Scanning tunneling microscopy and spectroscopy of Y-junction in carbon nanotubes

Z. Klusek a,*, S. Datta a, P. Byszewski b, c, P. Kowalczyk d, W. Kozlowski d

a Advanced Materials Research Institute, University of Northumbria, Ellison Building, Ellison Place, Newcastle upon Tyne, NE1 8ST, UK
b Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
c Institute of Vacuum Technology, Dluga 44/50, 00-241 Warsaw, Poland
d Department of Solid State Physics, University of Lodz, 90-236 Lodz, Pomorska 149/153, Poland

Abstract

Scanning tunneling microscopy and spectroscopy were used to observe the variations of electronic structure on the carbon nanotube Y-junction. The electronic structure derived from tunneling conductance maps showed natural metallic–metallic and semiconducting–metallic transitions close to the Y-junction, and the occurrence of metallic character of the whole Y-junction with the presence of additional resonant state at energy of 0.2 eV below the Fermi level. It is suggested that the state originates from heptagons forming the junction.

Keywords: Scanning tunneling microscopy; Scanning tunneling spectroscopies; Carbon; Surface electronic phenomena (work function, surface potential, surface states, etc.)

1. Introduction

The introduction of polygons with five and seven carbon atoms to the graphene sheet makes it possible to connect carbon nanotubes with different chiral vectors [1], allowing the formation of intramolecular electrically active junctions. When pentagon and heptagon are located at the opposite sides of the nanotube structure the axis of the two connected tubes makes an angle depending on their diameter up to about 30°. The angle can be smaller when the pentagon and heptagon are closer to one another. It is even possible to connect tubes of different diameters without bending them. Furthermore, it was shown that the more complex intramolecular junction like Y-type could be evolved from two bend junctions with different electronic characters (M–M, M–S, S–S, where S is semiconductor, M is metal) [2,3]. In this case, the Y-junction can be considered as three nanotubes joined via two triangular central spacers and the heptagons were found to fit well into the hexagonal network.

The electronic properties of intramolecular junctions are currently the focus of considerable interests. This is due to a theoretical analysis suggesting that the electronic structure of a junction differs considerably from that of the nanotube “bulk” region [1,4], and results in M–S transition and additional resonant states close to the Fermi level. The implications of these studies are especially important for molecular electronics devices [2,5–7].
Although, tunneling spectroscopy results for carbon nanotubes and carbon nanotubes with topological defects were presented previously [8–14], only a few experimental data in the high-energy range were published, especially for Y-junctions. The goal of this study is to gain a detailed understanding of the Y-junction tunneling spectra at 2 eV around the Fermi energy. These experiments are intended to identify the electronic band structure of the junction and additional resonant states around the Fermi level, if they exist. The results obtained will lead to a better understanding of the electronic structure of carbon nanotube defects, and electronic structure of nanotubes in general.

2. Experimental

A few micrograms of carbon nanotubes prepared in the electric arc were sonicated for 30 min in 2 cm$^3$ of 1,2-dichloroethane. Then a droplet of the solution was deposited on freshly cleaved (0001) basal plane of highly oriented pyrolitic graphite surface. After the treatment the sample was loaded in the UHV STM chamber. The STM/STS experiments were performed at room temperature with a VT-STM/AFM system in UHV condition (Omicron GmbH). The tips used were prepared by mechanical cutting from the 90%Pt–10%Ir alloy wires. Although, Au(1 1 1) surface is widely used as a substrate for nanotube deposition [8–14] we decided to use graphite. This was to avoid a small charge transfer that takes place between the gold substrate and the nanotube due to the difference in work functions. It results in a shift of the Fermi level [10,15], and $dI/dV$ asymmetry with respect to the bias voltage. However, similar effects can also be caused by particular tip geometry or point contact during STS measurements even on graphite [15].

3. Results and discussion

The STM image of a carbon nanotube Y-junction is shown in Fig. 1. The junction consists of a tube of $\sim0.4$ nm diameter (a) connected to two tubes of $\sim0.35$ nm diameter (b) and $\sim0.45$ nm diameter (c). The diameters were estimated from the height of tubes relative to the substrate assuming van der Waals distance between the substrate and the tube of 0.335 nm [16]. The horizontally measured diameters of the nanotubes were 16, 9 and 19 nm, respectively. However, the apparent horizontal width contains primarily tip convolution effects [17]. Further the mechanical deformation due to the interaction with the substrate and tip might lead to compression of nanotubes and anomalous low apparent height [13,16,17]. The unusual small tube height in the STM images can also be explained by the presence of minitips on the tip apex (carbonaceous contamination—carbon fibers, graphite clumps), which are in ohmic contact with the nanotube during scanning process [18].

An illustrative way of presenting spatially resolved spectroscopic data is to plot the $dI/dV$ quantity as a function of bias voltage and position along the tube [12,14]. In Fig. 2, we show tunneling conductance maps measured along the lines denoted as $\alpha$, $\beta$ and $\gamma$ in the inset of Fig. 1. From these measurements it is possible to extract
individual conductance curves. Fig. 3 shows $dI/dV$ curves taken from the vertical cross sections in Fig. 2 ($\alpha$-line, tube-a) at the position marked by #1 to #6. In the presented paper all the $dI/dV$ curves are shifted in vertical scale for the sake of clarity, and the $dI/dV = 0$ levels are marked by solid lines. The $dI/dV$ spectra recorded far from the Y-junction (#1, #2) reflect the metallic character of the tube. In this case, there is no energy gap and LDOS between the subbands is finite and roughly constant. Within a simple tight-binding model the separation $\Delta E_{\text{sub}}$ between the onsets of conductivity singularities is given by $\Delta E_{\text{sub}} = 6\gamma a_{c-c}/D$,

where $a_{c-c}$ is the nearest-neighbour carbon–carbon distance equal 0.142 nm, $D$ is the tube diameter and $\gamma$ means the $\pi-\pi$ energy overlap between neighbouring carbon atoms equal to 2.7 eV [1,14,19]. Taking into account the $\Delta E_{\text{sub\_tube-a}} = 3.2$ eV obtained from spectroscopic measurements (#1 in Fig. 3) one gets $D = 0.71$ nm. The discrepancy between the diameters measured from the STM height profile (~0.35 nm) and band-edge separation (0.71 nm) probably arises from mechanical deformation of the nanotube mainly caused by the tip. On the spectroscopic curves recorded close to the junction (#3 to #6) the main change is the appearance of well-defined two singularities located at 0.8 eV below and 0.8 eV above the Fermi level. The $dI/dV$ spectrum still reflects the metallic character, which is seen as a constant conductance plateau given by the distance between two singularities $\Delta E_{\text{sub\_junction}} = 1.6$ eV.

The $dI/dV$ curves recorded over the tube-c were similar to those presented in Fig. 3, i.e. the nanotube reflected metallic character, which was maintained up to the junction. However, it should be mentioned that the position of the peaks was slightly different due to the different nanotube diameter ($\Delta E_{\text{sub\_tube-c}} = 2.9$ eV).
Fig. 4 shows $dI/dV$ curves taken from vertical cross sections in Fig. 2 (β-line, tube-b) at the position marked by #7 and #8. The spectrum differs significantly from that recorded on tube-a and reflects the semiconducting character of this nanotube. The spectroscopic curve $dI/dV$ recorded far from the nanotube junction (#7) shows onsets of LDOS located at about 0.80 eV (V1), 1.63 eV (V2), below and at 0.78 eV (C1), 1.38 eV (C2) above the Fermi level. Since, the theoretical band gap for a semiconducting tube is given by $\Delta E_{\text{gap}} = 2\gamma a_{c-c}/D$ [1,14,19] then taking into account the $\Delta E_{\text{sub-tube-b}} = 1.58$ eV obtained from spectroscopic measurements (V1 C1 in Fig. 4) one gets 0.48 nm for the diameter of the tube-b, whereas the value measured from the height profile equals to ~0.35 nm. The separations between the singularities are given by $\Delta E_{V_{2-1}} = \Delta E_{C_{2-1}} = \gamma a_{c-c}/D = 1/2\Delta E_{\text{gap}} = 0.79$ eV and are comparable to the measured values $\Delta E_{V_{2-1}} = 0.83$ eV, $\Delta E_{C_{2-1}} = 0.6$ eV. The small discrepancy probably arises from neglecting the curvature of the nanotube and σ–π hybridization in simple tight-binding calculations [19]. On the spectroscopic curve recorded very close to the junction region (#8) the semiconducting character is changed to metallic

(LDOS between the subbands is finite) and an additional weak feature (RS) at about 0.25 eV below the Fermi level appears. The presence of RS was also observed on the curve #6 (junction region of the tube-a), though the magnification of the curve is required to enhance the feature. It was shown previously that the presence of a naturally semiconducting–metallic transition could be formed at the connection of two parts of a single nanotube if built in topological defects (pentagon, heptagon) allowed change of symmetry of the two parts [2,4].

The final stage of our studies was to measure the tunneling spectra on the Y-junction. Fig. 5 shows $dI/dV$ curves taken from γ-line at the position marked by #9 and #10. The spectra clearly show metallic character of the junction with the presence of additional resonant state at energy of 0.2 eV below the Fermi level—RS. The amplitude of the RS slightly varies over the junction, and assumes the maximal values at positions far from the center of Y-junction.

Summing up we observed natural metallic–metallic (tube-a, tube-c) and semiconducting–metallic (tube-b) transitions close to the Y-junction,
and the occurrence of metallic character of the whole Y-junction with the presence of additional RS at energy of 0.2 eV below the Fermi level. In our interpretation the RS may originate from carbon heptagons needed to form the Y-type junction structure. In such a model heptagons are located between each junction branch and are used to close hexagonal network [2,3]. As was shown theoretically the existence of heptagons in graphene network enhances the LDOS close to the Fermi level as results of the presence of additional resonant states [20]. It should be emphasized that the RS amplitude measured at different points over the junction showed maximal values at positions far from the center of Y-junction. The observations can be explained in terms of a decrease of the RS amplitude with increasing the distance from the defected region. Thus we can assume that the resonant state near the Fermi level appears only in the regions close to the heptagon rings located between each junction branch. Unfortunately, we were unable to distinguish different arrangements of carbon atoms using the STM because this method does not show atomic structure in crystallographic sense but the electronic structure of the surface near the Fermi level. The presence of various types of bonds in polygons can be detected mainly by the tunneling spectroscopy not by tunneling microscopy. However, more research needs to be done to clarify the influence of local surface defects on the tunnelling spectra.

4. Conclusions

In summary, we have studied the electronic structure of the carbon nanotube Y-junction by STM/STS. We found metallic–metallic and semiconducting–metallic transitions to be present close to the Y-junction. Furthermore, the occurrence of metallic character of the whole Y-junction with the presence of additional RS at energy of 0.2 eV below the Fermi level was observed. It is suggested that the resonant state originates from heptagons forming the junction.

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References