Anomalous Proximity Effect in an Inhomogeneous Disordered Superconductor

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(Received 5 February 2004; published 19 November 2004)

By combining very low temperature scanning tunneling microscopy and spectroscopy on a TiN film we have observed a nonuniform state comprising of superconducting (S) and normal (N) areas. The local density of states displays a spatial dependence between S and N different from the usual proximity effect. We conclude that mesoscopic fluctuations might play a major role in accordance with recent theories describing superconductor–normal-metal quantum transition.

DOI: 10.1103/PhysRevLett.93.217005 PACS numbers: 74.45.+c, 71.30.+h, 74.81.–g

In two dimensions, the superconductor-insulator transition (SIT) is traditionally described by two microscopic mechanisms [1]. In the first one, the Cooper pairs are all formed at $T = 0$ and become localized through the SIT. This is often referred to as the ''bosonic'' model and has been successfully applied to granular superconductors [2]. The onset of the superconductivity appears at a constant temperature but the transition becomes broader as the sheet resistance $R_\square$ approaches $\frac{h}{4e^2}$. This broadening is associated with quantum fluctuations of the phase of the order parameter due to the competition between the charging energy of the superconducting grains and the Josephson coupling between them. The resistance close to the SIT in most granular films displays a reentrant transition as a function of magnetic field or temperature [3]. Actually, the competition between Cooper pair and quasiparticle tunneling between superconducting grains can explain this nonmonotonic behavior. In these models, a zero resistance state appears when the network of superconducting islands percolate [4].

The second mechanism attributes the weakening of the superconductivity to a disorder enhanced Coulomb repulsion. Pair breaking is considered simultaneously with the decrease of both the superconducting critical temperature and the amplitude of the order parameter as the SIT is approached. This so-called ''fermionic'' scenario usually describes homogeneous thin films which keep a sharp superconducting transition until disorder becomes very close to a critical value [5]. By further increasing the disorder, by reducing the thickness, or by application of a magnetic field, these films can be driven into an insulating state with localized electronic excitations. However, there are theoretical predictions [6,7] and experimental observations [8–10] of an intermediate metallic phase.

Real samples are sometimes neither purely bosonic nor purely fermionic systems; granularity effects can be observed in homogeneous films [11] and a reentrant transition is not always present in granular films [12]. Moreover, to analyze experiments on nominally homogeneous films, the spatial dependence of the superconducting properties has nevertheless been considered [9,10]. In the light of these experiments, a two step scenario has been proposed where a Bose metal with no phase coherence precedes a localized electron insulator driven by amplitude fluctuations [7].

A double reentrant behavior very close to a SIT has recently been observed in disordered TiN thin films [13]. This SIT could be triggered either by a magnetic field or by increasing $R_\square$. It is worth noticing that such a double reentrance has also been observed in Josephson junction arrays and highly granular superconductors [14]. On the other hand, although granular, TiN films behave as homogeneous films with regard to the evolution of the superconducting critical temperature with $R_\square$ down to 500 mK, the double reentrant behavior appearing only below 150 mK. In this Letter, we report scanning tunneling spectroscopy on a similar but thicker TiN film with a lower $R_\square$ and in zero field, thus far away from the SIT. Nevertheless, we show that disorder induced inhomogeneities already exist in such a film, which are not detected by transport measurements.

TiN was prepared by dc reactive magnetron sputtering at 350 °C on thermally oxidized Si substrates. By sputtering a Ti target at various nitrogen partial pressures in an argon-nitrogen gas mixture, different TiN_δ compositions with $0.7 \leq \delta \leq 1.2$ were obtained [15]. We have been able to vary the room temperature electrical resistivity between 80 and 1100 $\mu\Omega$ cm by changing the nitrogen flow rate from 40 to 200 sccm [16]. In stoichiometric TiN films, the mean free path l is mainly limited by the grain boundaries and one gets $l \simeq L_g$, where L_g is the typical grain size. When the nitrogen flow rate is increased during the film preparation, Ti vacancies are introduced and one obtains overstoichiometric TiN_δ ($\delta > 1$) with $l < L_g$. Moreover, the Ti vacancies are not uniformly distributed inside the grains but are rather concentrated at their boundaries [17]. The film studied here has an intermediate resistivity of 270 $\mu\Omega$ cm, a mean free path $l = 5 \pm 1$ nm, and a thickness of 100 nm [16]. We estimate $L_g \simeq 20$ nm from scanning tunneling microscope (STM) images. It undergoes a sharp superconducting transition at $T_c = 4.68$ K as detected by $R(T)$ experiments.

We have combined topography and spectroscopy measurements with a STM cooled down to very low temperature in a dilution refrigerator. In order to probe the local density of states (LDOS), a small ac modulation of 20 μV rms was added to the sample-tip dc bias voltage V and the differential conductance $\frac{dI}{dV}$ obtained with a lock-in amplifier technique. V could be ramped at any position $\mathbf{r}$ to yield a curve $\frac{dI}{dV}(V)$ proportional to the LDOS $n(E, \mathbf{r})$ at an energy $E = eV$ with respect to the Fermi energy. Several spectra normalized by the conductance at high voltage ($V > \Delta$) are displayed in Fig. 1 for different temperatures. The superconducting gap values $\Delta(T)$ are obtained by convoluting a BCS density of states with a Fermi distribution function and are displayed in the inset. A weakly temperature dependent Dynes parameter in the range $\Gamma = 0.022$–0.027 mV is used to adjust the peak height [18]. The lowest indicated temperature of 250 mK is not the measured one which was 125 mK, but rather the temperature needed to correctly fit the spectrum. This indicates that the energy resolution of our STM is probably limited by unfiltered electromagnetic radiations which heat the electrons. We find $\Delta(T = 0) = 0.73$ mV and a ratio $\frac{\Delta}{kT_c} = 1.81$ not far from the theoretical BCS value of 1.76.

However, these spectra are not observed everywhere on the surface of the TiN film and at other locations a normal-metal–like flat LDOS is measured. In order to get an image of the superconducting and normal areas we set the bias to a voltage $V_0 = 0.75$ mV slightly above the BCS gap value. Two images were then recorded simultaneously: the topographic one $Z(x, y)$ and the spectroscopic one $\frac{dI}{dV}(x, y)$ at the given energy eV_0. When the tip is scanning above a superconducting region, the differential conductance signal increases because of the peak in the LDOS at V_0. Inversely, a flat LDOS is characterized by a lower output from the lock-in amplifier. The two images can be merged into a 3D colored picture

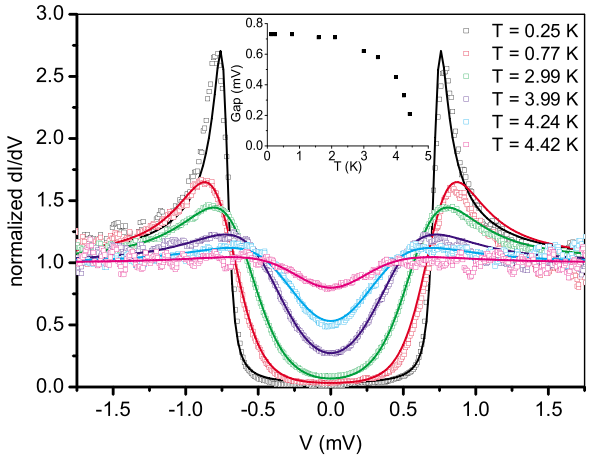

FIG. 1 (color). Several spectra taken at different temperatures at the same location and the corresponding BCS fits. Inset: Temperature dependence of the BCS gap.

[19], as shown in Fig. 2 for two different areas on the surface. The topography is rendered by the shaded perspective and the spectroscopy is depicted by the colors. The dark orange areas are normal, while the light yellow ones are superconducting. Sometimes, isolated grains stand higher on top of the surface. They can be either normal or superconducting. The lower panel in Fig. 2 shows several superconducting ones.

Once the electronic properties are identified everywhere on the scanned surface, it is then possible to measure the complete spectra along a line which crosses the boundary between a superconducting and a normal region. As an example, such a line is drawn in the upper panel of Fig. 2 and data are displayed in Fig. 3. Except for the truly gaped spectra which is labeled as the starting position $x_{\mathrm{exp}} = 0$ on the S side, none of the spectra are BCS-like. The distance d_{SN} over which the LDOS varies depends on the local granularity. It can be as long as 50 nm when the surface is smooth. For isolated superconducting grains such as those in the bottom panel in Fig. 2, the spatial variation of the LDOS is much more rapid and takes place within 10 nm, mainly inside the grain itself. However, these different spatial scales do not modify the form of the overall transition of the LDOS at the SN interface since the spectra evolve in the same manner between S and N wherever they are obtained on the surface of the sample.

The spatial dependence of the proximity effect at an SN interface can be described in the framework

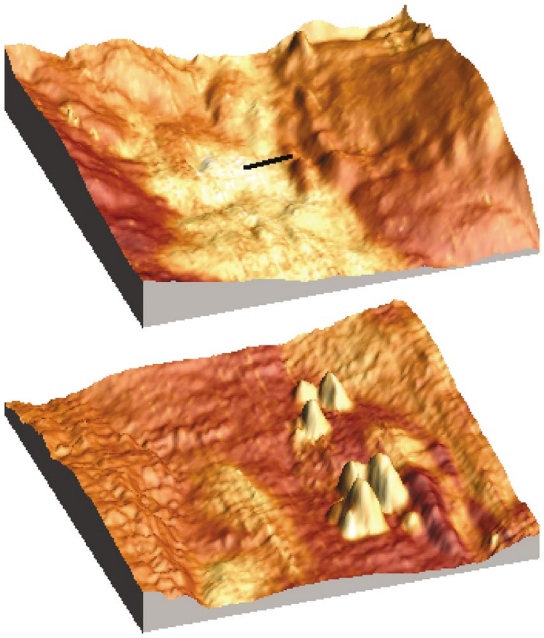

FIG. 2 (color). 3D images of two different areas of TiN. Top: 400×400 nm^2, $T = 143$ mK; the data of Fig. 3 were obtained along the drawn line. Bottom: 250×250 nm^2, $T = 258$ mK. The maximum height amplitude is 2 nm for both pictures. The coloring shows the LDOS at $V_0 = 0.75$ mV; the superconducting regions are yellow and the normal ones are orange.

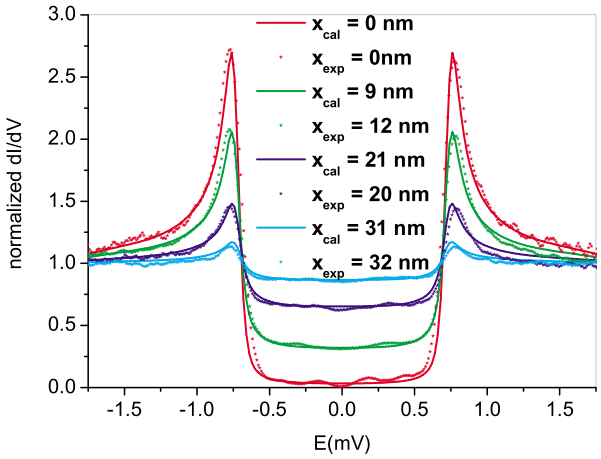

FIG. 3 (color). Spatial evolution of the LDOS for different positions x along a line of measured length $d_{SN} = 48$ nm between a superconducting and a normal region. The dotted lines are experimental data. The solid lines are numerical fits with Eq. (2), which has no adjustable parameter.

of the quasiclassical Green's functions by a complex pairing angle $\theta(E, \mathbf{r})$ [20]. The LDOS is related to θ by $n(E, \mathbf{r}) = n_0 \mathrm{Re}[\cos\theta(E, \mathbf{r})]$. In the dirty limit, i.e., $l \ll \xi = \sqrt{\hbar D/2\Delta}$ (D is the diffusion constant), $\theta(E, \mathbf{r})$ obeys the Usadel equation [21] which in one dimension can be written as

$$\frac{\hbar D}{2}\frac{\partial^2\theta}{\partial x^2} + [iE - \Gamma_{in} - 2\Gamma_{sf}\cos\theta]\sin\theta + \Delta(x)\cos\theta = 0, \tag{1}$$

where Γ_{sf} and Γ_{in} are the spin flip and the inelastic scattering rates, respectively. This description of the superconducting proximity effect at a mesoscopic scale has already been checked experimentally in SN heterojunctions with nanofabricated tunnel junctions and with STM experiments [22]. For infinite SN systems, it has been shown that the LDOS exhibits a V-shaped pseudogap with peaks below and above the Fermi level. These peaks are separated by an energy which decreases as a function of the distance from the interface in the normal side of the junction. Here instead, we observe U-shaped spectra with peaks that are pinned at the BCS energy Δ for any position between S and N. The LDOS is flat for energies smaller than Δ and increases as the tip is moved progressively away from the S region. We tried to fit these results using Eq. (1) and a self-consistently determined space dependent order parameter $\Delta(x)$ [23]. However, no set of parameters was able to correctly reproduce even qualitatively the shape of the spectra. One of the possible reasons for this failure could be that our film does not fulfill the dirty limit condition. Actually, we have $\xi = 6.5$ nm, which is slightly larger than l [16]. Moreover, since the scattering centers are concentrated at the grain boundaries, the electronic trajectories could be considered to be quasiballistic inside the grains. The projection in only one dimension of the Usadel equation might also be too crude an approximation.

It is nevertheless striking that we can reproduce with good accuracy our results if we assume θ varies linearly with distance between the BCS pairing angle on the S side ($x = 0$) and zero on the N side ($x = d_{SN}$):

$$\theta(x) = \theta_{BCS}\frac{d_{SN} - x}{d_{SN}}, \tag{2}$$

where $\tan(\theta_{BCS}) = \frac{i\Delta}{E+i\Gamma}$. The numerical results are shown in Fig. 3. We found excellent agreement between the experimental data and the calculations without any adjustable parameters. Δ and Γ are deduced from the spectrum taken above the BCS superconducting region and positions are chosen in order to match the measured LDOS at the Fermi energy. The slight differences between these positions and the measured ones reflect the granularity always present; the latter affects the measured value of the proximity length d_{SN} and can also perturb the pure linear behavior of Eq. (2). Although there is no obvious physical justification of this equation, we want to point out its universal character: it does not depend on any physical properties of the material such as scattering times, conductivities, or coherence lengths necessary to describe the usual proximity effect [24].

We want to discuss now the physical origin of the superconducting and normal clusters. In STM experiments, surface contamination must be seriously considered as a possible artifact for samples exposed to air. Nevertheless, there are easily recognizable signs which indicate the presence of adsorbates: (i) They usually degrade the quality of the images. (ii) At moderately low temperature, when they are frozen out, their positions are revealed as bumps in the topographic images. (iii) At very low temperature, they generally exhibit the LDOS of an insulator and give dark areas in spectroscopic images. As seen in the panels of Fig. 2, no such effects are visible. The transition between superconducting and normal areas is in places very smooth with no change in the noise in the data. This proves that the inhomogeneities are intrinsic to the sample. Moreover, we checked that they were indeed related to the amount of disorder by probing another film with a higher sheet resistance ($R_\square = 135\ \Omega$) and found very similar inhomogeneities but with a significantly smaller fraction of superconducting areas. These areas displayed a superconducting order parameter $\Delta = 0.68$ mV in concordance with a measured reduced superconducting temperature $T_c = 4.27$ K. However, we cannot rule out that, because of oxidation at intergrain boundaries for example, the surface of TiN itself is not representative of the bulk which could be more homogeneous. Another possible source of inhomogeneity could come from spatial variations of the nitrogen concentration in TiN_δ, since the BCS coupling constant, λ, depends on δ [25]. Following Ioffe and Larkin's pioneering work, strong statistical fluctuations of $\lambda(\mathbf{r})$ can lead to an in-

homogeneous system where superconductivity appears first in localized drops which percolate at T_c even far away from the SIT threshold [26]. A spatial distribution of the order parameter amplitude would give a broadened density of states as obtained by Hsu *et al.* [10] with large area tunnel junctions. Here, we would expect to observe well identified superconducting clusters with different BCS gap values. Since this is not the case, it seems therefore more likely that our film is made of well coupled superconducting grains with a unique Δ embedded in a normal-metal matrix where the Ti vacancies pile up. According to Feigel'man *et al.* [27] and Spivak *et al.* [27], quantum fluctuations in such a system make superconductivity unstable. Spatial variations of the size and the concentration of grains as well as mesoscopic fluctuations of the intergrain conductance can drive the film locally into either a normal-metal or a superconducting cluster. This is also consistent with the observed leveling off of the resistivity at very low temperature and with the reentrant field tuned transition observed in thinner TiN films. Indeed, when the film is closer to the percolation threshold of the superconducting network its global resistivity is then governed by a few bottlenecks and the associated mesoscopic fluctuations. According to Spivak and Zhou [28], these mesoscopic fluctuations can give a multiple reentrant transition between superconducting and normal metallic states.

In summary, despite a superconducting order parameter and a related critical temperature which mimic the disorder dependence of homogeneous films, we have observed inhomogeneities in thin TiN film of a nature similar to those invoked to explain macroscopic properties [9,10] and possibly described by a fluctuation driven superconductor–normal-metal transition for granular films [27]. It is very likely that, in order to understand the spatial dependence of the LDOS between superconducting and normal areas, one should go beyond the mean field Usadel equation: mesoscopic fluctuations could help explain the inhomogeneous superconducting state, the reentrant field tuned transition in TiN, and modify the proximity effect [29].

We are grateful to M. Houzet for helping us to resolve self-consistently the Usadel equation, and to M. Sanquer who initiated these experiments.

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