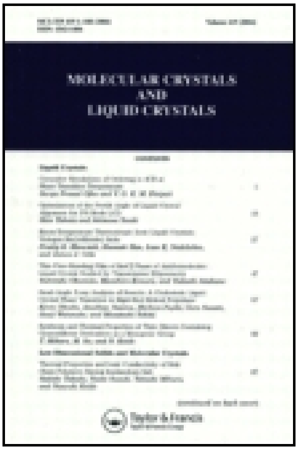

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We have measured Raman spectra of bromine doped single-walled carbon nanotubes (SWNTs) using various laser lines to clarify the electronic states of the doped SWNT. In the case of evacuated sample after full doping, two breathing mode peaks were observed simultaneously by visible laser excitations. We assigned the higher frequency peak to the doped SWNT bundles, and the other peak to the undoped portions in the sample. Intensity ratio between them decreased with decreasing excitation energy, and in the infrared region, the breathing mode band of the doped bundle was not observed. These results can be explained by a simple rigid band model.

Keywords: nanotubes; single-walled carbon nanotubes; doping; Raman scattering; electronic states

INTRODUCTION

Lee *et al.*[1] have reported that the bromine doped single-walled carbon nanotube (SWNT) bundles show a remarkable enhancement on conductivity and a typical metallic character in temperature dependence. At the same time, Rao *et al.*[2] have shown that the shift of Raman peak can be used as a effective scale of the charge transfer between SWNTs and dopants. When we discuss about Raman spectra of SWNTs, however, we have to take into account the fact that the resonance effect is dominant in this system. Because the sample contains many kinds of SWNTs with different chiral indexes that have different electronic states [3], we have to measure the Raman spectra for various excitation energies to see the detail of the electronic states of SWNTs and doping effects.

EXPERIMENTAL

SWNTs were prepared by a conventional electric arc method using NiY catalyst [4]. Transmission electron microscope (TEM) observation revealed that the bundle size of the SWNTs was much smaller than SWNTs by laser ablation method using NiCo catalyst [5] and that considerable amount of individual SWNTs existed in the sample. The sample for doping was homogenized by the ultra sonic agitation. Then it was dried and installed into a quartz ampoule. Saturated bromine vapor was introduced to the ampoule at room temperature after evacuation. Then the ampoule was sealed off. We prepared several samples with different depth of doping. In this report, however, we will show the results about the sample of which the ampoule was evacuated after doping.

Raman spectra were measured using a JOBIN YVON U1000 double monochromator and HAMAMATSU PHOTONICS photon counting system interfaced to a personal computer. Ar^+, dye and Ti-sapphire lasers were used for the excitation.

RESULTS AND DISCUSSION

Low frequency resonance Raman spectra for visible to near infrared excitation are shown in Fig. 1 (a). For visible excitation, two structures around 180 cm^{-1} and 240 cm^{-1} were observed. The structure around 180 cm^{-1} is similar to the breathing mode of the pristine sample. When we measured the fully doped sample, we observed only one peak around 260 cm^{-1}, which is consistent with

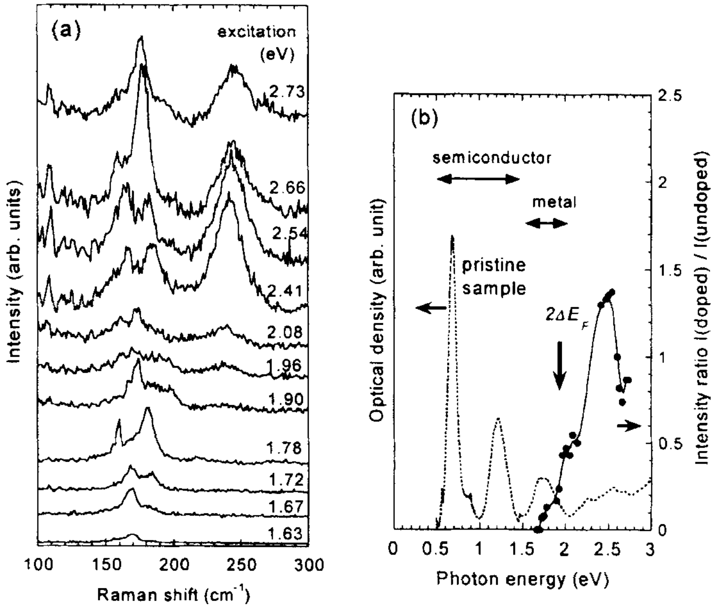

FIGURE 1. (a) Resonance Raman spectra of bromine doped SWNTs. Sample was evacuated after full doping. (b) Intensity ratio of breathing modes between doped and undoped portions. Dotted curve indicates an optical absorption spectrum of pristine sample. Background absorption was subtracted.

the results of Rao *et al.*[2] Further, it was found that heating in vacuum up to 250 °C was required to remove the bromine completely. Thus, we concluded that the structure around 240 cm^{-1} is the breathing mode of the partially doped SWNT bundles and the structure around 180 cm^{-1} is that of undoped portions namely, individual SWNTs in the sample.

Relative intensity of the breathing mode bands of doped bundles decreased with decreasing the excitation energy. The peak around 240 cm^{-1} disappeared for the near infrared excitation. Intensity ratio between doped and undoped portions is shown in Fig. 1 (b) as a function of the excitation energy. Optical absorption spectrum of the pristine sample is also indicated. It is clearly seen that the Raman intensity of doped portion arises around the third absorption peak of the pristine sample. It is already known that the first and second absorption peaks are due to the optical transition between spike like density of states of semiconductor SWNTs in the sample and that the third peak is originating from the metallic SWNTs. Further, the integrated intensity of breathing mode is roughly proportional to the optical absorption[6]. Thus, our present results indicate that optical transitions lower than 1.8 eV disappear by the bromine doping. Indeed, Chen *et al.*[7] have shown that the absorption peaks of SWNT solution at 0.67 and 1.2 eV disappeared after the bromine doping.

This result can be explained by a simple rigid band model. Initially, pristine sample contains both the metallic and semiconducting SWNTs. From the

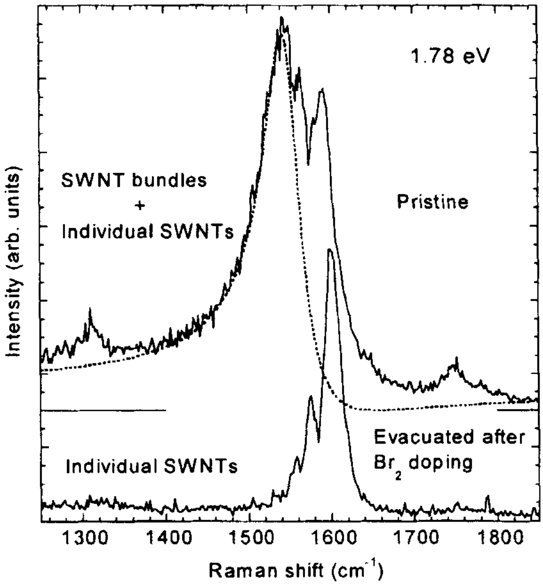

FIGURE 2. Near infrared Raman spectra of pristine and bromine doped SWNTs. Conditions of the measurement were the same. Dotted curve indicates the fitted Fano line shape. Here, ω_0 = 1548 cm^{-1}, 1/q = −0.25 and Γ = 27 cm^{-1}.

Raman and TEM observations, it was known that the diameters of constituent SWNTs spread from 1.1 to 1.5 nm and were weighted on 1.3 nm. Energy bands of SWNTs can be calculated by zone folding method[3]. For example, the first and second energy gaps of (10,10) SWNT are 1.7 and 3.23 eV, respectively. On the other hand, energy gaps of semiconductor (14,6) are 0.57, 1.09, 2.29 and 2.58 eV. Charge transfer from SWNT to bromine causes a change of Fermi energy for both kinds of SWNTs. If the energy shift ΔE_F is about -0.9 eV, optical transitions lower than 1.8 eV will disappear due to the lack of density of states. Consequently, we cannot observe any resonance Raman scattering. On the other hand, energy gaps larger than 1.8 eV are still effective for the resonance Raman scattering. The zone folding calculation indicates that observed resonance Raman peaks, excitaed in a range from 2 to 2.7 eV, are originating from the doped semiconductor SWNTs[6].

Now we pay attention to the individual SWNTs remaining in the doped sample. In the case of pristine sample, Fano line shape was observed when the excitation was at the optical transition of metallic SWNTs[6]. However, we did not observe Fano line shape for any excitation energy on the bromine doped SWNTs. Figure 2 shows infrared high frequency Raman spectra of the pristine and bromine doped SWNTs. As we mentioned above, the Raman signal from the bromine doped bundle could not be observed at this photon energy. Thus, the Raman spectrum of the doped sample indicates that of the individual SWNTs. On the other hand, the pristine sample contains both the bundles and individual SWNTs. Its Raman spectrum seems to be reproduced with a superposition of asymmetric Fano line shape and sharp Raman lines of individual SWNTs. If the Fano line shape is originating only from the metallic bundles, this result is quite reasonable. However, scanning tunneling spectroscopy measurements have indicated that armchair SWNT showed metallic behavior whether it was in bundle[8] or isolated[9]. It is still unknown why the individual SWNTs do not show Fano line shape.

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