STM/STS on Carbon Nanotubes at Low Temperature

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Abstract. Single-wall carbon nanotubes (SWNT's) prepared on the graphite substrate were investigated by a low temperature STM at 290 and 77 K. At 290 K, we obtained STM images of bundle structure. SWNT's with a diameter of about 1 nm are aligned closely in the bundle. From the tunneling spectra with high energy resolution obtained at 77 K, both metallic and semiconducting SWNT's were found in the same bundle. For the metallic SWNT, the conductance curve inside the first peak is finite and quite flat. The width between the first peaks is obtained as 1300 meV. Fine structures were observed just outside the first peak. The observed gap width for the semiconducting SWNT is 600 meV. The conductance curve due to the tunneling between SWNT's was observed.

INTRODUCTION

It is well known that electronic properties of carbon nanotubes depend on their chirality. It is important to elucidate the relation between the electronic state and the chirality for understanding the conduction mechanism in carbon nanotubes. The scanning tunneling microscope (STM) is a powerful tool to probe carbon nanotubes because it can obtain the structural image with the atomic resolution and investigate the local electronic state simultaneously. The spectroscopic measurement called as scanning tunneling spectroscopy (STS) is quite useful due to much less disturbance on the electronic state at the sample surface. It is important to reduce the thermal excitation which smears the spectrum in the spectroscopic measurement. STM and STS measurements on single-wall carbon nanotubes (SWNT's) were reported by Wildoer et al. [1] and Odom et al. [2] at 4.2 and 77 K, respectively. Recently, the peak splitting for the metallic SWNT is predicted [3, 4]. Further investigation with high energy resolution is needed for STS.

We have investigated the fine structure in the tunneling spectra on SWNT's using a low temperature STM. In this paper, we present STS results with high energy resolution on carbon nanotubes in bundles at 77 K. We found both metallic and semiconducting features in tunneling spectra of SWNT's in a bundle. The fine

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structure in the spectra observed for the metallic SWNT is discussed.

EXPERIMENTAL

Single-wall carbon nanotubes were synthesized by the conventional arc-discharge method with catalysts of Ni-Y (Ni:Y = 4.2:1 at. %). The SWNT sample for the STM measurement was prepared by dropping SWNT's agitated ultrasonically in ethanol on the cleaved KISH graphite. The cell which contains the STM unit is filled with a low pressure of helium gas as the thermal exchange. In the STS measurement, the tunneling differential conductance was measured directly by the lock-in technique, in which 1 kHz AC modulation with the amplitude of 15 mV was superposed in the sweep bias voltage.

RESULTS AND DISCUSSION

Figure 1(a) shows topographic image of a SWNT sample on the graphite substrate at 290 K with the tunneling current I=70 pA and the bias voltage V=150 mV. A bundle of nanotubes was found as pointed by an arrow in Fig. 1(a). The image indicates that SWNT's are aligned closely in parallel in each bundle. Although the atomic resolution is not obtained, individual SWNT's are imaged. Figure 2(b) shows the scan profile between A and B in Fig. 1(a). The profile across the bundle shows the arrangement of SWNT's which are closely spaced. The diameter of SWNT's is estimated as about 1 nm from the width of the corrugation.

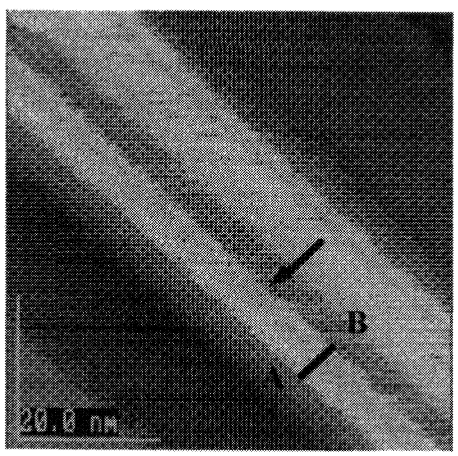

FIGURE 1(a). Topographic image of SWNT bundle. A bundle is pointed by an arrow.

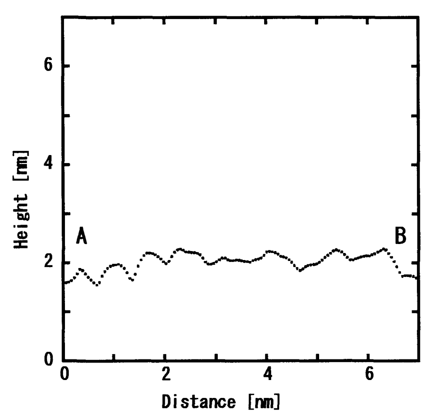

FIGURE 1(b). Profile between A and B. The distance is measured from point A.

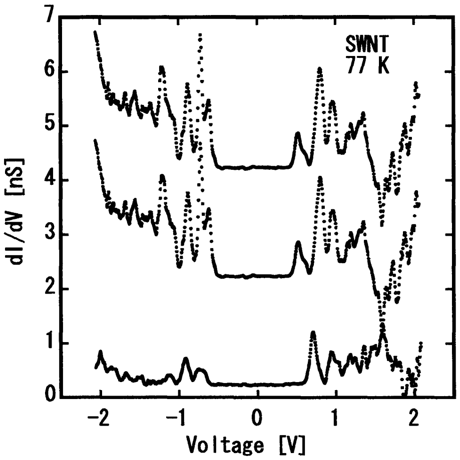

FIGURE 2. Tunneling differential conductance at 77 K. Spectra were obtained in sequence at the fixed position. The zero conductance line of each curve is shifted by two divisions for clarity.

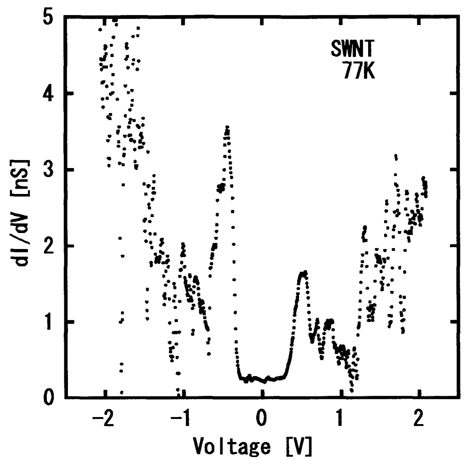

FIGURE 3. Tunneling spectra for the semiconducting SWNT at 77 K.

We succeeded to obtain tunneling spectra at the same bundle with varying the tip position at 77 K. In most cases, we obtained spectra which have finite conductance at zero bias voltage. Figure 1 shows the tunneling differential conductance curves obtained at the fixed position in sequence. Although the spectra are a little noisy, almost the same feature is reproduced. The conductance around the Fermi energy, which corresponds to zero bias voltage, is finite and flat. This indicates that the observed spectra corresponds to the electronic density of states (DOS) for the metallic SWNT. At about $V=\pm 650$ mV, the conductance shows a divergent peak like the gap edge. This peak corresponds to the van Hove singularity in the density of states for nanotubes [5]. The width between the first peak is almost consistent with that for the metallic SWNT reported by Wildoer et al. [1]. It is noteworthy that the conductance inside the first peak is much flat as compared with that in previous reports [1, 2].

Additionally, we found a few peaks located just outside the first peak at intervals of about 200 mV. Although there is a little shift in peak position, these structures are almost reproduced qualitatively as shown in Fig. 2. We point out the possibility that these fine structures are regarded as the splitting of the first peak. The first DOS peak for metallic nanotubes is predicted to split into two peaks due to the anisotropy of the Fermi surface depending on the chirality [3, 4]. Fine structures in present spectra might be related to this DOS splitting. However, the observed splitting width of about 200 meV is much larger than predicted one which is of the order of 10 meV. We need further investigation of the origin of these fine structures.

We found another type of tunneling spectra as shown in Fig. 3 at another SWNT in the same bundle. Although the conductance near the Fermi energy is finite and flat, the conductance value is smaller as compared with the metallic SWNT shown in Fig. 2. The width between the first peaks of about 600 meV is less than one half of that in Fig. 2. This width value is almost consistent with the estimation for the gap width in the semiconducting SWNT with a diameter of 1.2 nm. We consider that these spectra correspond to the semiconducting SWNT. We should note that both metallic and semiconducting SWNT's were found in the same bundle.

We point out the possibility of the tunnel junction between nanotubes. In rare cases, we found different conductance curves from above two types. The conductance is not flat near zero bias voltage. There are broad conductance peaks around $V=\pm 80$ mV. These features are partially explained by the tunneling between SWNT's which have different chirality [6]. It is likely that the tunneling junction between SWNT's is formed since nanotubes are contacted each other in a bundle.

In summary, SWNT's were studied by a low temperature STM. SWNT's aligned in a bundle were imaged at 290 K. Both metallic and semiconducting SWNT's were found in the same bundle by STS at 77 K. For the metallic SWNT, the conductance curve inside the first peak is quite flat. Fine structures just outside the first DOS peak were found in the tunneling spectra. For the semiconducting SWNT, the conductance value at zero bias voltage is much smaller than that in the metallic SWNT. The gap width of 600 meV is less than a half of the width between the first peaks in the metallic SWNT. The conductance curve, in which the peak appears at about $V=\pm 80$ mV, is partially explained by the tunneling between SWNT's in a bundle.

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