Ethanol Gas Adsorption Effect on Photoluminescence Spectra from Single-Walled Carbon Nanotubes

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1. Introduction

Single-walled carbon nanotubes (SWNTs) are cylindrical shape, as a rolled up graphene sheet, whose diameter is a few nm and length was a few µm. SWNTs have attracted attention in many fields since their discovery in 1993, because of their unique structures and properties.

SWNTs have van Hove singularities in the density of states owing to their one-dimensional structure, and showed optical transition between them. Semi-conducting SWNTs showed photoluminescence (PL) emission in near-infrared wavelength range, when they were dispersed in solutions with wrapping medium or they were suspended between a micro-structure. PL measurement was one of the important analysis techniques for determination of SWNT chirality ($n$, $m$) and investigation of optical properties. However, the optical transition energies ($E_{11}$, $E_{22}$, ...) which were obtained by PL measurement strongly depended on environmental conditions, such as species of wrapping medium, pH of solutions, temperature and so on. Therefore it was important to understand the environmental effects of the PL spectra.

In this paper, we studied the influence of gas atmosphere on PL spectra, as one of the environmental conditions. Ethanol gas, which adsorbed on graphite at room temperature, was used as ambient gas, and PL spectra were measured from SWNTs suspended between a pair of quartz pillars. From investigation of the effect of ethanol gas pressure on PL spectra, we discuss about the SWNT bundle structure.

2. Experiments

SWNTs were synthesized from cobalt metal catalysts based on alcohol catalytic chemical vapor deposition (ACCVD) method. In advance, quartz pillar structures were fabricated on quartz substrates by using photolithography technique. The pillar height and diameter were 5 and 2 µm, respectively, and the pillar spacing was 5, 7 or 10 µm. Silicon layer was deposited on the substrates except for the top of the quartz pillars, and then cobalt was deposited on the whole surface with a vacuum evaporator. Because the deposited cobalt except for the pillar tops became silicide with the silicon layer, they did not act as the catalyst of SWNT growth. Most SWNTs were grown from the top of the pillars and SWNTs suspended between pairs of pillars were obtained. In Ar/H2 mixture gas (3 % H2 by volume), the substrates were heated up to CVD temperature (850 °C) with an electronic furnace. At the CVD temperature, the CVD gas, which was ethanol gas bubbled with Ar/H2 gas, was introduced. The CVD time was 5 min. SWNTs were observed by scanning electron microscopy (SEM).

A Ti:sapphire laser, whose wavelength ranged from 700 to 830 nm, was used as the PL excitation laser. PL emission spectra were measured with a multi-array-channel InGaAs detector (900-1600 nm). The excitation laser was focused with an objective lens (50x), and the laser spot was approximately 2 µm in diameter. Since every pillar was numbered, the same SWNT was measured repeatedly.

PL measurement was performed in an environmental chamber. In the chamber, the temperature and the gas atmosphere were controlled. The sample was heated with a silicon heater by Joule-heating technique. Ethanol gas was used as ambient gas, and the pressure was controlled with a mechanical scroll pump and a gas mass-flow controller.

3. Result and Discussion

SEM image of SWNT suspended between a pair of quartz pillar is shown in Fig. 1. Most SWNTs were grown on the pillar top, and some of them were suspended. Because suspended SWNTs did not touch with any substrates or dispersed medium, they emitted sharp and intense PL spectra. PL maps measured from a (9,8) SWNT in ethanol gas ambient (50 Torr) and in vacuum (10-2 Torr) were shown in Fig. 2. In ethanol gas, the emission and excitation

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**Fig. 1** SEM image of SWNT suspended between a pair of quartz pillars.

**Fig. 2** PL maps from suspended a (9,8) SWNT (A) in ethanol gas and (B) in vacuum.
energies ($E_{11}$ and $E_{22}$) were almost the same as those in air [1]. On the other hand, both $E_{11}$ and $E_{22}$ in vacuum were blue-shifted, as shown in Fig. 2(B).

Figure 3 shows the ethanol gas pressure and temperature dependence of PL emission peak wavelength. PL emission peak rapidly shifted at a transition pressure. The peak slightly blue-shifted with decreasing ethanol gas pressure above the transition pressure, while no pressure dependence appeared below the transition pressure. All suspended SWNTs showed the energy transition depending on ethanol gas pressure, as shown in Fig. 3 and the transition pressure increased with increasing SWNT temperature. The ethanol pressure and temperature dependence of PL spectra were explained with the adsorption and desorption of ethanol molecules on SWNT surfaces [2]. Though ethanol molecules hardly adsorbed on SWNT surface below the transition pressure, ethanol molecules adsorbed and ethanol layer was formed on SWNT surface above the transition pressure. Adsorbed ethanol molecules increased the dielectric constant surrounding SWNTs, which changed the binding energy of excitons in SWNTs. Therefore PL spectra depended on the ethanol gas pressure.

PL spectra measured at various ethanol gas pressures are shown in Fig. 4(A). The peak width drastically increased at the transition pressure, although the peak width was almost the same above and below the transition pressure. The ethanol gas pressure dependence of PL spectra indicated that ethanol molecules uniformly adsorbed or desorbed on SWNT surface at the transition pressure.

On the other hand, some SWNTs showed complex PL spectra in ethanol gas atmosphere, as shown in Fig. 4(B). PL peak broadened or the multiple peaks appeared around the transition pressure and even below the transition pressure (less than $10^{-2}$ Torr), the complex PL peak feature remained. Moreover, the peak shape became sharp (spectrum after heating in Fig. 4(B)) after annealing in vacuum (100 °C).

The gas pressure dependence as shown in Fig. 4(B) indicated that some ethanol molecules were adsorbed more stably and the adsorption and desorption phenomena did not occur uniformly over the SWNT. If the suspended SWNT was in bundle and touched with other SWNTs, an additional adsorption site, such as interstitial sites [3] which had higher desorption energy, existed. Therefore, we considered that isolated SWNT, which was not contiguous with any SWNT, showed clear pressure dependence as shown in Fig. 4(A), while bundles SWNTs showed complicated pressure dependence.

Interestingly, there was no significant difference of PL spectra between the isolated SWNTs and the bundled SWNTs. It indicated that the SWNTs in bundle emitted PL spectra if it did not touch with metallic one and both the structure and the dielectric constant were not affected by the neighboring SWNTs.

4. Conclusions

PL spectra from suspended SWNTs were measured in ethanol gas atmosphere and they showed the ethanol gas pressure dependence. However, some SWNTs showed clear pressure dependence, though the others did complex one. We considered that the complex pressure dependence come from SWNTs in bundle, because the adsorption site of isolated SWNTs was only the surface and bundled SWNTs had additional sites, such as interstitial sites.

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References