Electron Scattering in Intrananotube Quantum Dots

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Intratube quantum dots showing particle-in-a-box-like states with level spacings up to 200 meV are realized in metallic single-walled carbon nanotubes by means of low dose medium energy Ar⁺ irradiation. Fourier-transform scanning tunneling spectroscopy compared to results of a Fabry-Perot electron resonator model yields clear signatures for inter- and intravalley scattering of electrons confined between consecutive irradiation-induced defects (interdefects distance ≤ 10 nm). Effects arising from lifting the degeneracy of the Dirac cones within the first Brillouin zone are also observed.

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The experimental realization of quantum dots (QDs) [1] has led to new concepts for applications in promising fields like nanoelectronics, nanophotonics, and quantum information or computation [2–4]. Frequently, for these applications a QD needs to be contacted by source, drain, and gate electrodes. For semiconductor heterostructures the excitation energies of contacted QDs are usually so small that the devices can only be operated at cryogenic temperatures. A promising candidate for room temperature active dots are intranotube QDs formed within a single-walled carbon nanotube (SWNT) by means of two local defects [5]. For defect separations of order 10 nm the dot excitation energies are well above 100 meV and thus large compared with $k_B T$ at room temperature. Furthermore, the remaining sections of the SWNT to either side of the confining defects provide natural source and drain electrodes. So far, SWNT-based QD prototypes have been realized by tunneling barriers at metal-nanotube interfaces and/or by gate electrodes [6]. Several authors have analyzed defect-induced standing waves by means of scanning tunneling microscopy (STM) [7–9]. However, a detailed description of the scattering dynamics of electrons in and out of the QD is absent. Elaborate studies have only been reported for epitaxial graphene with defects, where an analysis of standing waves in Fourier space has permitted distinguishing between contributions to the wave modulation due to inter- and intravalley scattering [10]. In this Letter we investigate electron standing waves in intratube QDs created in SWNTs irradiated with medium energy Ar⁺ ions. This promising alternative to build intratube QDs has been suggested by observations of electronic confinement in metallic SWNTs due to intrinsic defects [11]. We first show that by virtue of this technique it is indeed possible to realize QDs with a level spacing considerably larger than the thermal broadening at room temperature. Then, by means of Fourier-transform scanning tunneling spectroscopy combined with a Fabry-Perot electron resonator model, we are able to describe the dominant

scattering mechanisms and to identify contributions from inter- and intravalley scattering.

Our measurements were performed in a commercial (Omicron), ultrahigh vacuum LT-STM setup at ~ 5 K. Extremely pure high-pressure CO conversion SWNTs [12] with an intrinsic defect density < 0.005 nm⁻¹ were deposited onto Au(111) surfaces from a 1,2-dichloroethane suspension [13]. *In situ* irradiation with medium energy Ar⁺ ions was performed in a way to achieve a defect density of about 0.1 nm⁻¹ [14]. Figure 1(a) shows a three-dimensional (3D) STM image of a ~ 50 nm long portion of an armchair SWNT irradiated with ~ 200 eV ions. Defects induced by medium energy Ar⁺ ions appear typically as hillocks with an apparent height ranging from 0.5 Å to 4 Å and a lateral extension between 5 Å and 30 Å. We recorded consecutive and equidistant dI/dV spectra (proportional to the local density of states [15]) along the tube axis. Typical $dI/dV(x, V)$ data sets, called dI/dV scans in the following, consist of 150 dI/dV spectra recorded on topography line scans of 300 pts. Figure 1(b) shows a dI/dV scan with a spatial resolution $\Delta x = 0.34$ nm recorded along the horizontal dashed line drawn in Fig. 1(a), running over seven defect sites (d1–d7). A third order polynomial fit has been subtracted from each dI/dV spectrum to get a better contrast. Defect-induced modifications in the local density of states are revealed as one or more new electronic states at different energy values, spatially localized on the defect sites. First-principle calculations show that medium energy Ar⁺ ions essentially give rise to single vacancies, double vacancies, and also C adatoms on SWNTs [16]. Based on these results we can confidently assume that the created defects in the present work are mainly of vacancy type.

Several broad discrete states characterized by a modulation of the dI/dV signal in the spatial direction are observed in the negative bias range between d3 and d4 and between d5 and d6, and in the positive bias range between d2 and d3. These states show a discrete number

FIG. 1 (color). (a) Three-dimensional topography image [22] of a ~ 50 nm long portion of an armchair SWNT exposed to 200 eV Ar^+ ions, recorded in the constant current mode with a sample-tip bias voltage (V_s) of 1 V (sample grounded) and a tunneling current (I_s) of 0.1 nA, $T = 5.3$ K. (b) Corresponding dI/dV scan with background subtraction, recorded along the horizontal dashed line in (a), $\Delta x = 0.34$ nm. The dI/dV spectra are recorded through a lock-in detection of a 12 mV rms (~ 600 Hz) ac tunneling current signal added to the dc sample bias under open-loop conditions ($V_s = 0.9$ V, $I_s = 0.3$ nA). (c) Energy spacings between discrete states visible in (b) in the negative bias range between defect sites d3–d4 (~ 7.9 nm) and d5–d6 (~ 9.9 nm).

of equidistant maxima following a regular sequence $i, i + 1, i + 2 \dots$ for increasing $|V_{\text{bias}}|$, similar to the textbook 1D particle-in-a-box model. Within this model it is possible to estimate the level spacing around the charge neutrality point (CNP) for discrete states observed, for example, in short SWNTs [7,17]. Assuming a linear dispersion $E = \hbar v_F k$ around the two inequivalent Fermi points $\mathbf{K}$ and $\mathbf{K}'$ for a SWNT with finite length L , the energy spacing is then given by

$$\Delta E = \hbar v_F \frac{\pi}{L} = \frac{\hbar v_F}{2L} \approx \frac{1.76}{L} \text{ eV nm} \quad (1)$$

with L in nm and the Fermi velocity $v_F = 8.5 \times 10^5 \text{ m s}^{-1}$ [7]. The energy spacings $\Delta E_{a1} - \Delta E_{a4}$ in the negative bias range between d3 and d4 and $\Delta E_{b1} - \Delta E_{b4}$ between d5 and d6 are reported in Fig. 1(c). Using the sequence of maxima we can determine the level spacing closest to the CNP: $\Delta E_{a1} = 0.22$ eV ($\Delta E_{b1} = 0.18$ eV) between d3 and d4 (d5 and d6). This corresponds to a defect distance of $L = 8$ nm ($L = 9.78$ nm) for the defect separation d3–d4 (d5–d6), in good agreement with the measured value at the center of the defect sites $L \approx 7.9$ nm ($L \approx 9.9$ nm) [18]. These results show artificial defect-induced electron con-

finement regions in metallic SWNTs, i.e., intratube QDs. It is important to note that spatially close defects can be generated with our method, allowing level spacings which are much larger than the thermal broadening at room temperature of $k_B T \approx 25$ meV.

Figure 2(a) shows a ~ 16 nm long section of a metallic SWNT exposed to 200 eV Ar^+ ions with four defect sites (d1–d4). A line-by-line flattened topography image of the same tube between defects d2 and d4 is displayed in 2(b) with the corresponding dI/dV scan recorded along the horizontal dashed line. Two discrete states are clearly visible in the negative bias range between d3 and d4, at energies $E = -0.22$ eV and $E = -0.39$ eV. The measured energy spacing of about 170 meV fits well with the value of 177 meV obtained from Eq. (1) for a defect separation of about 9.5 nm. Line profiles of dI/dV signals recorded between the drawn red arrows in 2(b) and displayed in 2(c) show a clear oscillatory behavior characterized by a rapid oscillation with an average wavelength of 0.7 nm modulated by a slower variation of the amplitude. This slow modulation, which shows a decreasing wavelength for increasing $|V_{\text{bias}}|$, has been fitted with the function $|\psi(x)|^2 = A + B \sin(2kx + \phi)$, where ϕ is an

FIG. 2 (color). (a) Three-dimensional STM topography image [22] of a metallic SWNT treated with 200 eV Ar^+ ions, showing four defects, d1–d4. (b) Line-by-line flattened topography image of the tube in (a) including defects d2–d4, with the corresponding dI/dV scan recorded along the horizontal dashed line. $V_s = 0.8$ V, $I_s = 0.32$ nA, $T = 5.21$ K, $\Delta x = 0.1$ nm. (c) dI/dV line profiles of the first two modes in the negative bias range, recorded between the red arrows drawn in (b). (d) $|dI/dV(k, V)|^2$ map calculated from the dI/dV scan in (b) between the red arrows. (e) Differential conductance calculated within the Fabry-Pérot electron resonator model for a (7,4) SWNT with a defect distance of 9.5 nm, intra- and intervalley scattering parameters equal to 0.35 for both impurities, with the corresponding $|dI/dV(k, V)|^2$ map in (f).

arbitrary phase and the factor 2 originates from the fact that $|\psi(x)|^2$ is probed.

More details on the observed oscillatory behavior are obtained by means of Fourier-transform scanning tunneling spectroscopy, where line-by-line Fourier transforms are performed on the dI/dV scan in Fig. 2(b), between the positions indicated by the red arrows. From the resulting $|dI/dV(k, V)|^2$ map in 2(d), we observe that the Fourier spectrum of each discrete state is composed of several components [20]. Whereas the individual low frequency peaks between $k = 0$ and $k = 4 \text{ nm}^{-1}$, with a high intensity for each discrete state, correspond to the slow modulation discussed above, the rapid oscillation in dI/dV is produced by several components around $k = 11 \text{ nm}^{-1}$ and $k = 17 \text{ nm}^{-1}$. These Fourier components are aligned along sloped lines, indicating the energy dispersive nature of these features. Around $k = 17 \text{ nm}^{-1}$, a unique positively sloped line is clearly visible, with $dE/dk \approx 0.32 \text{ eV nm}$, whereas two lines with positive and negative slopes can be distinguished around $k = 11 \text{ nm}^{-1}$, with a measured slope of about 0.3 eV nm .

In order to fully explain the experimental features, we use a Fabry-Perot electron resonator model [see Fig. 3(a)] considering interference at a fixed energy of electron states scattered by impurities. These states can be easily identified considering an unrolled SWNT, i.e., a graphene sheet showing periodic strings of defects along the circumfer-

ential direction. The impurities break the translational invariance along the SWNT axis, allowing low energy electron scattering among the six valleys or Dirac cones of the first Brillouin zone. The momenta exchanged in these processes can be decomposed in axial k_A and circumferential k_C components with respect to the tube axis. The former give rise to the interference pattern resulting in the standing waves, whereas the latter modulate the intensity of the standing waves in a nonlinear way; i.e., a larger k_C component leads to a lower intensity. In the calculated $|dI/dV(k, V)|^2$ maps, these standing waves give rise to intensities at k values corresponding to the axial component k_A . Therefore, the $|dI/dV(k, V)|^2$ maps show a weighted projection of the 2D space of possible scattering vectors along the axial direction. The situation is depicted in Fig. 3(b). Two distinct scattering mechanisms take place: intra- and intervalley scattering. For the first process within the same valley the momentum exchange is small, even zero at the CNP [green process in 3(c)]; the second process connects different valleys [blue, red, and black processes in 3(b) and 3(c)]. Both scattering mechanisms are related to the presence of single vacancies and double vacancies [19].

This analysis reduces the scattering processes to a series of weighted 1D scattering events among electrons with a linear energy dispersion and axial momenta k_{A_i}, k_{A_j} [see Fig. 3(c)]. We model the impurities as deltalike potentials placed at a distance L , and the STM tip is included by allowing electron tunneling to an external electrode [21] [see Fig. 3(a)]. Figure 2 shows a comparison between the measured 2(b) and the calculated 2(e) local density of states for the case of a SWNT with two identical impurities. The measured SWNT has a chiral angle $\theta \approx 21^\circ$ and shows three dispersion lines at $k = 6.1, 10.7$, and 16.8 nm^{-1} , compatible with a (7,4) metallic SWNT. The numerically evaluated $|dI/dV(k, V)|^2$ map shown in 2(f) unveils a richer structure than the experimental one. These differences can be attributed to the finite resolution of the tip. The components centered around $k = 0 \text{ nm}^{-1}$ are more intense than the others because they are associated with intravalley scattering occurring at all six valleys. In the measured $|dI/dV(k, V)|^2$ the dispersion lines around $k = 10.7$ and 16.8 nm^{-1} show a more intense signal for the positive slope branch than for the negative one. For the component centered at 16.8 nm^{-1} , the negative slope branch is almost missing. Similar behavior has been observed in all samples investigated. For armchair SWNTs, this effect has been related to an interplay between symmetry properties of defects and electronic bands resulting in a suppression of $\pi \rightarrow \pi$ scattering [8]. However, in our case of chiral SWNTs the relation between the parity of the π and π^* band is more complex, and there is no obvious explanation of the observed branch asymmetry. Since our observations are of pivotal importance to the electric transport properties of real SWNT devices, this issue certainly deserves further in-depth experimental characterization and theoretical explanation.

FIG. 3 (color). (a) Outline of the experimental setup and of the Fabry-Perot resonator model. (b) Sketch of the graphene valleys at a fixed energy for a (7,4) metallic SWNT. The parallel horizontal $\mathbf{k}$ lines are reminiscent of the quantization in the circumferential direction. (c) Sketch of the 1D-scattering processes between two nonequivalent valleys: intravalley (green arrows) and intervalley scattering (red, blue, and black arrows). The processes indicated by black arrows are only relevant if a commensurability condition is fulfilled. k_{A_i} and k_{A_j} are the CNP axial momenta components of valleys i and j , respectively.

FIG. 4 (color). (a) STM current error image [22] of a metallic SWNT with two defect sites d1 and d2 produced by an exposition to 1.5 keV Ar⁺ ions, with the corresponding dI/dV scan recorded along the horizontal dashed line. Interference pattern visibility is improved via a background subtraction. (b) Corresponding $|dI/dV(k, V)|^2$ map limited to low frequencies contributions. $V_s = 0.8$ V, $I_s = 0.3$ nA, $T = 5.3$ K, and $\Delta x = 0.22$ nm. (c) Calculated dI/dV scan for a (10,7) SWNT with a length of 18.5 nm corresponding to the average distance between the defects d2 and d3. The intra- and intervalley impurity strengths are equal to 0.025 and 0.05 for the left and the right impurity, respectively. (d) Corresponding $|dI/dV(k, V)|^2$ map limited to low frequencies contributions.

If the commensurability condition $L = m\pi/\Delta k_A$, with m an integer and L the defect separation, is not fulfilled, intervalley scattering takes place only between electrons with opposite direction of motion and implies an asymmetry of the spots in the $|dI/dV(k, V)|^2$ along the positive and negative slope branches. Contrarily, intravalley scattering always fulfills this condition with $m = 0$, therefore showing symmetric spots around $\Delta k_A = 0$ [see Fig. 3(c)].

Figure 4(a) shows a current error image of a metallic SWNT which has been exposed to 1.5 keV Ar⁺ ions, and the corresponding $dI/dV(x, V)$ scan recorded along the tube axis through two defect sites labeled d1 and d2. Here, instead of clear “textbooklike” modes as shown in Fig. 2, we observe curved stripes in the interference pattern between defects d1 and d2. However, the corresponding $|dI/dV(k, V)|^2$ on the right-hand side clearly shows well-defined small momentum spots with an average energy separation of about 90 meV in good agreement with Eq. (1) giving $\Delta E \simeq 95$ meV for a measured defect separation L of about 18.5 nm. These features are also captured

by the Fabry-Perot electron resonator model if the two impurities have different scattering strengths λ , as shown for the simulated dI/dV scan with $\lambda_L = 0.05$ and $\lambda_R = 0.15$ in Fig. 4(b). There is now a clear asymmetry characterized by stripes showing an increasing curvature when moving from the weaker left to the stronger right impurity. There can also be energy dependent differences in the scattering strengths of the defects leading to energy dependent asymmetries in the standing wave pattern as seen in Fig. 1. The choice of ion energy can significantly change the type of defects produced and could therefore potentially be used as a parameter to control to some extent the scattering configuration [14].

In summary, studying intratube QDs in SWNT by Fourier-transform scanning tunneling spectroscopy in combination with simulation, we provided an analysis of the dominant electron scattering processes. Clear signatures for inter- and intervalley scattering were observed, and scattering effects arising from lifting the degeneracy of the Dirac cones were identified.

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