



## Absorption spectra of high purity metallic and semiconducting single-walled carbon nanotube thin films in a wide energy region

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### ABSTRACT

Absorption spectra of high purity metallic and semiconducting single-walled carbon nanotubes separated by the density-gradient ultracentrifugation method have been measured in the wide energy region from 1 meV to 5 eV. In the high purity metallic nanotube sample, a strong and broad absorption band has been observed at 0.06 eV. This observation suggests that the optical properties of even high purity metallic nanotube bundles cannot be explained by the simple Drude conduction model. We discuss the origin of these absorption bands for metallic and semiconducting nanotube samples by considering the existence of a small energy gap in metallic nanotube bundles and plasmon resonance.

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## 1. Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs), considerable research effort has been expended in investigating their optical and dielectric properties from the viewpoint of both basic research and device applications. As-produced SWNTs always contain both metallic and semiconducting SWNTs. In order to use SWNTs in devices such as field-effect transistors, it is necessary to separate and purify the metallic and semiconducting SWNTs. Recently, by using the density-gradient ultracentrifugation method, we obtained high purity metallic and semiconducting SWNTs [1].

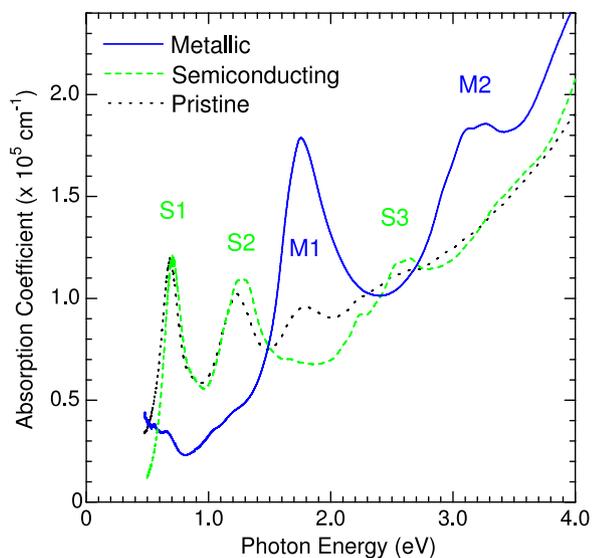
The dielectric and optical properties of SWNT films have been studied by several researchers [2–5]. The real part of the conductivity increases with frequency up to 0.8 THz [2] and shows a peak at around 0.02 eV [4]. These results are explained not by the simple Drude conduction model, but by the Maxwell–Garnett model; in the latter model, metallic SWNTs are embedded in semiconducting SWNTs, which are regarded as a dielectric host. On the other hand, experimental results on the temperature dependence of the absorption spectra [3] and results of pump-probe measurement [5] in the far-infrared

region suggest that the far-infrared absorption band is due to interband transitions in the nanotubes. However, in the previous works, metallic and semiconducting SWNTs were mixed, and therefore the intrinsic electronic structures of high purity metallic and semiconducting SWNTs, i.e., SWNT crystals, were not brought out. Using well-separated SWNTs, we can investigate the intrinsic optical properties of metallic and semiconducting SWNTs, especially in the infrared and terahertz (THz) energy region. In this study, we measured absorption spectra of high purity metallic and semiconducting SWNT thin films in a wide energy region (from THz to UV).

## 2. Samples and experimental

The high purity metallic and semiconducting SWNT thin films were prepared by using the density-gradient ultracentrifugation (DGU) method [1]. The surfactant and other contamination were carefully removed, as described in previous work [6]. No oxygen and iodine signals from surfactants and other molecules used in DGU were detected within the experimental limit of 0.5% by X-ray photoelectron spectroscopy (XPS) measurement [7]. For optical measurements, purified SWNTs were placed on quartz or Si substrates. The thickness of the SWNT thin films was about 300 nm. In these thin film samples, SWNTs are bundled, as confirmed by X-ray diffraction [6]. The diameter of the bundle was about 5 nm.

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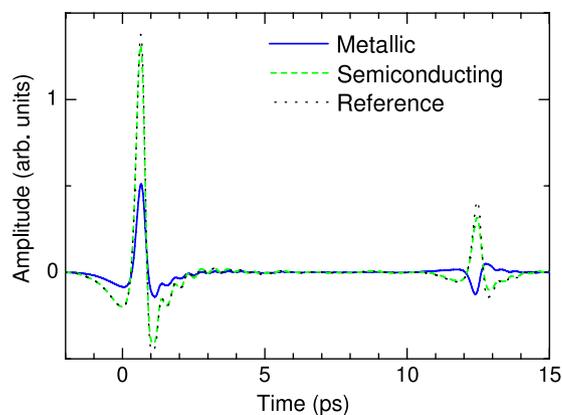
**Fig. 1.** (Color online) Near-infrared and visible absorption spectra of pristine (dotted black curve), high purity semiconducting (broken green curve), and metallic (solid blue curve) SWNT thin films.

Absorption spectra were measured by UV–visible spectrometry, Fourier transform infrared (FT-IR) spectroscopy, and THz time domain spectroscopy.

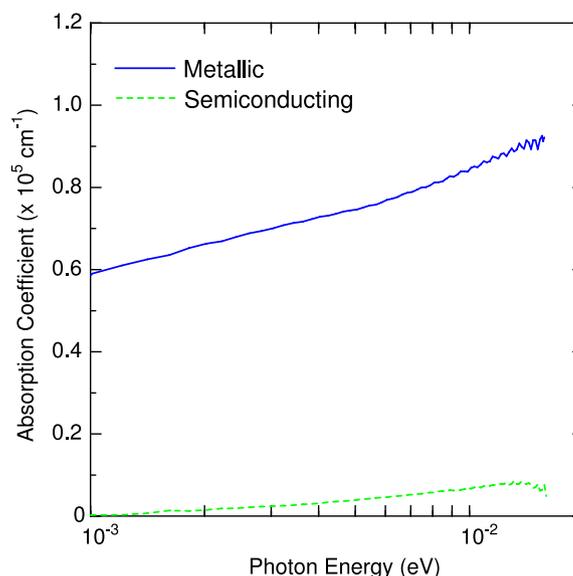
The dotted curve in Fig. 1 shows the near-infrared and visible absorption spectra of pristine SWNT thin films. Broad absorption bands are observed at 0.70 eV (S1), 1.24 eV (S2), and 1.77 eV (M1). The S1 and S2 bands are attributed to an optical transition in the semiconducting SWNTs, while the M1 band is due to the metallic SWNTs. The mean tube diameter estimated from the absorption spectrum is about 1.4 nm. As seen in the absorption spectrum, both metallic and semiconducting SWNTs are present in the pristine SWNT sample. Solid and broken curves denote the absorption spectra of high purity metallic and semiconducting SWNTs, respectively. In the case of the high purity metallic SWNT sample (solid curve), both the M1 band and M2 bands can be observed at about 3.20 eV, which corresponds to the optical transition between the second valence and conduction bands. The S1 and S2 bands cannot be observed in this sample. In addition to the M1 and M2 bands, an absorption increase is observed below 0.5 eV. In the absorption spectrum of the high purity semiconducting SWNTs (broken curve), S1, S2, and the higher energy transition S3 at about 2.5 eV can be observed, and metallic bands, i.e., the M1 and M2 bands, cannot be observed. From these absorption spectra of the high purity samples, we can estimate the purity of both the metallic and semiconducting SWNT samples. The estimated purities are higher than 95%.

### 3. Results and discussion

Fig. 2 shows the transmitted THz waveforms of the metallic (solid curve) and semiconducting (broken curve) SWNTs films and the reference quartz substrate (dotted curve). The signals around 12 ps result from reflections at the boundary between the sample and vacuum. Comparing the reflected signals for the reference substrate and the sample films, the phase of the reflected signal for the metallic SWNTs sample is opposite to that for the other signals. This shows that the sample has a metallic nature. The transmitted amplitude in the case of the metallic SWNT sample is much smaller than that in the case of the semiconducting SWNTs sample. This result indicates that the absorption in the case of the metallic SWNTs sample is much larger compared to the case of the semiconducting SWNTs sample. Using the transmitted waveforms



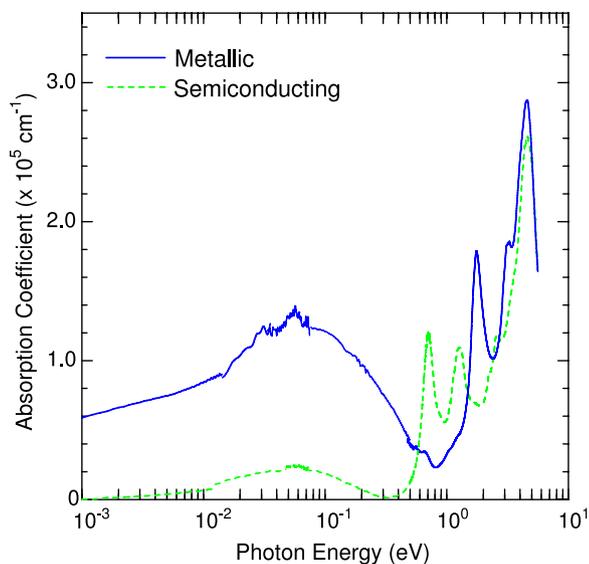
**Fig. 2.** (Color online) Transmitted THz waveforms of metallic (solid blue curve) and semiconducting (broken green curve) SWNTs and the reference substrate (dotted black curve). The signals around 12 ps correspond to reflections in the samples.



**Fig. 3.** (Color online) Absorption spectra of metallic (solid blue curve) and semiconducting (broken green curve) SWNT films in THz energy region.

of the SWNT samples and reference substrate, we can obtain the absorption spectra in the THz region. Fig. 3 shows the absorption spectra of metallic (solid curve) and semiconducting (broken curve) SWNTs. The spectra are normalized by the film thickness. The semiconducting SWNT film is almost transparent in the THz energy region. On the other hand, in the case of the metallic SWNT film, the absorbance increases with the frequency. The shape of the absorbance spectra of metallic materials usually conforms to the simple Drude theory. According to the theory, the absorbance is expected to show a maximum in the dc region, and it decreases with an increase in the frequency. However, the observed spectra show the opposite behavior. A similar behavior has been reported for unseparated SWNT samples [3–5]. The dielectric properties have been explained by considering particle plasmon resonance, i.e., the Maxwell–Garnett model [8]. In the previous studies, metallic SWNTs were surrounded by semiconducting SWNTs, which can be regarded as an effective dielectric medium. The electrodynamic response of such an effective medium cannot be described by the simple Drude model; however, they can be described by the Maxwell–Garnett model. Further, the non-Drude behavior of our high purity metallic SWNTs cannot be ascribed to the existence of semiconducting SWNTs.

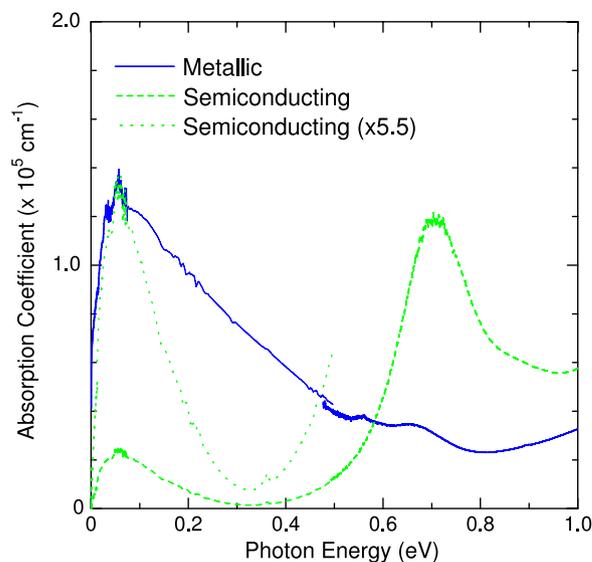
Fig. 4 shows the absorption spectra of the metallic and semiconducting SWNT thin films on a log-energy scale. In the



**Fig. 4.** (Color online) Absorption spectra from the THz region to the ultraviolet region for metallic (solid blue curve) and semiconducting (broken green curve) SWNT films on a log-energy scale.

spectrum of metallic SWNTs, there is a broad absorption band in the 0.02–0.2 eV region. In our high purity metallic SWNTs sample, the metallic SWNTs form a bundle. Furthermore, because the sample does not contain any residual molecules used in the separation processes [7], a metallic SWNT is not surrounded by any dielectric media. Thus it is difficult to understand this broad absorption band by using the Maxwell–Garnett model. Simple theoretical studies predict that only the “armchair” SWNT is truly metallic and that other “metallic” SWNTs have a small energy gap [9–11]. The energy gap in non-armchair “metallic” SWNTs with a tube diameter of 1.4 nm is estimated to be about 0.05 eV [10]. Other theoretical studies suggest that the bundled metallic SWNTs have a small pseudo energy gap [12]. This energy gap is about 0.2 eV. Thus, our experimental result is consistent with theoretical predictions. We need to consider another possibility of the origin of this absorption band for the metallic SWNT sample. In this sample, the metallic SWNTs are bundled, and the diameter of the bundle is about 5 nm; it contains about 15 nanotubes with tube diameter of 1.4 nm. Thus, in the air, the metallic SWNT samples can be regarded as a composite of a metallic SWNT bundle and air, which may show plasmon resonance like a metallic particle in a dielectric medium. We cannot exclude this possibility and we need further investigation to determine the origin of this absorption band. The temperature dependence of the absorption spectra is one of such methods to discuss the origin of absorption band. Although we have not measured the temperature dependence of the absorption spectra, Kampfrath et al. reported the temperature dependence of this band for a pristine (mixture of semiconducting and metallic) SWNT sample. They explained the weak temperature dependence by a simple model based on an ensemble of two-level systems [5]. This suggests that the small energy gap in the metallic SWNT bundle sample may be more appropriate as the origin of the absorption band in the 0.02–0.2 eV region.

It is worth mentioning the origin of the absorption band observed at around 0.06 eV in the high purity semiconducting SWNT sample. The IR absorption peak energy for both metallic and semiconducting SWNT samples is about 0.06 eV. From the absorption spectra in the visible region, the residual metallic SWNTs in the semiconducting SWNT sample constitute less than 5% of the sample. The peak coefficients for metallic and semiconducting SWNT samples are  $1.3 \times 10^5 \text{ cm}^{-1}$  and



**Fig. 5.** (Color online) Absorption spectra for metallic (solid blue curve) and semiconducting (broken green curve) SWNT films in the expanded energy scale. The dotted green curve shows the magnified spectra to compare the spectral shape of metallic and semiconducting SWNT samples.

$0.23 \times 10^5 \text{ cm}^{-1}$ , respectively. If the observed absorption band in the semiconducting SWNT sample originates from the residual metallic SWNTs in the semiconducting SWNT sample, the absorption coefficient should be less than  $0.065 \times 10^5 \text{ cm}^{-1}$ . Fig. 5 shows the absorption spectra of metallic and semiconducting SWNT samples to compare the spectral shape in the IR absorption bands. Although the absorption peaks for both samples are similar, the overall spectral shapes of these absorption bands are different, especially in the higher energy region. The existence of midgap states due to defects in SWNTs has been reported theoretically [13–15] and experimentally [16,17]. For example, both point defects such as Stone–Wales defects [13] or vacancies [14,16] and line defects [15] form midgap states near the Fermi level. Such defect states are considered to be possible origins of observed absorption bands in the semiconducting SWNT sample. Another possibility is the plasmon resonance of the residual metallic SWNT tubes in the high purity semiconducting SWNT sample. The residual metallic SWNTs are embedded in semiconducting SWNTs, which are regarded as a dielectric host. If the origin of the 0.06 eV absorption band in the semiconducting SWNT sample is the plasmon resonance, the IR absorption band observed for the metallic SWNT sample should not originate from the plasmon resonance, because the environments surrounding the metallic SWNTs in the high purity metallic and semiconducting SWNT samples are completely different, and this may lead to the different resonance energy.

#### 4. Conclusion

In summary, the absorption spectra of high purity metallic and semiconducting SWNT thin films have been measured in a wide energy region (from THz to UV). In the absorption spectrum of semiconducting SWNTs, there is weak absorption band below the S1 fundamental absorption band. In the case of high purity metallic SWNT samples, the absorption spectrum does not show Drude-like spectral shape; the absorbance increases with frequency up to 3.5 THz (0.015 eV) and shows a broad absorption band around 0.02–0.2 eV.

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## References

- [1] M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp, M.C. Hersam, *Nat. Nanotechnol.* 1 (2006) 60.
- [2] T.I. Jeon, K.J. Kim, C. Kang, S.J. Oh, J.H. Son, K.H. An, D.J. Bae, Y.H. Lee, *Appl. Phys. Lett.* 80 (2002) 3403.
- [3] A. Ugawa, A.G. Rinzler, D.B. Tanner, *Phys. Rev. B* 60 (1999) R11305.
- [4] N. Akima, Y. Iwasa, S. Brown, A.M. Barbour, J.B. Cao, J.L. Musfeldt, H. Matsui, N. Toyota, M. Shiraishi, H. Shimoda, O. Zhou, *Adv. Mater.* 18 (2006) 1166.
- [5] T. Kampfrath, K. von Volkman, C.M. Aguirre, P. Desjardins, R. Martel, M. Krenz, C. Frischkorn, M. Wolf, L. Perfetti, *Phys. Rev. Lett.* 101 (2008) 267403.
- [6] Y. Miyata, K. Yanagi, Y. Maniwa, T. Tanaka, H. Kataura, *J. Phys. Chem. C* 112 (2008) 15997.
- [7] P. Ayala, Y. Miyata, K. De Blauwe, H. Shiozawa, Y. Feng, K. Yanagi, C. Kramberger, S.R.P. Silva, R. Follath, H. Kataura, T. Pichler, *Phys. Rev. B* 80 (2009) 205427.
- [8] R.W. Cohen, G.D. Cody, M.D. Coutts, B. Abeles, *Phys. Rev. B* 8 (1973) 3689.
- [9] N. Hamada, S. Sawada, A. Oshiyama, *Phys. Rev. Lett.* 68 (1992) 1579.
- [10] C.L. Kane, E.J. Mele, *Phys. Rev. Lett.* 78 (1997) 1932.
- [11] Y. Akai, S. Saito, *Physica E* 29 (2005) 555.
- [12] Y.K. Kwon, S. Saito, D. Tomanek, *Phys. Rev. B* 58 (1998) R13314.
- [13] V.H. Crespi, M.L. Cohen, A. Rubio, *Phys. Rev. Lett.* 79 (1997) 2093.
- [14] A.J. Lu, B.C. Pan, *Phys. Rev. Lett.* 92 (2004) 105504.
- [15] M.U. Kahaly, S.P. Singh, U.V. Waghmare, *Small* 4 (2008) 2209.
- [16] S. Lee, G. Kim, H. Kim, B.-Y. Choi, J. Lee, B.W. Jeong, J. Ihm, Y. Kuk, S.-J. Kahng, *Phys. Rev. Lett.* 95 (2005) 166402.
- [17] K. Iakoubovskii, N. Minami, Y. Kim, K. Miyashita, S. Kazaoui, B. Nalini, *Appl. Phys. Lett.* 89 (2006) 173108.