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STM/STS investigation of carbon nanotubes deposited on Bi_2Te_3 surface

Research Article

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Abstract: This paper reports our scanning tunneling microscopy and spectroscopy (STM/STS) study of double-walled and multi-walled carbon nanotubes (CNTs) of different diameter deposited on Bi_2Te_3 (narrow gap semiconductor). The approximate diameter of the studied double-walled and multi-walled CNTs was 2 nm and 8 nm, respectively. Crystalline Bi_2Te_3 was used as a substrate to enhance the contrast between the CNTs and the substrate in the STS measurements performed to examine peculiarities of CNT morphology, such as junctions, ends or structural defects, in terms of their electronic structure.

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Keywords: carbon nanotubes • STM/STS • Bi_2Te_3

1. Introduction

Since the discovery of carbon nanotubes [1] much attention has been paid to their electronic properties. The main finding of theoretical investigations [2, 3] was a strong dependence of the electronic band structure of a nanotube on its chirality and diameter. These theoretical results [4] were verified by experimental studies, in which the properties of nanotubes, either metallic or semiconducting, were shown to depend on the tube diameter. This dependence can be investigated by scanning tunneling microscopy (STM) and spectroscopy (STS). In STS the tunneling current is measured as a function of the bias voltage with the STM tip positioned above the nanotube and the feedback loop switched off. In most experiments reported so far the CNTs were deposited on HOPG(0001) [5, 6] or Au(111) surfaces [7]. Silicon surfaces were used in some studies performed in search of applications in electronic devices [8]. The major reasons for using bismuth telluride as a substrate in our study are its atomically flat terraces, necessary to recognize the nanotubes on the surface, specific electronic properties (Bi_2Te_3 is a narrow gap semiconductor) which enhance the contrast in the current imaging tunneling spectroscopy (CITS), as well as relatively long stability and cleanness of samples exposed to air. Our purpose was to study the topography and the

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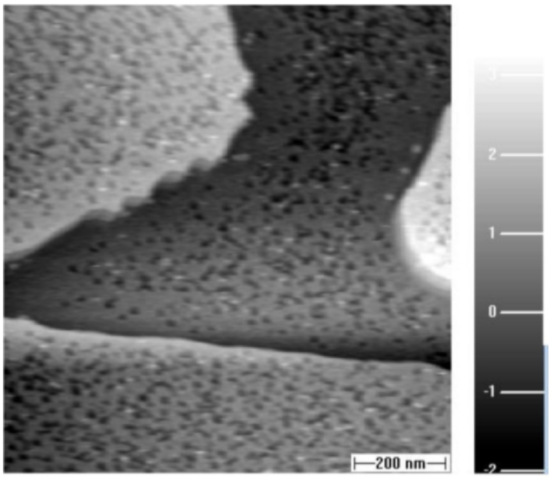

Figure 1. STM image of the Bi_2Te_3 surface etched by heating at 420 K for a few hours (scan range 1x1 μm^2). The step height and the hole depth are 1 nm, approximately.

electronic structure of double- and multi-walled carbon nanotubes (MWCNs), particularly at their morphological peculiarities such as junctions, ends or structural defects.

2. Experimental details

The carbon nanotubes were grown by plasma-enhanced hot filament chemical vapor deposition onto a nickel thin film on a display glass [9]. The experiment was performed in two parts, in which 2 nm and 8 nm diameter CNTs were studied separately. In each case the diameter distribution was focused near the mean value (90 per cent of population), as determined by scattering methods. The Bi_2Te_3 surface was cleaved and etched by annealing at 480 K for about 2 hours to obtain a clean surface with well-developed terraces of different height and trenches. The nanotubes were immersed in water-free 99.99 per cent pure ethanol (fast evaporation) and then dropped on the clean Bi_2Te_3 surface. Subsequently the sample was placed in an UHV STM system and degassed at 420 K for a few hours. The STM measurements were carried out at parameters typical of narrow gap semiconductors: polarization voltage of 0.5 V, tunneling current of 0.08÷0.2 nA, and scan rate of 1÷2 Hz.

3. Results

The obtained images of the Bi_2Te_3 surface revealed large atomically flat terraces with etched triangular holes (see Fig. 1). The depth of the latter, about 1 nm, corresponds well to the total thickness of every five consecutive layers. Considering the structure of the Bi_2Te_3 unit cell [10] and the fact that the crystal cleaves along the Te-Te bonds, we conclude that only tellurium layers were uncovered.

In the first part of the study we examined 8 nm diameter nanotubes (henceforth referred to as CNT8nm), which were over 1 micron in length (see Fig. 2A). We observed many structural peculiarities such as junctions and scales (see Figs. 2 and 3), which were the very object of our interest. The studied CNT8nm appeared composed of sections with approximate length of 30 nm (see Figs. 2B and 3A) and two kinds of junction between them. In Fig. 3A a junction between parallel sections is indicated by line A, intersecting the profile line; the CNT diameter at this site increases by 0.5 nm, approximately, as we move in the direction indicated by the arrow. Line B in Fig. 3A indicates

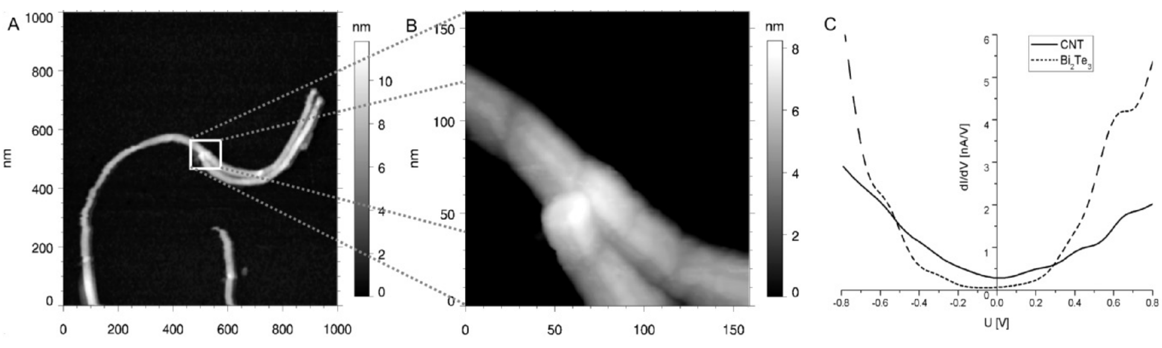

Figure 2. (A) STM image of a CNT with a Y junction; (B) higher magnification of the junction area with visible scales along the nanotube; (C) averaged dI/dV curves taken over the CNT and the Bi_2Te_3 substrate.

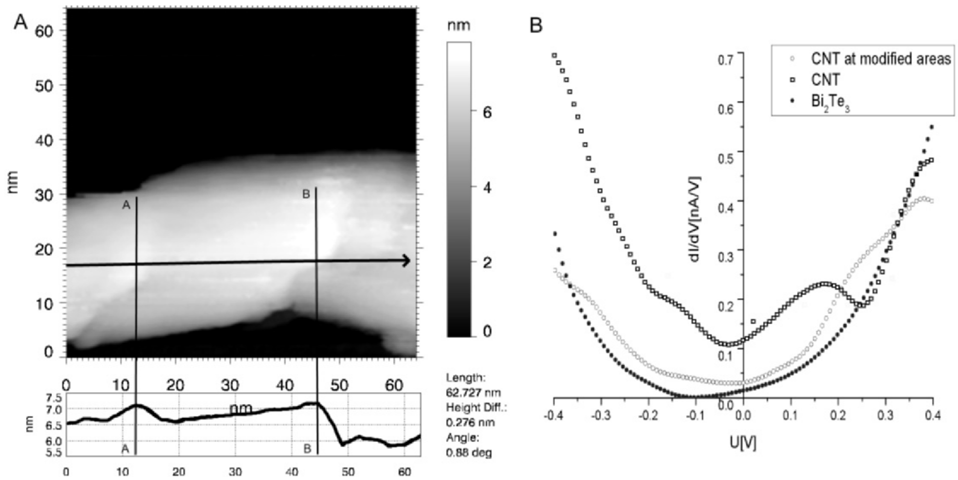

Figure 3. (A) STM topography image of a CNT with profile line below. Lines A and B indicate junctions between CNT sections. The image range is 65x65 nm^2. (B) Superimposed plot of dI/dV curves taken over a CNT thickening, along the CNT, and over the substrate.

a junction between sections that are not parallel; at this site the diameter across the ridge decreases by ca. 1 nm behind the junction. The described morphological details are presented in Figs. 2 and 3. The dI/dV curves taken over the studied CNTs showed their metallic nature (no energy gap), in contrast to the semiconducting substrate (Fig. 2C). CITS measurements over the Y junction did not show any new features in the local density of states (LDOS). The dI/dV curves taken over the junctions show much lower LDOS than at straight parts of the nanotubes (see Fig. 3B). The averaged dI/dV curves taken along the CNT8nm revealed two surface states, one at 0.14 eV below the Fermi level (occupied state) and the other at 0.17 eV above the Fermi level (empty state). Those features were not observed in defective areas (see Fig. 3B).

In the next stage of the experiment we studied 2 nm diameter CNTs (henceforth referred to as CNT2nm). Although many of them were found to be more than 1 micron long, the most interesting CNT2nm was a 250 nm long nanotube (see Fig. 4A) which can be regarded as a one-dimensional object. Calculated from the I/V characteristics taken over the CNT2nm, dI/dV curves show a metallic character of the investigated nanotubes. The LDOS minimum was found to be shifted below the Fermi level (see Fig. 4B).

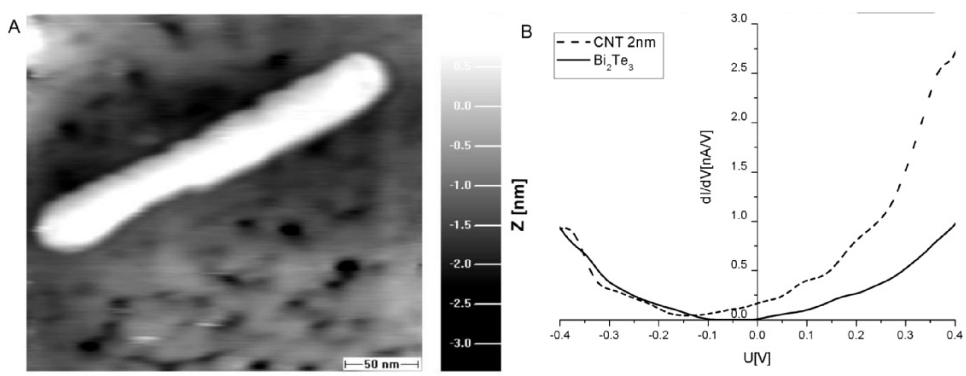

Figure 4. (A) STM image of a double-walled CNT2nm about 250 nm long. (B) dI/dV curves taken over the CNT and the Bi_2Te_3 substrate.

4. Discussion

As indicated by our results, in CNT8nm the nanotube diameter remains constant within a single section, and so does the number of walls. A junction between two parallel sections involves a change in nanotube diameter, which implies that adjacent sections differ in number of walls. In most cases the number of walls in adjacent sections of the studied nanotubes differed by one. Whether the other type of junction is characteristic of the CNT8nm structure or a result of nanotube positioning during deposition on the surface, we cannot determine directly from STM measurements (some complementary techniques, e.g. scattering methods, would be necessary). In the case of MWNTs the metallic character of the straight parts was predictable, but modified electronic properties could be expected in Y junction areas. In single-walled nanotubes (SWNTs) Y junctions are mostly caused by structural defects in the graphene sheet (heptagons present therein) [11, 12]. Although the dI/dV curves are reported to show some variations in local density of states at and around Y junctions in SWNTs [13, 14], no similar effect was observed in the studied MWNTs. This might be due to a different chirality of the inner walls, and the consequent screening of the electron properties of the core tube. Moreover, the outer wall can be composed of a number of shreds rather than of a single graphene sheet. Nevertheless, contrary to the results reported in [13], the obtained spectra (recalculated into dI/dV curves) revealed no new state in the Y junction area, most probably because of the shredded structure of the outer wall. The STS measurement showed some structural defect-related differences in LDOS along the nanotube. The decrease in LDOS would suggest a breakage in one of the inner walls rather than in the outer one. The observed two surface states at 0.14 eV below the Fermi level and at 0.17 eV above the Fermi level are probably a consequence of wall coupling. None of these states was predicted by computer simulations. The shifted LDOS minimum in the CNT2nm might be substrate-related, as suggested by the asymmetric dI/dV characteristic of Bi_2Te_3 (see the dI/dV plots in Figs. 2C, 3B and 4B). The performed STM study indicates that double-walled CNTs have less structural defects than multi-walled ones.

5. Conclusions

The results of our UHV STM study of 8 nm and 2 nm diameter carbon nanotubes deposited on Bi_2Te_3 show that CNT8nm nanotubes have a heterogeneous structure slightly wrinkled at junctions between sections. The obtained dI/dV characteristics indicate a decrease in density of states in the vicinity of the wrinkles. Two asymmetric states, one at 0.14 eV below and the other at 0.17 eV above the Fermi level, were found in the studied CNT8nm nanotubes. Although the CNT2nm and CNT8nm nanotubes under investigation were produced by the same method, their structure proved different.

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