High-yield production of single-wall carbon nanotubes in nitrogen gas

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Received 30 November 2002; in final form 26 January 2003

Abstract

To see roles of an ambient gas on the formation process of single-wall carbon nanotubes (SWNTs), we have prepared SWNTs by laser ablation with Ne, Ar, Kr and N_2 gases and estimated the abundances of SWNTs mainly by Raman spectroscopy. The abundance of SWNTs was found to depend systematically on the pressure and the molecular mass of the ambient gas, and the highest abundance was obtained in N_2 at 1000 Torr. Only N_2 produced thinner SWNTs than any other gases, which suggests that the size of nanotube precursors is sensitively affected by the internal freedom of ambient gas.

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1. Introduction

In a synthesis process of single-wall carbon nanotube (SWNT) by laser ablation, 500 Torr argon gas has been used empirically as an ambient gas [1]. Recently, Jost et al. studied the correlation between abundances of SWNTs and conditions of ambient gas by using several inert gasses with various pressures [2]. They showed that the abundance of SWNTs was systematically changed and was roughly scalable by the pressure and molecular weight of the ambient gas. Zhang et al. synthesized SWNTs in a nitrogen atmosphere and confirmed that nitrogen was not reactive in the formation process [3]. However, detailed experimental condition has not yet been optimized to get high-purity SWNTs.

The present report is aimed to get the highest abundance of SWNTs by laser ablation using several inert gases at various pressures. The abundances and diameter distributions of the produced SWNTs were precisely checked by scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical absorption spectroscopy and Raman spectroscopy.

2. Experimental

SWNTs were synthesized by laser ablation using a Ni/Co (0.6/0.6 at.%) carbon composite rod. Details of the equipment are described elsewhere [4]. A quartz tube was heated to 1200 °C by an electric furnace, since SWNTs were found to result in the highest yield at 1200 °C when this catalyst was used in nitrogen atmosphere as well as in argon [5]. This indicates that the temperature for the optimum yield of SWNTs does not depend on the kind of ambient gas. The second harmonics of the Nd:YAG laser pulse (532nm, 10Hz, 300mJ/pulse) was focused on the surface of the composite rod which was rotating inside of the quartz tube. Neon, argon, krypton, and nitrogen were used as ambient gases. Gas pressure was set between 100 and 1500 Torr. Previous studies [5,6] clearly demonstrated that the diameter distribution of SWNTs was influenced by the flow rate of the ambient gas inside the quartz tube. The following reasoning can account for this effect. Though the temperature gradient in the central area of the furnace is very small, it is much larger near the exit (from 1200 °C to room temperature). Thus the growth process of SWNTs is significantly affected by the gradient when the flow rate (of ambient gas and, as a result, carbon and metal particles) is varied. In the present work the flow rate (linear velocity) of the ambient gas, instead of the velocity (pumping speed, cm^3/s), was fixed to 0.88 cm/s, so that the vaporized carbon and metal species could feel identical temperature-gradient history during the growth of SWNTs inside the furnace.

The abundance of SWNTs in the raw soot was investigated by SEM and TEM observation. The precise diameter distribution and the purity of SWNTs were estimated by Raman and optical absorption spectroscopy.

3. Results and discussion

3.1. Estimation of the abundance of SWNTs

Typical tangential-mode Raman spectra of raw soot synthesized under different conditions are shown in Fig. 1(a). A double peak appearing at 1593 cm^{-1}, so-called the G-band, is characteristic of SWNT, and a broad peak around 1350 cm^{-1}, the D-band, is usually regarded as the Raman mode of amorphous carbon. For a low-purity sample, the intensity ratio, G/D, reflects the abundance of SWNTs in the soot and is often used as an index of purity of the SWNT sample [5]. However, as indicated by a solid curve in Fig. 1(a) high-purity SWNTs have a narrower peak due to defects on the wall of SWNTs at the position of the D-band [7], and this narrow peak is higher for a sample of higher purity. Therefore, this G/D ratio is not a suitable index of purity for a high-purity sample. Basically, the Raman intensity of SWNT is strongly enhanced by the resonance effect [8, 9]. Since the resonance effect of amorphous carbon is much weaker, the absolute Raman intensity of the G-band is always a good index of purity of the sample. In this work, therefore, we measured the Raman spectra with great care to keep reproducibility, and then the integrated intensity of the G-band was used to evaluate the purity of SWNTs. The results are plotted in Fig. 1(b) as a function of the ambient gas pressure.

As shown in Fig. 1(b), the abundance of SWNTs depends on the ambient gas. The best abundance was obtained with N_2 at 1000 Torr and the second best cases were Ar at 1000 Torr and Ne at 1500 Torr; Kr at 800 Torr showed the lowest abundance. This finding can be explained as a systematic change in the abundance by their molecular masses, 20, 28, 40 and 84 for Ne, N_2, Ar and Kr, respectively. Namely, the abundance of SWNTs increases from Ne to N_2 with the molecular mass and then decreases from N_2 to Kr. A similar tendency has been reported [2].

In addition, the abundance of SWNTs strongly depends on the gas pressure. The Raman intensity of Ar at 1000 Torr is 1.8 times as large as that at 500 Torr. For all the gases the abundance first increases linearly with pressure, and then exhibits a broad maximum at an optimum pressure excepting Ne. According to a simple model introduced in Ref. [2], Ne gas should take the optimum pressure around 2000 Torr, far beyond our experimental condition. Indeed, our result suggests that the optimum pressure of Ne gas should exceed 1600 Torr. The most important outcome of the present

study is the very high abundance observed for N_2 at 1000 Torr, which has never been reported.

SEM images of untreated raw soot synthesized in various gases are shown in Figs. 2(a)-(d). Many amorphous carbon materials, like lumps of cotton in their SEM images, were observed in Fig. 2(d); this displays low purity of the SWNTs produced in Kr. The amount of amorphous carbons appearing in Fig. 2(a) and (b) are much less than that in Fig. 2(d). SWNTs seem to have gathered with higher density in Fig. 2(a) than the others. On the other hand, TEM images (not shown) have also indicated a similar tendency of the abundance. Especially, many bare metal particles are found in the TEM image of the N_2 sample, whereas metal particles in the other samples are covered with amorphous carbon. These bare metal particles indicate that all the surrounding amorphous carbon is converted to SWNTs. These intuitive estimations of the abundance using SEM and TEM observations are consistent with that of purity by the Raman analysis.

3.2. Low-frequency Raman spectra of SWNTs

Figure 3 indicates the Raman spectrum of the soot produced in each condition described above. The Raman peaks observed in this range are the radial breathing modes (RBMs) of SWNTs, of which the frequency is proportional to the inverse diameter of SWNTs [10, 11]. The RBM spectra for rare gases are essentially independent of the gas and the pressure. As mentioned in Sec. 2, the gas flow rate was adjusted to a constant value to avoid variation in the temperature gradient inside the furnace that influences the diameter distribution of SWNTs [5,6]. Figure 3 shows hardly any change in the diameter distribution of SWNTs in all ambient gases and at all pressures (except for N_2). This suggests that the molecular mass of rare gas is inessential for controlling the diameter distribution of SWNTs. Moreover, the gas pressure does not influence their diameter distribution. For N_2, however, the RBM peaks show blue shifts of 20 cm^{-1} from those of rare gases. According to a simple relationship between the RBM frequency and the diameter of SWNTs [11], a shift of 20cm^{-1} corresponds to a decrease of 0.2 nm in the diameter distribution. This change can be achieved for rare gas if the furnace temperature is lowered by 50 °C [5].

The reason why only the SWNTs grown in N_2 was thinner than the others is probably related to the fact that only N_2 is a diatomic molecule and its vibrational degree of freedom affects the cooling process of vaporized carbon by collision. Actually, spontaneous emission from vaporized carbon clusters observed with a high-speed video camera indicates that black body radiation from high-temperature carbon particles in N_2 atmosphere fades out more quickly than in Ar [12, 13]. This strongly suggests that N_2

gas cools carbon vapor more effectively than rare gases. The mean diameter of SWNTs is known to become thinner as the ambient temperature is lowered [5]. Thus an additional cooling process due to an extra internal freedom in a diatomic gas may lower the effective growth temperature of SWNT by about 50 °C compared with rare gases.

3.3. Optical absorption spectra of thin films including SWNTs

Since the energy gap of SWNT is widened as its diameter becomes thinner, a difference in the resonance effect should be taken into account in the use of Raman intensity to study the abundances of SWNTs with different diameters [9]. Since nitrogen gas was found to generate thinner SWNTs, we have measured optical absorption to confirm its high purity. The spectra of soot synthesized in Ar and N_2 at 1000 Torr are shown in Fig. 4. Since the thickness of each film is unknown, the absorption intensity is normalized at the highest absorption peak around 5 eV. A broad peak around 5eV originates from the π-plasmon of amorphous carbon while that of SWNTs appears at 4.5 eV [9]. Soot prepared in Ar gas shows a broad peak at 4.8 eV (see Fig. 4), and that in N_2 at 4.5 eV with a shoulder at 5 eV. On the other hand, three peak structures appearing in the infrared (IR) region are optical transitions between spikes in the density of states due to 1D-van Hove singularities in SWNTs. The N_2 sample shows more intense IR absorption peaks than the Ar sample. These spectral features apparently indicate that carbons in the N_2 sample are less amorphous than in Ar. Furthermore, the peak positions for the IR absorption for the N_2 sample are slightly higher. This finding is consistent with the conclusion derived from the Raman analysis that nitrogen produces thinner SWNTs than argon.

4. Summary

We have used neon, argon, nitrogen and krypton as ambient gases for laser ablation to see the role of the ambient gas. Raman spectra, SEM, TEM and optical absorption spectra indicate systematic changes in the abundances of SWNTs as a function of molecular mass and the pressure of the ambient gas. The highest purity of synthesized SWNTs has been obtained with nitrogen at 1000 Torr, where the Raman intensity is 1.8 times as high as that with argon at 500 Torr. Moreover, only nitrogen gas is found to produce SWNTs thinner than others by about 0.2 nm. A higher cooling rate in the nitrogen gas, probably due to the additional cooling by the vibrational degree of freedom, may cause a smaller precursor of SWNTs.

The results obtained in the present work indicate that the pressure and the molecular mass of the ambient gas are not sensitive parameters to control the mean diameter

distribution of SWNTs obtained by laser ablation. However, they are found to be important parameters for achieving higher abundance of SWNTs in soot generated by this method. The highest abundance of SWNTs has been obtained with N_2 at 1000 Torr. Still higher abundance with controlled diameter distribution may be achieved by a similar laser vaporization procedure in a mixed gas phase, where the effect of molecular mass can be optimized.

Acknowledgements

The authors are grateful to Y. Misaki for TEM observation. This work was supported in part by a Grant-in-Aid for Scientific Research (A) No. 13304026 by the Ministry of Education, Science, Sports, Culture and Technology of Japan, and in part by the research project from Japan Society for the Promotion of Science. K.T and Y. Ao. acknowledge the financial support from Industrial Technology Research Grant in 2001 from New Energy and Industrial Technology Development Organization (NEDO) of Japan, and a Grant-in-Aid by Japan Society of the Promotion of Science.

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Figure captions

Fig. 1. (a) Typical Raman spectra of soot produced by laser ablation excited by 488 nm Ar^+ laser. A dotted curve indicates a spectrum of the soot produced in 300 Torr Ar, and a solid curve in 1000 Torr N_2. To see details of the D-band parts, the spectra are magnified vertically and one shifted upward. For relative estimation of the purity of SWNTs, all Raman spectra were recorded under the same setup. (b) Integrated intensity of the G-band (from 1470 to 1670 cm^{-1}) as a function of the ambient gas pressure in Ne (open circles), Ar (solid triangles), Kr (solid squares), and N_2 (solid circles).

Fig. 2. Typical SEM images of soot produced in 1000 Torr (a) N_2, (b) Ar, (c) Ne, and (d) Kr gases.

Fig. 3. Low-frequency Raman spectra of (a) soot synthesized in Ar (thick solid), Ne (dotted) and Kr (thin solid); (b) soot synthesized in Ar (solid) and in N_2 (dotted).

Fig. 4. Optical absorption spectra of thin films of soot. Upper spectra show soot produced in 1000 Torr Ar (dotted) and N_2 (solid). Lower spectra are purified SWNTs (solid) and amorphous carbon (dotted) as references.

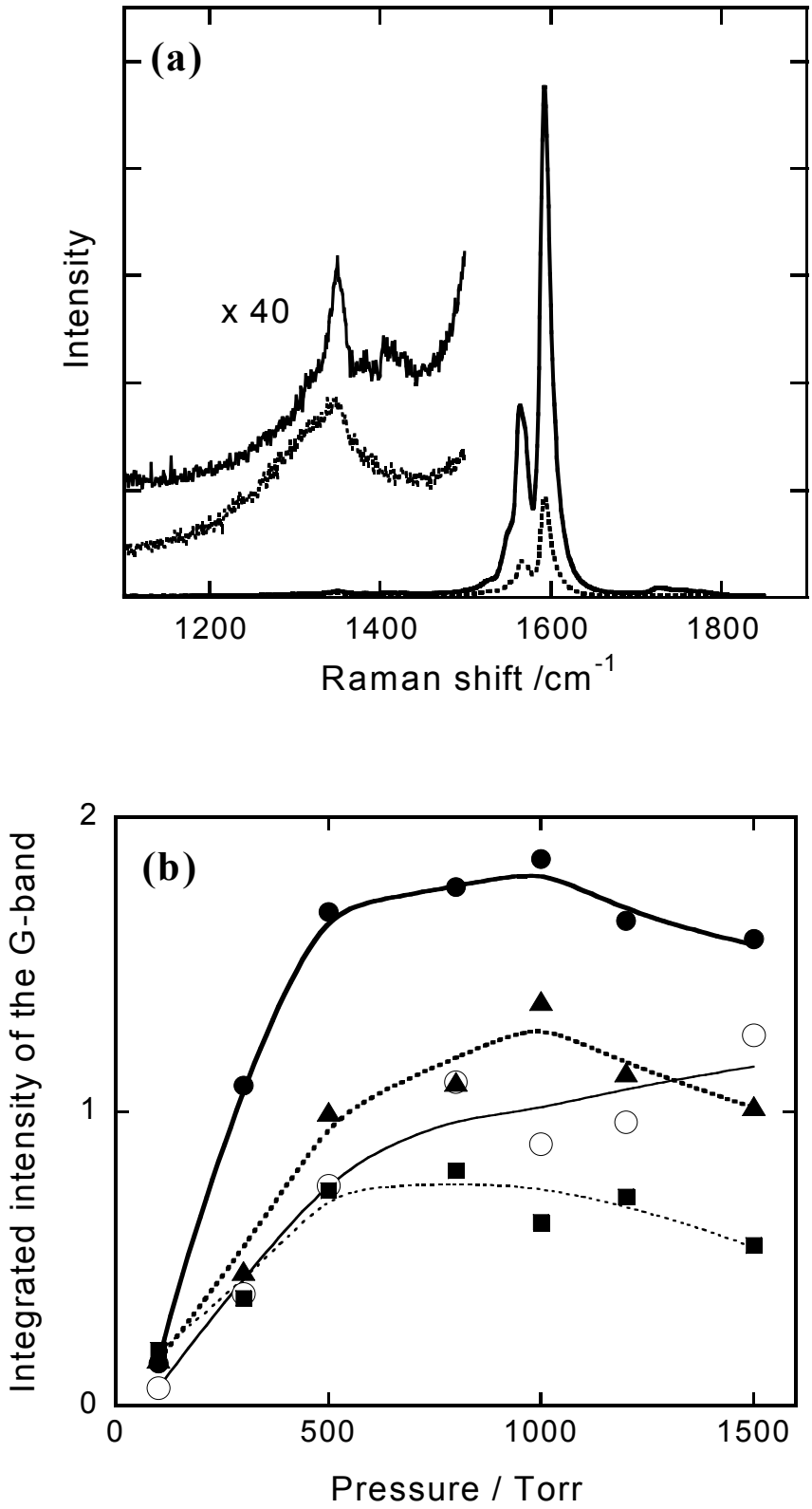

Figure 1, Nishide et al.

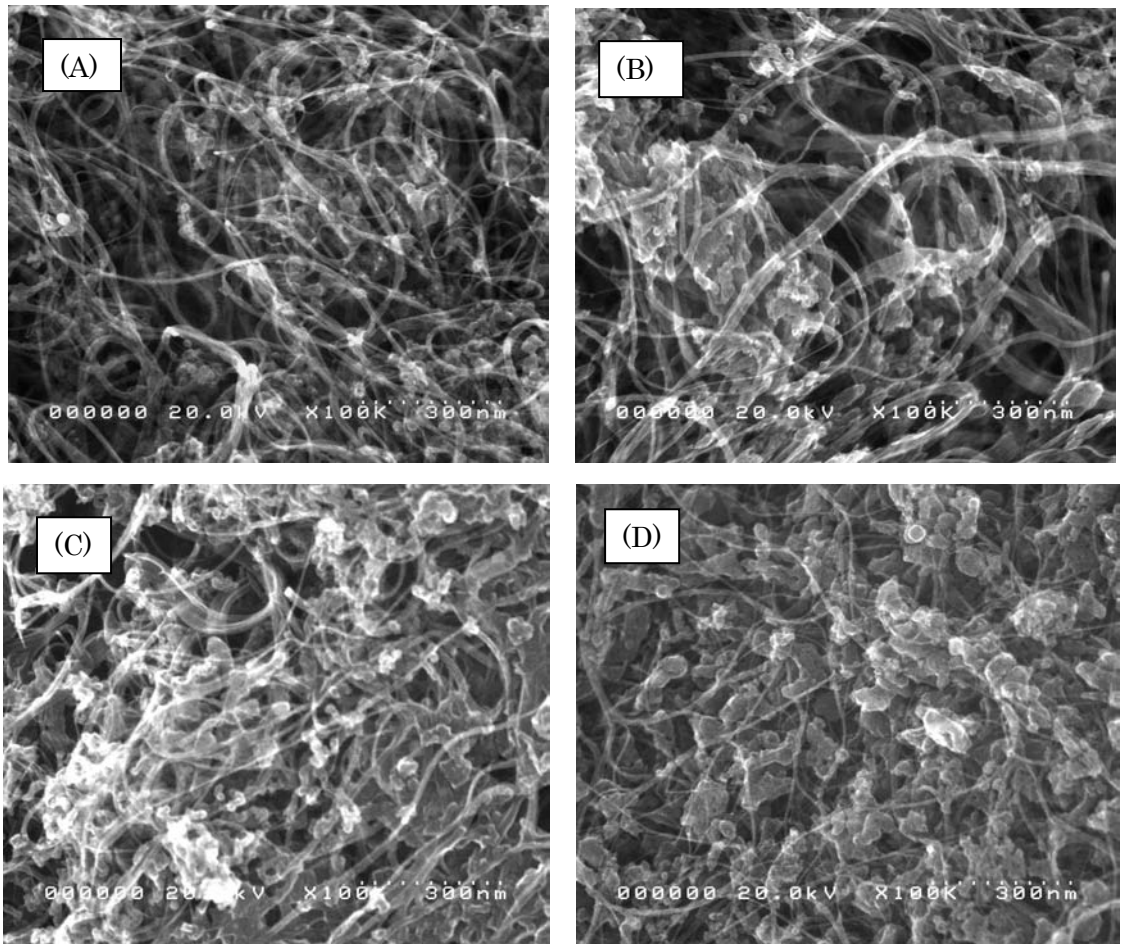

Figure 2 Nishide et al.

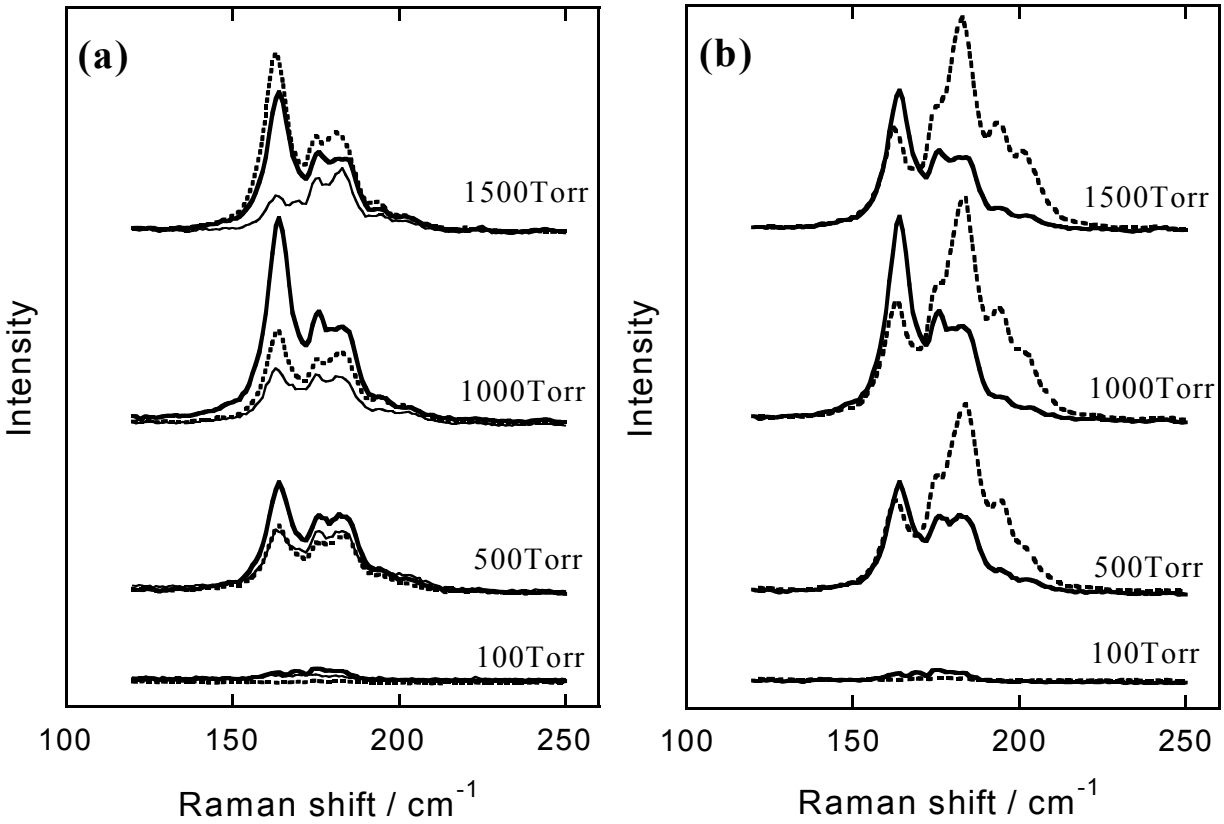

Figure 3, Nishide et al.

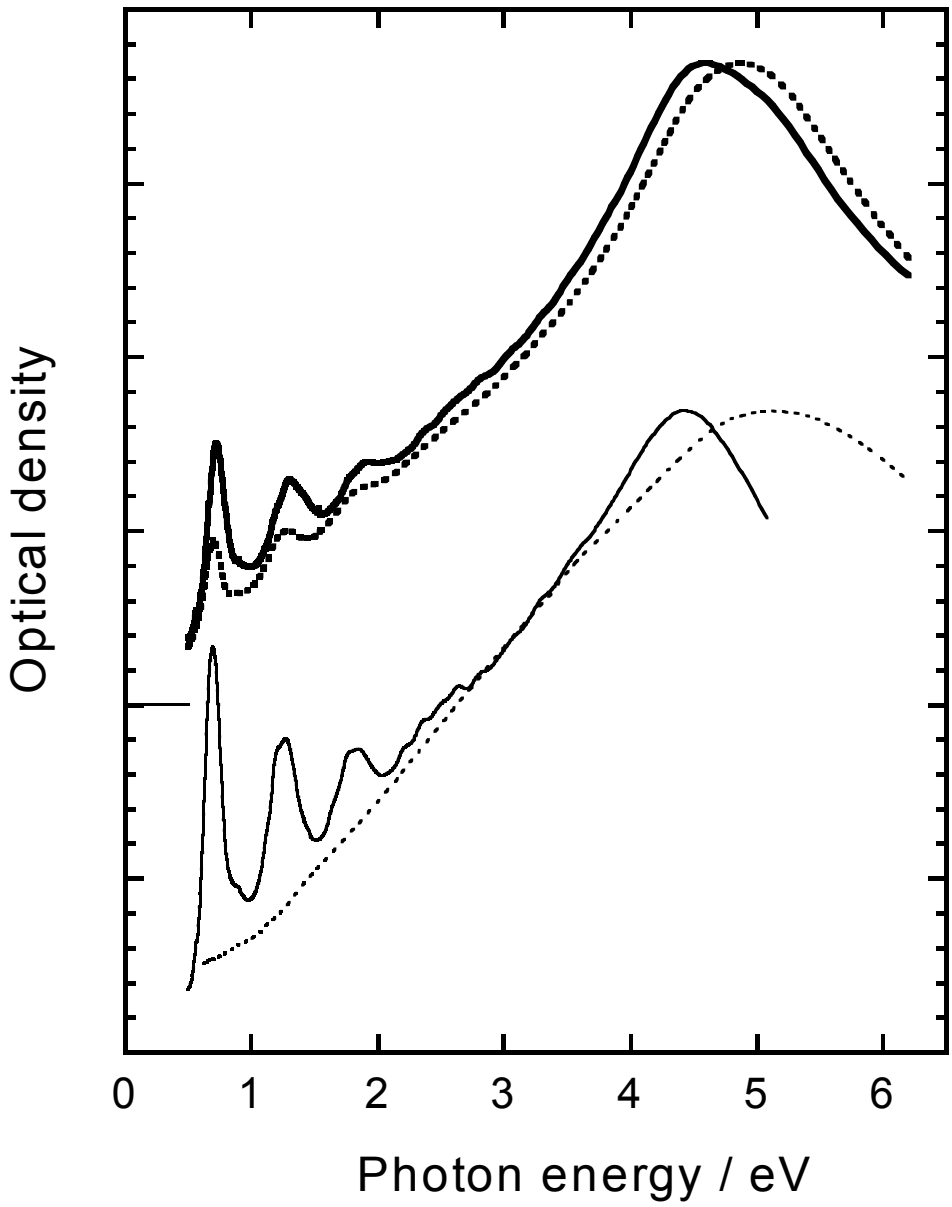

Figure 4, Nishide et al.