Optical Absorption Properties of Single-Walled Carbon Nanotubes*

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1. Introduction

Single-walled carbon nanotubes (SWNTs) are 1 dimensional (1D) tubular material with sp^2 bonded graphene wall. Their unique geometry gives rise to sharp divergences in electronic density of states and consequently leads to characteristic discrete energy subbands. Since these inter-subband energy corresponds to near infrared (NIR) to visible (vis) range, many innovative optical application of SWNTs have been proposed thus far. The 1D geometry of SWNTs would be highly advantages for polarization-sensitive optical devices, provided their anisotropic optical absorption properties were appropriately understood.

So far, quite few studies have investigated anisotropic optical absorption of SWNTs. Previous studies were done on weakly aligned SWNT films prepared by dispersing SWNTs in gel [1] or polymer matrices [2]. However, the measured range was limited only below 3.5 eV because of ultra-violet (UV) absorption of the employed matrix. Therefore, the well-known remarkable UV absorption of SWNTs, which forms absorption baselines in vis-NIR region, has not been examined deeply and thus not clarified well. In this study, using our vertically aligned SWNT (VA-SWNT) film directly grown a quartz substrate, we have elucidated polarization dependent optical absorption properties of SWNTs for wide energy range of 0.5 - 6 eV and explained origin of the remarkable UV absorption of SWNTs [3].

2. Experimental procedure

Co-Mo bimetallic catalyst is supported on an optically polished quartz substrate by dip-coating method [4,5]. Using the alcohol CCVD method [6,7], a VA-SWNT film is directly grown on the substrate [8,9]. Optical absorption of the VA-SWNT film is measured by NIR-vis-UV spectrophotometer equipped with a rotatable substrate holder and a polarizer. We defined *s*- (*p*-) polarization so that incident electric vector is parallel (perpendicular) to rotation axis of the substrate.

3. Result and Discussion

Inset of Fig. 1 shows an FE-SEM image of the VA-SWNT film that was measured in this study. From HR-TEM measurement, it has been found that average diameter and its standard deviation are ~ 2.0 nm and ~ 0.4 nm, respectively [10]. Raman scattering spectra of the sample exhibits sufficiently high quality [8] and anisotropy [11]. Figure 1 shows optical absorption spectrum measured from $\theta = 0°$ to 45° at a step of 7.5°. The spectrum is nearly the same regardless of θ in case of *s*-polarization while the spectrum is dependent on θ in case of *p*-polarization, which is confirmed by the multiple-dipole model for VA-SWNT film [10]. This result shows that, not only inter-subband absorption below 2.5 eV, but also the remarkable UV absorptions at ~ 4.5 and 5.25 eV exhibits remarkable and different dependencies on the incident light polarization.

Component of these UV absorption peaks have actually been seen in past optical absorption or electron

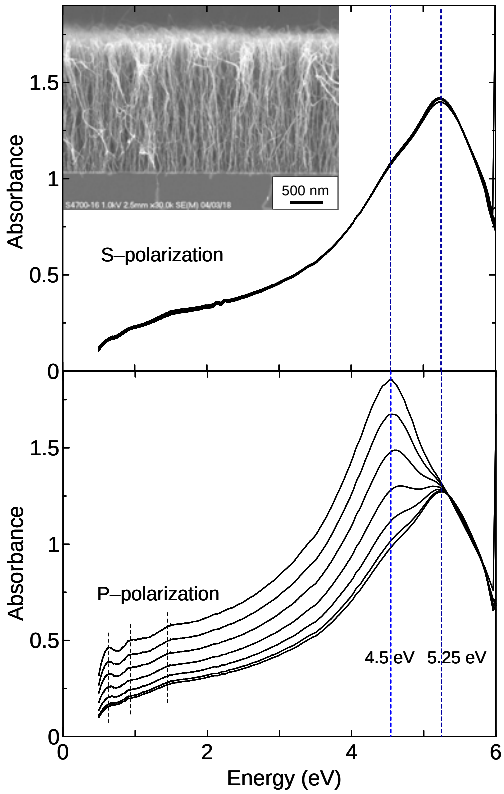

Fig. 1. Absorption spectra of a VA-SWNT film. Incident angle θ was varied from 0° to 45° at a step of 7.5°. Polarizations are '*s*' (upper panel) and '*p*' (lower panel) to the substrate plane. Inset shows a cross-sectional FE-SEM image of the measured SWNT film.

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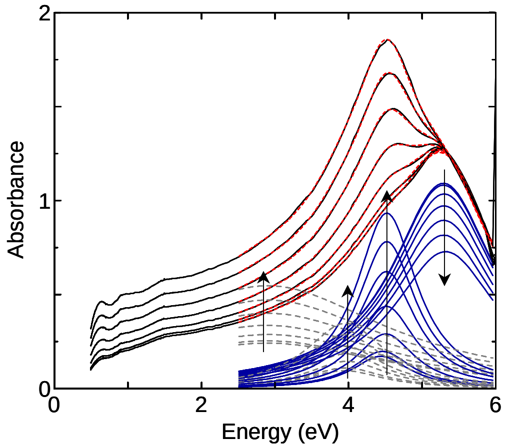

Fig. 2. Fitting of absorption spectra by four Lorentzian curves. Arrows indicate the change of each curve as θ changes from 0° to 45°. Red dotted lines represent the sum of the four curves.

energy loss spectroscopy (EELS) studies performed on randomly oriented SWNT films, however, considerable discrepancies have been seen in their discussions. Since energies of these peaks are almost independent of synthesis method and diameter of the sample, it is deduced that they are originating from optical properties of graphite and that these correspond to maxima of Im{$\varepsilon_\perp$} in the direction parallel to SWNT axis and Im{-$\varepsilon_{\|}^{-1}$} in perpendicular to SWNTs axis, respectively.

Based on such findings, it has become possible to evaluate physical degree of alignment, or *nematic order parameter* (S), of the SWNT film [10]. In the present case, the polarization dependence of only one dipole has to be extracted in order to calculate S. For this purpose, the spectra shown in Fig. 1 were decomposed into 4 Lorentzian curves whose positions were given based on the experimental result shown in Ref. 12. Figure 2 shows the result of Lorentz decomposition of measured spectra. The dependence of ~ 4.5 eV peak height on θ is plotted in Fig. 3a, from which S is calculated to be ~ 0.74.

Furthermore, using thereby obtained S and spectra shown in Fig. 1, bare optical absorption cross section of SWNT for each light polarization $\sigma_{\|}$ and $\sigma_\perp$ has been determined as shown in Fig. 3b. This result indicates that that even inter-subband absorption region below 3 eV there exists small but meaningful $\sigma_\perp$ that is contributed by π plasmon excitation at ~ 5.25 eV.

4. Conclusion

In summary, we have determined anisotropic optical absorption properties of SWNTs for 0.5 - 6 eV, from the measurements on our VA-SWNT film grown on a quartz substrate. It was revealed that the absorption features of SWNTs located at ~ 4.5 and 5.25 eV have remarkable and different dependencies on incident light polarization. Due to the fact that these absorption peaks were observed at almost the same positions regardless of

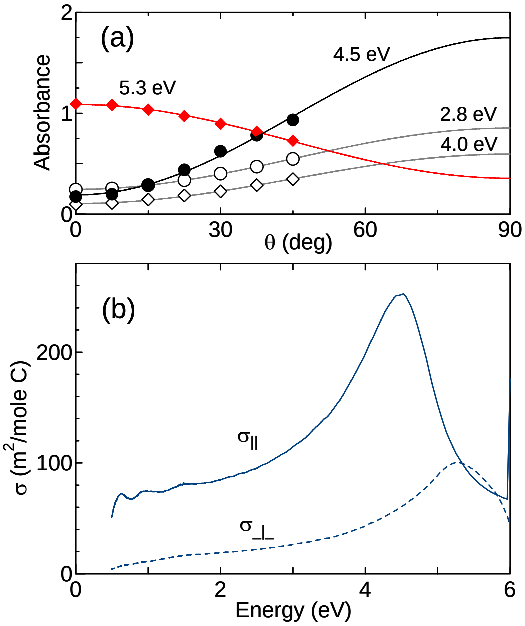

Fig. 3. (a) Dependence of each Lorentzian amplitude on θ. Curves fitted by $\sin^2\theta$ and $\cos^2\theta$ are also shown. (b) Calculated bare optical cross-sections parallel ($\sigma_{\|}$) and perpendicular to ($\sigma_\perp$) the SWNT axis.

SWNT diameter and/or preparation method, they are reasonably attributed to the maxima in Im{$\varepsilon_\perp$} (~ 4.5 eV) and Im{-$\varepsilon_{\|}^{-1}$} (~ 5.25 eV), that are originating from optical properties of graphite. These results imply an important possibility of investigating unresolved optical properties of graphite in the direction parallel to the *c*-axis by optical absorption measurements of aligned SWNT films.

Reference

[1] M. F. Islam, et al., *Phys. Rev. Lett.* **93** (2004) 037404.
[2] M. Ichida et al., *Appl. Phys. A* **78** (2004) 1117.
[3] Y. Murakami et. al., *Phys. Rev. Lett.* **94** (2005) 087402.
[4] Y. Murakami et. al., *Chem. Phys. Lett.* **377** (2003) 49.
[5] Y. Murakami et. al., *Jpn. J. Appl. Phys.* **43** (2004) 1221.
[6] S. Maruyama et. al., *Chem. Phys. Lett.* **360** (2002) 229.
[7] Y. Murakami et. al., *Chem. Phys. Lett.* **374** (2003) 53.
[8] Y. Murakami et. al., *Chem. Phys. Lett.* **385** (2004) 298.
[9] S. Maruyama et. al., *Chem. Phys. Lett.* **403** (2005) 320.
[10] Y. Murakami et. al., *Carbon*, in press.
[11] Y. Murakami et. al., *Phys. Rev. B* **71** (2005) 085403.
[12] H. Lee et al., *Jpn. J. Appl. Phys.* **42** (2003) 5880.