Ultrafast Relaxation Dynamics of Photoexcited Carriers in Metallic and Semiconducting Single-walled Carbon Nanotubes

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We have investigated carrier relaxation dynamics in both metallic and semiconducting single-walled carbon nanotubes by means of femtosecond pump-probe experiments. The femtosecond excitation pulse bleaches the absorption bands of both metallic and semiconducting tubes. In the metallic tubes, the change in the absorption spectra vary from bleaching to broadening. The relaxation aspects of the spectral features change from internal thermalization to electron temperature cooling. In the semiconductor tubes, the nonradiative channel governs the recovery behavior via trapping at defects in the SWNTs.

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1. Introduction

Depending on the helical arrangement, a single-walled carbon nanotube (SWNT) can be either a metal or a semiconductor. Since the electronic structure of a SWNT is quasi-one-dimensional (1D), a SWNT is a suitable system for studying carrier scattering and relaxation mechanisms in 1D metals and semiconductors. Since the discovery of SWNTs, especially metallic SWNTs, much effort has been devoted to studying the carrier scattering of these unique quasi-1D electronic structures. Many transport measurements have been made to investigate the scattering properties of electrons in the ground state.¹²) Recently, the carrier dynamics of excited states have been studied using time-domain photoelectron measurements,³⁴) and the electron-electron and electron-phonon scattering rates of photoexcited carriers have been evaluated. It is interesting to investigate how the optical spectra of metallic tubes change after photoexcitation.

Several studies have also investigated the carrier relaxation dynamics of semiconducting SWNTs. Chen et al. demonstrated that semiconducting SWNTs have an exciton decay time of less than 1 ps.⁵) Lauret et al. conducted femtosecond pump and probe experiments of SWNT films.⁵) They investigated the recovery dynamics of the nonlinear optical signal related to the interband transition and π-plasmon and observed the nonlinear spectral changes at several photon energies. Since the relaxation dynamics and processes appear as changes in the absorption over a wide spectral range, in order to discuss the physical origin of relaxation, we need to study the temporal evolution of the nonlinear optical spectral change using white continuum femtosecond pulses with a wide spectral range. Recently, Koroyvancock et al. made femtosecond two-color pump-probe measurements of semiconducting SWNTs.⁷) They observed the change in spectral absorption after femtosecond photo excitation and discussed the origin of the change with respect to state filling effects and induced absorption owing to the exciton transition. However, they did not discuss the diameter or temperature dependencies of the relaxation dynamics. Both dependencies are important for determining the origin of the relaxation of photoexcited carriers.

In a semiconducting SWNT, the strong Coulomb interaction between an electron and a hole produces the exciton transition in the fundamental absorption.⁶) Previously, we reported that there is a strong Coulomb correlation between an electron and a hole in the fundamental absorption in semiconducting SWNTs. Such a Coulomb interaction enhances the oscillator strength of the exciton state.⁶) This effect may increase the radiative recombination rate in the lowest photoexcited state (the exciton state) in a semiconducting SWNT. In fact, strong photoluminescence has recently been observed for semiconducting SWNTs in micelles.¹⁰) Conversely, in many cases, SWNT thin film samples, including our sample, do not show any photoluminescence, which suggests that non-radiative recombination is the main process in the relaxation dynamics. In such samples, the electron-phonon interaction and carrier trapping at defects may play significant roles in the relaxation dynamics as non-radiative transitions.

In this paper, we report the relaxation dynamics of photoexcited carriers in both semiconducting and metallic SWNTs using femtosecond transient absorption spectroscopy over a wide probing photon energy range. The relaxation behavior depends on the probing photon energy, which is related to the tube diameter. We discuss the relaxation dynamics of photoexcited carriers in terms of electron-phonon and electron-electron interactions, cooling of the hot electron temperature, and carrier trapping at defects, the incidence of which is related to the tube diameter.

2. Experimental

SWNTs were prepared using the laser vaporization...
method.\textsuperscript{11)} The mean tube diameter was about 1.22 nm, as determined using Raman spectroscopy.\textsuperscript{12)} Thin-film samples for optical measurements were prepared by spraying a SWNTs/ethanol suspension on a quartz substrate. Transient absorption measurements in the subpicosecond time region were made using a conventional pump and probe setup. Femtosecond pumping pulses were generated from the second harmonic of an amplified Ti:sapphire laser system. The pump photon energy was \(3.10\) and \(1.55\) eV. Transient absorption spectra were measured with a white continuum probing beam generated by self-phase modulation in a water cell. InGaAs and Si photodiode arrays were used as detectors for the near IR (0.74–1.08 eV) and visible (1.14–2.90 eV) regions, respectively. The pump laser fluence is about \(200\) \(\mu\)J/cm\(^2\). This fluence is in a range where the photo-induced absorption change is proportional to the pump fluence. With such excitation conditions we did not observe a significant change in absorption spectrum suggesting a drastic modification of electronic states in SWNTs.

3. Results and Discussion

The solid curve in Fig. 1(a) shows the absorption spectrum of a SWNT film with a mean tube diameter of 1.22 nm. Three broad absorption bands are observed at \(\lambda\) (A) 0.8, (B) 1.4, and (C) 2.0 eV. The broken and dotted curves in Fig. 1(a) show the respective calculated absorption spectra of semiconducting and metallic SWNTs with a mean diameter of 1.22 nm.\textsuperscript{13)} Comparing the calculated and observed spectra, bands A and B are attributed to optical transitions from the valence band to the conduction bands in semiconducting SWNTs, and band C is attributed to metallic SWNTs.\textsuperscript{9,11)} The spectral position of the calculated absorption agrees well with the observed absorption bands B and C, but band A is located at a higher energy. The blue shift is ascribed to the Coulomb effect acting on the fundamental optical transition.\textsuperscript{8,9)} Figure 1(b) shows the differential absorption spectrum for delay time \(t_d = 0\) ps, just after the pumping pulse. An absorption decrease was observed for the energy regions (i) 0.7–0.9 eV, (ii) 1.2–1.6 eV, (iii) 1.7–2.3 eV, and (iv) higher than 2.3 eV with vibrational structure. The absorption changes for (i), (ii), and (iv) are attributed to the semiconducting tubes, and (iii) is owing to the metallic tubes. The decrease in absorbance is induced by photoexcited electrons and holes, and we will explain the origin of the absorption change and how its relaxation dynamics depend on the tube diameter in the temporal evolution of the absorption change.

3.1 Metallic SWNTs

The solid curve in Fig. 2(a) shows the absorption spectrum of a SWNT sample in the energy range 1.6–2.6 eV. The broad C absorption band is observed. Figure 2(b) shows the differential absorption spectra for delay times \(t_d = 0, 0.4, 1.0,\) and 4.0 ps after the pumping pulse. For \(t_d = 0\) ps, a large absorption decrease was observed in the 1.70–2.25 eV energy region, and small dips were observed at \(2.36\) and \(2.55\) eV. The dip energies correspond to the absorption peak positions indicated by the dots in Fig. 2(a). The absorption decrease below 1.65 eV is attributed to the second optical transition in a semiconducting tube (band B), the absorption bleaching from 1.67 to 2.15 eV belongs to the metallic tube (band C), and the small dips originate from
semiconducting SWNTs. A large negative change in the absorbance (absorption decrease) is observed for band C at the initial (\(t_d = 0\) ps) stage. By contrast, at a later stage (\(t_d > 0.4\) ps), both negative and positive signals (absorption increase) are observed. These spectral changes imply that different relaxation mechanisms are involved at the initial and later stages.

Figure 3 shows the temporal evolution of the absorption change measured at 1.80, 1.90, 2.05, and 2.28 eV. In order to consider the origin of the different spectral changes in the initial and later time regions, we fit the time evolutions to the sum of two exponential decay components with different decay times, i.e.,

\[
\Delta A(h\omega) = I_1(h\omega) \exp\left(-t/t_1(h\omega)\right) + I_2(h\omega) \exp\left(-t/t_2(h\omega)\right).
\]

The solid curves in Fig. 3 show the best fit results using two exponential decay components for all the decay curves: one with a short decay time of \(t_1 \sim 0.2\) ps and one with a long decay time of \(t_2 \sim 1.5\) ps. Although the fast decay component \(I_1\) is negative for all of the curves, the sign of the slow decay component \(I_2\) depends on the energy; it is negative at 1.90 and 2.05 eV, and positive at 1.80 and 2.28 eV. Neither decay time depends strongly on the photon energy.

Recently, the carrier dynamics of metallic SWNTs have been studied using femtosecond time-resolved photoemission spectroscopy.\(^{1,4}\) Hertel et al. observed the electron distribution directly, and found two different relaxation mechanisms, i.e., internal thermalization via an electron–electron interaction at the early stage, and the cooling of hot electron temperatures via an electron–phonon interaction in the later time region. Here, we will explain the temporal evolution of the photoinduced spectral change in band C using the relaxation dynamics observed by Hertel et al.\(^{1,4}\)

For the early time stage, photoexcitation produces the non-equilibrium electron distribution. The bands that are owing to the optical transition of band C are partially occupied by photoexcited electrons and holes. These carriers block the optical transition and cause an absorption decrease in band C. In this time region, we observe the absorption decrease in band C, as seen in Fig. 2(b). After the early stage, the electron distribution becomes a pseudo-Fermi–Dirac distribution in which the electron temperature exceeds the lattice temperature. In our excitation condition, the electron temperature is estimated to be lower than \(\sim 2,000\) K, considering the specific heat of the lattice and electron system in a SWNT.\(^{1,4}\) Nevertheless, the ‘hot’ electron temperature is too low to distribute electrons and holes in the bands that correspond to band C, because the energy separation of these bands from the Fermi level is \(\sim 1\) eV, which corresponds to \(\sim 12,000\) K. The absorption decrease partially recovers with the disappearance of the non-equilibrium electron distribution as a fast recovery component of the absorption change. In a graphite system, this dynamic occurs within the 50-fs time region.\(^{15}\) The observed 200-fs relaxation is much slower than that for graphite. This indicates that the lack of energy and momentum conservation for electron–electron scattering in the 1D band suppresses the electron–electron scattering rate in a SWNT. For the late time region, the electron temperature exceeds the lattice temperature. This higher electron temperature causes the spectral broadening in the metallic C band. In our results, we observe broadening of band C after \(\sim 0.5\) ps in Fig. 2(b). The laser-heated electron gas cools to the lattice temperature via the electron–phonon interaction,\(^{1,4}\) on a picosecond timescale, and the absorption change recovers as the electron temperature decreases.

Note that Lauret et al. observed induced absorption (increased absorbance) at the center of bands B and C.\(^{6}\) They interpreted the induced absorption as resulting from a redshift of \(\pi\)-plasmon resonance owing to carrier injection via photo excitation. We observed both an increase and a decrease in the absorbance around band C. Although we explained the nonlinear absorption changes around band C using the non-equilibrium carrier distribution and cooling of hot electrons, the redshift of the \(\pi\)-plasmon also appears in the absorption change.

### 3.2 Semiconducting SWNTs

Figure 4(a) shows the absorption spectrum of a SWNT sample in the near IR region. Broad A and B absorption bands are observed. Figure 4(b) shows the differential absorption spectra for delay times of \(t_d = 0, 0.4, 1.0,\) and \(4.0\) ps after the pumping pulse. Absorption bleaching in bands A and B was observed in the 0.74–0.95 and 1.15–1.65 eV energy regions. The decreased absorbance means that the photoexcited electrons and holes have not relaxed to the ground state configuration. For all the delay times, the spectral shape of the nonlinear absorption change is similar to the linear absorption band. This means that the absorption change originates from the simple state filling of valence and conduction bands.

The broad A and B absorption bands include optical transitions in SWNTs of various diameters in the sample.\(^{9}\) Therefore, the tube diameter can be selected using the probe photon energy. Figure 5 displays the temporal evolution of the absorption change measured at 0.76 and 0.79 eV for band A, and at 1.29 and 1.41 eV for band B. The decay
behaviors can be fitted to the sum of the two exponential decay components with the different decay times. The solid curves in Fig. 5 show the best fit results with a short decay time of 1.0 ps for 0.76 eV, 0.8 ps for 0.79 eV, 0.6 ps for 1.29 eV, and 0.5 ps for 1.41 eV, and with a long decay time of ~5 ps for all the decay curves. The short decay time depends on the probing photon energy. The open circles and triangles in Fig. 6 show the decay time of the fast component for bands A and B as a function of the probing photon energy, respectively. For both bands A and B, the decay time decreases with increasing photon energy in a broad absorption band. As the peak energy of bands A, B, and C depends on the tube diameter, we can estimate the respective tube diameters from the probing photon energy. The inset of Fig. 6 shows the decay rate of the fast components for bands A and B as a function of the estimated tube diameter. We can estimate the respective tube diameters from the probing photon energy. The observed decay time of ~1 ps in a semiconducting SWNT is consistent with the absence of photoluminescence, and this decay time should be determined using a nonradiative recombination process. Candidates for such a process are (i) multi-phonon emission, (ii) the Auger process of electrons and holes, (iii) energy transfer to the metallic tubes, and (iv) trapping at defects. If the Auger process governs the relaxation, the decay time should depend on the excitation intensity, because the numbers of scattering electrons and holes are proportional to the excitation intensity. The decay time does not depend on the excitation intensity. When multi-phonon emission is the main channel of a nonradiative recombination process, the decay rate depends on the strength of the electron–phonon interaction. However, the simple tight-binding models predict that the electron–phonon coupling constant does not depend on the tube diameter for zigzag tubes.
observed diameter dependence of the decay rate is too large for the change in the electron–phonon interaction. Conversely, if excited carriers are relaxed by energy transfer to the metallic tubes, the decay rate is determined by the energy transfer rate from a semiconducting to a metallic tube. The top of the valence and bottom of the conduction bands of a semiconducting tube overlap with the metallic linear band in the energy diagram. As this overlap does not change over our diameter range, the transfer rate does not depend on the tube diameter. Therefore, it is difficult to explain the tube-diameter dependence of the decay time using the energy transfer.

These results indicate that the observed nonradiative process is attributable to trapping at defects in a SWNT. As such a defect, we propose a Stone–Waals (SW) type defect, i.e., a five–seven member ring defect in a six member rings roll. Pan et al. have reported the formation energy of a SW type defect for SWNTs of various chiralities and diameters using tight-binding calculations.\(^\text{17}\) The defect formation energy of a SWNT is smaller than that for graphite, and it becomes smaller with decreasing tube diameter. For a zigzag tube, the formation energy is \(\sim 2.7\) eV for a 1.2-nm diameter tube and \(\sim 2.6\) eV for a 1.0-nm tube. This type of defect forms during the growth of a SWNT. The defect density is proportional to \(\exp(-E(d)/k_B T)\), where \(d\) is the tube diameter, \(E(d)\) is the formation energy of a SW defect with a tube diameter of \(d\), \(k_B\) is the Boltzmann constant, and \(T\) is the temperature during the SWNT growth period. If we use a temperature of 1,300 K, which is the furnace temperature, the defect density of a 1.0-nm diameter tube is about three times greater than that of a 1.2-nm tube. As the trapping rate at a defect is proportional to the defect density, the rate increases as the tube diameter decreases. This results in a larger decay rate for smaller diameter SWNTs, as seen in the inset of Fig. 6.

The decay rate of band B is larger than that of band A. Band B also arises from the optical transition for a semiconducting tube as band A. Therefore, for band B, the same relaxation dynamics exist, i.e., trapping to the defects. Moreover, nonradiative relaxation owing to an interband relaxation channel from band B to A exists. This causes the higher decay rate of band B as compared to that of band A.

### 4. Summary

We investigated the diameter-dependent relaxation dynamics of photoexcited carriers in semiconducting and metallic single-walled carbon nanotubes. In the metallic tubes, we observed the thermalization and cooling processes of hot electrons via both electron–electron and electron–phonon interactions as the spectral change in absorption spectra after photoexcitation. These processes can be observed as the bleaching and broadening of the metallic absorption band. In the semiconducting tubes, the absorption bleaching after photoexcitation recovers via the nonradiative channel within \(\sim 1\) ps. The decay time decreases with increasing probing photon energy, which means that the relaxation rate increases with decreasing tube diameter. This suggests that the nonradiative relaxation in a semiconducting SWNT is governed by the trapping at defects.

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