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Tunneling spectroscopy on carbon nanotubes using STM

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Abstract

Single-wall carbon nanotubes (SWNTs) prepared on the graphite substrate were investigated by a low-temperature scanning tunneling microscope at 77 K. From the tunneling spectra with high-energy resolution obtained at 77 K, both metallic and semiconducting SWNTs 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 due to the anisotropy of equi-energy contours around the K point were observed just outside the first peaks. The observed gap width for the semiconducting SWNT is 600 meV. The conductance curve, which has broad peaks around $V = \pm 80$ mV was also observed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electronic properties of carbon nanotubes depend on their chirality. 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 useful since it can obtain the electronic density of states with less disturbance on the sample surface. STM and STS measurements on single-wall carbon nanotubes (SWNTs) 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 reported [3,4].

We have investigated the fine structure in the tunneling spectra on SWNTs using a low-temperature STM. In this manuscript, we present STS results with high-energy resolution on SWNTs in bundles at 77 K.

2. Experimental

SWNTs 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 SWNTs agitated ultrasonically in ethanol on the

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cleaved KISH graphite. The cell which contains the STM unit is filled with a low-pressure 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 an amplitude of 15 mV was superposed in the sweep bias voltage.

3. Results and discussion

In STM imaging measurement, we always observed the bundle structure of SWNTs. Topographic image of a SWNT sample on the graphite substrate shows bundles. The image indicates that SWNTs are aligned closely in parallel in the bundle. Although the atomic resolution is not obtained, individual SWNTs are imaged. The scan profile across the bundle shows the arrangement of SWNTs which are closely spaced. The diameter of SWNTs is roughly estimated as about 1 nm from the width of the corrugation.

We succeeded to obtain tunneling spectra at the same bundle with varying the tip position at 77 K. The tunneling differential conductance curves for the metallic (Fig. 1(A)) and the semiconducting (Fig. 1(B)) SWNTs were found in the same bundle. The conductance for the tunneling spectra shown in Fig. 1(A) is finite and flat around zero bias voltage, which corresponds to the Fermi energy. The finite conductance at the Fermi energy indicates the metallic feature. Therefore, the conductance curve in Fig. 1(A) corresponds to the electronic density of states (DOS) for the metallic SWNT. At about $V = \pm 650\,\mathrm{mV}$, the conductance shows a divergent peak, which corresponds to the van Hove singularity [5]. The width between the first peak is almost consistent with that for the metallic SWNT reported by Wildoer et al. [1]. Additionally, we note that the conductance inside the first peak is much flat as compared with that in previous reports [1,2].

We found a few peaks located just outside the first peak at intervals of about 200 mV. We point out the possibility that these fine structures are regarded as the splitting of the first peak. The DOS peak for metallic nanotubes is predicted to split into two peaks due to the anisotropy of equi-

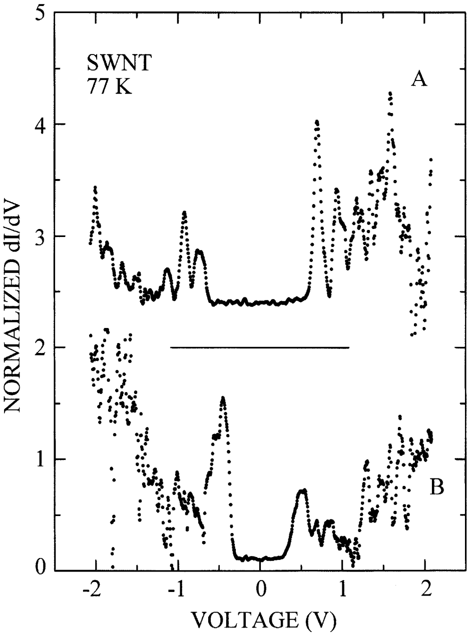

Fig. 1. Normalized tunneling differential conductance for the (A) metallic and (B) semiconducting SWNT in the same bundle. Each curve is normalized at $V = 2\,\mathrm{V}$.

energy contours around the K points [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 the predicted one which is of the order of 10 meV. We need further investigation of the origin of these fine structures.

We also found tunneling spectra for the semiconducting SWNT as shown in Fig. 1(B) at different SWNTs in the same bundle. The conductance around zero bias voltage is much smaller than that in the metallic SWNT shown in Fig. 1(A). The flat and reduced conductance near the Fermi energy shows a clear semiconducting gap structure. The width between the first peaks of about 600 meV is less than one half of that in Fig. 1(A). This width value is almost consistent with the estimation for the gap width in the semiconducting SWNT with a diameter of 1.2 nm.

In rare cases, we found different conductance curves from above two types as shown in Fig. 2. The conductance is not flat near zero bias voltage. There are broad conductance peaks around $V = \pm 80\,\mathrm{mV}$. These features are partially

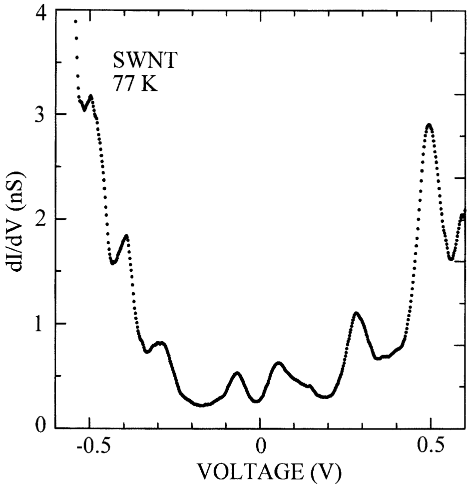

Fig. 2. Tunneling spectra with conductance peak at low energy.

explained by the tunneling between SWNTs which have different chirality [6]. It is likely that the tunneling junction between SWNTs is formed since nanotubes contacted each other in a bundle. However, there is another possibility; pseudogap in the bundle. For the bundle consists of the metallic SWNT with the same chirality, it is predicted that there is the pseudogap with a gap width of about 200 meV at the Fermi energy [7,8]. The observed conductance peaks around $V = \pm 80\,\mathrm{mV}$ might be due to the pseudogap.

In summary, SWNTs were studied by a low-temperature STM. Both metallic and semiconducting SWNTs were found in the same bundle by STS at 77 K. For the metallic SWNT, fine structures just outside the first DOS peak were found in the tunneling spectra. For the semiconducting SWNT, the conductance at zero bias voltage is much smaller than that in the metallic SWNT. The obtained gap width of 600 meV is almost consistent with the estimated gap for the semiconducting SWNT with a diameter of 1.2 nm.

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