Direct observation of confined states in metallic single-walled carbon nanotubes

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We investigated the local density of states (LDOS) of extended individual metallic single-walled carbon nanotubes using low-temperature scanning tunneling spectroscopy. We observed that the LDOS oscillates with energy close to the Fermi level. The oscillation period of about 50 meV varies with position on the nanotube. Maps of the LDOS reveal that the peaks in the oscillation are related to confined states. The widths of the peaks increase with increasing distance from the Fermi level. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1598282]

Single-walled carbon nanotubes (SWCNTs) are considered promising candidates for molecular electronics.[1] It is therefore highly desirable to understand their electronic properties in detail. In particular, the effect of defects on transport properties must be understood and is currently under debate. Early experiments generally assumed ballistic transport in SWCNTs. Indeed, the mean free path in individual as well as in ropes of metallic SWCNTs appeared to be restricted by the contacts.[2–4] Later experiments, however, found evidence for defects in semiconducting SWCNTs by using an atomic force microscope (AFM) tip to locally change the transport properties of the tube.[5] Theory work explained both results by stating that all defects larger than the lattice constant do not lead to backscattering within metallic tubes, whereas backscattering is present in semiconducting tubes.[6,7] More recently, low-temperature transport measurements using individual metallic SWCNTs have been interpreted in terms of disorder-induced quantum dots (QDs).[8,9] According to theory, a corresponding backscattering could originate from certain arrangements of vacancies.[10]

Here, we also found disorder-induced QDs in SWCNTs, which are directly probed by low-temperature scanning tunneling spectroscopy (STS). At the Fermi level E_F, we find a reduced dI/dV magnitude surrounded by a number of peaks. The position of the peaks depends on the location within the tube, and maps of the local density of states (LDOS) reveal that the peak intensity is sharply restricted to a certain region of the tube, as expected for confined states.

Our scanning tunneling microscope (STM) operates in ultrahigh vacuum ($p < 10^{-10}$ mbar) at low temperature ($T = 14$ K), and is described in Ref. 11. STM images are recorded in constant-current mode with the voltage V_{sample} applied to the sample. The differential conductivity $dI/dV \propto \mathrm{LDOS}$[12] is recorded by lock-in technique ($V_{\mathrm{mod}} = 2-10$ mV) with tip–surface distance stabilized at voltage V_{stab} and current I_{stab}.

In order to permit STM and STS on SWCNTs, we sonicate the raw SWCNT material in dichloroethane and deposit a droplet of the solution on a freshly evaporated Au/mica surface. This is a common technique for preparing SWCNTs on Au.[13] After checking the surface contamination with AFM, the sample was transferred into the STM.

Although the sample preparation is done in air, very reproducible STM images revealing atomic resolution are obtained. The inset of Fig. 1 shows an example. Using a technique described in Ref. 14, we relate this SWCNT to a (15,6)-type with a chiral angle of 13.9°. According to $(n - m)/3 = (15-6)/3 = 3 =$ integer, such a tube is metallic.

Metallic SWCNTs can be identified additionally either by their finite dI/dV magnitude close to E_F or by their relatively large separations between subbands of about 2 V.[13] A spectrum of such a nanotube is shown in Fig. 1. As in Ref. 13, the subband features are not symmetric around 0 V, which has been attributed to a charge transfer from the tube to the Au substrate. Au has a higher work function (5.3 eV) than graphite (4.5 eV), suggesting a hole-doping of the SWCNTs.

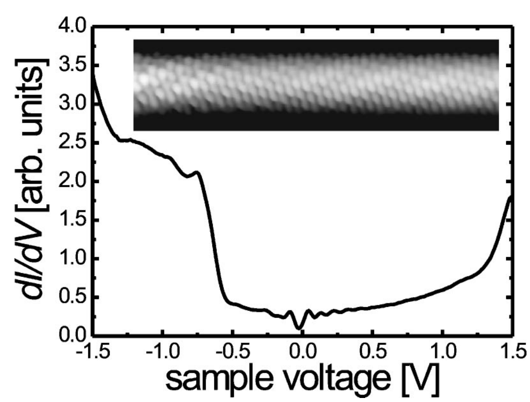

FIG. 1. dI/dV spectrum of a metallic SWCNT. Subband features as well as oscillations near the Fermi energy are visible. These oscillations are shown in more detail in Fig. 2(c) ($V_{\mathrm{stab}} = 1.5$ V, $I_{\mathrm{stab}} = 300$ pA). Inset: atomically resolved STM image of a SWCNT ($I = 1$ nA, $V_{\mathrm{sample}} = -50$ mV, 2.3 nm $\times$ 9 nm).

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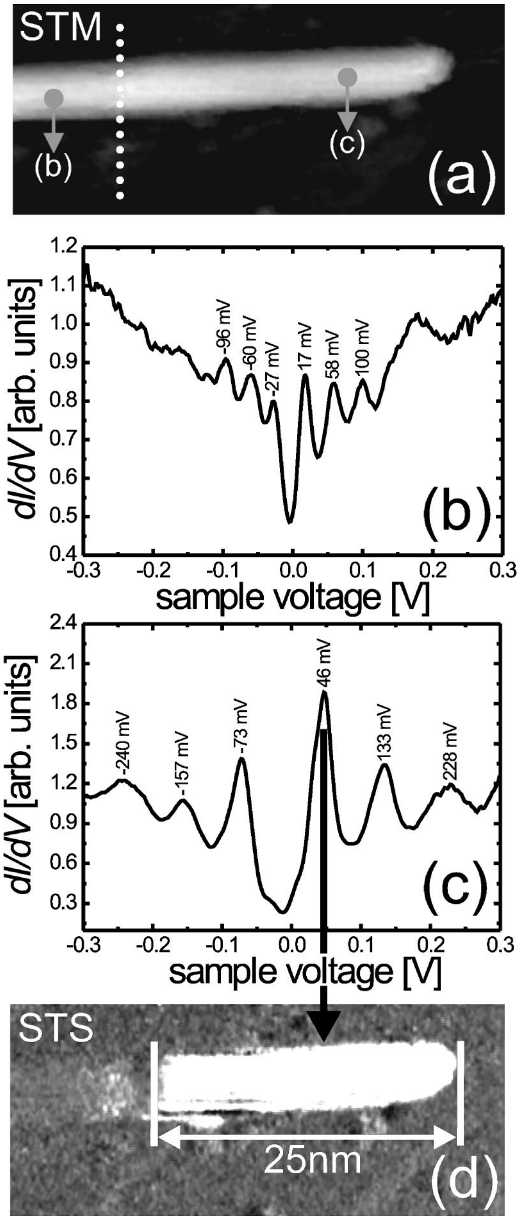

FIG. 2. (a) STM image of a SWCNT end ($I = 300$ pA, $V_{\text{sample}} = 46$ mV, 45 nm$\times$19 nm). (b) STS data on the left-hand side of the dotted line in (a). (c) STS data on the right-hand side of the dotted line in (a) (zoom of the STS data shown in Fig. 1 into the region close to E_F). All STS data in (b) and (c) are taken with $V_{\text{stab}} = -300$ mV, $I_{\text{stab}} = 300$ pA, and $V_{\text{mod}} = 3$ mV. (d) Simultaneously recorded spatially resolved STS image, $V_{\text{stab}} = 46$ mV [first peak in Fig. 2(c)], $I_{\text{stab}} = 300$ pA and $V_{\text{mod}} = 10$ mV.

Surprisingly, there are features close to E_F. Besides a dip at E_F, a number of nearly equidistant peaks is found, as shown more clearly in Figs. 2(b) and 2(c). The features look like a damped oscillation starting at E_F with a period of about 87 meV in Fig. 2(c). At another position of the tube, the energy difference between the peaks is different, for example, about 38 meV, as shown in Fig. 2(b). This change in periodicity appears quite abruptly at the dotted line in Fig. 2(a). To demonstrate this, the spatially resolved dI/dV signal at the energy of the 46-mV peak of Fig. 2(c) is shown in Fig. 2(d). It clearly reveals that the 46-mV peak is restricted to an area of 25 nm right of the dotted line. The same restriction has been found for the other prominent peaks in Fig. 2(c).

Peaks in the LDOS restricted to a certain area are strong indications for confined states. Confined states have previously been found by STS after shortening individual SWCNTs.[15,16] However, they have never been reported on extended tubes with lengths of about 2000 nm, as in the present case. In order to verify that the peaks are indeed confined states, we calculate whether the peak separation ΔE is consistent with the size of the confined regions. Therefore we use the approximate formula $\Delta E = h v_F / 2L$, with $v_F = 8 \times 10^5$ m/s being the Fermi velocity. For $\Delta E_1 = 87$ and $\Delta E_2 = 38$ meV, we get $L_1 = 19$ and $L_2 = 44$ nm, respectively. L_1 fits approximately with the measured 25-nm restriction length of the 46-mV peak. Thus, we assign the observed peaks close to E_F to confined states within the SWCNT.

Confinement in an extended tube obviously requires scattering. We could not identify the type of scatterer. However, we can rule out a significant bending of the nanotube at the end of the confined region from STM images. In addition, there is no step edge in the metallic substrate below the tube at this position. Moreover, we can rule out a large contaminant since we observe only a small elevation of 0.7 Å at the scattering point in line scans of STM images. Thus, the data suggest that the scatterers are either intrinsic or single adsorbates below, within, or above the tube.

Regardless of their exact nature, our data directly show that localized scatterers can lead to significant backscattering. This backscattering has a strong influence on the transport properties of the tube: It modifies the LDOS near the Fermi level and decreases the transmittance of individual modes. The effect of two partly transmitting barriers on the transport properties of SWCNTs has been measured by Liang *et al.*,[17] and was described in terms of Fabry–Perot-like electron modes in the nanotube. Pursuing this analogy, the energy- and position-dependent LDOS measurements reported here amount to spatial maps of these Fabry–Perot modes, with defect sites playing the role of reflecting barriers. A similarly pronounced modulation of the transmittance can be expected.

This transmission is, of course, related to the LDOS at E_F. Since we do not find peaks at E_F, the remaining dI/dV magnitude appears to be related to the widths of the surrounding peaks. These widths are much larger than the estimated energy resolution of the experiment $\delta E = \sqrt{(3.3\,kT)^2 + (2.5\,V_{\text{mod}})^2} = 8.5$ meV. For example, the full width at half-maximum of the 46-meV peak is 47 meV. The width increases with increasing distance from E_F, suggesting lifetime effects guided by electron–electron interaction. A simple broadening by the escape of the electrons towards the Au substrate would usually not be symmetric around E_F. Electron–phonon interaction in SWCNTs is known to be weak.[18] Thus, only electron–electron interaction remains as a possible cause. The same magnitude and energy-dependence of the peak widths is also observed for shortened SWCNTs.[19] A similar lifetime broadening in SWCNTs can also be deduced from the phase coherence of scattered electron waves observed by STM.[20] In contrast, time-resolved photoemission data of SWCNT bucky papers revealed an electron lifetime close to E_F which corresponds to a broadening of only 4 meV.[21] Since the SWCNTs used in all STM measurements are directly deposited on a Au substrate, which is not the case within the bucky papers used for photoemission, it might be that lifetime effects in SWCNTs depend significantly on the substrate.

In summary, we find quantized states within extended individual metallic SWCNTs confined by defects. They appear as peaks in the dI/dV curves close to E_F which are restricted to certain areas. Our work, thus, shows that defects can lead to significant backscattering within individual metallic SWCNTs, resulting in confined states. Moreover, we found an increase of the peak-widths with increasing voltage.

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