Terahertz absorption and dispersion of fluorine-doped single-walled carbon nanotube

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We present experimental and theoretical results on the absorption and dispersion of a single-walled carbon nanotube (SWNT) with and without fluoride (F) doping in the frequency range of 0.2–3 THz. Under the doping conditions, the power absorption, index of refraction, and the real and imaginary parts of the conductivity are decreased compared to those for pure SWNTs because the charge transfer to the F2 molecule will be increased. Our measurement of pure SWNT agrees well with the Maxwell-Garnett and Drude models. However, the F-doped SWNT requires adding a Lorentz oscillator term for good agreement between theory and measurement. © 2005 American Institute of Physics. [DOI: 10.1063/1.2001751]

I. INTRODUCTION

Recently there has been increasing interest in carbon nanotube (CNT) devices. CNT device properties can be optimized by doping. While the microwave and infrared properties of the CNTs have been previously measured, they were measured only for undoped pure single-walled carbon nanotubes (SWNTs) by the Kramers-Kronig analysis. More recently, spectroscopic measurements of SWNT have been made with subpicosecond terahertz electromagnetic pulses. The previous terahertz experiments measured the frequency response up to 0.8 THz (Ref. 3) and 2 THz. In this paper, we report an experimental study in frequency range of 0.2–3 THz on the properties of fluorine (F)-doped SWNT films prepared by the solvent casting method. The broadband terahertz spectrum allows a more precise analysis of the measured results. In addition, we observed the 2.4-THz phonon spectrum along the c direction for the F-doped SWNT.

In the simple Drude model for a conductive metal, the key parameters describing the dynamics of a free carrier in a material are the plasma frequency \( \omega_p \) and the carrier damping rate \( \Gamma = 1/\tau \), where \( \tau \) is the carrier collision time. Unlike a crystal material, a SWNT has a network of crossed CNTs. This structure exhibits both the metallic properties of the CNT itself and the semiconducting properties of a CNT junction. Therefore the dynamic of free carriers responds well along the CNT itself as a conductive metal but that of free carriers responds poorly at the CNT junction. This has been modeled by the Drude-Lorentz model.

Another consideration in the analysis is the background dielectric constant. CNTs have empty air space created by the network of nanotubes in the film. This condition creates an effective medium with two different dielectric constants. To explain the dynamic response of such a medium, the Maxwell-Garnett (M-G) model is introduced, where CNTs are embedded in a dielectric air host.

II. EXPERIMENT

We used raw HiPCO (high-pressure CO) SWNT powder (Carbon Nanotechnologies Inc.) for fluorination. This powder was placed on a Ni boat in the fluorine reaction chamber in order to prevent erosion. The reaction process was similar to the process described in previous reports. The chamber was pumped out to \( 10^{-2} \) torr and purged with nitrogen gas to remove residual oxygen gas and moisture. F2 gas was then introduced and the pressure was maintained at 0.1 bar at room temperature for a given reaction time. After the reaction, the chamber was pumped out again to \( 10^{-2} \) torr and nitrogen gas was refilled prior to extraction of the powder sample. We note that the fluorination condition was rather mild compared to previous works where the SWNTs disintegrated. The pure and F-doped SWNT powders were immersed in an isopropanol solution and sonicated for dispersion for 10 min. SWNT films were obtained by dropping the prepared solution on an undoped silicon substrate.

The samples were placed into a terahertz time-domain spectroscopy (TDS) system as illustrated in Fig. 1. A detailed description of the entire system has been previously published. Figure 2(a) shows the reference terahertz pulse without sample, and Figs. 2(b) and 2(c) show signal terahertz pulses with pure SWNT and F-doped SWNT, respectively.
The reference terahertz pulse has a signal-to-noise (S/N) ratio of 5000:1, while the S/N ratios of the sample terahertz pulses have 3500:1 and 200:1 for Figs. 2(b) and 2(c), respectively. These S/N ratios are much larger than those obtained by a general Fourier transform infrared (FTIR) spectroscopy measurement. The terahertz pulse amplitude in Fig. 2(c) is 20 times less than that of Fig. 2(a). However, despite this reduction in amplitude, the signal is still more than 200 times larger than the rms noise. Figure 2(d) shows that the spectra of the measured terahertz pulses extended to 3 THz.

The coherent terahertz TDS data contain both the amplitude and phase information of the terahertz pulses so one can simultaneously retrieve both the power absorption coefficient and index of refraction of a sample of known thickness. In our case, the measured average thicknesses of the SWNT films are 3.8 μm for the F-doped SWNT film and 7 μm for the pure SWNT film with roughly ±10% deviation. To obtain precise measurements, more uniform samples are needed.

The spectra of the reference and signal pulses, obtained by fast Fourier transform, are shown in Fig. 2(d). The complex signal spectrum $A_s(\omega)$ and the complex reference spectrum $A_r(\omega)$ can be described as

$$A_s(\omega) = A_r(\omega) [\exp(i\beta_0)]/t(\omega),$$

where $\beta_0 = 2\pi d/\lambda_0$ accounts for the air space displaced by the sample. For our experimental setup, with a relatively small power absorption in a low-frequency range and a thin sample, multiple reflection of the terahertz pulse occurs between the two surfaces of the sample. An approximately 10% adjustment is needed to remove the multiple reflection effect in the low-frequency range. However, because the power absorption coefficient is extremely large in the high-frequency range, the multiple reflection effect is negligible. For this situation the frequency-dependent complex amplitude transmission $t(\omega)$ is given by the Fabry-Perot interference equation,

$$t(\omega) = \frac{t_{12}r_{21}\exp(-\alpha d/2)\exp(i\beta)}{1 + t_{12}r_{21}\exp(-\alpha d/2)\exp(i2\beta)}.$$  

$t_{12}$ and $r_{12}$ are the complex Fresnel transmission and reflection coefficients from air into the sample; $t_{21}$ and $r_{21}$ are the transmission and reflection coefficients from the sample into the silicon plate, which has an index of refraction of 3.417 in the terahertz frequency range. The propagation vector is $\beta = 2\pi n_2 d/\lambda_0$; $n_2(\omega)$ is the complex index of refraction, given by $n_2(\omega) = n_1(\omega) + i\alpha(\omega)$; $d$ is the film thickness; $\alpha(\omega)$ is the power absorption, given by $\alpha = n_4 \pi /\lambda_0$. Using the Fabry-Perot analysis of Eq. (2) and the measured ratio of
The measured power absorption of pure SWNT (dots) shows a smooth frequency-dependent curve. However, the power absorption of the F-doped SWNT (circles) linearly increases with frequency. The power absorption in the high-frequency range increases more rapidly than that of the low-frequency range due to the F-doping process. Because the originated SWNT has a high plasma frequency, the power absorption gradually increases with increasing frequency. This characteristic curve of power absorption is very similar to our pure and F-doped SWNTs. Therefore high plasma frequencies are expected for both pure and F-doped SWNTs. The power absorption is reduced by about 50% at our peak frequency. The F atoms easily bond to the sidewall of SWNTs because the energy of the F-carbon bonding is stronger than that of carbon-carbon bonding. A F$_2$ molecule approaches the nanotube wall and is dissociatively chemisorbed. The energy gain after chemisorption is about $-5$ eV for SWNTs. When a F$_2$ molecule is first physisorbed, no significant charge transfer will occur. As the F$_2$ molecule approaches the tube, the bond becomes weaker and the amount of charge transfer from the nanotube to the F$_2$ molecule will be increased. Recent researches have predicted the bonding charge change by F functionalization from $sp^2$ to $sp^3$. This bonding charge change would reduce the density of free carriers, consequently leading to the magnitude reduction of the absorption and dispersion.

The properties of SWNT have been changed from metallic to semiconductor by the F-doping process. The measured index of refraction $n_r$ decreases rapidly in the low-frequency range and then monotonically decreases in the high-frequency range. Both indices of refraction asymptotically approach a constant value. We assumed that the index of refraction approached 1.8 as used in Ref. 4. The effective SWNT’s dielectric constant ($\varepsilon_{\text{eff}}$) is 1.8, the square of the high-frequency limit of the measured $n_r(\omega)$.

Similar to semiconductors, the conducting SWNT’s frequency-dependent dielectric response $\varepsilon(\omega)$ is assumed to be described by the following general relationship:

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{eff}}^\infty + \frac{i\sigma}{\omega\varepsilon_0} = (n_r + i n_i)^2,$$

where $\sigma(\omega)$ is the frequency-dependent complex conductivity and $\varepsilon_0$ is the free-space permittivity. The real part $\sigma_r(\omega)$ and imaginary part $\sigma_i(\omega)$ of the conductivity can be obtained from Eq. (3) and are shown in Figs. 3(c) and 3(d). Clearly, our pure and F-doped SWNT conductivities do not follow the simple Drude model, which has a Lorentzian line shape centered at zero frequency and decreases with increasing frequency.

**III. RESULTS**

Because the SWNT films are composed of SWNT and air, we consider the effective medium to be a carbon nanotube network embedded in an air medium. To explain the dynamic response of such a medium, the M-G model was introduced, which is given by

$$\varepsilon_{\text{eff}} = \varepsilon_i + \frac{[N + f(1 - N)]\varepsilon_m + (1 - N)(1 - f)\varepsilon_i}{N(1 - f)\varepsilon_m + (fN + 1 - N)\varepsilon_i},$$

where $f$ and $N$ are the filling factor and geometrical factor of the M-G model, respectively. $\varepsilon_i$ is the background dielectric constant to SWNTs, and $\varepsilon_m$ is the dielectric constant of the SWNT network, which may be composed of metallic and
semiconducting carbon nanotubes. This combination of materials can be modeled by a combination of the Drude term and localized Lorentzian absorption, given by

$$e_{\text{m}}(\omega) = e_{\text{SWNT}}^\infty - \frac{\omega_p^2}{\omega^2 + \Gamma_i \omega} + \sum_j \frac{\omega_{pj}^2}{(\omega_j^2 - \omega^2) - i\Gamma_j \omega},$$

where $e_{\text{SWNT}}^\infty$ is the dielectric constant of the SWNT network, $\omega_p$ is the plasma frequency, $\Gamma_i$ is the damping rate, $\omega_j$ is the phonon frequency, $\Gamma_j$ is the spectral width, and $\omega_{pj}$ is the oscillator strength of the Lorentz oscillators. The dielectric constant of the effective medium at infinite frequency and the effective dielectric constant are $e_{\text{m}}(\infty) \approx 1.87^2$ and $e_{\text{eff}}^\infty = 1.8^2$, respectively, as used in Ref. 4. The first and second terms in Eq. (5) are the well-known Drude model for a conductive metal. In the simple Drude model, the key parameters describing the dynamics of free carriers in a material are $\omega_p$ and $\Gamma = 1/\tau$, where $\tau$ is the carrier collision time. The third is a Lorentz oscillator term by phonon mode. The fitting parameters are shown in Table I.

The pure SWNT sample needed a combination of the M-G model and the Drude model. A very good fit is shown in Fig. 3. However, the F-doped SWNT sample needed the M-G model combined with not only the Drude model but also the single Lorentzian oscillation term in Eq. (5). We discovered that the phonon frequency of F-doped sample is 2.4 THz, which is very similar to what is found in Ref. 4. The characterization of the pure sample has mainly electron behavior. However, through the F-doping process, the characterization of the F-doped sample has both electron and phonon behaviors. The fitted damping rate was $\Gamma/2\pi = 3.5$ and 7.5 THz for pure SWNT and F-doped SWNT, respectively, corresponding to the collision times of $\tau = 46$ and 21 fs. This was closely related to the effective scattering length of nanotubes. The collision time of $\tau = 21$ fs for the F-doped SWNT is approximately 1/8 of high doped GaAs (Ref. 16) and three times that of a conducting polymer.17

In summary, pure and F-doped SWNT films were characterized by terahertz TDS which fit well with the M-G model combined with the Drude-Lorentz model. By the F-doping process, the properties of pure SWNTs are changed from metallic to semiconductor in the terahertz frequency range. Because of the F-doping process, during which the F2 bond becomes weaker, the amount of charge transfer from the SWNT to the F2 molecule will be increased. Therefore the characterization of pure SWNT has mainly electron behaviors. However, the characterization of F-doped SWNT has both electron behaviors across the spectrum and phonon responses around the 2.4-THz resonance frequency.

**ACKNOWLEDGMENT**

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**Table I. Theoretical fitting parameters for the measurements presented in Figs. 5(a)–5(d).**

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<thead>
<tr>
<th>Parameter</th>
<th>$\omega_p/2\pi$ (THz)</th>
<th>$\Gamma/2\pi$ (THz)</th>
<th>$\omega_1/2\pi$ (THz)</th>
<th>$\omega_2/2\pi$ (THz)</th>
<th>$\Gamma/2\pi$ (THz)</th>
<th>$N$</th>
<th>$f$</th>
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<tr>
<td>Pure</td>
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<tr>
<td>F-doped</td>
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<td>6.0</td>
<td>2.4</td>
<td>3.0</td>
<td>0.1</td>
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