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Description	

Temperature dependence of photoconductivity at 0.7eV in single-wall carbon nanotube films

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Abstract

Temperature dependence of photoconductivity has been investigated for single-wall carbon

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nanotube (SWNT) films at 0.7eV. In order to clarify the effect of atmosphere on photoconductivity, measurements have been performed under helium and nitrogen gas flow in the temperature range from 10 K to room temperature (R.T.) and from 100 K to R.T., respectively. Photoconductive response monotonously increases with a decrease in temperature and tends to saturate around 10 K. No clear difference in photoconductive response under different atmosphere was observed. We discuss the mechanism of photoconductivity at 0.7eV.

**Keywords: carbon nanotube, single-wall carbon nanotube, photoconductivity,
temperature dependence**

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. Actually, the findings of many properties of NTs, such as single electron transport [4,5], spin transport [6], rectification [7,8], switching function [9] and tunable electronic structure by magnetic fields [10,11], have opened up a route towards the single-molecule electronic-devices. For applying NTs to electronic devices, more detailed physical- and chemical-properties of semiconducting and metallic phases have to be individually clarified. To date, however, selective growth of a single phase of NTs has not been achieved; both the metallic and semiconducting phases can coexist even in a single-wall carbon nanotube (SWNT) bundle [12]. Although Collins et al. [13] demonstrated a method for leaving only the semiconducting SWNTs from the mixture of two phases by burning the metallic NTs, this technique is quite difficult. As an easier approach to evaluate transport properties of semiconducting SWNTs in the mixture sample of two phases, we proposed photoconductivity measurements [14-16]. The photoconductivity excitation spectrum shows two peaks around 0.7 and 1.2 eV, which correspond to the first and second peaks of the optical adsorption spectrum in semiconducting NTs [14-18].

There are two subjects to be solved to discuss the photoconducting properties of semiconducting SWNTs. One is the origin of carrier. Theoretical and experimental studies on optical adsorption suggest that almost all of the lowest interband-transition intensity is transferred to the exciton transition [17-19]. Supposing it is true, photoconductive response at 0.7 eV is caused by dissociation of excitons into free carriers (electrons and holes). Then the

mechanism of photoconductivity is still unclear. Another is the effect of atmosphere on transport properties of SWNTs. The electronic states and transport properties of SWNTs strongly depend on the atmosphere, *i.e.*, kinds of gases surrounding samples [20-23].

In this work, we have investigated temperature dependence of photoconductivity in SWNT films and discuss the mechanisms of photo-carrier generation. In order to clarify the effect of atmosphere on photoconductivity, measurements have been performed under helium (He) and nitrogen (N₂) gas flow.

2. Experimental details

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 [18,24]. Observations by transmission electron microscopy (TEM) revealed that soot is composed mainly of SWNTs and also amorphous carbons and metal particles. 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 $100 \mu\text{m} \times 100 \mu\text{m}$ 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 $10 \mu\text{m}$ gap was evaporated in vacuum on to the surface of the film samples and connected to a dc regulated power supply (100.00mV). The narrow gap of $10 \mu\text{m}$ was chosen in order to

reduce the number of junctions between SWNTs in the current pass, because the resistance of the junctions dominates the total resistance of the sample and obscures the intrinsic transport properties of SWNTs. The samples were mounted in a continuous-flow cryostat and cooled by flowing the vapor of liquid He and liquid N₂ in the temperature range from 10 K to room temperature (R.T.) and from 100 K to R.T., respectively. As a light source, an optical parametric oscillator (OPO) excited by a pulsed Nd:YAG laser was used. The photon energy was set to 0.7 eV and the pulse duration was 5 ns. The temporal profiles of the laser pulse and the photocurrent were monitored with a digitizing oscilloscope. In order to avoid 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 signal-to-noise (S/N) ratio of photocurrent was low because the signal was extremely weak. Therefore we could not observe in the low intensity range of incident light. The resistance of samples in the dark is ca. 110 Ω at R.T. and 850 Ω at around 10 K.

3. Result and discussion

Figure 1 shows the temporal evolution of photocurrent for various incident light intensities at 150K. Photoconductive response with a 5ns width can be observed and increases with an increase in incident light intensity. Figure 2 shows the relationship between the photocurrent peak height and the incident light intensity under He gas flow for various temperatures. At the range of low incident light intensity, photocurrent shows a rapid increase whereas it shows a tendency of saturation at the high intensity region. This saturation is often observed under intense light intensity and might be due to lack of replenishment of carriers [25]. Although steepest slope at the low intensity region should be used for the determination of

photoconductive response, it is difficult because of the low S/N ratio and the limited data points; we estimated photoconductive response from the slope of the data at the incident light intensity of about 150 nJ/pulse in Fig.2 at each temperature. Temperature dependence of photoconductive response for data measured under He and N₂ gas flow is shown in Fig. 3. Data of previous work (Ref. 14) are also plotted for comparison. Although photoconductive response reveals some difference in the absolute value between data measured under He and N₂ atmosphere, the general tendency is similar to each other. As for this work, effect of the adsorption of the flowing gases on photoconducting properties can be negligible. The observed photoconductive response increases with a decrease in temperature, and shows the saturation around 10 K in this work. From Fig. 3, one can see the great difference in degree of enhancement of photoconductive response at low temperature between data measured under He gas flow in this work and data in ref. 14, although sample preparation process and measurement condition are almost the same in both measurements. This might be due to the underestimation of photoconductive response at low temperatures. As mentioned above, we estimated their values from the slope of the data at a certain fixed incident light intensity. 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. Therefore we discuss the carrier generation mechanism by considering only the general tendency of temperature dependence of photoconductive response. Photoconductive response increases with a decrease in temperature for all samples and measurement conditions. If free carriers are created through thermal dissociation of excitons,

number of free carriers will decrease with a decrease in temperature, and then, photoconductive response will decrease, which is contrary to the experiment result. Our results naively support that photo-carrier originates from the usual interband transition. Very recently, photoconductivity was observed in SWNTs with the diameter of 0.4 nm [26,27]. Since these samples have more strong one-dimensional structure, binding energy of exciton is expected to be much larger than our samples. It is expected that the comparison the photoconducting properties between these samples gives valuable information to solve this problem.

4. Conclusion

We have measured the temperature dependence of photoconductivity at 0.7eV in single-wall carbon nanotube films. Photoconductive response increases with a decrease in temperature. There is no clear difference in photoconductive response under He and N₂ gas flow. Our results show that the photoconducting properties are hardly affected by the atmosphere. For the origin of carrier in photoconductivity, our results support interband transition rather than dissociation of exciton.

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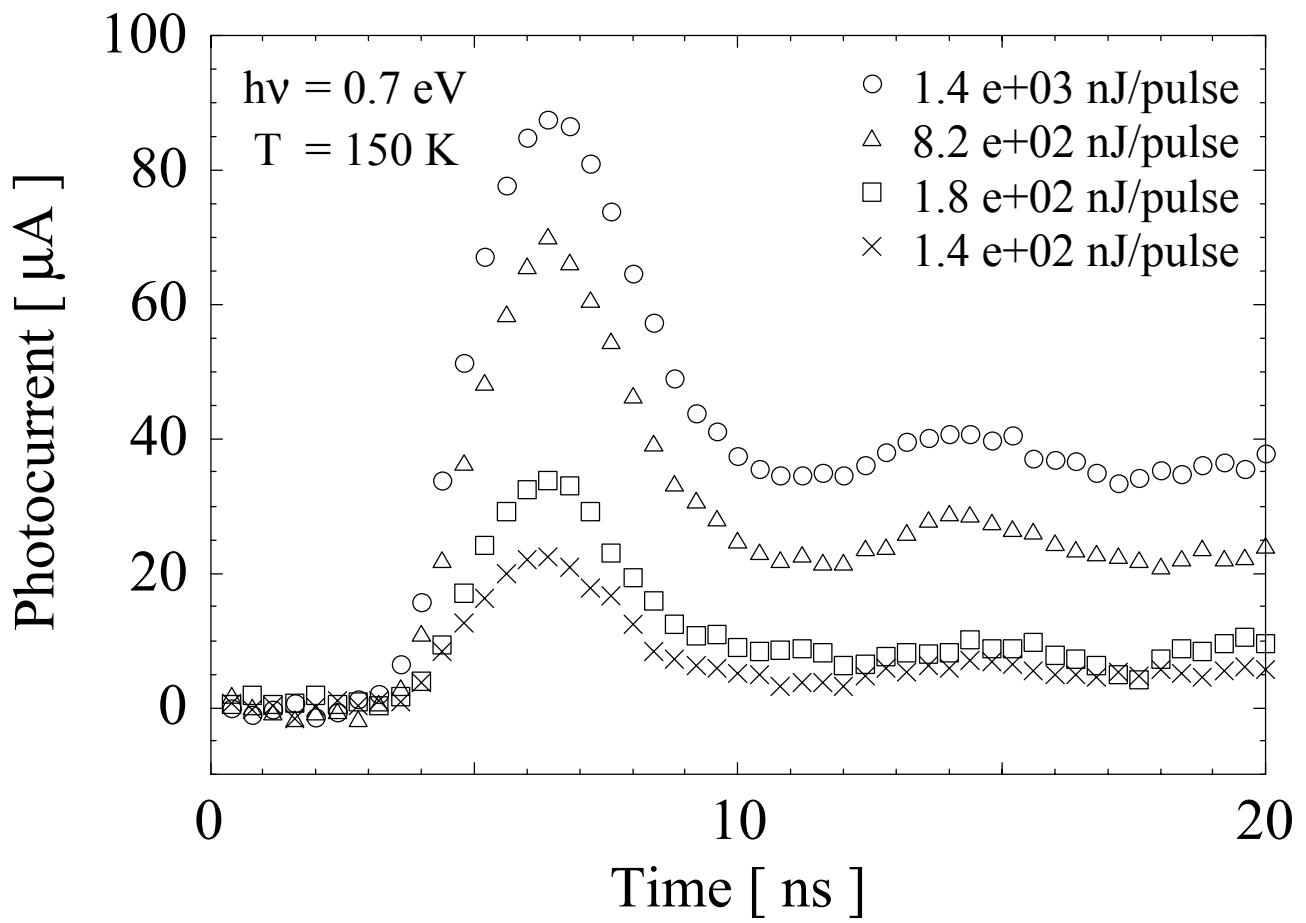
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Figure Captions

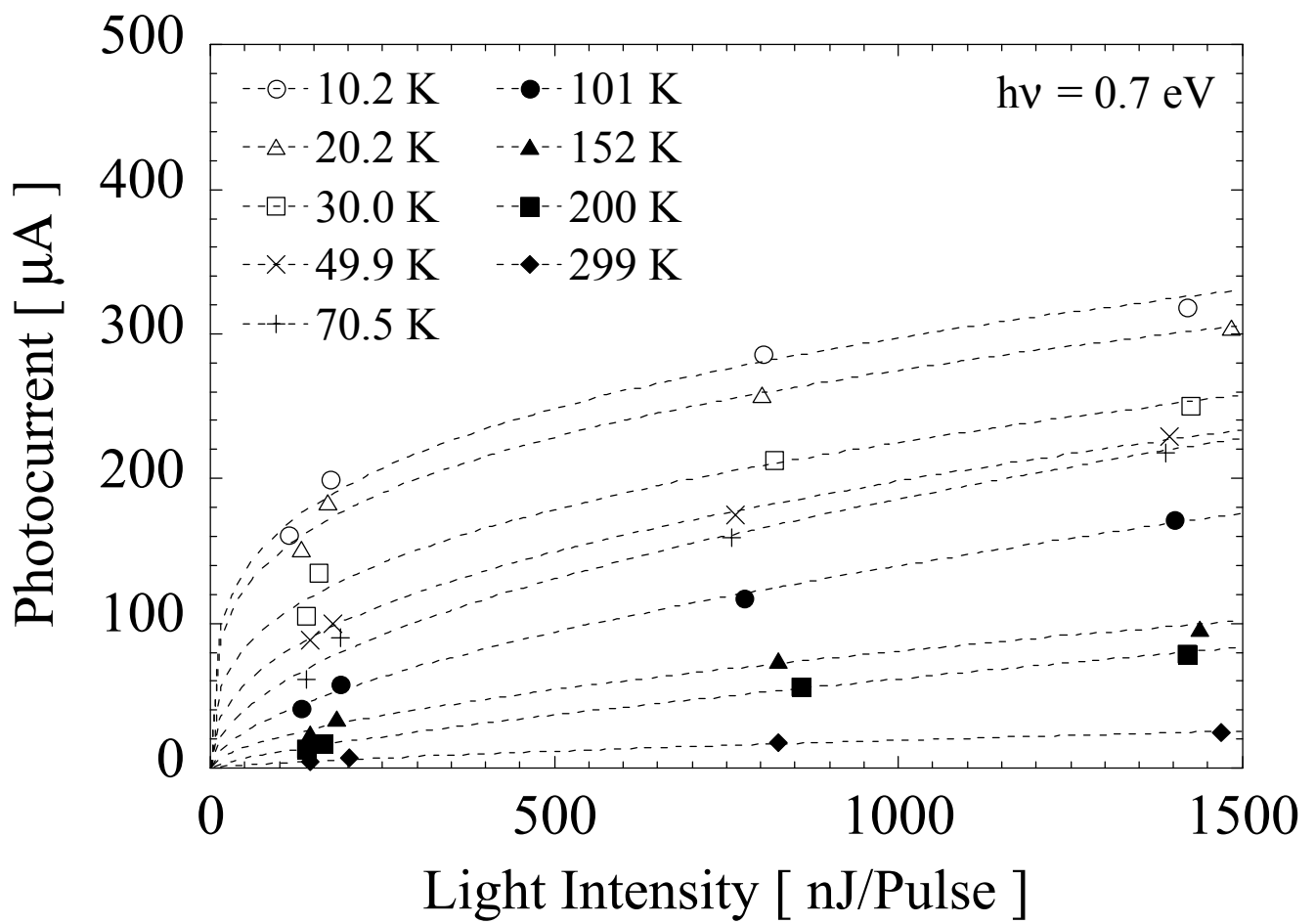
Figure 1. Temporal evolution of the photocurrent for various incident light intensities at 150K.

Figure 2. Incident light intensity dependence of photocurrent. Lines are guide to the eye.

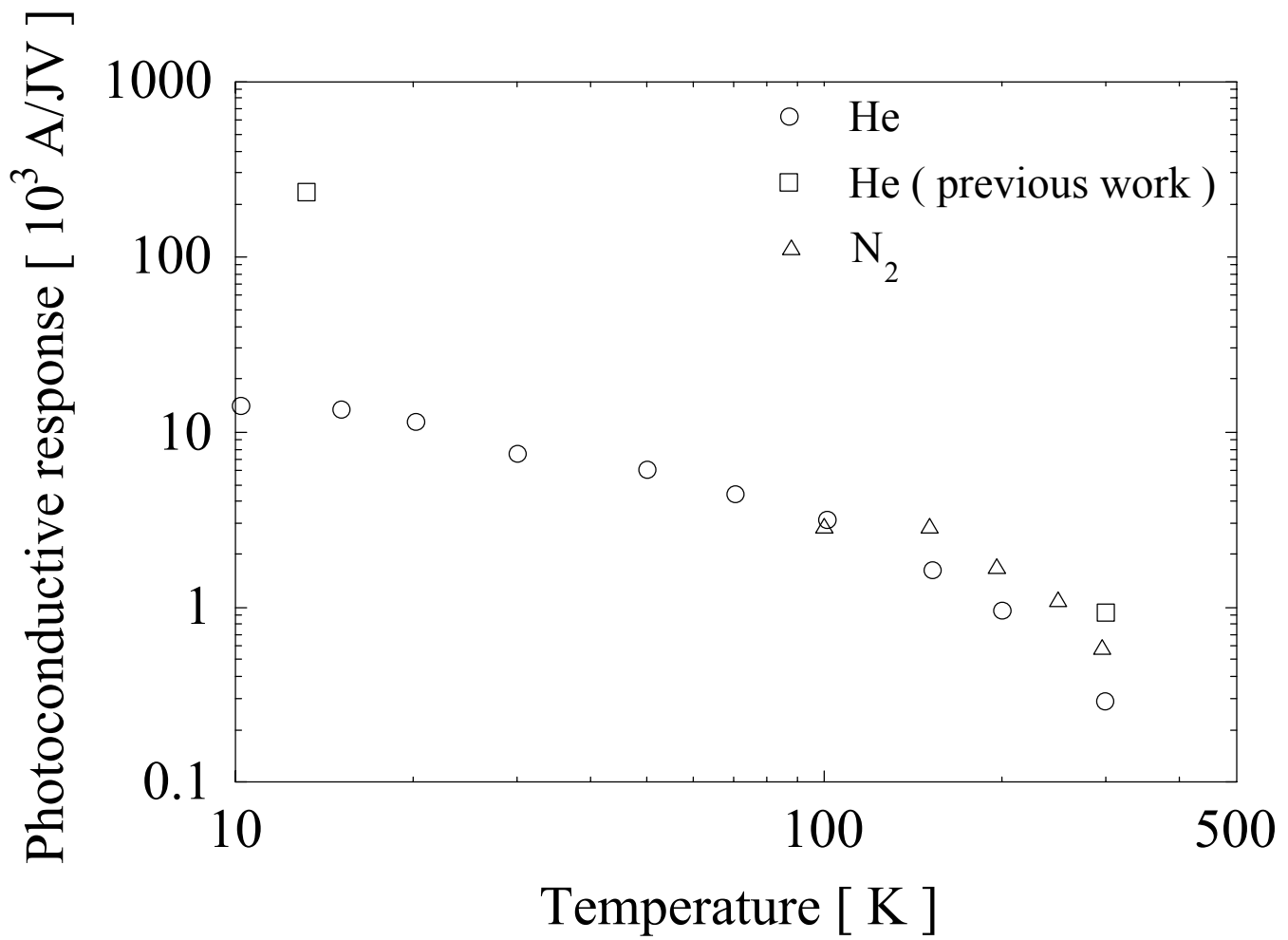
Figure 3. Temperature dependence of the photoconductive response at 0.7 eV for data measured under He (), N₂ () gas flow and data in ref. 14 ().



Y.Matsuoka et al. Figure 1.



Y.Matsuoka et al. Figure 2.



Y.Matsuoka et al. Figure 3.