Suppression of Superconductivity in Zinc Nanowires by Bulk Superconductors

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Transport measurements were made on a system consisting of a zinc nanowire array sandwiched between two bulk superconducting electrodes (Sn or In). It was found that the superconductivity of Zn nanowires of 40 nm diameter is suppressed either completely or partially by the superconducting electrodes. When the electrodes are driven into their normal state by a magnetic field, the nanowires switch back to their superconducting state. This phenomenon is significantly weakened when one of the two superconducting electrodes is replaced by a normal metal. The phenomenon is not seen in wires with diameters equal to or thicker than 70 nm.

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Superconductivity in quasi-one-dimensional (1D) nanowires (NWs) has attracted considerable attention in the last two decades [1–6]. When the wire diameter is smaller than its phase coherence length $\xi(T)$, finite dissipative resistance due to thermally activated phase-slip [6,7] and possibly also quantum phase-slip processes [1–3] is found below the superconducting transition temperature T_c. When such a superconducting nanowire (SNW) is connected to two normal metal (N) electrodes [8], a fraction of the wire, due to the proximity effect (PE) [9], is found to be resistive.

When a SNW is connected to two strongly superconducting bulk electrodes, the total combined system is expected to be superconducting below the T_c of the SNW and the electrodes [10]. The superconductivity of the wire is expected to become more robust through its coupling with the superconducting reservoirs. In this Letter, we report results that are contrary to this expectation in a system consisting of superconducting zinc nanowires (ZNWs) sandwiched between two bulk superconductors (BSs) of different materials (Sn and In). We found evidence that the superconductivity of ZNWs of 40 nm in diameter is suppressed either completely or partially when the BSs are in the superconducting state. When the BSs are driven normal by a magnetic field (H), the ZNWs switch back to their superconducting state, exhibiting an "antiproximity effect" (APE) behavior.

Bulk zinc (Zn) is a conventional type I superconductor (S) with a transition temperature at 0.85 K and a critical magnetic field of 50 Oe. Its superconducting coherence length in a bulk crystalline sample, ξ_0, at $T = 0$ K is found to be as large as 2.0 μm [11]. ZNWs were fabricated by a simple template-assembly electrodeposition technique [12], where the diameter and the length of the ZNWs are easily controlled by the pore diameter and the thickness of the porous membranes (PM) made of polycarbonate and anodic aluminum oxide. The electrolyte was prepared by dissolving 4.7 g $ZnCl_2$ into 200 ml distilled water, and then mixed with 40 ml saturated KCl and 0.5 g gelatin. Deposition was made at room temperature under a constant voltage of -0.1 to -0.4 V with a pure bulk Zn bar as the anode. Structural characterization of the ZNWs was made via transmission electron microscopy (TEM). Images shown in Fig. 1(a) indicate that the majority of the ZNWs has a polycrystalline structure with grain size ranging from the wire diameter up to a few hundred nanometers. High resolution TEM showed that the grains are primarily oriented with the $[0001]$, $[11\bar{2}0]$, and $[1\bar{1}00]$ directions along the length of the wires [13]. Dislocations were observed near the surface and inside the crystalline grains.

Electrical transport was carried out with a physical properties measurement system (PPMS), equipped with a ^{3}He insert and a superconducting magnet. The experimental arrangement is shown schematically in the inset of Fig. 1(b). In this configuration, high-purity (99.9999%) Sn or In wires of 0.5 mm diameter were mechanically squeezed onto the two sides of a membrane, making electrical contact to the ZNWs embedded in the membrane. The details of this technique can be found in Ref. [3]. The measured resistance (R) from this structure includes contributions from BS electrodes, ZNWs, and the two BS/ZNW interfaces. Figure 1(b) shows the normalized

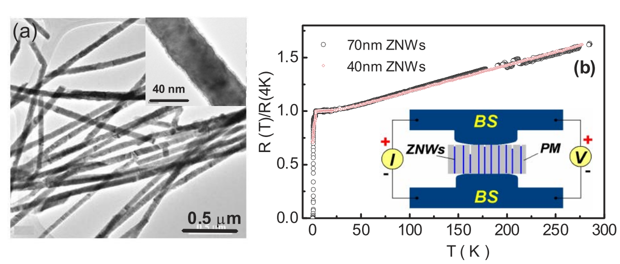

FIG. 1 (color online). (a) TEM images of freestanding ZNWs and a magnified segment showing crystalline structure. (b) $R(T)/R(4\text{ K})$ vs T of 70 and 40 nm ZNWs between bulk In electrodes from 0.47 to 300 K, and the schematic of transport measurement.

$R(T)/R(4\ \mathrm{K})$ of two In/ZNWs/In samples with ZNWs of 70 and 40 nm in diameter and 6 μm in length. These two R-T curves appear to collapse onto each other and show metallic behavior from 300 down to 4.0 K with a residual resistance ratio (RRR) of ~1.6. The metallic behavior of the sample implies metallic contacts between the BSs and ZNWs. With this technique, 38 samples of different configurations were measured. Reproducible results are always found on samples of similar configurations. In this Letter, we show figures of seven representative samples: $Z1$, $Z2$, $Z3$, $Z4$, $Z5$, $Z6$, and $Z7$. The numbers of ZNWs making contact to BSs in these samples are estimated by using a resistivity of $\rho_{\mathrm{Zn}}(4\ \mathrm{K}) \sim 18.2\ \mu\Omega\,\mathrm{cm}$ at 4 K [14] and the drop in resistance when ZNWs are cooled from the normal to the superconducting state. They are, respectively, 11, 4, 6, 1, 55, 13, and 5 for $Z1$–$Z7$. The estimates for multiple wires are correct to within 30% and the estimate of a single wire for $Z4$ should be accurate given the limits in uncertainty in resistivity (20%) and the wire dimensions (10%). In a careful study of single-crystal Zn, the product of the elastic electron mean-free path ℓ_e and resistivity ρ_{Zn} at 4.2 K was found to be $2.2 \times 10^{-11}\ \Omega\,\mathrm{cm}^2$ [11,15]. Using this relation and $\rho_{\mathrm{Zn}}(4\ \mathrm{K})$ of 18.2 $\mu\Omega$ cm, the ℓ_e and the superconducting phase coherence length, $\xi(0) \sim (\xi_0 \ell_e)^{1/2}$, of our ZNWs are estimated to be 12 and 155 nm, respectively. The presence of dislocations or other defects inside the ZNWs is likely the reason for the reduced RRR of 1.6 and a ℓ_e that is much smaller than the grain size.

Figure 2(a) shows R-T curves of sample $Z1$ (diameter, $d = 70$ nm; length, $L = 6\ \mu$m) with bulk Sn electrodes, measured at different magnetic fields. At $H = 0$ Oe, the resistance of the system shows a small drop near 3.7 K, and then a much larger drop near 1.0 K before decaying to zero below 0.7 K. These resistance drops have their origins from

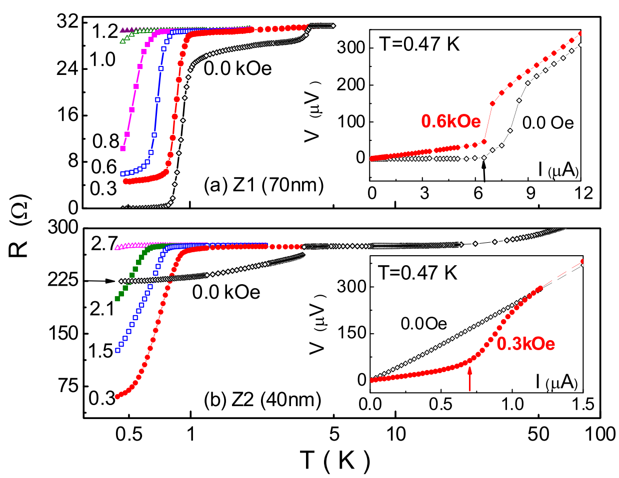

FIG. 2 (color online). R-T curves of (a) $Z1$ and (b) $Z2$ with Sn electrodes under different magnetic fields ($H \perp$ ZNWs). The length of the ZNWs is 6 μm. The insets show the V-I curves at $H = 0.0$ and 0.3 kOe, respectively.

the superconducting transitions of bulk Sn and ZNWs, respectively. The fact that zero resistance of the system was found below 0.7 K shows that the entire Sn/ZNWs/Sn system is superconducting at low temperatures, consistent with expectations. When bulk Sn is driven into the normal state under a field 0.3 kOe, the system shows only one large drop around 1.0 K due to the superconducting transition of the ZNWs. Superconductivity in the ZNWs persists because its critical field is enhanced to 1.2 kOe at 0.47 K by their reduced diameter. The inset of Fig. 2(a) shows V-I curves at 0.47 K at $H = 0$ and 0.6 kOe. Regardless of whether the bulk Sn is superconducting or normal, the V-I curves of the system show a well-defined critical current, $I_c \sim 6.0\ \mu$A, below which the ZNWs are in the superconducting state. The linear dependence of V on I seen at $I < I_c$ at $H = 0.6$ kOe reflects the Ohmic metallic nature of the interfaces between normal Sn and ZNWs.

Figure 2(b) shows R-T curves of sample $Z2$ ($d = 40$ nm, $L = 6\ \mu$m) with bulk Sn electrodes, measured at different H. The R-T curve at $H = 0$ Oe shows the expected drop at 3.7 K, the T_c of Sn. However, in strong contrast to the data of $Z1$, there is no sign of a drop or even a change in the slope near 1.0 K, the T_c of ZNWs. The large finite resistance found at 0.47 K confirms that the ZNWs reside in the "normal" state. When the bulk Sn electrodes are driven to the normal state by a field of 0.3 kOe, a prominent resistance drop is seen around 1.0 K, indicating the superconductivity of the ZNWs is recovered. The results shown in R-T curves are supported by V vs I scans at 0.47 K. At $H = 0$ Oe, when bulk Sn is superconducting, the V-I curve of the system shows Ohmic linear behavior at all excitation current. Under a field of 0.3 kOe, when bulk Sn is normal, the V-I curve of the ZNWs shows a change in shape at a critical current I_c of ~0.6 μA.

Measurements were also made on three In/ZNWs/In samples with ZNWs of 40 nm in diameter but of different lengths. The lengths of the ZNWs in samples $Z3$, $Z4$, and $Z5$ are 6, 2, and 35 μm, respectively. The ZNWs in $Z5$ were made in a porous alumina membrane; all other samples reported here were made with polycarbonate membranes. The R-T curves of $Z3$, $Z4$, and $Z5$ are, respectively, shown in Figs. 3(a)–3(c). Sample $Z3$ ($L = 6\ \mu$m) at $H = 0$ Oe shows a broad transition near 1.0 K with a limited resistance drop that ends with a finite resistance of 100 Ω at 0.47 K. When the bulk In electrodes are driven normal by a field of 0.3 kOe, a larger and sharper resistance drop near 1.0 K is observed. A similar but stronger suppression effect [Fig. 3(b)] is seen in sample $Z4$, which is a single wire of 2 μm. The measured R at $H = 0$ Oe shows a smooth decrease from 3.4 to 0.47 K, with no resistance drop near 1.0 K. The application of a magnetic field of 0.3 kOe, as in samples $Z2$ and $Z3$, results in a sharp resistance drop near 1.0 K. The V-I scans in the inset of Figs. 3(a) and 3(b) support the R-T measurements, namely, a well-defined I_c is found only when

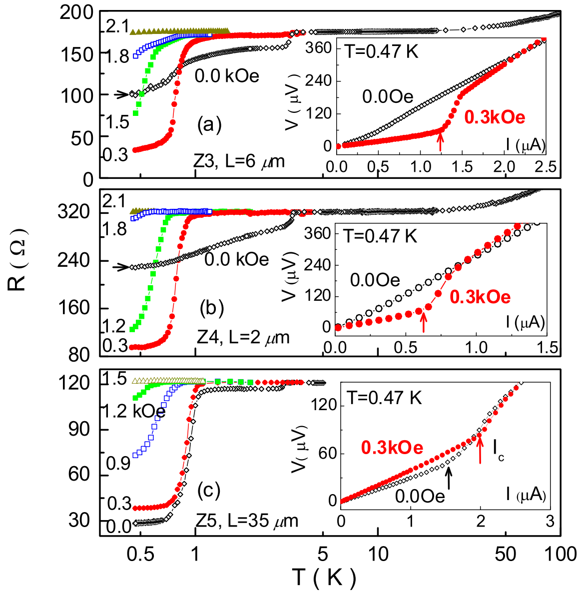

FIG. 3 (color online). *R-T* curves of (a) *Z*3, (b) *Z*4, and (c) *Z*5 with indium electrodes under different fields ($H \perp$ ZNWs). The diameter of the ZNWs is 40 nm. The insets show the *V-I* curves of the specific sample measured at 0.0 and 0.3 kOe, respectively.

the In electrodes are normal at $H = 0.3$ kOe. The results in *Z*4 closely resemble that of *Z*2 of 6 μm in length with Sn as the BS. These results indicate that Sn as BS is more effective than indium in suppressing superconductivity in ZNWs and the APE is reduced when the length of the ZNWs is increased from 2 to 6 μm. When the length is increased to 35 mm as in *Z*5, no obvious sign of the APE is seen in the *R-T* curves. However, the *V* vs *I* scans at 0.47 K measured under two different fields show an increase in critical current I_c from 1.6 μA at 0 Oe to 2.0 μA at 0.3 kOe.

Figure 4 shows *R-H* scans of sample *Z*4 at different temperatures. At 1.2 K, the ZNWs are in the normal state and the discontinuous rise in *R* at 0.245 ± 0.01 kOe with increasing *H* pinpoints the critical field of bulk indium. Scans at 0.47 and 0.75 K, below the T_c of the ZNWs, show sharp drops in *R* as *H* is increased above 0.27 ± 0.01 kOe, the H_c of indium at these temperatures. These scans show clearly that the abrupt switching of ZNWs from a superconducting to a nonsuperconducting state (and vice versa)

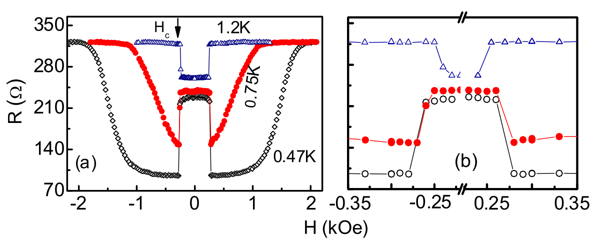

FIG. 4 (color online). (a) *R-H* curves of sample *Z*4 at 0.47, 0.75, and 1.2 K. (b) Magnified *R-H* curves near H_c.

bears a negative correlation with the state, namely, superconducting or normal, of the BS.

In order to understand the effect of BS/ZNWs interfaces on the observed phenomenon, control experiments were carried out with samples *Z*6 and *Z*7. Sample *Z*6 has a configuration of Ag/ZNWs/Sn. Sample *Z*7 has a configuration of Sn/ZNWs/Sn, but the interface resistance is approximately 10 times higher than that of *Z*2. The diameter and the length of the ZNWs in these two samples are the same as in *Z*2 and *Z*3, namely, 40 nm and 6 μm, respectively. *R-T* curves for sample *Z*6 by themselves show no obvious evidence of APE. A clear signature of the effect, as in the case of sample *Z*5, is found in the *V-I* curves. The I_c at $H = 0.3$ kOe, with the Sn electrode in the normal state, is higher than that at zero field. The result in *Z*6 shows that the APE is present even when one of the two electrodes is a normal metal, but it is much weaker. In sample *Z*7 with high interface resistance [Fig. 5(b)], the only signature of the APE in the *R-T* curves is the slightly lower *R* value at 0.3 kOe as compared to that at zero field below 0.75 K. An increase in the critical current at 0.3 kOe, as compared to that at zero field, is also found. We have also made measurement on 40 nm ZNWs sandwiched between two Au electrodes. The ZNWs always showed a superconducting transition near 1.0 K. These control experiments support the conclusion that the BS is responsible in suppressing superconductivity in ZNWs and the effect is reduced when the coupling between the ZNWs and BS is reduced.

One possible source of the APE is that it is an artifact of electrical noise. One may argue that when the BSs are in the superconducting state, they are more efficient in absorbing high frequency noises which in turn heat the ZNWs into the normal state. This explanation cannot explain the finding that the strength of the APE is material dependent, strongest with Sn, weaker with In, and weakest with Pb as the electrodes [16]. It is also difficult to understand how electrical noise can give rise to the observed

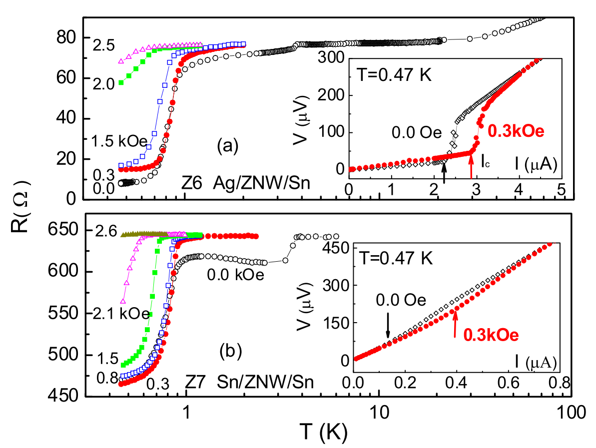

FIG. 5 (color online). (a) *R-T* curves of (a) *Z*6 and (b) *Z*7 with Sn as the BS. $L = 6$ μm; $d = 40$ nm. The insets show their *V-I* curves at $H = 0.0$ and 0.3 kOe, respectively.

systematic dependence on the length of ZNWs. Nevertheless, we have made measurements with all electrical leads equipped with low pass π filters, both at room temperature and inside the cryostat adjacent to the sample. The measurements with low temperature filters were carried out in a conventional dilution refrigerator cryostat instead of the PPMS cryostat. The results measured with or without filters showed the same APE behaviors.

We do not as of yet have a satisfactory explanation of the observed effects. A very speculative explanation is that the symmetry of the superconducting order parameter in a thin (40 nm) ZNW is different from that of bulk and thick ($d \geq$ 70 nm) wires. When superconductors of different pairing symmetries are placed in contact with each other, the mismatch of the order parameters can disrupt the superconducting transport through the system [17]. However, if there is a symmetry change as the diameter of the ZNW is decreased from 70 to 40 nm, one would expect also a significant difference in the transition temperature. This is not seen.

It is likely that the APE has its origin in the BS/ZNW interfaces. At a SN junction or various hybrid structures [18,19], the electron transport behavior can be understood in the framework of Andreev reflection (AR) [9,20]. A direct consequence of AR leads to an enhanced total conductance through the SN interface which is the origin of the PE [9,18,19]. Our system can be considered as a SNS system above 1.0 K. The R-T curves at $H = 0$ Oe between 1.0 K and the T_c of BS do show PE, where the total resistance was found to decrease significantly with decreasing temperature when the BSs are in the superconducting state. However, none of the theoretical models in the AR framework can explain the observed APE behavior below 1.0 K.

Since the diameter of our ZNWs is significantly smaller than the estimated phase coherence length ~155 nm, 1D dissipation due to thermal and quantum fluctuations is expected to give rise to nonzero resistance at all temperatures below T_c [1–3]. These dissipation mechanisms, e.g., phase-slip events, are expected to be much more important in the thinner, 40 nm rather than 70 nm, wires [1,3]. Martin-Rodero *et al.* [21] considered a model consisting of a narrow superconducting channel of length $L \gg \xi_0$ coupled to two wider superconducting electrodes, resembling our system. This theory predicted the existence of a region of phase-slip center of length ξ_0 at the center of the channel where the magnitude of the order parameter is nearly zero at $T = 0$ K or suppressed at nonzero temperatures. This prediction bears resemblance to our data for samples $Z3$, $Z5$, and $Z7$ showing partial suppression. However, the theory did not predict the complete destruction of superconductivity in the channel (as shown in $Z2$ and $Z4$) and cannot explain our data in $Z6$ when one electrode was replaced by a normal metal. Since the channel material in the model is the same as the bulk electrodes, it was assumed that the order parameter in the constriction is the same as its bulk value of the electrodes. This assumption is not realized in our experiment where the wire and the electrodes are different superconductors. Because of experimental difficulties, we have not been able to make measurements with bulk Zn as BS electrodes. However, measurements made on Sn NWs with a diameter of 40 nm and length of 6 μm between bulk Sn electrodes [3] did not show any evidences of APE. The superconducting coherence length of the Sn wires was determined to be 55 nm, considerably smaller than that in ZNWs. Measurements extending to thinner Sn wires with 6 μm or shorter length might be helpful in understanding the current effect. It would be also very interesting to extend the theory of Martin-Rodero *et al.* to the case of when the wire and the electrodes are superconductors of different energy gaps.

In conclusion, a novel antiproximity effect was found in a system consisting of 40 nm ZNWs sandwiched between two BS electrodes (Sn or In). A quantitative understanding of this phenomenon may require a realistic model of the superconducting order parameter in the 1D limit and how it is altered through the interface when it is coupled to neighboring bulk superconducting reservoirs.

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