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PHOTOCONDUCTIVITY OF SINGLE-WALL CARBON NANOTUBE FILMS

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Abstract

Time-resolved photoconductivity measurements were carried out on single-wall carbon nanotube (SWNT) films at various temperatures. Photoconductivity excitation spectra show two clear peaks around 0.7 and 1.2 eV. Observed peaks in the spectra correspond to the optical absorption between symmetrical bands of semiconducting SWNTs. The analysis of this feature allows insight into the transport properties of semiconducting SWNTs. Signal profiles in the photoresponse at low temperatures depend strongly on the sample, while intensity of the photoresponse monotonously increases with a decrease in temperature for all samples. Photo-induced current for a sample decays rapidly after the laser pulse irradiation. For another sample, on the other hand, it decreases gradually and remains up to a few hundred nano seconds, showing the existence of trapping sites in the nanotubes.

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1. Introduction

Carbon nanotubes (NTs) [1] have attracted great attention as potential electronic materials because of the one-dimensional tubular network structure on a nanometer scale. The variety of band structures of the NTs, being either semiconducting or metallic depending on the chirality and the diameter of the tube [2,3], is also a novel feature. For applying NTs to electronic devices, more detailed transport properties of semiconducting single-wall carbon nanotubes (SWNTs) have to be individually clarified. To date, however, selective growth of NTs has not been achieved: both the semiconducting and metallic SWNTs can coexist even in a single bundle [4]. Although Collins *et al.* [5] demonstrated a method for leaving only the semiconducting SWNTs from the mixture of semiconducting and metallic ones by burning only the metallic ones, this technique is quite difficult. To overcome this difficulty, we proposed photoconductivity measurements [6-10]. The photoconductivity excitation spectra show two peaks around 0.7 and 1.2 eV, which correspond to the first and second peaks of the optical absorption spectrum in semiconducting NTs, E_{11}^s and E_{22}^s [11,12]. By evaluating the properties of photoconductivity, their own character of semiconducting SWNTs can be extracted from the mixture sample of semiconducting and metallic SWNTs. The photoconductivity of NTs has high potential not only to the practical application to the optical devices, such as high spatial resolution detector, nano-sized optical switch *etc.*, but also to the fundamental characterization of the semiconducting NTs.

In this paper, we report on properties of photoconductivity originating from semiconducting SWNTs. We discuss variation of the temperature dependence of photoconductivity in terms of transport properties of semiconducting-SWNT circuits.

2. Experimental

The samples of SWNT bundles were synthesized by evaporation of composite rods of nickel (Ni), yttrium (Y) and graphite in helium atmosphere by arc discharge [12,13]. The diameter of the SWNTs used here is determined to be about 1.4 ± 0.2 nm by the Raman frequency of a breathing mode and TEM observation. The typical length of SWNT bundles estimated by scanning electron microscopy (SEM) is a few micrometers. To prepare film samples, soot-containing SWNTs was dispersed in methyl alcohol by ultrasonic vibrator, and suspension of SWNTs was dropped on glass substrate. The typical film sample size is about $100 \times 100 \mu\text{m}^2$ and the thickness of the film is between 300 and 500 nm. The samples were annealed in vacuum at 10^{-6} Torr and 673 K for 2 hours to remove the absorbed gasses and methyl alcohol from samples. A pair of gold electrodes separated by a 10 μm gap was evaporated in vacuum on to the surface of the film samples and connected to a dc regulated power supply (100 mV). The samples were mounted in a continuous-flow cryostat. For measurements on the temperature dependence, samples were cooled by flowing the vapor of liquid He in the temperature range from 10 K to room temperature (R.T.). As a light source, an optical parametric oscillator (OPO) excited by a pulsed Nd:YAG laser with the duration time of 5 ns was used. The photon energy was set to in the range of 0.5 to 2.8 eV. The temporal profiles of the laser pulse and the current were monitored with a digitizing oscilloscope. In order to reduce spurious ringing in the fast

pulse detection, we were obliged to use the input impedance of the oscilloscope (50Ω) as the reference resistor despite the obvious disadvantage of lower sensitivity. The resistance of samples in the dark is ca. 100Ω at R.T. and order of $1k\Omega$ at around 10 K.

3. Results and Discussion

Fig. 1 shows temporal evolution of photo-induced current for various incident light intensities for sample #1 at 13.2 K. The current properly follow the laser pulse shape: signal profile with a 5 ns width can be observed and increases with an increase in incident light intensity. The oscillatory structure for time $t > 10$ ns is considered to be due to ringing in the circuitry. Here, we derived the signal intensity by fitting the first peak in the signal profile with a Gauss function. The relationship between the signal intensity and the incident light intensity for various photon energies is shown in Fig. 1(b). Below $10 \mu\text{A}$, the signal intensity responds linearly to incident light intensity. On the other hand, it shows saturation behavior above $10 \mu\text{A}$; this saturation is often observed under intense light intensity and might be due to lack of replenishment of carriers [14]. Therefore, we estimate the photoresponse from the deepest slope of the signal intensity vs. incident light intensity curves in Fig. 1(b).

Photon energy dependence of photoresponse, *i.e.*, photoconductivity excitation spectra for two film samples of SWNTs #1 and #2 at room temperature are shown in Fig. 2. Optical absorption spectrum for the sample made by the same method is also presented as a reference. Two clear peaks in photoconductivity excitation spectra at R.T. are observed around 0.7 and 1.2 eV. These energies are very close to the first and second peaks of the optical absorption spectrum in semiconducting NTs with a diameter of 1.4 nm, E_{11}^s and E_{22}^s . Therefore they correspond to the electron excitation between symmetrical bands of semiconducting NTs. From this result, we can conclude that the photoconductivity originating from the semiconducting SWNTs occurs, and that this technique can be used for studying the electronic transport properties of semiconducting NTs.

As a first step of extraction and study on transport properties of the semiconducting SWNTs, we focus on the most simple process: photocarrier produced by the laser pulse with the energy of $E_{11}^s \approx 0.7$ eV. Figs. 3(a) and (b) show the temporal evolution of photo-induced current for various incident light intensities for samples #1 and #3 at R.T., respectively. Data at 13.2 K for the sample #1 in Fig. 3(c) show almost the same behavior to those at R.T., except for the enhancement in the intensity. On the other hand, they change drastically for the sample #3 at 10.2 K, as shown in Fig. 3(d). The current shows a pronounced tail superposing on the oscillatory structure after the first peak observed in Figs. 3(a)-(c). This tendency becomes remarkable at low temperatures.

Temperature dependence of photoresponse normalized by the data at R.T. for samples #1 and #3 are shown in Fig. 4. Although photoresponse increases monotonously with a decrease in temperature in both samples, the degree of enhancement at low temperatures are different between these two samples. This difference is attributed to three reasons. One of them is an intrinsic behavior of semiconducting SWNTs. As shown in Fig. 3(d), the current is distributed to wide time scale, which cannot contribute to the photoresponse in Fig. 4, because we derived the photoresponse by fitting *the first peak* in the signal profile in the present definition. This behavior will be discussed later. Next one is the underestimation of photoconductive response at low temperatures in the sample #3. As discussed above the photocurrent does not respond linearly to incident light intensity but tend to saturate at high light intensity region. This effect is much larger in sample #3, because experiments were performed under rather high incident light intensity as shown in Figs. 3(b) and (c). Therefore, the effect of saturation on them becomes larger at higher intensity, namely, at lower temperature. This difference might be due also to differences in conditions of contact between SWNTs and/or SWNTs and electrode; loose

contacts can cause the reduction of photoconductive response at low temperatures where carrier must hop by thermal activation for conductance.

Considering rather small enhancement of the first-peak intensity and the tail in the signal profile of the current, it is plausible that trapping of photocarrier affects the photoconductive properties of the sample #3 at low temperatures. This result suggests that quality of semiconducting SWNTs is various even in the sample produced by the same method. Although this fact has not been pointed out clearly so far, it is very important information from the viewpoint of application of semiconducting SWNTs to electronic devices. In addition, our results show photoconductivity is very sensitive to the quality of semiconducting-SWNT circuits. Further experiments will clarify the mechanism of electron trapping in the semiconducting SWNTs.

4. Conclusions

We have investigated properties of photoconductivity in SWNT bundles. Photoconductivity excitation spectra show good correspondence to the optical absorption spectrum of the semiconducting SWNTs, showing that we can extract the transport properties of semiconducting SWNTs from the mixture sample of the semiconducting and the metallic SWNTs. Temporal evolution of profile and its intensity strongly depend on the sample and temperature. The origin of this variation is considered to be due to the difference in trapping effect of the circuits consisting of semiconducting SWNTs. This result suggests that quality of semiconducting SWNTs is various even in the sample produced by the same method, and that photoconductive properties are very sensitive to it. We can propose that photoconductivity measurements are very effective and powerful technique for evaluating electronic circuit and devices consisting of semiconducting SWNTs.

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Fig. 1. (a) Temporal evolution of photo-induced current for various incident light intensities for sample #1 at 13.2 K. (b) Incident light intensity dependence of photoresponse.

Fig. 2. Photoconductivity excitation spectra for two film samples of SWNTs (#1, #2) at room temperature. Optical absorption spectrum for the sample made by the same method is also presented with a dotted line as a reference. Background of optical absorption which is almost linearly increases with photon energy in this region was subtracted.

Fig. 3. Temporal evolution of photo-induced current for various incident light intensities for (a) sample #1 at R.T., (b) sample #3 at R.T., (c) sample #1 at 13.2 K, (d) sample #3 at 10.2 K.

Fig. 4. Temperature dependence of the photoresponse at 0.7 eV for the samples #1 and #3 normalized by the data at R.T.

Fig. 1.

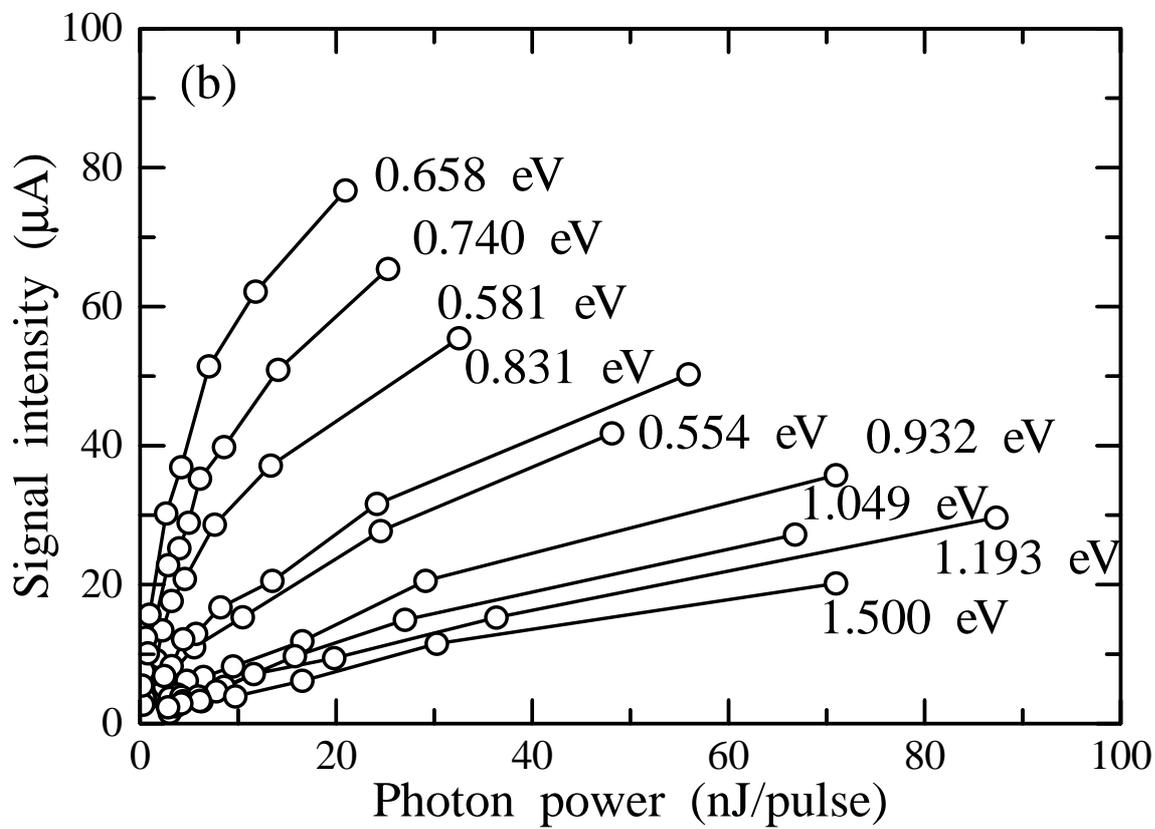
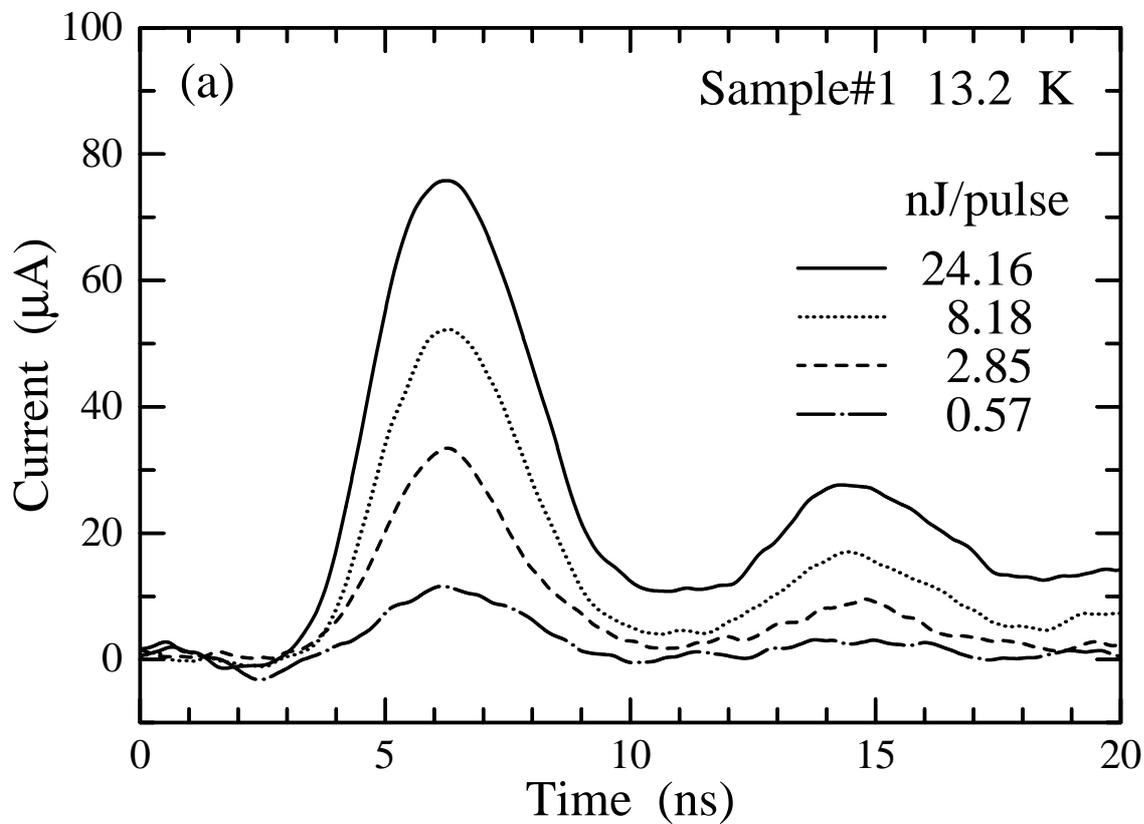


Fig. 2.

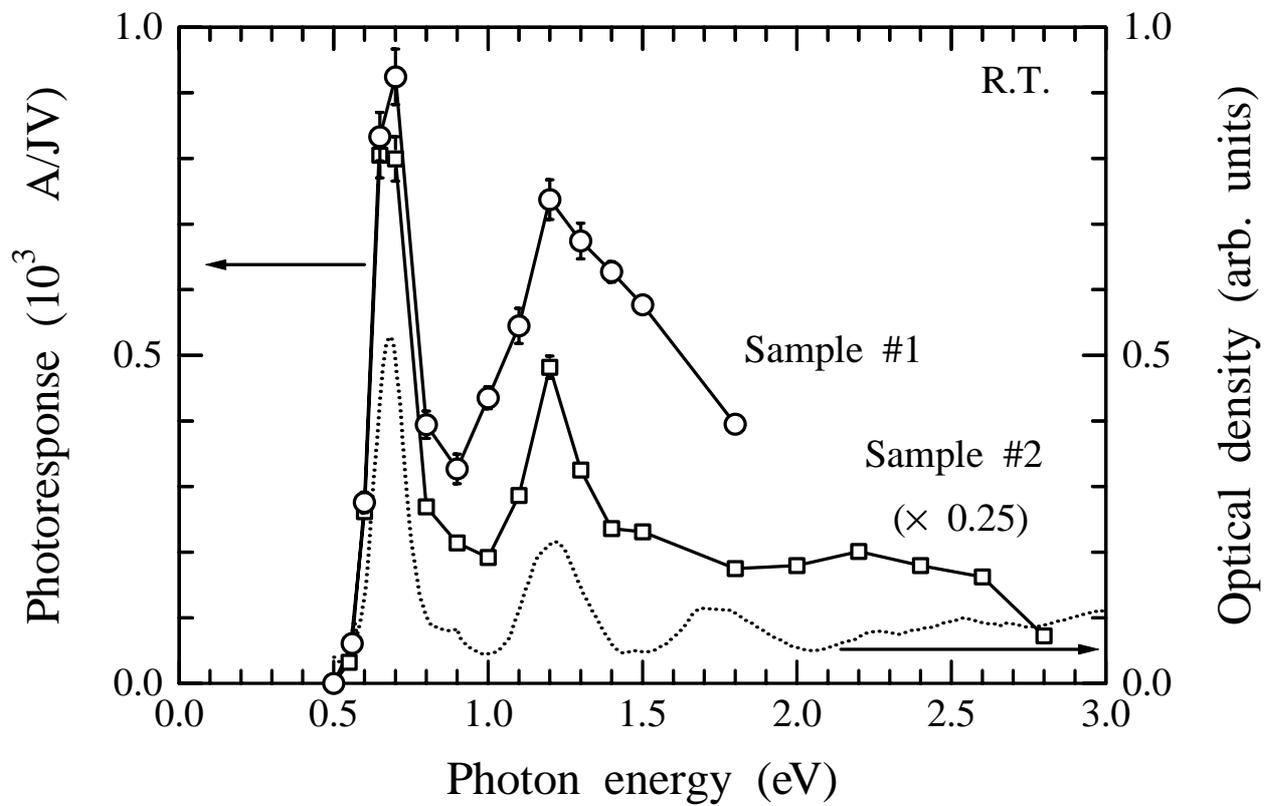


Fig. 3.

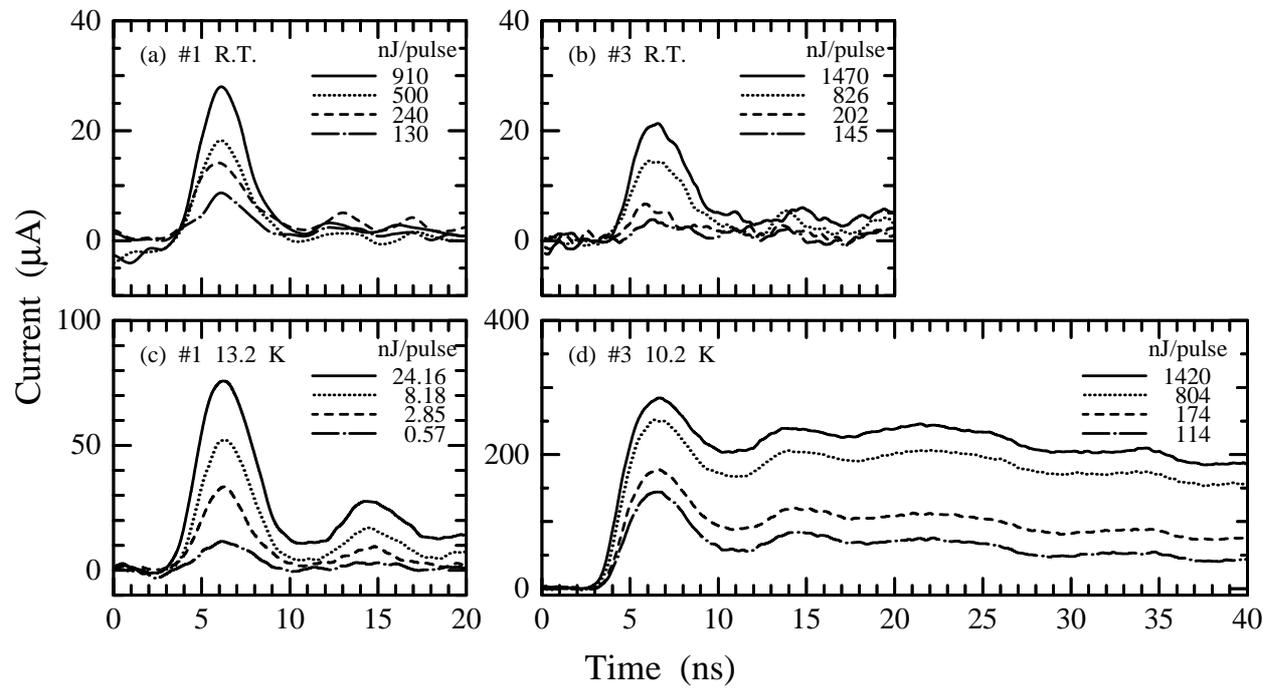


Fig. 4.

