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4. Mesoscopic superconductivity

Superconductivity in molecular wires

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Abstract. We show experimental evidence of a proximity-induced superconducting transition in individual single-walled carbon nanotubes with normal state resistance much large than the quantum of resistance. The critical current of samples is extensively studied as a function of temperature and magnetic field. We also studied an influence of electron and ion beams radiation on the superconducting properties of carbon nanotubes.

Superconductivity in molecular systems (inorganic and organic) has been studied for 25 years on macroscopic samples consisting of a huge amount of molecules [1]. The discussions about the mechanism of superconductivity in these systems are still in progress. Discovery of a proximity effect in carbon nanotubes, i.e. the induction of superconductivity in a nonsuperconducting material that is connected to superconducting leads [2, 3], has allowed to begin study of superconductivity in individual molecules. A single-walled carbon nanotube (SWNT) is a molecular wire with diameter about 1 nm and, when connected, its room temperature (RT) resistance is larger than the quantum of resistance, $R_Q = \hbar/(2e)^2 \sim 6.5\ \mathrm{k\Omega}$ ($\hbar$ is the Plank constant, e is the charge of an electron). There are theories stating that superconductivity is impossible in wires with normal resistance, R_N, larger than R_Q [4]. Recently these theories have received experimental confirmation [5]. In this paper we show data on single SWNTs which have $R_N \gg R_Q$ (up to $R_N \sim 10R_Q$) and nevertheless undergo a proximity-induced superconducting transition.

The sample fabrication, described elsewhere [6], consists in the laser soldering of a suspended nanotube to superconducting electrodes, using Au or In. Because it is suspended between the edges of the slit in a membrane (Fig. 1), the nanotube can be imaged in a high-resolution transmission electron microscope (HRTEM). The study in HRTEM shows that the nanotubes do not contain catalytic particles and drops of a melt with diameter ≥ 1 nm. Particles of smaller dimensions and individual atoms are outside detection range, and it is quite possible that the nanotubes contain impurity atoms of catalyst (Y, Ni) and solder (Au, In). Concerning the atoms of catalyst, it was found that their average density is 1 atom per every 4 nm of length of a tube, i.e. 1 atom out of 500 carbon atoms [7]. Outside detection range there are also impurity atoms (O, N, H) adsorbed on the surface of nanotubes, and nanotube structure defects (5–7 defects, vacancies). As a result of laser soldering, the gas impurities can partially desorb, and part of natural defects can anneal. Thus a real nanotube is a nonhomogeneous conductor which contains defects and differs from the ideal model (Fig. 1). Nevertheless, the resistance of a real nanotube can be close to ideal value of 6.5 kΩ as the scattering on defects is strongly suppressed [8]. Due to this fact, ballistic transport in some tubes is possible even at room temperature [9]. We have also measured an almost ideal RT resistance value for some samples: $R \sim R_Q$ for individual SWNTs and MWNTs (multi-walled nanotubes), and $R \sim R_Q/N$ for ropes of SWNTs (here N is the number of tubes in a rope).

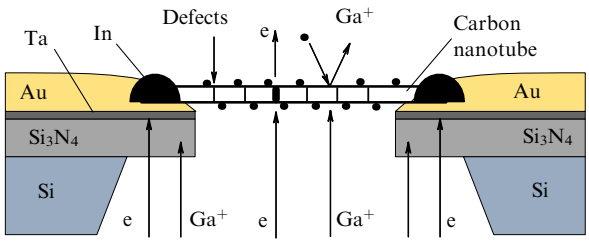

Figure 1. Schematic of a sample.

However, the resistance of an overwhelming majority of samples largely exceeded the ideal value. Since 1994, we have measured the RT resistance of more than 3000 individual MWNTs, SWNTs, and ropes of SWNTs. Only about 30 samples had resistance close to ideal. It was possible to select nanotubes with low resistance quite fast, due to our unique deposition technique [6]. Deposition of a nanotube, measurement of its resistance, removal, if its resistance is too large, and deposition of a new tube take about 5 minutes. Proximity-induced superconductivity was observed [2] in selected nanotubes with low resistance.

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We have also tried to create superconducting nanowires by deposition of thin layer (no more than 3 nm) of the metals such as In, Sn, Re, Mo–Ge on top of small ropes of SWNT. Surprisingly, we always observed an increase of the resistance of the sample (SWNT rope plus metal) after deposition and we never detected any superconducting transition down to 1.5 K. Sometimes, the deposition was destroying ropes. TEM observations of these samples always indicated a granular structure with crystallites in the nanometer range.

Here we present low-temperature measurements of 3 individual SWNT mounted on Ta/Au/In superconducting contacts. Their RT resistances are $R_N = 9$ kΩ, 28 kΩ and 41 kΩ. For correct interpretation of transport measurements it is crucial to know what part of the tube resistance is due to the contacts: for a ballistic tube the entire resistance is due to the contacts, and in case of bad (low-transmission) contacts the resistance can largely exceed R_Q [9]. In our case, it is known for tubes SW1 and SW3. Tube SW1 was exposed to the electron beam of an electron microscope. The area of the contacts was shielded by a layer of membrane and metal opaque to electrons with an energy of 100 kV, so that only the part of the tube outside contacts (Fig. 1) was irradiated. The resistance of this sample after irradiation increased to 20 kΩ, due to the radiation defects, and it is certain that this part of resistance (about 11 kΩ) is not due to contacts. The measurements presented here were obtained after this modification of the sample. Sample SW3 was exposed to the 30 kV Ga+ ion beam of a focused ion beam machine. As in the case of the electron beam, the ions did not reach the contact area, being 'stuck' in the shielding membrane. The extremely small radiation dose, 10^{13} ions cm^{-2}, corresponded to 3 ions passed through a nanotube. The irradiation resulted in essential decrease of resistance of the sample down to 13 kΩ, apparently owing to the desorption of impurity atoms (in [10] all nanotubes were irradiated by Ga ions with a dose of 2×10^{14} ions cm^{-2}, and their resistance remained very low, as low as 200 Ω). This definitely proves that the most part of resistance of SW3 before irradiation, 41 kΩ, is not due to contacts. Therefore the samples are nonhomogeneous one-dimensional (1D) conductors, whose resistance is determined by contacts and internal defects. For sample SW2 we have no direct measurement of the influence of defects on resistance.

The measurement of temperature dependence of resistance shows that all three of the samples undergo a proximity-induced superconducting transition with critical temperature $T_c \sim 0.5$ K, which is the T_c of the superconducting electrodes (Fig. 2). This is the main result of this paper. Moreover, besides the $R(T)$ dependence, the magnetic field dependence of the resistance (Fig. 2), and the differential resistance vs.. current curves (Fig. 3) definitely show the superconducting character of the transition. For samples SW1 ($R(T)$ dependence for this sample was presented in [2]) and SW2 the transition is complete and the resistance drops from 26 kΩ down to less than 1 Ω, the value defined by the sensitivity of measurements ($I = 1$ nA, $V = 1$ nV). Supercurrents of the order of 100 nA are measured [2]. The resistance of sample SW3 does not go to zero, but saturates at a value of 1.5 kΩ.

This induced superconductivity in 1D conductors with $R_N \gg R_Q$ seems to be in contradiction with theoretical predictions. This could be due to the fact that the nanotubes cannot be considered as homogeneous wires. Also, the theory [4] predicts that superconductivity cannot

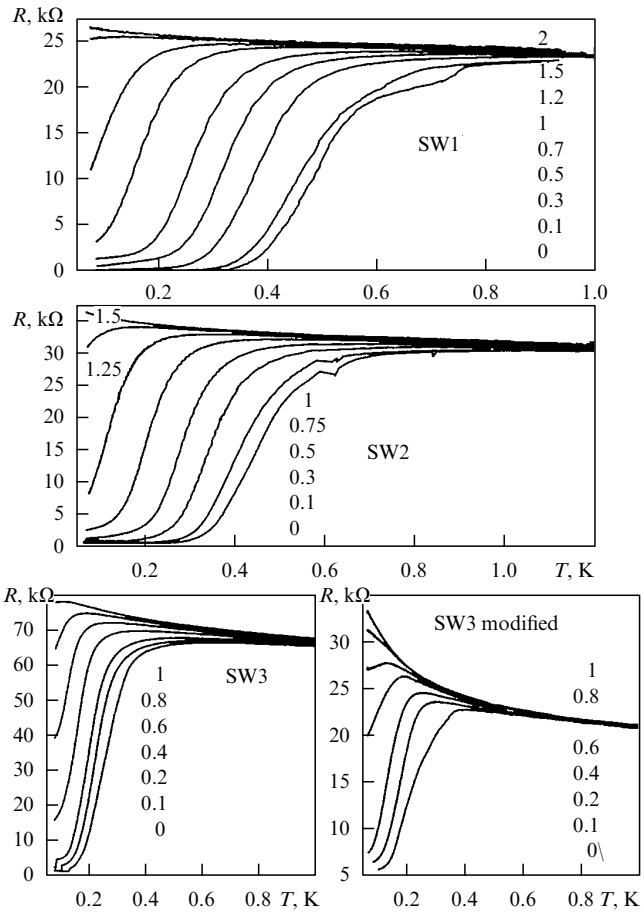

Figure 2. Resistance as a function of temperature for all samples, in various magnetic fields (fields are indicated in Teslas to the right of the curves). SW1 is 0.3 μm long and is mounted on Ta/Au contacts. Room temperature resistance of SW1 was 9 kΩ after desposition and before TEM observation, and 20 kΩ afterwards. SW2 is 0.15 μm long and is mounted on Ta/Au/In contacts. SW3 is 0.2 μm long and is mounted on Ta/Cr/Au/In contacts.\

exist in homogeneous diffusive wires of diameter less than 10 nm. However, superconductivity in such wires built in porous media (glasses, zeolites and asbestoses) was investigated more than 30 years ago, and a superconducting transition was observed even for wires with diameter about 2 nm [11].

In addition, we note that superconducting single-electron transistors, consisting of two Josephson junctions in series with $R_N \sim 50$ kΩ, are another example of systems through which supercurrents flow even though the normal-state resistance of the junctions is larger than R_Q [12]. In the case of Josephson junctions, it is known that the electromagnetic environment of the junctions must be taken into account to describe the magnitude of the maximum supercurrent. It is therefore probable that in a similar manner, the normal state resistance of the nanotubes may not be the only parameter which determines whether or not a superconducting transition is possible, but that the circuit in which the nanotube is embedded probably plays a role as well.

Finally, we would like to add that a similar effect has observed in another kind of molecular wires — double-stranded DNAs [13].

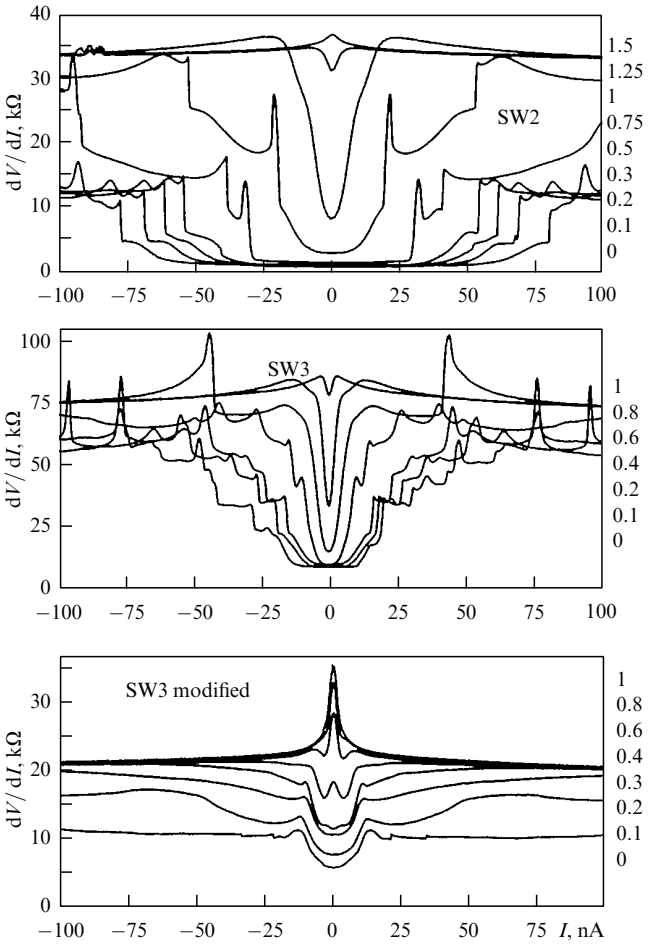

Figure 3. Dufferential resistance as a function of current for samples SW2, SW3 and SW3m, at $T = 70$ mK. (Fields are indicated in Teslas to the right of the curves).

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Scanning tunneling spectroscopy on superconducting proximity nanostructures

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Abstract. We investigated the local density of states (LDOS) of a normal metal (N) in good electrical contact with a superconductor (S) as a function of the distance x to the NS interface. The sample consists of a pattern of alternate $L = 1$ μm wide strips of Au and Nb made by UV lithography. We used a low temperature scanning tunneling microscope and a lock-in detection technique to record simultaneously $\mathrm{d}I/\mathrm{d}V(V,x)$ curves and the topographic profile $z(x)$ at 1.5 K. We scanned along lines perpendicular to the strips. All the spectra show a dip near the Fermi energy, which spectral extension decreases from the superconducting gap Δ at the NS interface to zero at distances $x \gg \xi_N$ where $\xi_N \simeq \sqrt{\hbar D_N/2\Delta} \simeq 53$ nm is the coherence length in the normal metal. Our measurements are correctly described in the framework of the quasi-classical Green's function formalism. We numerically solved the 1D Usadel equation and extracted a decoherence time in gold of 4 ps. We also investigated the LDOS of small ridges of Au deposited on the top of the Nb lines. In this case, $L \leq \xi_N$ and the spatial variations of the spectra depend on the exact shape of the Au ridge. However, our results are consistent with a predicted minigap related to the Thouless energy.

1. Introduction

It is actually believed that all the experiments on normal metal – superconductor (NS) heterostructures can be understood from a unified point of view based on the theory of non-equilibrium superconductivity [1, 2]. The underlying Usadel [3] equations governing this proximity effect introduce a coherence length $\xi_N \simeq \sqrt{\hbar D_N/2\Delta}$ (Δ is the superconducting gap and D_N is the diffusion coefficient of the N metal). Depending on the ratio L/ξ_N where L is the size of the N metal, different behaviors are predicted [2]. On the one hand, when $L \gg \xi_N$ (infinite system), the superconducting correlations induced in N lead to a depression of the electronic density of states around the Fermi energy E_F. The energy scale of this dip in the LDOS vanishes to zero at increasing distances from the NS interface. On the other hand, when L is comparable to ξ_N (finite system) the LDOS shows a space independent minigap E_g whose width is related to the Thouless energy $E_{Th} = \hbar D/L^2$.

Several experiments address the spatial variations of the LDOS either in the infinite case at a scale larger than ξ_N [4] or with a much higher resolution but only in a finite geometry [5 – 7]. We report here measurements of the LDOS by scanning tunneling spectroscopy on Nb/Au proximity junctions. Since STM allows a high energetic and spatial resolution in conjunction with sample topography we are able to spatially resolve the LDOS in the normal metal as a function of the distance x to the NS interface (x can vary from zero to several coherence lengths with a resolution of a few nanometers). Moreover, we can discriminate between the two situations: $L \leq \xi_N$ and $L \gg \xi_N$ within the same sample.

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