Evidence of quantum phase slip effect in titanium nanowires

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Electron transport properties of titanium nanowires were experimentally studied. Below the effective diameter ≲ 50 nm all samples demonstrated a pronounced broadening of the $R(T)$ dependencies, which cannot be accounted for thermal fluctuations. An extensive microscopic and elemental analysis indicates the absence of structural or/and geometrical imperfection capable to broaden the $R(T)$ transition to such an extent. We associate the effect with quantum fluctuations of the order parameter.

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Since the early years of experimental studies in superconductivity it has been noticed that the superconducting transition $R(T)$ has always a finite width. Very often the broadening can be accounted for sample inhomogeneity. However, soon it became clear that, at least in low dimensional samples, the transition width remains finite even with the refined material purity and improved fabrication. The effect has been attributed to fluctuations typically more pronounced in objects with reduced dimensionality. The finite resistance $R(T) \sim \exp(-F_0/k_B T)$ at a temperature $T$ below the critical temperature $T_c$ of a quasi-one-dimensional superconducting channel with cross section $\sigma$ has been explained by the thermal fluctuations of the order parameter: the so called thermal activation of phase slips (TAPS)\cite{Pikovski:1998, Fetter:1993}. Here the condensation energy $F_0 \sim B_c^2 \xi \sigma$ of the smallest statistically independent volume $\xi \sigma$, where $\xi$ is the superconducting coherence length and $B_c$ is the critical magnetic field, competes with the thermal energy $k_B T$. The effect manifests itself only sufficiently close to the critical temperature, and in extremely homogeneous samples with micrometer-size diameter (e.g. pure whiskers) leads to the experimentally observable width of the $R(T)$ transition of about few mK\cite{Pikovski:1998, Fetter:1993, Kuprianov:1998}. In less homogeneous objects (e.g. lithographically fabricated nanowires) separation of the impact of the thermal fluctuations from the trivial inhomogeneity-determined $R(T)$ broadening is rather problematic. Nevertheless with development of nanotechnology it became clear that in extremely narrow superconducting wires, with diameters ≳ 10 nm, the shape of the $R(T)$ transition by no means can be explained by sample inhomogeneity or/and thermal fluctuations. The effect has been attributed to quantum fluctuations, also called - quantum phase slips (QPS) - and has been observed in a rather limited number of experiments studying the transport properties of ultra-narrow nanowires made of various superconducting materials: amorphous MgGe\cite{Kuprianov:1998, Kuprianov:1999, Kuprianov:2000}, In and In - Pb\cite{Jannett:2003, Balslev:2004, Balslev:2005}, A\cite{Jannett:2003, Balslev:2004, Balslev:2005} and InO\cite{Scarborough:2009}. Though the subject of a reliable experimental confirmation of the quantum fluctuation phenomenon in quasi-one-dimensional superconductors is still under debate, there is a consensus in the scientific community, that if exists, it should be observed in extremely narrow samples with characteristic diameters ≳ 10 nm. Unfortunately, at these scales an independent and reliable analysis of a nanostructure homogeneity is rather problematic. The uncertainty leaves a room for a critically-oriented scientist to attribute the experimentally observed deviations of the $R(T)$ superconducting transition shape from the well-established TAPS model to sample inhomogeneities: structural (impurities, grain boundaries) or geometrical (constrictions). In this paper we demonstrate that with proper selection of material (superconducting titanium) the obvious deviations of the $R(T)$ transition shape from the TAPS model become pronounced already at scales ≲ 10 nm, which dramatically simplifies both the sample fabrication and makes the structural analysis more reliable compared to the 10 nm case.

So far a rather limited number of models has been...

FIG. 1: (Color online). SPM image of typical part of a titanium nanowire. Horizontal plane indicates the interface between the metal and the sputtered Si substrate. The experimental error in definition of the interface position provides the main contribution to uncertainty in determination the sample cross section. Inset: profile of the top part of the sample.
proposed to describe the impact of quantum fluctuations on transport properties of quasi-one dimensional superconductors. Following one may describe the QPS contribution to the effective resistance of a superconducting wire with length $L$ and cross section $\sigma$ as:

$$R(T) \simeq b \frac{\Delta(T) S_{\text{QPS}}^2}{\xi(T)} \exp(-2S_{\text{QPS}})$$

(1)

where $b$ is an unimportant constant which remains the same for all samples; $\Delta(T)$ and $\xi(T)$ are the temperature-dependent superconducting energy gap and coherence length, respectively. The QPS action $S_{\text{QPS}} = A(R_Q/R_N)(L/\xi)$, where $R_Q = \hbar/2e = 6.47\,\text{k}\Omega$ is the 'superconducting' quantum resistance and $R_N$ is the wire resistance in the normal state. Constant $A$ is of the order of unit and, unfortunately, cannot be determined more precise within the model\textsuperscript{20,21,22}. The mean free path $\ell$ and the constant $A$ are the two fitting parameter of the QPS model. Note that the mean free path is not a truly free parameter and with acceptable accuracy can be estimated from the normal state resistivity as the product $\ell\rho_N$ is the material constant. Two other parameters of the model - the critical temperature $T_c$ and the normal state resistance $R_N$ - are deduced from the the experimental $R(T)$ dependencies. Recovering that for a 'dirty limit' superconductor $\ell \ll \xi$ the coherence length $\xi \simeq \sqrt{\xi_0}$, where the 'clean' coherence length $\xi_0 \simeq hv_F/\Delta$ and $v_F$ is the Fermi velocity, one may conclude that with the exponential accuracy $R(T) \propto \exp(-aT_c^{1/2}/\sigma/\rho_N)$. As the Fermi velocity does not vary much between conventional superconductors being of the same order as $v_F \simeq 1.79 \times 10^6\,\text{m/s}$ for titanium, the constant $a$ should be basically material-independent. So far in the rather limited number of experiments claiming the observation of QPS phenomena\textsuperscript{20,21,22} the efforts were mainly concentrated on reducing the sample cross section $\sigma$. However, the material issue was largely ignored: for the smallest obtainable dimension $\sigma$, obviously limited by available fabrication capabilities, the ultra-low temperature superconductors with high normal state resistivity are of advantage.

In this paper titanium has been selected as the suitable material for demonstration of the QPS phenomenon. The critical temperature $T_c$ of the titanium nanowires is below $400\,\text{mK}$. The low-temperature resistivity $\rho_N$ is significantly larger than for the majority of single-element superconductors and varies from $\approx 1.0 \times 10^{-6}\,\Omega\cdot\text{cm}$ for the 2D films to $\approx 3.2 \times 10^{-6}\,\Omega\cdot\text{cm}$ for the sub-30 nm nanowires. Utilizing for titanium the product $\ell\rho_N \approx 10 \times 10^{-16}\,\Omega\cdot\text{cm}^2$, which slightly varies from different literature sources\textsuperscript{21,22}, one gets that in our nanowires the mean free path $\ell$ is of the order of 1 nm, which correlates with the independent transmission electron microscope (TEM) analysis indicating the corresponding size of the defect-free areas. From the technological point of view titanium is an easy-to-handle material. The nanowires with different lengths $L$ between 1 $\mu$m and 100 $\mu$m were fabricated using conventional lift-off technique: soft-mask e-beam lithography followed by e-gun evaporation at a residual pressure $\approx 10^{-9}\,\text{mBar}$ on naturally oxidized Si/SiO$_2$ substrate. The mentioned difference in normal state resistivity $\rho_N$ between the wide films and the thin nanowires presumably originates from the pressure gradient between the bottom of the narrow groove in the resist mask and the rest of the vacuum chamber. In the former case, being an effective getter material, Ti 'absorbs' the residual gas and the not-completely-evacuated organics leading to formation of a dirtier sample. After the analysis with the scanning electron and scanning probe microscopes (SEM and SPM, respectively), the samples showing no obvious defects were cooled down in $^3\text{He}$-$^4\text{He}$ dilution refrigerator down to temperatures $T \approx 50\,\text{mK}$. Conventional four-probe DC and low-frequency ($< 20\,\text{Hz}$) lock-in AC techniques were used to measure the $R(T)$ dependencies. Special care was taken not to overhear the samples. Very low excitation currents down to 30 pA were used to ensure the linear response. The refrigerator and the front-end battery powered analogue pre-amplifiers were located inside the electromagnetically shielded room being connected to the external electronics via low-pass RC filters. An extensive multi-stage RLC filtering of the signal lines inside the refrigerator effectively reduced the impact of the noisy electromagnetic environment. In a separate experiment using the same measuring set-up, the increase of the effective electron temperature $T_e$ deduced from the shape of the $I-V$ dependence of a normal-insulator-superconductor junction\textsuperscript{23}, was found to be at the level $\delta T_e \simeq 20\,\text{mK}$ above the base temperature $T_b$\textsuperscript{24}.

Both the co-deposited 2D films with characteristic thickness $d \approx 40\,\text{nm}$ and the as-fabricated relatively ‘wide’ $w > 60\,\text{nm}$ nanowires showed an abrupt superconducting transition at a critical temperature $T_c \approx 400\,\text{mK}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{resistance.png}
\caption{(Color online) Resistance vs. temperature for the same titanium nanowires with length $L = 20\,\mu$m and progressively reduced effective diameter $\sqrt{\sigma}$ indicated in the plot and specified with accuracy $\pm 2\,\mu$m. Inset: normal state resistance per unitlength vs. inverse cross sections for several sample with different length $L$ indicated in $\mu$m.}
\end{figure}
The low-energy ion etching to reduce the wire effective diameter \( \sqrt{\sigma} \) is indicated in the plot in nm and are specified with accuracy \( \pm 2 \text{ nm} \).

(Figs. 2 and 3). The experimentally measurable width of the \( R(T) \) transition \( \Delta T_c \approx 20 \text{ mK} \) of these 'thick' samples can be qualitatively understood in terms of the TAPS model and the inevitable mild inhomogeneity, e.g. few percent variation of the cross section \( \sigma \). Due to the re-deposition of the sputtered material the inevitable imperfections are smoothed-out resulting in the surface roughness of the processed samples approaching \( \pm 1 \text{ nm} \) (Fig. 1). The method enables the study of a size-dependent phenomenon on a same structure with progressively reduced characteristic dimension eliminating the artefacts of the samples fabricated in different experimental runs. Further decrease of the nanowires cross sections leads to (i) reduction of the critical temperature \( T_c \), and (ii) broadening of the \( R(T) \) transition (Figs. 2 and 3). The first effect is well-known for low dimensional superconductors, though the origin of the phenomenon is still under debates.

As the size dependence of \( T_c \) is observed not only in nanowires, but also in wide 2D films, we believe that the effect is not related to the essentially 1D phenomenon under discussion - phase slips (thermal or quantum).

Homogeneity of samples is the key point in interpretation of experimental \( R(T) \) data within any model derived for a homogeneous superconducting channel of uniform cross section \( \sigma \). Critically oriented reader might always argue that the observed broad \( R(T) \) transition is the result of a trivial sample inhomogeneity: either structural (e.g. local variation of the critical temperature along the wire) or geometrical (e.g. constrictions). The two cases should be analysed separately. Let us first consider the structural inhomogeneity. Obviously all real samples do have a certain level of structural inhomogeneity originating from various sources: grain boundaries, finite size of the sample, proximity effect at the interface with wider parts of the structure, etc. We would like to note that all our samples, including the thinnest wires with a typical sheet resistance \( R_{\square} \lesssim 200 \text{ \Omega} \), are still comfortably on the metal side of a 'dirty' titanium. Formation of a network of weakly coupled metal grains and the corresponding Coulomb effects have been observed in deliberately oxidized titanium films with the sheet resistance \( R_{\square} \) exceeding few k\( \Omega \). All our samples above the critical temperature demonstrate \( I - V \) dependencies without any non-linearities, which otherwise might indicate the existence of weak links (Fig. 4), and the dependence of the normal state resistance \( R_N \) on diameter follows the expected Ohm's law (Fig. 2, inset). If the transport properties of the nanowires would be determined by the presence of the weak links, then at low temperatures the non-linear \( I - V \) characteristics should be sample-dependent. For example, various parts of a long multi-terminal nanowire should demonstrate some 'fingerprint' features related to formation of weak links particular for each sub-sample, which is not the case (Fig. 4).

An extensive TEM analysis (Fig. 5) cannot reveal any suspicious structural imperfections inside the metal matrix: the material bulk looks exactly the same for the sputtered and for the non-sputtered samples. The polycrystalline nanostructures consist of compactly packed grains with the average size of defect-free area \( \approx 3 \text{ nm} \), which correlate well with the the best-fit value \( l \approx 1 \text{ nm} \) used in calculations. The elemental depth profiles (Fig. 6) were determined by means of Time-of-Flight Elastic Recoil Detection Analysis (TOF-ERDA) using 8.015 MeV \( ^{35}\text{Cl}^{+} \) incident ions.
at the surface \((1.7 \times 10^{16} \text{ atoms/cm}^2)\) and at the interface \((5.5 \times 10^{15} \text{ atoms/cm}^2)\) corresponds to the thickness of about 1.9 nm and 0.8 nm, respectively, for the surface TiO\(_2\) and the boundary with SiO\(_2\)/Si with the corresponding density \(4.0 \text{ g/cm}^3\) and \(2.2 \text{ g/cm}^3\). The thickness of the material with the high concentration of oxygen correlates well with the high-resolution TEM analysis data (Fig. 5). The bulk concentration of oxygen \(\simeq 0.4\) at. % inside the titanium matrix was determined by comparison of the experimental energy spectra with the ones obtained by Monte Carlo simulations\(^2\). Given that the average microcrystall size is \(\sim 3\) nm, one can easily estimate that inside the titanium bulk there is less than one oxygen atom per defect boundary. Concentration of other than oxygen elements inside the titanium matrix was found to be even smaller. The observation eliminates the possibility of the weak link(s) formation due to non-metallic grain interfaces capable to block the metal-to-metal supercurrent. To summarize, all available at our disposal methods of analysis - SEM, TEM, SPM and TOF-ERDA - give us confidence to state that (i) our nanostructures are as homogeneous, as a conventional thin film titanium can be; and (ii) - what is even more important - our method of reduction of the nanowire cross section by the low energy ion sputtering does not introduce new defects. At acceleration energies \(\simeq 1\) keV the penetration depth of the \(Ar^+\) ions inside the titanium matrix is below 3 nm making the method virtually non-destructive: the thickness of the ion-damaged layer is comparable to the thickness of the naturally grown oxide. Hence, if there are some inevitable 'intrinsic' structural defects, they cannot appear in thinner samples contributing to broadening of the \(R(T)\) transition. If we assume that there exist some mysterious and undetectable mechanism which degrades the wire homogeneity with reduction of its diameter (e.g. recovery of hidden in the bulk caverns or/and grain boundaries, blocking the supercurrent), it is reasonable to assume that the mechanism should manifest itself individually for each particular sample leading to a unique 'fingerprint' on the \(R(T)\) and the \(I - V\) dependencies. However, a large statistics of samples states the opposite: the shape of the broadened \(R(T)\) transitions is universal and reproducible for different samples of the same effective diameter (Fig. 3).

Now let us turn to the alternative critics dealing with geometrical inhomogeneity: the inevitable variation of a nanowire cross section. One might argue that the \(R(T)\) broadening originates from the well-known TAPS mechanism: due to the strong exponential dependence \(R(T) \sim \exp(-\sigma)\) the contributions coming from the parts with different cross sections \(\sigma_{\text{local}}\) wash-out the otherwise sharp \(R(T)\) dependence. First, we would like to note that with reduction of the wire dimensions (by ion sputtering) the shape of the \(R(T)\) transition becomes more consistent between the samples with close values of the cross sections (Fig. 3). The observation supports the earlier statement that the ion beam etching polishes the surface making the sample geometrically more uniform: the as-fabricated 'wide' nanowires have larger variation of the cross section \(\sigma\) compared to the thinner ('polished') samples. Here we would like to stress, that the uncertainty of the effective diameter specified in Figs. 2 and 3 reflects the experimental error in determination of the cross section and not the actual roughness of the surface, which for the multiply sputtered samples does not exceed \(\pm 1\) nm (inset in Fig. 1). The error mainly comes from the uncertainty in determination of the position of the interface between the metal and the sputtered substrate (Fig. 1). In SEM the contrast between the two light materials - Ti and Si - is not sufficient to determine the position of the interface with accuracy better than \(\pm 2\) nm. While the tip deconvolution effect, typical for SPM analysis of essentially 3D nanostructures, leads to the basically same uncertainty. Summarizing, we would like to state that by standards of the modern nanotechnology and microscopic analysis our nanowires are so 'large' that it is almost impossible to overlook a pronounced constriction. Even in the worst case scenario, in the sputtered samples the variation the cross sections along the wire is below \(\pm 10\%\). The contribution of such a moderate geometrical imperfection on the shape of the \(R(T)\) transition determined by thermal fluctuations has been analysed\(^2\), by no means it can account for the experimentally observed

FIG. 5: (a) Bright field low-resolution TEM image of the cross section of a typical 35 nm thick Ti film on Si substrate. (b) Bright field high-resolution TEM image of the Ti / Si interface. Inset: Fast Fourrier Transform (FFT) indicates the single crystal nature of the metal grains forming the film.
pronounced broadening of the $R(T)$ dependencies. One may come to the same conclusion just analysing Fig. 2: the reduction of the wire average diameter from 58 nm to 33 nm leads to a negligible broadening of the TAPS fits (dashed lines) compared to the experimental data (symbols). For sufficiently narrow nanowires no realistic set of fitting parameters of the TAPS model can explain the broad experimental $R(T)$ dependencies (e.g. Fig. 2, symbols).

On the contrary, the QPS model provides reasonable agreement with the experiment (Fig. 2, solid lines). In simulations of the theoretical QPS-governed $R(T)$ dependencies (Eq. 1) for each sample (cross section) the best fit critical temperature $T_c$ corresponds to the onset of superconductivity, the mean free path $\ell \approx 1$ nm and the numerical constant $A \approx 0.3$ were kept as free parameters. At temperatures $T \ll T_c$ the negative magnetoresistance of about few percent has been observed in the thinnest samples at very small magnetic fields $\lesssim 3$ mT. Similar effect has been earlier reported in ultra-narrow lead$^{21}$ and aluminum$^{22}$ nanowires. The origin of the phenomenon is not yet clear. One alternative$^{23}$ employs possible formation of a charge imbalance region accompanying each phase slip event. This non-equilibrium region, if exists, would provide dissipation outside the core of a phase slip. Within a certain range of (small) magnetic fields the corresponding Ohmic contribution can be suppressed by the magnetic field more effective than the superconducting gap, resulting in the negative magnetoresistance. However, so far the validity of the charge imbalance concept has been only demonstrated at temperatures sufficiently close to $T_c$ and its applicability to QPS is by no means obvious. The charge imbalance scenario responsible for the negative magnetoresistance$^{24}$ still requires a solid theoretical justification.

It should be noted that the both models (QPS and TAPS) were derived assuming that the phase slips are the ‘rare’ events. In other words, the justified comparison with experiment is valid only in the limit $R(T) \ll R_N$. The QPS effect is an essentially low temperature phenomenon when quantum fluctuations of the order parameter dominate over the thermal fluctuations, with the latter being important only sufficiently close to the critical temperature $T \rightarrow T_c$. Contrary to the QPS, extrapolation of the TAPS mechanism down to lower temperatures violates the Ginzburg criterion $(T_c - T)/T_c \ll 1$ of the model applicability$^{25}$. This is an additional (theoretical) argument why the broad experimental $R(T)$ transitions (Figs. 2 and 3) cannot be explained in terms of thermal fluctuations$^{26,27}$, even if one would assume in those samples the presence of extended and unrealistically narrow constrictions $\sqrt{\sigma} \sim 1$ nm (overlooked in all microscopes!).

In conclusion, we have studied titanium nanowires with progressively reduced cross sections. An extensive microscopy and elemental analysis revealed no obvious structural or geometrical imperfections. Neither the normal state, nor the superconducting transport properties provided any signature of a non-Ohmic behavior to be associated with ‘hidden’ structural defects. The thickest samples demonstrated relatively sharp $R(T)$ superconducting transitions with the shape which can be qualitatively understood by the model of thermally activated phase slips (TAPS)$^{28,29}$ and the inevitable mild inhomogeneity of the samples$^{30}$. However for the nanowires with diameters $\lesssim 50$ nm the width of the $R(T)$ transition broadens well above the limits which can be explained by the TAPS model with a realistic set of parameters. For the thinnest samples with diameters $\lesssim 30$ nm the temperature dependence of the experimentally measured resistance $R(T)$ is very weak and does not extrapolate to zero at $T \rightarrow 0$. By the standards of modern nanotechnology and microscopic analysis the structures are so ‘large’ that speculations about trivial inhomogeneity overlooked in SET, TEM and SPM microscopes could be ruled out with a high level of confidence. We associate the pronounced broadening of the $R(T)$ transitions with quantum fluctuations of the order parameter - the so-called quantum phase slips (QPS)$^{20,21,22}$. Additionally to the importance for the basic knowledge about nanoscale superconductivity, the subject of quantum fluctuations is expected to lead to a new class of devices: quantum standard of electric current$^{36}$, qubits$^{37}$ and various QPS-based systems$^{38,39}$.

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