional to the product of power absorption and the real index of refraction \( \sigma(\omega) = \epsilon(\omega)n_1(\omega)\epsilon_0 \), the noise of power absorption is amplified by the steep decrease of the real index of refraction. This results in a steep decrease of the real conductivity from 0.1 to 0.15 THz. In general, the real conductivity decreased by 20–40% in the measurement frequency range after hydrogen functionalization.

To analyze these property changes, the experimental results were fitted with the Maxwell–Garnett model, which is described thoroughly in Ref. 11. In the simulation, the dielectric host material was assumed to be glassy carbon, and conducting particles to be SWNTs. The geometrical factor value of the SWNTs was set to one-third because the SWNTs can be regarded as randomly oriented long cylinders. Other fitting parameters are shown in Table I. The plasma frequency was reduced to two-thirds after hydrogen functionalization. This means that the number of free carriers is reduced because the plasma frequency is proportional to the square root of the carrier density.

Recent simulations have also predicted the bonding change by hydrogen functionalization from \( sp^2 \) to \( sp^3 \). The hydrogen ions could be easily bonded to the dangling bond of SWNTs because the energy of hydrogen-carbon bonding is smaller than that of carbon-carbon bonding. This would reduce the density of free carriers, consequently leading to the magnitude reduction of the index of refraction and conductivity.

In conclusion, the frequency-dependent optical constants and electrical conductivities of the hydrogen-functionalized SWNTs were measured for the range between 0.2 and 1.5 THz. The magnitude reduction of the index of refraction and electrical conductivity after hydrogen functionalization were observed. Using the Maxwell–Garnett model, the experimental results were fitted, which resulted in the reduction of plasma frequency. This reduction resulted in a decrease in the number of free carriers, which can be evidence of bonding change from \( sp^2 \) to \( sp^3 \) by hydrogen functionalization. In other words, the bonding change by functionalization induces the reduction of free carriers, resulting in the reduction of conductivity.

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