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Photoconductivity in Semiconducting Single-Walled Carbon Nanotubes

Akihiko FUJIWARA[*1], Yasuyuki MATSUOKA[*2], Hiroyoshi SUEMATSU[*3], Naoki OGAWA[1], Kenjiro MIYANO[1*4], Hiromichi KATAURA[2], Yutaka MANIWA[2], Shinzo SUZUKI[3] and Yohji ACHIBA[3]

Department of Physics, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[1]*Department of Applied Physics, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[2]*Department of Physics, School of Science, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachi-oji, Tokyo 192-0397, Japan*

[3]*Department of Chemistry, School of Science, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachi-oji, Tokyo 192-0397, Japan*

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We have observed the photoconductive response of film samples of single-walled carbon nanotubes for the first time. Two peaks in the photoconductivity excitation spectra around 0.7 and 1.2 eV are observed at room temperature, which can be interpreted as a photocurrent in semiconducting nanotubes. At a low temperature, we found a marked change in the intensity of the spectrum. In this paper, we discuss this temperature dependence and the mechanism of photoconductivity.

KEYWORDS: carbon nanotube, SWNT, photoconductivity, electronic structure, nanotechnology

[*1] E-mail address: fujiwara@phys.s.u-tokyo.ac.jp

[*2] Present address: Network Service Systems Laboratories, NTT Corporation, 3-9-1 Midori-cho, Musasino-shi, Tokyo 180-8585, Japan.

[*3] Present address: Materials Science Division, SR Research Laboratory, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan.

[*4] Present address: Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan.

Since the discovery of carbon nanotubes (NTs),[1] they have attracted much attention as a very interesting electronic material because of the one-dimensional tubular network structure in the nanometer scale.[2,3] The variety of band structures of the NTs, being either semiconductive or metallic depending on the chirality and the diameter of the tube,[4–6] is also a novel feature. The discovery of the many functions of NTs[7–15] has opened up the possibility of applications to nanoscale electronic devices. To date, however, the electronic transport properties of semiconducting NTs has been largely unexplored, though understanding them is important for basic study on semiconducting nanotubes and for the application of semiconducting NTs to nanotechnology.

In this letter, we report the photoconducting properties of single-walled carbon nanotubes (SWNTs) with a diameter of about 1.4 nm. We found that 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 SWNTs. Our results clearly show that SWNTs can act as a semiconductor with photoconducting function despite the one-dimensional electronic structure. We also discuss the mechanism of photoconducting behavior and mobility of SWNTs.

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.[16,17] 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.

For preparing film samples for photoconductivity measurements, suspension of as grown SWNTs in methyl alcohol was dropped on a 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. 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. The narrow gap of 10 μm 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 helium cryostat. As a light source, an optical parametric oscillator (OPO) excited by a pulsed Nd:YAG laser was used. The photon energy was in the range of 0.5 to 2.8 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 (50 Ω) as the reference resistor despite the obvious disadvantage of lower sensitivity. The resistance of samples in the dark is ca. 100 Ω at room temperature (RT) and ca. 700 Ω at 13.2 K.

Figure 1(a) shows the temporal evolution of photocurrent for various incident light intensities at RT. Photoconductive response with a 5 ns width can be observed and increases with increasing incident light intensity. The relationship between the photocurrent peak height and the incident light intensity for various photon energies is shown in Fig. 1(b). Below 10 μA, the photocurrent intensity responds linearly to incident light intensity. On the other hand, it shows saturation behavior above 10 μ A; this saturation is often observed under intense light intensity and might be due to lack of replenishment of carriers.[18] Therefore, we estimate the photoresponse from the slope of the linear part in Fig. 1(b) (photocurrent $\leq$ 10 μ A); results are shown in Fig. 2. Two clear peaks in photoconductivity excitation spectra at RT are observed around 0.7 and 1.2 eV. These energies are very close to the first and second interband gaps of semiconducting SWNTs with a diameter of 1.4 nm. In addition, these spectra are very similar to the optical absorption spectra of SWNTs prepared by the same method.[17,19] From this result, we can conclude that the photoconductivity originating from the semiconducting SWNTs occurs, and that this technique is very effective for studying the electronic transport properties of semiconducting NTs.

The photoconductivity measurement was repeated at 13.2 K and the results, are shown in Fig. 3, in which the data at RT are also plotted for comparison. In all energy regions, the photoconductivity response at 13.2 K is much higher than that at RT, whereas the optical absorption is hardly enhanced even at a low temperature.[20] Moreover, the enhancement strongly depends on the photon energy. We focus on the temperature (T)

dependence of the peak intensities around 0.7 and 1.2 eV as shown in Fig 4. The first (E = 0.7 eV) and second (1.2 eV) peaks generally follow $T^{-\frac{3}{2}}$ and $T^{-\frac{1}{2}}$ dependence, respectively. T dependence of photoconductivity $\Delta\sigma(T)$ can be represented by

$$\Delta\sigma(T) = \Delta n(T) e\mu(T) = \Delta n(T)\frac{e^2}{m^*}\frac{l(T)}{v(T)}, \tag{0.1}$$

where $\Delta n(T)$, e, $\mu(T)$, m^*, $l(T)$ and $v(T)$ are carrier numbers increased by light irradiation, carrier charge, mobility of charge carrier, effective mass of charge carrier, mean free path and thermal velocity. Therefore, the photon-energy dependence of $\Delta\sigma(T)$ should be attributed to that of $\Delta n(T)$ and/or e, $\mu(T)$.

Firstly, we consider a case where $\Delta n(T)$ strongly depend on $\mu(T)$ as in the case of conventional semiconductors. We can expect $T^{-\frac{3}{2}}$ dependence of $\mu(T)$ in the regime of the diffusive transport due to electron-phonon interactions, because $l(T)$ and $v(T)$ respectively follow T^{-1} and $T^{\frac{1}{2}}$. On the other hand, some experimental results[21,22] show that NT behaves as a ballistic conductor even at RT. In this case, $l(T)$ is expected to be limited to the nanotube length and to become independent of temperature. Therefore, $\Delta\sigma(T)$ is expected to follow $T^{-\frac{1}{2}}$. Although $T^{-\frac{3}{2}}$ and $T^{-\frac{1}{2}}$ dependence of $\Delta\sigma(T)$ can be explained by possible models, it is unlikely that the different conduction mechanisms, *i.e.*, diffusive and ballistic transport, coexist in the same SWNT. In addition, if generated charge carriers rapidly relax to the lowest energy band and follow it as photocurrent, $\mu(T)$ must be independent of the photon energy.

Taking account of this contradiction, we also adopt the photon-energy dependence of $\Delta n(T)$ as the origin of that of $\Delta\sigma(T)$. Ando[23] claimed that almost all of the lowest interband-transition intensity is transferred to the exciton transition. This prediction is applied to the interpretation of the optical absorption experiments:[17,19] the first peak in optical absorption is assigned to this exciton transition, while others are ascribed to the interband transition. In this case, the mechanisms of photoconductivity at the first and the second peaks are qualitatively different from each other: the former and the latter originate from the dissociation of the exciton and the usual interband transition, respectively. In this case, $\Delta n(T)$ can show different T dependence between the first and second peaks.

Though simple models are applied in the above discussions, the mechanism of photocarrier creation, the transport properties of photocarriers and their T dependences are still not clear. This problem is also related to the lifetime of excited photocarriers and complex current pass including junctions between SWNTs. In this way, this intricate T dependence of $\Delta\sigma(T)$ cannot be understood only from experiments on photoconductivity. Therefore, more detailed experiments on the temperature dependence of photoconductivity excitation spectrum of an individual SWNT and the comparison of them with the temperature dependence of optical absorption will clarify the mechanism of photoconductivity and transport properties of semiconducting SWNTs.

In conclusion, we have observed the photoconducting effect of SWNTs for the first time. We find two peaks around 0.7 and 1.2 eV in photoconductivity excitation spectra corresponding to the first and second gaps of semiconducting SWNTs. This result shows that the SWNTs may actually function as a photoconducting material in nanotechnology. On the other hand, enhancement of the photoconductive response is observed at low temperature, and it strongly depends on the excitation energy. Further experimental studies will clarify this unusual temperature dependence and mechanism of photoconductivity, which was not achieved in this study.

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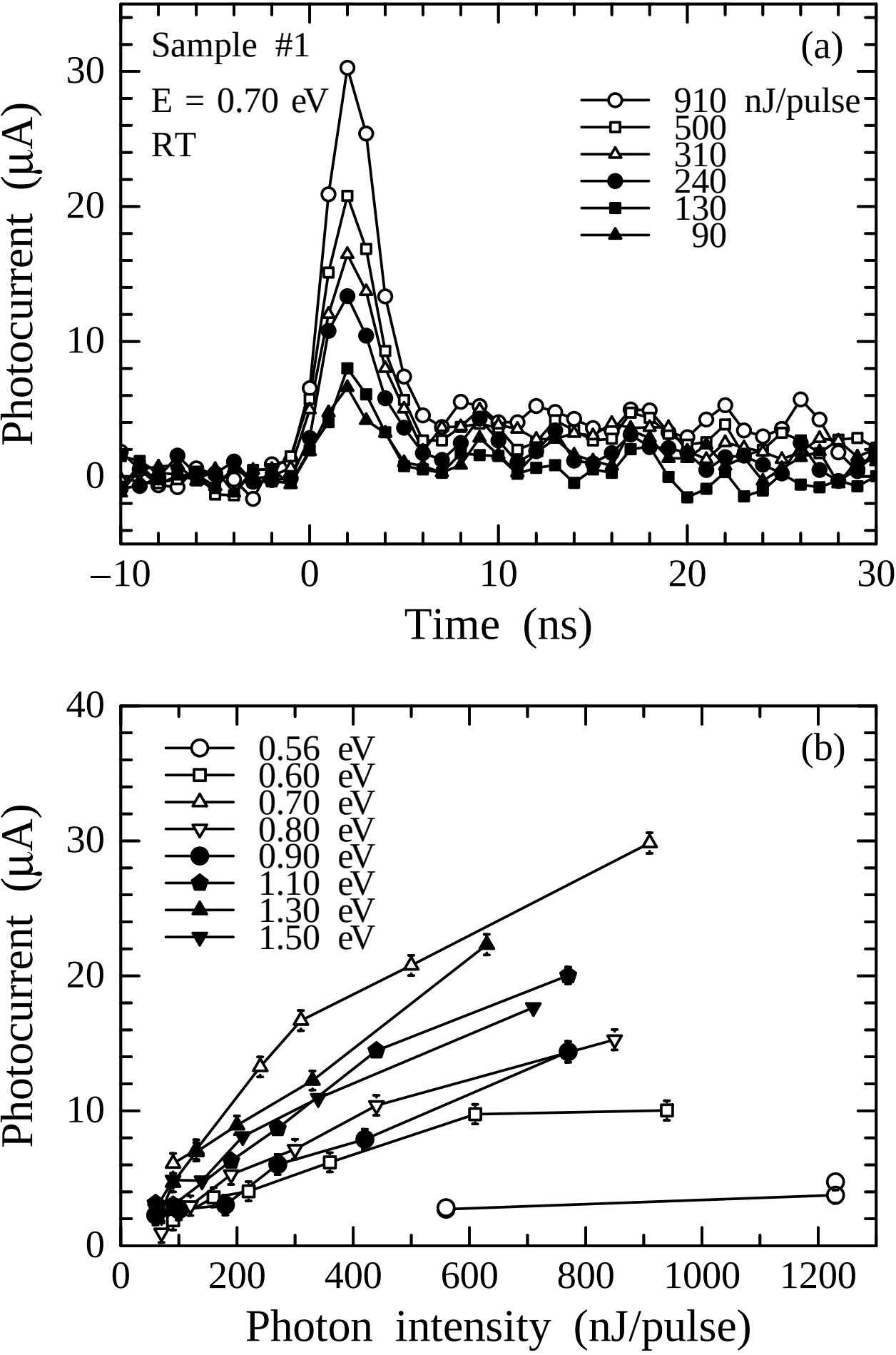
Figure captions

Fig. 1. (a) Temporal evolution of the photocurrent for various incident light intensities at room temperature. (b) Incident light intensity dependence of photoresponse.

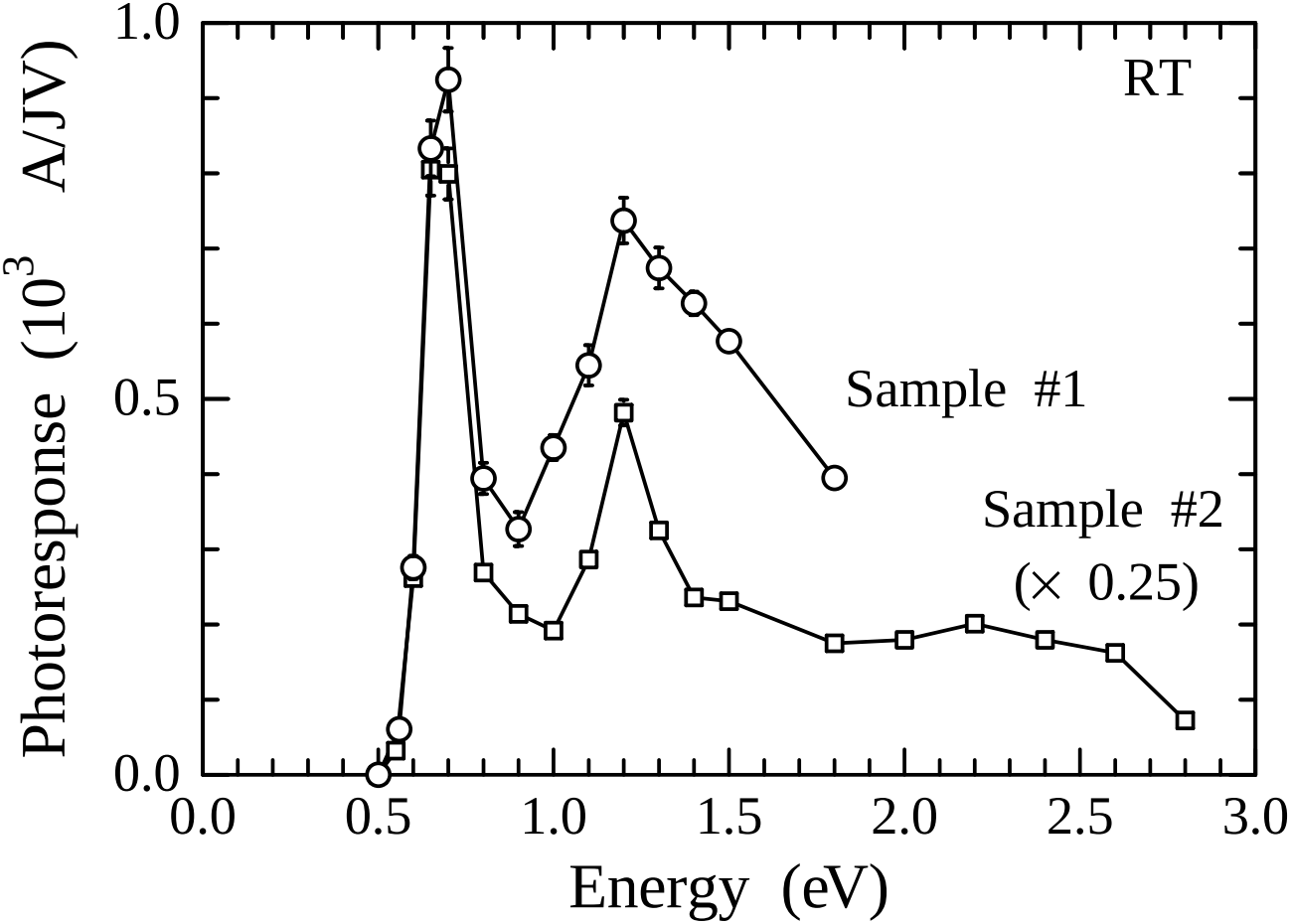
Fig. 2. Photoconductivity excitation spectra for two film samples of SWNTs at room temperature.

Fig. 3. Photoconductivity excitation spectra for data at 13.2 K and room temperature. Data are plotted in semi-logarithmic scale.

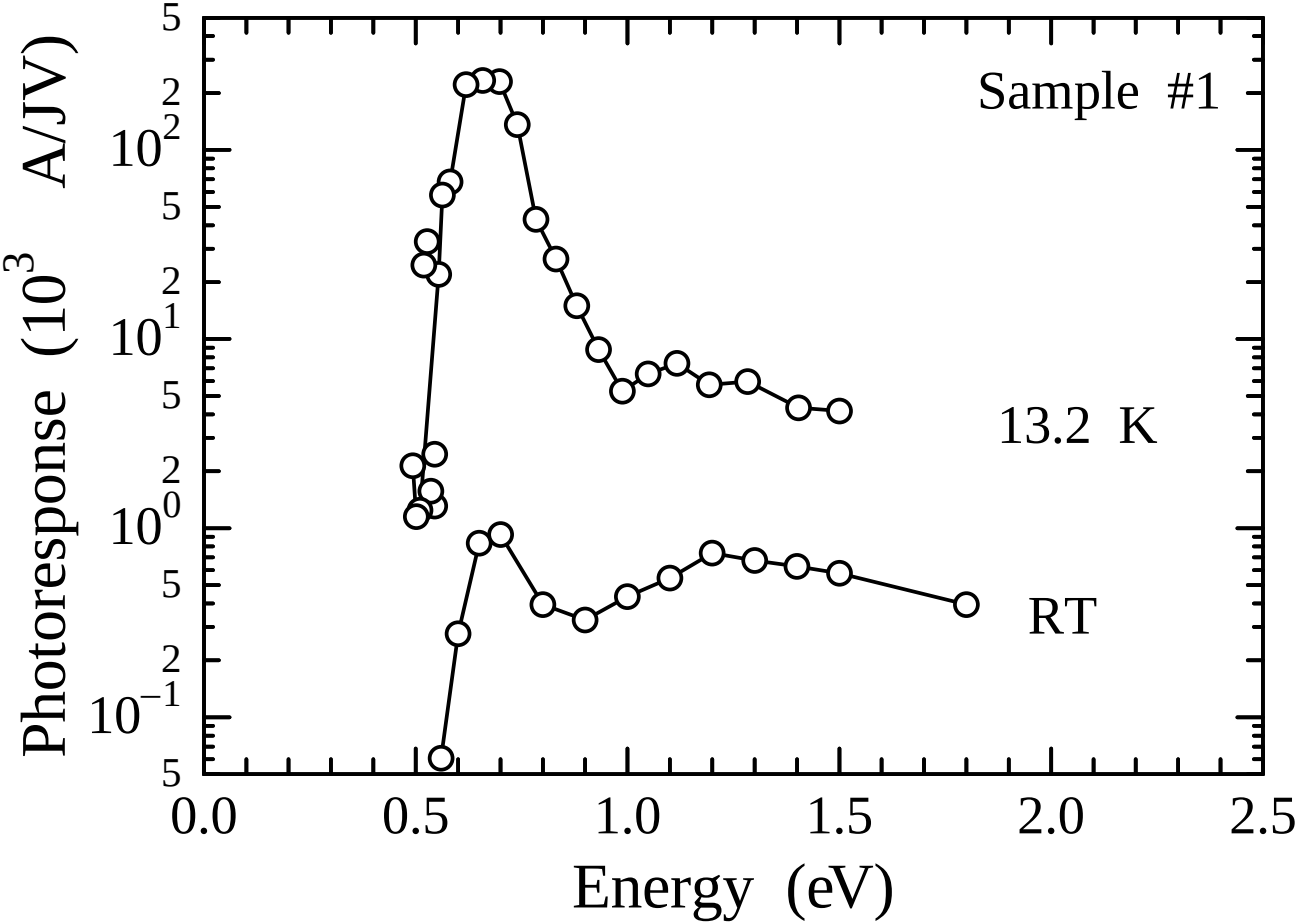
Fig. 4. Temperature dependence of the peak values of photoconductivity excitation spectrum around 0.7 and 1.2 eV.



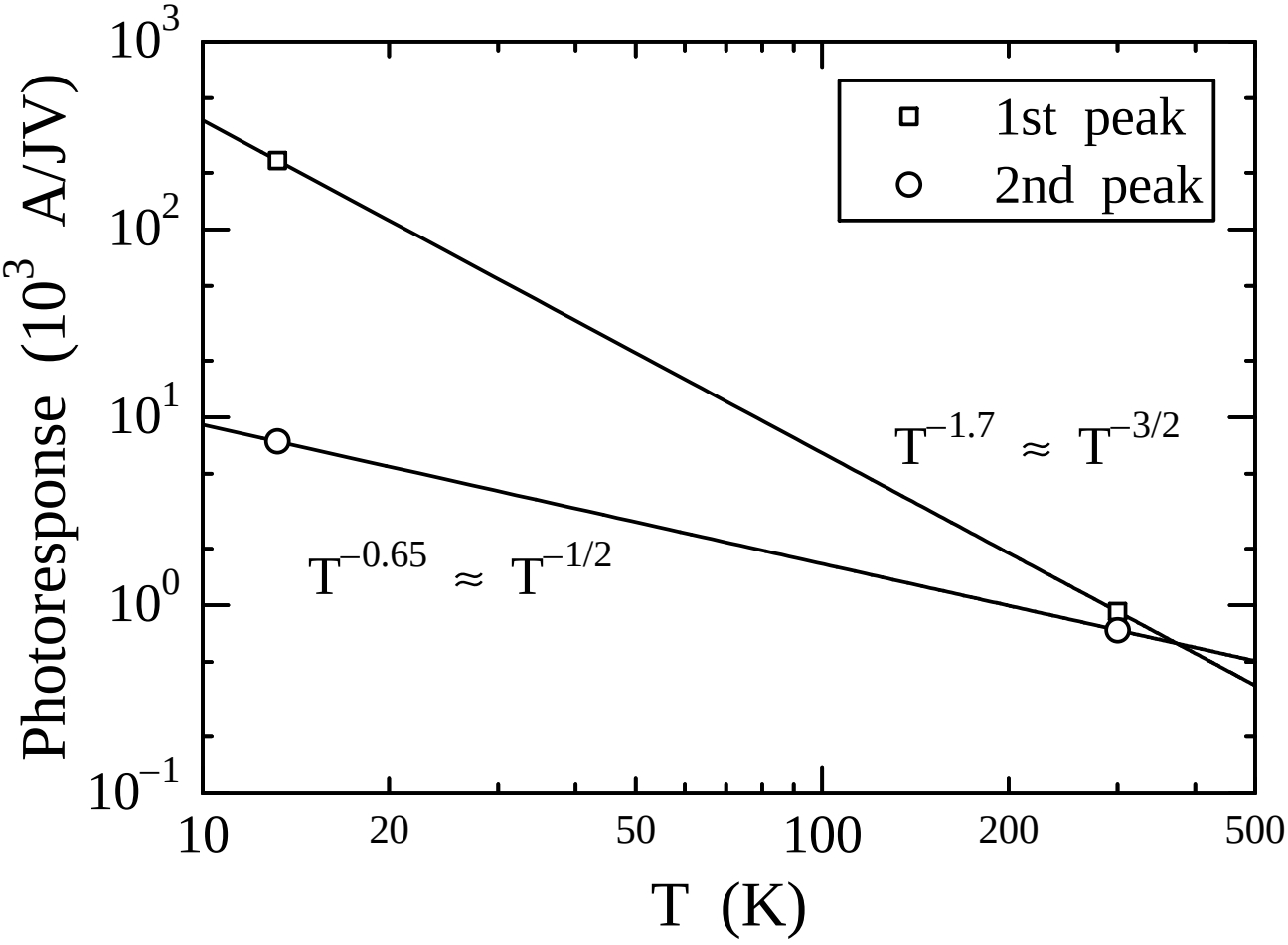
A. Fujiwara et al. Fig. 1



A. Fujiwara et al. Fig. 2



A. Fujiwara et al. Fig. 3



A. Fujiwara et al. Fig. 4