Long-range superconducting proximity effect in template-fabricated single-crystal nanowires

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Abstract. A long-range superconducting proximity effect is investigated in single-crystal nanowires of Zn, Sn, and Pb, of length up to 60 μm, electrochemically deposited into the pores of anodic aluminum oxide membranes and polycarbonate membranes. Using an in situ self-contacting method, single nanowires are electrically contacted on both ends to a pair of macroscopic film electrodes of Au, Sn, or Pb pre-fabricated on both surfaces of the membranes. Superconductivity in the nanowires is strongly suppressed when Au electrodes are used. When electrodes having higher superconducting transition temperatures are used, the nanowires become superconducting at the transition temperatures of the electrodes. Microscopy analyses of the structure and the chemical composition of the nanowires are presented, which demonstrate a sharp interface between the nanowires and the macroscopic film electrodes. Measurements of the I-V characteristics provide evidence that this proximity effect occurs along the length of the nanowires.

1. Introduction
The suppression of superconductivity in one-dimension (1-D) has been studied in amorphous and granular materials [1-5]. These nanowires (NWs) are typically highly disordered. Recently, NWs formed by electroplating metals into porous membranes have attracted much attention. They can be granular [6], polycrystalline [7], or single crystalline [8], providing a largely unexplored parameter space in which new superconducting effects may be studied in 1-D.

When a superconducting NW is in contact with normal metal electrodes, parts of the NW near the contacts become resistive due to the proximity effect (PE) [9]. The penetration length of the PE is expected to be shorter than the thermal length $L_T = 2\pi\hbar v_F/k_B T$ in the clean limit and $(\hbar D/k_B T)^{1/2}$ in the dirty limit, where $\hbar$ is Planck’s constant, $v_F$ is the Fermi velocity, $k_B$ is the Boltzmann constant, and $D$ is the electron diffusivity. In the clean limit, $L_T$ is about 2 μm at 7.2 K and 3.8 μm at 3.7 K for Sn and Zn. This picture is consistent with reports on the PE in carbon nanotubes [10] and e-beam patterned Al NWs [11]. However, there are exceptions. For example, a modulation of $T_c$ on a length scale of 60 μm was observed [12] in lithographically patterned Al films. In this report, we present experimental results of the PE in single crystalline Zn, Sn, and Pb NWs of length up to 60 μm.

2. Experimental details
Zn, Sn, and Pb NWs of diameter $d = 30-250$ nm and length $L = 6$ or 60 μm were fabricated by electroplating metals into the pores of either 6-μm-thick polycarbonate (PC) membranes or 60-μm-thick anodic aluminum oxide (AAO) membranes from Whatman Co. and SPI Supplies Inc. The
electrolytes were 4.7 g ZnCl₂ dissolved in 200 ml water for plating Zn, a 16.72 g of Sn(BF₄)₂ solution at 50% wt with 200 ml of water for plating Sn, and a 16.2 g Pb(BF₄)₂ 50% wt solution in 200 ml water with 6.72 g HBF₄ and 3.0 g HBO₃ for plating Pb. The reducing potentials relative to an Ag/AgCl reference were 1.1-1.2 V for Zn, 0.4-0.5 V for Sn, and 0.4-0.5 V for Pb, while using a Pt anode. As shown by Fig. 1(a), we applied an in situ method [13] for self-contacting a single NW with a negligible contact resistance, using a thick (~300 nm) cathode and a thinner (50-100 nm) front electrode evaporated on the two membrane surfaces. Plating was initiated at the cathode to fill the pores not blocked by the front electrode, and terminated to obtain a single NW in contact with the electrodes as the potential difference between the two electrodes suddenly dropped to zero when the first NW contacted the front electrode. The resistance of the NW was then measured in a pseudo 4-probe configuration with each electrode connected to a pair of current and voltage leads. Au, Sn, and Pb electrodes were used to study how superconductivity was modified in the NWs. We believe it is crucial to form contacts with a near-perfect transparency. In this regard, this in situ method [13] likely has an advantage over the other contacting methods such as electron-beam lithography.

![Figure 1(a): Sketch showing the self-contact method. (b): A TEM image of a slice of an AAO membrane. EDS mappings of Zn and Pb elements on the same slice are shown in (c) and (d), respectively.](image)

The structure and composition of the NWs were investigated in a number of approaches using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), electron diffraction pattern (EDP) and energy dispersion spectroscopy (EDS). Free-standing NWs were extracted using a centrifuge after the membranes were dissolved. Selected-area EDP patterns were taken along the length of the NWs. In each case, the EDP patterns showed an identical geometry without rotation, indicating that the NWs were single crystalline with the lattice structures of their respective superconducting bulk phases. To investigate NWs preserved in the pore channels, we embedded AAO membranes with NWs in epoxy. The samples were then microtomed parallel to the NWs to produce slices about 150 nm in thickness. In some slices, the cathode/NW interface was visible, as shown by the TEM image in Fig. 1(b) for a slice of membrane with Zn NWs grown using Pb electrodes. A portion of the Pb cathode near the top of the image and the Zn NWs in the pore channels appear as dark contrast due to their larger scattering-absorption effect compared to that of the Al₂O₃ matrix. Fig. 1(c) is an EDS mapping of the element Zn in the plane of the slice. Mapping of the element Pb is shown in Fig. 1(d). The Zn and Pb profiles in (c) and (d) match the dark contrast in (b). All EDS studies revealed a sharp interface between the NWs and the electrodes.

3. Results

The resistance \( R \) of single Zn, Sn, and Pb NWs was measured down to 1.8 K in a Quantum Design physical properties measurement system (PPMS). The \( T_c \) of bulk Pb, Sn, and Zn are, respectively, \( T_c(Zn) = 0.88 \) K, \( T_c(Sn) = 3.7 \) K, and \( T_c(Pb) = 7.2 \) K. For 6-μm-long Pb and Sn NWs in contact with
Au electrodes, we did not observe any signature of superconductivity down to 1.8 K, however, when 6-μm-long Zn and Sn NWs were in contact with superconducting electrodes having a higher $T_c$, they became superconducting at the $T_c$ of the electrodes. This is shown by the top frames in Fig. 2 for Sn NWs. For 60-μm-long NWs, superconductivity in Pb and Sn NWs was only partially suppressed by Au electrodes as shown by Fig. 2(d) for Pb NWs, yet, superconductivity induced by Pb electrodes in Zn and Sn NWs was robust, as shown by Fig. 2(e). Fig. 2 illustrates a PE in NWs up to 60 μm in length. These single crystalline NWs had large residual-resistance-ratios (RRR) of up to 50, as shown by Fig. 2(f). In the clean limit, the thermal length $L_T$ is 2 μm at 7.2 K and 3.8 μm at 3.7 K for Sn and Zn. For 6-μm-long NWs, coherence over the length $L_T$ cannot be excluded as the origin of the PE in 6-μm-long NWs. However, $L_T$ is much too short to account for the PE in the 60-μm-long NWs.

Figure 2. Top: $R$ vs. $T$ for 6-μm-long Sn NWs of indicated diameters with electrodes of (a) Au, (b) Sn, and (c) Pb. Bottom: $R$ vs. $T$ for 60-μm-long NWs of $d = 200$ nm. (d): Pb NWs are fully superconducting with Pb electrode (lower two curves) but only fully superconducting with Au electrodes (upper two curves). (e): Superconducting at $T_c$(Pb) for Zn and Sn NWs with Pb electrodes. (f): $R$ vs. $T$ up to 300 K showing the large RRR values of Sn and Zn NWs.

Figure 3(a): $I$-$V$ curves measured at 2 K on one 60-μm-long Sn NW with Pb electrodes for fields (transverse to the NWs) between 0.8 and 2.5 kOe for curves from the right to the left. (b) Filled triangles show $I_c$ vs. $H$ obtained from $I$-$V$ curves measured at 2 K and open triangles show $I_c$ vs. $T$ obtained from $I$-$V$ curves measured in zero-field.

Figure 3(a) shows the typical current-biased $I$-$V$ curves measured on one 60-μm-long Sn NW with Pb electrodes, at 2 K for various transverse field values between 0.8-2.5 kOe. Approaching $H_c$, the $I$-$V$ showed reproducible and regular steps identical to those seen in superconducting whiskers and microbridges [14]. We identify the critical current $I_c$ by the first step in an $I$-$V$, or, when the slope of an
$I-V$ shows a sudden increase from the slope at zero-bias for $H$ very close to $H_c$. Fig. 3(b) is a plot of $I_c$ vs. $H$ (filled triangles) at 2 K, showing that $H_c$ is 1.3-1.4 kOe, consistent with $H_c = 1.35$ kOe of the Pb film electrodes measured at 2 K. The steps in the $I-V$s reveal the successive establishment of spatially localized phase-slip centers (PSCs) as certain spots along a NW have smaller $I_c$. Associated with a PSC is an oscillating gap parameter in a core length $2\xi(T)$, with $\xi \approx 230$ nm well below $T_c$ for Sn. The length of the PSCs is twice the nonequilibrium quasi-particles diffusion length $\Lambda_{Q}$. Following Skocpol et al. [14], we found $2\Lambda_{Q} \approx 10$ μm using the voltage steps and the corresponding $I_c$, consistent with early results from Sn microbridges [14] and recent results from electroplated Sn NWs. Similar multiple steps were also observed in $I-V$s measured between 6.5-7.2 K (near $T_c(Pb)$) in zero field, and we plot $I_c$ vs. $T$ in Fig. 4(c) for $H = 0$ showing that $T_c = T_c(Pb)$ as indicated by the arrow. We note that similar measurements in 6-μm-long NWs observed single step only, possibly because this length was shorter than $2\Lambda_{Q}$. We interpret the multiple steps observed in 60-μm-long NWs as evidence that the observed PE occurs along the length of the NWs and is not limited to the interface region between the NWs and the electrodes.

4. Conclusions
In summary, we have observed a long-range superconducting PE for NWs in contact with bulk film electrodes formed by an in situ electrochemical deposition process. With electrodes having a higher critical temperature $T_c$, single-crystal Zn and Sn NWs of length up to 60 μm are superconducting at the $T_c$ of the electrodes. The $I-V$ curves measured at various $H$ and $T$ provide evidence that this PE occurs along the length of the NWs. A number of analysis techniques, using the SEM, TEM, EDS, EDX, and XRD, have been applied to verify the structure and the chemical composition of the samples. The interface between the NWs and the film electrodes appears sharp based on cross-sectional TEM and EDS mapping investigation.

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