Terahertz conductivity of anisotropic single walled carbon nanotube films

Tae-In Jeon and Keun-Ju Kim
Division of Electrical and Electronics Engineering, Korea Maritime University, Pusan 606-791, Korea

Chul Kang, Seung-Jae Oh, and Joo-Hiuk Son
Department of Physics, University of Seoul, Seoul 130-743, Korea

Kay Hyeok An, Dong Jae Bae, and Young Hee Lee
Department of Physics, National Research Laboratory for Carbon Nanotubes, Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Korea

(Received 18 June 2001; accepted for publication 6 March 2002)

Absorption and dispersion of singlewalled carbon nanotube films were measured using an optoelectronic THz beam system for THz time-domain spectroscopy. The anisotropically aligned nanotube films were prepared through simple mechanical squeezing with a bar coater. The angle-dependent absorption and dispersion values were then measured. Results indicate that the index of refraction decreases with increasing frequency (0.1–0.8 THz), whereas the real conductivity increases with increasing frequency. The real conductivity measured is not congruent with the simple Drude model, but it follows a Maxwell–Garnett model, where the nanotubes are embedded in a dielectric host. © 2002 American Institute of Physics. [DOI: 10.1063/1.1476713]

Singlewalled carbon nanotube (SWCNT) films can be easily fabricated on a substrate, but the dc and ac transport phenomena from such films have yet to be clearly understood. The ac transport phenomena, in particular, need to be clarified before developing possible applications of SWCNT films for electromagnetic wave shielding materials. SWCNT films have manifested varying behaviors in different frequency regions. The infrared properties of SWCNTs have been measured over 15–5000 cm⁻¹, where the real conductivity extracted using the Kramers–Kronig model was explained using a modified Drude model combined with low-frequency localized absorption. Recently, the dielectric properties of SWCNT films have been studied by electromagnetic waves up to 500 GHz, where the real conductivity decreases with increasing frequency, in accordance with Drude conduction model. However, the results from those experiments are not consistent when overlapping frequency regions are taken into consideration. This may be ascribed to different sample preparation conditions or experimental errors in the upper or lower limits of the measured frequency regions. These discrepancies make it difficult to carry out a complete analysis of the electrical properties of SWCNT films from the low frequency to the far infrared range.

Anisotropically aligned SWCNT films have been prepared using a high magnetic field of 25 T, where the anisotropy in the room temperature dc conductivity \( \sigma_{dc} \) ranges from 6 to 24. However, high magnetic fields are not widely accessible, limiting the number of samples that can be produced. A simpler method of fabricating these films is thus desirable.

In this letter, we characterize the ac conductivities of anisotropically aligned SWCNTs in the THz frequency region from 0.1 to 0.8 THz using THz time-domain spectroscopy (THz-TDS). The SWCNT films were prepared through simple mechanical squeezing using a bar coater. The anisotropy of the ac conductivity is found to be smaller than that of dc conductivity due to ac coupling between individual SWCNTs. The real conductivities do not follow a simple Drude model in our frequency range.

SWCNT powder was synthesized using a traditional arc discharge with catalytic transition metals. The pristine powder was a mixture of SWCNTs and carbonaceous particles. It also contained a mixture of transition metals of about 15 wt % in the sample. For the purified sample, this powder was heated at 470 °C for 30 min to remove carbonaceous particles and then refluxed in HNO₃ solution to remove transition metals. The metal content was reduced to less than 1 wt %. This tar was mixed with 5 wt % binder (methyl cellulose, which is water soluble) in distilled water and sonicated for 3 h. The thin film was obtained by mechanically squeezing the slurry on a glass slide using a bar coater. Both the pristine film and the purified film were prepared in this manner. The thickness of the films was typically a few tenths of a micron. This thin film was placed into the THz-TDS system described below and shown in Fig. 1. The sample was placed in the incident THz beam path and rotated to a particular angle with respect to the beam polarization to measure anisotropies.

A high-performance optoelectronic setup was used to generate and detect the subpicosecond pulses of freely propagating THz electromagnetic radiation. A transmitting and receiving GaAs antennas consisting of a micron-size dipole antenna embedded in a coplanar transmission line were driven optoelectrically using 6 mW, 80 fs pulses from a mode-locked Ti:sapphire laser. The THz system was located in dry, airtight box to eliminate the effects of water vapor on the THz beam. Two electromagnetic pulse shapes are measured using the THz-TDS technique, the input (reference) pulse and the output (transmitted) pulse whose shape has been modified as it passed through the SWCNTs being studied. The frequency-dependent absorption and dispersion of
the sample can be obtained using Fourier analysis of the input and output pulses.

The output THz signal includes the sample’s power absorption and index of refraction. The measured output signal is

\[
\text{output THz}(\omega) = \text{input THz}(\omega) \exp \left( -\frac{d\alpha(\omega)}{2} \right) \times \exp \left( i \frac{2\pi}{\lambda} n(\omega) d \right),
\]

where \(\alpha\) is the power absorption coefficient, \(d\) is the thickness of the sample, \(\lambda\) is the free-space wavelength, and \(n\) is the index of refraction of a given sample. The power absorption coefficient and index of refraction can be determined using Eq. (1) with the measured input and output THz signals. The frequency dependent complex dielectric constant \(\varepsilon\) is equal to the square of the complex index of refraction \(n = n_r + in_i\). The imaginary index is determined by measuring the power absorption coefficient \(\alpha = 4\pi n_i/\lambda\). The dielectric response for the SWCNTs is described by the following general relationship:

\[
\varepsilon = \varepsilon_{\text{CNT}} + i \frac{\sigma}{\omega \varepsilon_0},
\]

where \(\varepsilon_{\text{CNT}}\) is the dielectric constant of SWCNTs, \(\sigma\) is the complex conductivity, and \(\varepsilon_0\) is the free-space permittivity.

The power absorption data measured using different orientations for the pristine and purified samples are shown in Fig. 2(a). The absorption coefficient of the purified sample shows a consistent increase with increasing frequency, whereas that of the pristine sample saturates at a high frequency. This indicates that the pristine SWCNTs are longer than those in the purified sample on the average; this is consistent with tube lengths being shortened in the purification process.5 During the purification process, larger sizes of CNTs are statistically attacked more frequently than smaller ones by oxidative wet etching, transforming them into smaller ones. Power absorption of parallel oriented films is always larger than those with perpendicular orientation for both pristine and purified samples, while the absorptions at 45° remain inbetween the two extremes. In the parallel orientation, the polarization direction of the incident THz beam coincides with the alignment of the tube axis, as shown in Fig. 1. The power absorption of the parallel orientation is always larger than that of the perpendicular orientation. Although our reference signal has frequencies to 1 THz, we consider our data to be accurate only up to 0.8 THz, due to the excessive attenuation caused by the thick SWCNT samples.

The relative phase of the Fourier components is obtained since the electric fields of the THz pulses are measured. This phase information determines the relationship between the index of refraction and frequency, as shown in Fig. 2(b). The index of refraction manifests a gradual increase with decreasing frequency. This trend is similar to that yielded by lightly
doped semiconductors,\textsuperscript{7} reflecting the fact that our SWCNT mats are composed of metallic and semiconducting tubes.\textsuperscript{3} The purified sample shows a larger index of refraction, suggesting higher conductivity for the purified samples compared to the pristine sample.

Given the measured power absorption and index of refraction, the general relationship of Eq. (2) determines the real conductivity, as shown in Fig. 2(c). Using electrical four-point probe measurement, the parallel ($\sigma_\parallel$) and perpendicular ($\sigma_\perp$) components of the dc conductivity at room temperature are 87 and 33 (1/Ω cm) for the purified sample and 4.4 and 1.9 for the pristine sample, respectively. The respective anisotropies ($\sigma_\parallel / \sigma_\perp$) are 2.64 and 2.27 for the purified and pristine samples. The conductivities are smaller than the previously reported values.\textsuperscript{1,2} This is partly due to the fact that 5\% of the polymer binder was introduced during the film coating. The respective densities of the films are 0.4 and 0.34 g/cm$^3$ for the purified and pristine samples, which are again smaller than the previously reported values.

Metal and doped semiconductor materials usually follow a simple Drude theory that has maximum conductivity at the dc region and the conductivity decreasing with increasing frequency. Conductivity in our SWCNT films increases with increasing frequency for both samples, disagreeing with the Drude model in our frequency range. However, this behavior has already been reported by previous measurements\textsuperscript{1,9,10} outside the THz frequency range. To describe our sample, the CNT films are considered as individual tubes joined at junctions. The CNTs are composed of metallic and semiconductive tubes, while the junction serves as an insulator. Therefore, our sample may be viewed as CNTs embedded in an effective dielectric medium. The electrodynamic response of such an effective medium can be explained using the Maxwell–Garnett model\textsuperscript{9,10}, which predicts conductivity in our THz frequency range to increase with increasing frequency. However, in our measurements, an exact fit with the Maxwell–Garnett model becomes ambiguous due to the limited frequency region of the current study. In previous infrared measurements of randomly disordered CNT mats, conductivity decreased with increasing frequency from 0.1 to 0.2 THz, following the Drude model.\textsuperscript{5} We have likewise observed this decline in conductivity in the same frequency region with the randomly oriented SWCNT mat and then the conductivity increase after 0.2 THz.\textsuperscript{11}

The purified sample manifested higher conductivity than the pristine sample in all the orientations studied. In the purification process, the crystallinity of the individual tubes is improved by heat treatment. This enhances the conductivity of the individual nanotubes, and the conductivity of the entire film. The transition metals and carbonaceous particles were also removed in the purified samples. While the metals in the insulating medium will manifest a Drude- like behavior, the nonmetals contained in the medium are not conductive. Between the two limits of conductivity, the resonance peak shifts from dc to higher frequencies in a log scale figure.\textsuperscript{9,10} The increase in conductivity shown by our purified sample continues up to 0.8 THz, while the maximum conductivity in the pristine sample is around 0.4 THz on a log scale, as shown in Fig. 2(c). The resonance peak shifts to higher frequencies because the purified sample contains less metals and carbonaceous particles than the pristine sample. The inset in Fig. 2(c) reflects a persistent decrease in the anisotropy. This suggests that the ac conductivity of the aligned SWCNT mat is dominantly governed by the electromagnetic interactions between the aligned nanotubes, i.e., the coupling between CNTs in the mat is enhanced with increasing frequency, thus increasing conductivity in the mat. We are investigating the possibility of reducing anisotropy in the ac conductivity using an additional polymer binder.

In summary, we applied noncontact THz-TDS to investigate the transport phenomena of anisotropically aligned SWCNT films prepared by simple mechanical squeezing using a bar coater. The power absorption shows maximum at parallel film orientation to the THz beam polarization, and reaches minimum for perpendicular orientation. The ac conductivity of the aligned films increases with increasing frequency, following the Maxwell–Garnett model. A persistent decrease in anisotropy with increasing frequency is explained by the electromagnetic wave interactions between CNTs in the mat. The decline in conductivity at the low frequency region is correlated to an effective medium of the CNTs in the mat. A more rigorous analysis of the conductivity with frequency dependence will be undertaken in future work.

This work was supported by Korea Research Foundation Grant No. KRF-2000-015-DP0163.