TEMPERATURE-DEPENDENT TIME-DOMAIN TERAHERTZ SPECTROSCOPY OF HIGHLY ALIGNED SINGLE-WALLED CARBON NANOTUBES

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Using time-domain terahertz spectroscopy (TD-TS), the radiation absorption tendencies of highly-aligned, length-controlled single-walled carbon nanotubes (SWNTs) were studied in the far-infrared range (at frequencies between 0.3 and 4.5 THz). TD-TS is extremely valuable due to its ability to provide time-resolved amplitude and phase information from the electric field transmitted through the sample. From this data, the frequency dependence of a number of parameters, including refractive index, dielectric constant, and complex conductivity of a sample may be derived and analyzed, yielding a great deal of information about the carrier dynamics of the sample. Previous studies of carbon nanotubes in the THz range have attempted to analyze their data through the classical Drude model. However, a characteristic non-Drude peak at 4.0 THz was repeatedly verified, and its origin has not been understood. To analyze the mechanism responsible for this peak, we studied the THz wave absorption characteristics of the SWNTs using TD-TS at a wide range of temperatures (from 40 to 300 K) and alignments of the SWNTs with respect to the THz electric field polarization (from 0 to 90˚). The absorption tendencies of the SWNTs were found to be highly anisotropic, with strong absorption when the axis alignment was parallel to the polarization direction, and no absorption when the SWNT alignment was perpendicular to the THz polarization. The strength of the 4.0 THz peak was also found to be also highly dependent on the angle between SWNT alignment and THz field polarization, with the peak at its strongest with the parallel oriented SWNTs, and nonexistent in the perpendicularly oriented SWNTs. Surprisingly, the 4 THz peak was rather stable as a function of temperature, both in intensity and spectral position, which exclude some of the proposed explanations for its origin.

Temperature Dependent Time-Domain Terahertz Spectroscopy of Highly Aligned Single-Walled Carbon Nanotubes

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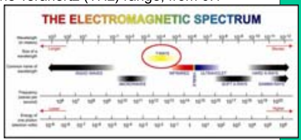
Background

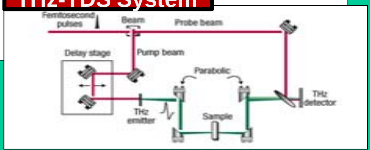
➢Terahertz spectroscopy takes advantage of the many quantum excitations in the Terahertz (THz) range, from 0.1-10 THz, to characterize semiconductor carrier properties.



➢The newest THz probing technique is Time-Domain Terahertz Spectroscopy (TD-TS). In TD-TS, the electric field transmitted through the sample is measured coherently, allowing calculation of the sample's effect on both the amplitude and phase shift of the original polarized THz wave.

➢From the transmission coefficients measured, the frequency dependent complex values of a sample's dielectric constant, refractive index, and conductivity may be precisely obtained

THz-TDS System



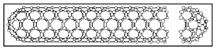
Carbon Nanotubes

➢Single-Wall Carbon Nanotubes (SWNTs) display two striking optical features in the THz range:
1) Extremely anisotropic radiation absorption[1]
2) Unexplained non-Drude absorption peak at 4.0 THz

➢ While the first feature is primarily due to the 1-D quantum SWNT structure, there are two proposed explanations for the absorption peak:

1) Interband absorption in semi-metallic, small gap SWNTs
2) Plasmon excitation along the SWNT axis.

➢ If SWNTS do indeed show plasmon resonance at THz frequencies, SWNTs would have very great potential as THz radiation emitters and sensors.



1. L. Ren, C. L. Pint, L. G. Booshehri, W. D. Rice, X. Wang, D. J. Hilton, K. Takeya, I. Kawayama, M. Tonouchi, R. H. Hauge, and J. Kono, "Carbon Nanotube Terahertz Polarizer," *Nano Letters* **9**, 2610 (2009).

Project Goals

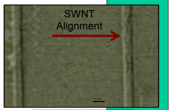
➢Use TD-TS to study and confirm the validity of the reported non-Drude 4.0 THz absorption peak using highly aligned, length controlled SWNTs.

➢Test temperature dependence of both peak location and intensity to gain insight into the mechanism behind Drude model deviation

➢Explore temperature dependence of the THz absorption anisotropy displayed by highly aligned SWNTs.

Methods

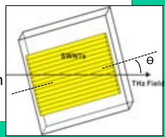
➢ SWNT samples were grown using a Fe-based CVD process onto a vertically patterned SiO_2 wafer to maintain high alignment. Samples were then transferred to a sapphire substrate using high-temperature H_2O etching, allowing a great degree of length control.



SWNT sample displays extremely high alignment with controlled length of 45 µm, as shown by optical microscopy

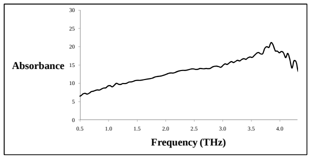
➢Each sample was tested at temperatures ranging from 40-300K .
➢At each temperature, a minimum of 3 tests were averaged to create the TD waveform.
➢TD waveforms were converted into the frequency domain using a fast Fourier transform (FFT).

➢ After each round of testing, samples were rotated so that the SWNTs' alignment axis formed angles ranging from 0˚ to 90˚ with the THz field polarization direction.



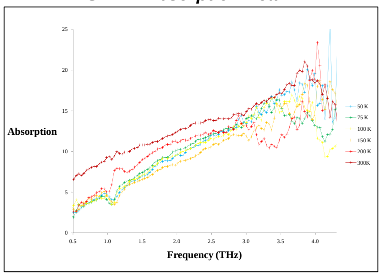
Results

0˚ Aligned SWNT THz Absorbance at 300K



➢ An absorption peak at 4.0 THz was consistently observed for SWNT samples.
➢ The validity of this peak was tested using 3 methods:
   1) Dynamic range analysis of absorption data
   2) Phase shift stability analysis
   3) Statistical system precision analysis
➢ Each analysis tool used indicated that data between 0.5 and 4.3 THz could be considered valid.

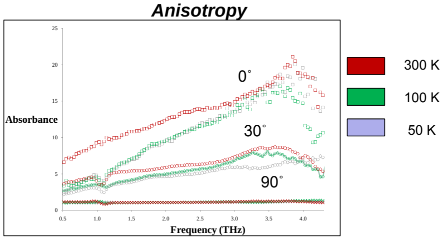
Temperature Dependence of 0˚ Aligned SWNT Absorption Peak



➢ Temperature dependence of data is weak and inconclusive.

Results Contd.

Temperature Dependence of SWNT Absorption Anisotropy



➢Temperature effects are negligible compared to anisotropy effects.
➢The intensity of the 4.0 THz absorption peak is strongly dependent on the polarization angle.

Conclusions

➢SWNT sample displayed a characteristic non-Drude absorption peak at 4.0 THz that was repeatedly confirmed and verified using several methods.

➢Lack of strong temperature dependence indicates that interband absorption is not likely to be the cause of the peak, rendering plasmon oscillation the most probable explanation.

➢Lack of peak position dependence on temperature may be due to adsorbed donors occupying the conduction band

➢Extremely anisotropic SWNT THz absorption effects are relatively independent of temperature

➢4.0 THz peak intensity is also shown to be heavily anisotropic.

Further Work

➢Annealed samples may be tested in the same manner, to check the possibility of donors causing temperature independence of absorption tendencies.

➢Length dependent TD-TS study of SWNTs will be necessary for confirmation of THz-frequency plasmon excitation.

➢After confirmation of THz-frequency plasmon oscillation, studies using SWNTs as THz emitters and sensors may begin.

➢TD-TS testing should be extended to graphene to test its optical properties in a similar manner.

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