Optical Properties of Hydrogen- and Fluorine-Doped Single-Walled Carbon Nanotubes

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We measured the reflectivities of various single-walled carbon nanotubes (SWCNTs) by using integrated spheres in the spectral range between 0.5 eV and 6.0 eV. The SWCNTs were made using an arc-discharge method with yttrium as a catalyst and were purified using a standard procedure. The SWCNTs were doped either by atomic hydrogen or fluorine gas for functionalization. We directly fitted the reflectivity spectra to the Drude-Lorentz equation without using Kramers-Kronig transformation. Combining the reflectivity and the resonance Raman data, we assigned chiral indices \((n, m)\) to the optical structures in the reflectivity spectra. We discuss the modifications of the various optical structures found in the SWNTs after postgrowth treatments of hydrogen and fluorine functionalization. This optical study shows that a reflectivity measurement can resolve the chiral indices and the diameters of SWNTs with the assistance of Raman spectroscopy. We observed an increase in the \(\pi\)-plasmon energy of F-doped and H-doped SWCNTs compared to that of the purified ones. We observed a weakening of van Hove singularity transitions in fluorinated SWCNTs and a large enhancement of the intensities of the \(S_{11}\) peaks in hydrogenated ones. For hydrogenated SWCNTs, we also measured and discuss the infrared absorption spectra, which show the incorporation of hydrogen to SWNTs.

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I. INTRODUCTION

Carbon nanotubes (CNTs) are very interesting nano-materials in terms of basic science and applied engineering. Single-walled carbon nanotubes (SWCNTs) are very promising in applications such as field emission displays, nanoelectronics, hydrogen storage, and nanocomposites [1–3]. The SWCNTs are considered to be a quasi-one-dimensional (1D) system because of the high aspect ratio of length to diameter. The characteristic Van Hove singularities arise from the quantized motion of electrons along the circumferential direction and have been verified experimentally and theoretically. To investigate the electronic properties, various methods have been used, such as photoluminescence, resonant Raman spectroscopy, electron energy loss spectroscopy, optical absorption, and reflectivity [4–8]. Among them, optical absorption and reflectivity are excellent methods to investigate the electronic structures of SWCNTs in the form of a thin film on a substrate. For example, Itkis et al. used near-infrared (NIR) reflectivity to investigate the electronic structures of SWCNTs near the Fermi level [7]. In particular, the reflectivity spectra can be used to investigate an opaque sample in the ultra-violet region, which is inaccessible with the optical absorption method.

A Kramers-Kronig (KK) transformation may be used to fit the dielectric function from the measured reflectivity. However, the dielectric function estimated by means of the KK transformation is not accurate near the boundary of the spectral range. Another method is direct fitting, where the dielectric function is fitted from the reflectivity spectra by assuming an appropriate line-shape formula for the dielectric function. Assuming an
ambient-substrate interface, the reflectance ($r$) is given by $(n + ik - 1)/(n + ik + 1)$. Note that the complex refractive index $(n + ik)$ is the square root of the dielectric function ($\varepsilon$). This direct fitting method is free from the uncertainties of the boundary values of the dielectric functions KK-transformed from the reflectivity data [9].

Electronic excitations in SWCNTs can be explained in terms of various plasmon-like excitations. At very high energy, the $\pi$ and $\pi - \sigma$ plasmons occur near 6 eV and 23 eV, respectively. At intermediate energies, there are several excitations, each of which is related to a specific Van-Hove $\pi$-electron transition in the energy range between 0.5 to 4 eV. At very low energy, a propagating charge density wave can occur along the nanotube. The quasi-1D nature leads to an increase in exciton energy and binding energy due to an enhanced Coulomb effect with decreasing diameter for Van Hove transitions [10].

Functionalization of CNTs is a useful method to transform the electronic structure of CNTs and can be carried out by using a postgrowth process treatment of doping with hydrogen or fluorine. Hydrogenation of CNTs was shown to increase the energy gaps [11]. Fluorination of CNTs modifies the electronic structures to be metallic or semiconducting, depending on the coverage and the method of fluorination [12].

In the present work, we measured the reflectivities of various purified SWCNTs, which were subsequently doped with hydrogen (H) or fluorine (F). We performed Drude-Lorentz lineshape fitting to the reflectivity data and obtained the parameters for various excitations. Using reflectivity and resonance Raman data, we assigned chiral indexes $(n, m)$ to the peaks in the reflectivity data. We discuss the changes in the peak energies and intensities after postgrowth treatment. We measured the infrared absorption spectra of hydrogenated SWCNTs and compared the peak wave numbers with literature values.

II. EXPERIMENT

The SWCNTs were synthesized by using a dc arc-discharge method with nickel and yttrium as catalysts. The total amount of the catalysts in a graphite powder was fixed at 5 wt%. A purification was performed following the standard procedure [8]. The synthesized SWCNT powder was heated at 450 °C for 50 min in air to remove carbonaceous particles. In order to remove the catalysts, we immersed the annealed powder in 6-M hydrochloric acid for 24 hours. This process was repeated several times until the color of the acid was unchanged. The sample was then washed in deionized water several times. The carbon nanotubes were deposited on quartz glass with a thickness of several $\mu$m. Hence, the samples were opaque for the whole measurement range. After the purification, we hydrogenated or fluorinated the purified CNTs.

The hydrogenation of SWCNTs was carried out inside a vacuum chamber at a base pressure of $1.0 \times 10^{-9}$ Torr. Before hydrogenation, we annealed the purified SWCNTs at 1300 K for 30 min to remove carbonyl and hydroxyl functional groups, which had been accidentally attached during the purification process. The SWCNT powders were then exposed to atomic hydrogen, which was generated by using a hot tungsten filament at about 2500 K. The exposure continued for 24 hours at a hydrogen pressure of $5 \times 10^{-5}$ Torr.

Fluorination of the SWCNT powder was carried out in a fluorine reaction chamber made by Ni and SUS-316 in order to prevent erosion. The chamber was heated at 150 °C while purging by nitrogen gases at a chamber pressure of $10^{-2}$ Torr to remove the residual oxygen gases and moisture. $F_2$ gas was then introduced, and the pressure was maintained at 0.2 bar for 10 minutes at 150 °C. After the reaction, the chamber was pumped out again to $10^{-2}$ Torr and was refilled with nitrogen gas prior to extraction of the sample. The F/C ratio of these fluorinated SWNTs was determined to be 0.2 by using X-ray photoemission spectroscopy. [13]

We measured the reflectivity spectra of the various SWCNTs by using a spectrophotometer (JASCO model V-570) in the range of 190 – 2500 nm. We note that the purified, hydrogenated, and fluorinated CNTs originated from different pieces of the purified one. In order to include the scattering from the rough surface of the SWCNT films, we used an integrating sphere. We used a micro-Raman system (Renishaw invia basic) with an Ar$^+$ laser (excitation energy: 514.5 nm, 2.41 eV) and a notch filter with a cutoff wavenumber of 50 cm$^{-1}$ and micro-Raman system (Renishaw 1000) with Ar$^+$ laser (excitation energy: 785 nm, 1.58 eV) and a He-Ne laser (excitation energy: 632.8 nm, 1.96 eV) and an interference notch filter with a cutoff wave number of 50 cm$^{-1}$. We also used a FT-Raman spectrometer (Bruker IFS-66/S) with a Nd-YAG laser (excitation energy: 1064 nm, 1.17 eV) and a Rayleigh line rejection filter with a spectral range of 50 – 3600 cm$^{-1}$, for the Stokes shift. If the absolute reflectivity from the intrinsic properties of the CNTs is to be estimated, the loss of reflectivity due to scattering from rough surfaces should be taken into account. In this work, we adopted an integrating sphere method. Normalization of the reflectivity against gold-coated carbon nanotube films is another useful method to estimate the intrinsic reflectivity of CNTs [14]. However, the gold coating may affect the hydrogenation or the fluorination due to bombardment of the thin films with gold atoms. Therefore, we did not measure the reflectivity of gold-coated CNTs.

III. RESULTS AND DISCUSSION

Figure 1 shows the radial breathing modes (RBMs) of the Raman spectra for the purified SWCNTs in the spectral range between 100 cm$^{-1}$ and 250 cm$^{-1}$ for various
laser excitation energies. The one-dimensional nature of the nanotubes with small diameters induces resonant Raman spectra. The sample contains nanotubes with different diameters and chiralities. The energy gaps between the subbands of the valence band and the conduction band depend on the diameters and the chiralities. The nanotubes are excited whenever the laser excitation energy is in resonance with the energy gaps. The RBM is inversely proportional to the diameter,

$$\omega(\text{cm}^{-1}) = \frac{239}{d(\text{nm})} + 8.5$$

for bundles [15, 16]. Once we obtained the diameters via this empirical formula, we were able to assign either the metallic or semiconducting nature of the nanotubes from Kataura plots [17]. The tube diameter can be calculated as

$$d(n, m) = \frac{a \pi}{\sqrt{n^2 + m^2 + nm}}$$

where (n,m) is the index vector and a = 0.246 nm is the lattice constant of graphite [18]. The energy gaps, $E_{ii}$ (i = 1,2,3), vary with the chirality and the diameter. The nanotubes are excited in the phonon spectra when the laser energies are in resonance with the energy gaps $E_{ii}$. If the tight-binding approximation is used, $E_{ii}$ can be modeled as a function of diameter [18]:

$$E_{11}(S) = \gamma_0 a/d$$
$$E_{22}(S) = 2\gamma_0 a/d$$
$$E_{33}(S) = 3\gamma_0 a/d$$

where $\gamma_0$ is a tight-binding overlap interaction parameter with an assumed value of 2.9 eV.

Figure 2 shows the reflectivity spectra of (a) purified, H-doped, and F-doped SWCNTs in the spectral range between 0.5 eV and 6.0 eV, and (b) enlarged plots in the near-infrared region, 0.5 – 2 eV. In Fig. 2(a), the peak energy of the $\pi$-band plasmon is increased, particularly in the H- and F-doped SWCNTs. We can also see a drastic increase of the reflectivity in the H-doped SWCNT compared to that in the purified SWCNT. The F-doped SWCNTs show comparable reflectivity intensity to that of the purified SWCNT whereas the peaks due to the Van Hove subband-to-subband (VHS) transitions were damped substantially.

We used the Drude-Lorentz equation to fit the optical structures of the plasmons in the measured reflectivity spectra. The Drude-Lorentz equation is a phenomenological equation and is a generalization of the Drude equation. The Drude-Lorentz equation incorporates collective excitations associated with interband transitions, as well as plasmon excitations associated with intraband transitions. The equation can be derived from the dipole oscillator model. The Drude-Lorentz equation is given by [6,19,20]

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau_D} + \sum_j \frac{A_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j}$$

where $\varepsilon_\infty$ is the high-frequency dielectric constant, $\omega_p (= \sqrt{ne^2/(m^*\varepsilon_0)})$ is the Drude plasma frequency, $\tau_D$ is the Drude lifetime, and $m^*$ is an optical effec-
tive mass. The second term is the contribution of the Drude plasmon (intraband transition). The third term is due to the various Lorentz oscillators (interband transition). The \( j \)-th oscillator has the following parameters: oscillator strength \( A_j \), center frequency \( \omega_j \), and damping constant \( \gamma_j \). The oscillator strength \( A_j \) may be expressed as the square of the plasma oscillator strength, \( \omega_{pj} = \sqrt{n_j e^2/(\varepsilon_0 m^*_j)} \) with \( n_j \) being the density of electrons of the \( j \)-th oscillator and \( m^*_j \) being their optical effective mass. The \( j \)-th plasma peak frequency is equal to \( \sqrt{\omega_j^2 + \omega_{pj}^2} \), which is the peak frequency of the plasmons in the spectra (\( \text{Im}(-1/\varepsilon(\omega)) \)) of electron energy loss spectroscopy \[21\].

In the case of VHS transitions we may neglect the plasmon-like characteristics because the transitions occur between discrete delta-like densities of states and because the oscillator strength \( A_j \) will be roughly proportional to the square of the interband transition matrix element between valence subbands and conduction subbands \[22\]. Therefore, the oscillator strength should also depend on the details of the band structures. For example, a disorder induced by dopants may affect the oscillator strength.

Figure 3 shows the reflectance spectra and their fits using Eq. (4) for (a) purified, (b) H-doped, and (c) F-doped in the near infrared range. The VHS transition peaks and the \( \pi \) to \( \pi^* \) plasmon peak were fit using Eq. (4). We also fitted the reflectivity in the visible-ultraviolet region, and the fit matched the raw data very well. (not shown here) In the near-infrared range, however, the fitting deviated slightly from the raw data near the peak energies. We attribute this to an enhanced exciton interaction due to a quasi-1D effect. \[10\]

Resonant Raman data suggested that the SWCNTs had several diameters: 1.33, 1.36, 1.39, 1.42, 1.48, 1.52, 1.53, 1.55, 1.64, 1.68, and 1.69 nm. Compared to the Kataura plot modified by Saito et al. \[18\], we can classify the metallicities of the RBM by using the resonance Raman energies \( E_R \) and the RBM wave numbers \( \nu_{RBM} \), as shown in Fig. 1. In order to determine the chiral indices \( (n, m) \), we also used the reflectivity peak energies \( E_{ii} \) in addition to \( E_R \) and \( \nu_{RBM} \). We compared the experimentally determined parameters with the calculated values from Eqs. (1), (2), and (3). We incorporated uncertainties in the \( E_R \) and \( E_{ii} \) as \( \pm 0.1 \) eV whereas that of \( \nu_{RBM} \) was assumed to be \( \pm 2 \) cm\(^{-1}\). Making tables of \( E_R, E_{ii}, \) and \( \nu_{RBM} \) as functions of chiral indices \((n, m)\) and comparing them to the experimental values within the uncertainties, we could determine the chiral indices \( (n, m) \). Thus, we assigned the peak energies in the reflectivity spectra as \( S_{11,a}(0.64 \text{ eV}), S_{11,b}(0.73 \text{ eV}), S_{22,a}(1.17 \text{ eV}), S_{22,b}(1.33 \text{ eV}), \) and \( M_{11,c}(1.72 \text{ eV}) \). \[13, 14\] Here, \( a, b, \) and \( c \) correspond to diameters (chirality) of 1.55 nm ((16, 6) or (12, 11)), 1.39 nm ((16, 3)), and 1.53 nm, ((14, 8)), respectively, and \( S (M) \) stands for semiconducting (metallic) transitions, and 11 (22) means the first (the second) \( \pi \) subband-to-\( \pi^* \) subband transition. The measured (calculated) main wave numbers \( \nu_{RBM} \) were 162.3 (163.5 or 161.7), 180.4 (181.0), and 165.2 (166.8) cm\(^{-1}\), respectively. No other diameters were observed in the reflectance spectra, suggesting that the populations of other tubes were below our detection limit. Therefore, reflectivity spectra can determine the SWCNTs with the most populous chiral indices, when used with resonance Raman data. For a summary, we refer to Table 1.

In the case of H-doped SWCNTs, the VHS peak energies were similar to those for the purified ones. However, we can see a large enhancement of \( S_{11} \) transitions in the spectrum of H-doped SWCNT compared to those in the spectrum of the purified one, as shown in Fig. 3. In
the case of F-doped SWCNTs, $S_{11}$ transitions were significantly damped, $S_{22}$ transitions were shifted to 1.40 eV, and $M_{11}$ transitions disappeared. Table 2 shows the center energy, the plasma oscillator strength, and the broadening of the $\pi$ band plasmon. The center energy of the plasmon increased significantly for F-doped SWCNTs. The center energy of H-doped plasmon increased about 0.1 eV compared to that of the purified one. The fitted gapless plasmon energies were 0.531 eV, 0.548 eV, and 0.645 eV for purified, H-doped, and F-doped SWCNTs, respectively, which suggests that the free carriers increase with F-doping.

The degradation of the VHS peaks in the F-doped SWCNT should be attributed to an increased disorder due to the formation of covalent sp$^3$ bonds. It appears that F doping significantly increases the energy separation between $\pi$ and $\pi^*$ bands, according to Table 2. Kazaoui et al. investigated the doping effects on the VHS transitions by using optical absorption and attributed the decrease in the VHS transition intensities to electron filling or depletion from specific bands. As dopants, they added Br$_2$ and I$_2$ as acceptors, and K and Cs as donors [23]. In the case of F-doping, a similar mechanism may also apply to the decreased VHS transition amplitudes. Structural disorder induced by F-doping was investigated by Lee et al. [13]. Plank et al. observed that SWCNTs gained more disordered sp$^3$ bonds with increasing fluorination [24].

In H doping, the Van Hove transitions were more pronounced with sharp peaks, and the Drude intensity, due to increased free electrons, increased significantly compared to those of the purified SWCNTs. This phenomenon could be attributed to H-passivation of dangling bonds and defects in the purified SWCNT, which is very well known in amorphous or polycrystalline silicon films. The enhanced $S_{11}/S_{22}$ peak intensity ratio in the H-doped SWCNTs compared to that in the purified ones is also attributed to H-passivation of dangling bonds and defects and to the transformation of sp$^3$ into sp$^2$ states in the purified SWCNTs. It has been suggested that an enhanced exciton interaction due to the quasi-1D effect will cause a blue shift of the VHS transition energies, especially for the $E_{11}$ transition, which is the lowest subband-to-subband transition ($v_1 \rightarrow c_1$) [10]. Performing transport experiments to a single SWCNT, Kim et al. reported that H functionalization of a single SWCNT grown by using chemical vapor deposition opened a band gap of 1.88 eV in metallic SWCNT and 4.4 eV from 0.8 eV in semiconducting SWCNT [11]. However, our reflectivity spectra for the H-doped SWCNT suggested no discernible increase in the band gaps.

The plasmon peak near 5 eV arises between the center of the $\pi$ states (bonding states) and the $\pi^*$ states (antibonding states) with an additional energy shift due to the plasma oscillator strength. This plasmon is typically found in a poly-carbon and graphite [25, 26]. In Table 2, the increase in the $\pi$ band plasmon peak energy in H-doped, and especially in F-doped SWCNTs is attributed to an increased separation between the centers of $\pi$ and $\pi^*$ bands.

Figure 4 shows the FTIR spectra of purified and hydrogenated SWCNTs. Figure 4(a) and (b) are the spectra of stretching modes and bending modes, respectively, of C-H bonding. In Fig. 4(b), the 1353 cm$^{-1}$ and 1438 cm$^{-1}$ peaks may be assigned to the bending modes of the C-H vibrations, which arose from functionalization
by H atom, according to Khare et al. [27]. We note that our peaks were red-shifted by about 30 cm$^{-1}$ compared to the values of 1382.5 and 1467.0 cm$^{-1}$ in their results. In the case of hydrogenated amorphous carbon films, using infrared absorption spectroscopy, Zvonareva and colleagues observed 1372 and 1436 cm$^{-1}$ peaks and assigned them to the sp$^3$ CH$_3$ symmetric mode and the sp$^3$ CH$_2$ (or sp$^3$ CH) mode, respectively [28]. Our peaks at 1532 and 1569 cm$^{-1}$ were assigned to the C=C double bond or the C=O bond in carbonyl group. The 1689 cm$^{-1}$ peak in Fig. 4 is of unknown origin. In Fig. 4(a), the 2844, 2912, and 2951 cm$^{-1}$ peaks are assigned to C-H stretching vibrations in the CH$_2$ and the CH$_3$ groups. Using infrared spectroscopic ellipsometry, Heitz et al. observed and assigned the CH bending modes as 1375 (symmetric sp$^3$ CH$_3$) and 1465 (asymmetric sp$^3$ CH$_3$) and stretching modes as 2847 (symmetric sp$^3$ CH$_2$), 2912 (sp$^3$ CH), and 2959 (asymmetric sp$^3$ CH$_3$) [29].

IV. CONCLUSION

We measured the reflectivities of various single-walled carbon nanotubes by using an integrated sphere in the spectral range between 0.5 and 6.0 eV. The SWCNTs were post-treated with either atomic hydrogen or fluorine gas. Our reflectivity spectra fitted the Drude-Lorentz model well. We discussed the changes in the Van-Hove-like transition energies and intensities in the SWCNTs after post-growth treatment. Particularly, by incorporating the RBM wave number, the Raman resonance energy, and the VHS energy of reflectivity, we could determine the chiral indices (n, m) and the diameters for major single-walled carbon nanotubes. We observed an increase in the π-plasmon energy of F-doped and H-doped SWCNTs compared to that of the purified ones. We observed a weakening of the VHS transitions in fluorinated SWCNTs, which may be due to sp$^3$ formation. The large enhanced intensities of the S$_{11}$ peaks in hydrogenated SWCNTs are attributed to H-passivation and to transformations from sp$^3$ to sp$^2$ states.

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