

Electroless template grown superconducting lead and tin nanotubes

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Abstract

Lead and tin nanotubes were synthesized by electroless deposition in a nanoporous polymer membrane without sensitization, activation or a reducing agent. A thick Pb or Sn layer is evaporated on one side of the membrane and provides the metallic ions needed to grow the tubes in an aqueous solution. The nanotubes' geometry and composition were investigated by means of electron microscopy, energy dispersive x-ray spectroscopy and ultramicrotomy. Electrical measurements obtained on such superconducting nanotubes are compared with solid wire characteristics. This spontaneous growth could explain some recent results obtained on superconducting nanowires showing an anomalous long-range proximity effect.

Among the different techniques used to synthesize mesoscopic superconductors, electrodeposition into alumina and polymer membranes is now widely used [1]. Superconducting nanowires made from a variety of materials with a wide range of diameters have been synthesized allowing the investigation of one dimensional superconductivity phenomena [2, 3] and flux-line penetration in a confined geometry [4, 5]. More recently, this template technique has been used to develop nanowires appropriate for the study of the proximity effect at superconductor–normal interfaces [6–8]. On the other hand, metallic nanotubes have also been fabricated by covering the walls of the pores of nanoporous media [9–11]. In most cases these nanotubes are synthesized by chemical (electroless) reduction of metal ions, which normally requires reducing agents and a metal catalyst that must be applied to the pore walls. This catalyst is usually formed with sensitization and activation steps. In the present work, we present an electroless synthesis of lead (Pb) and tin (Sn) nanotubes without sensitization, activation or a reducing agent. The simplicity of their synthesis makes this technique attractive to study superconductivity in this particular geometry. Some electrical transport measurements performed on these superconducting nanotubes are also presented.

The nanotubes were prepared using 21 μm thick nuclear track etched polycarbonate membranes [12] having uniform pore diameters of either 250 or 480 nm and a pore density of $4 \times 10^7 \text{ cm}^{-2}$. One face of the membrane is first coated with a thick layer of Pb or Sn, which closes all the pores. The

other face is then exposed to an appropriate acidic electrolyte for a few minutes, sufficient for the electroless growth of the tubes. Three different baths were used. The first one, named BPb, contained 40.4 g l⁻¹ lead tetrafluoroborate (Pb(BF₄)₂), 33.6 g l⁻¹ tetrafluoroboric acid (HBF₄) and 15 g l⁻¹ boric acid (H₃BO₃). The second, BSn, contained 41.8 g l⁻¹ tin tetrafluoroborate (Sn(BF₄)₂) and 33.6 g l⁻¹ HBF₄. It is noted that BPb and BSn are baths commonly used to make Pb and Sn nanowires by electrodeposition [13]. The third bath, BH, contained only 33.6 g l⁻¹ HBF₄ and is therefore free of Sn or Pb ion species. Lead nanotubes were obtained by electroless deposition using the three different baths, while for the growth of Sn nanotubes only baths BSn and BH were used. The nature of the thick coating layer at the bottom of the pores appeared to be of major importance. Using a Pb or Sn layer, pure Pb or Sn metallic nanotubes are formed when solution BPb or BSn is used, respectively. On the other hand, nanotubes grown from a Pb layer using bath BSn (containing Sn⁺⁺ ions) turned out to be made of Pb with only 12 wt% Sn inclusion, as determined by energy dispersive x-ray spectroscopy measurements in a transmission electron microscope (TEM) after having dissolved the membrane with dichloromethane. Moreover, nanotubes have also been synthesized using bath BH, initially free from metallic ions, which further indicates that the thick coating layer is able, by itself, to provide the material needed for nanotube growth. In contrast, when a membrane coated with a thick gold layer is immersed in BPb or BSn, no electroless deposition takes place (solid wires are formed under the application of a voltage).

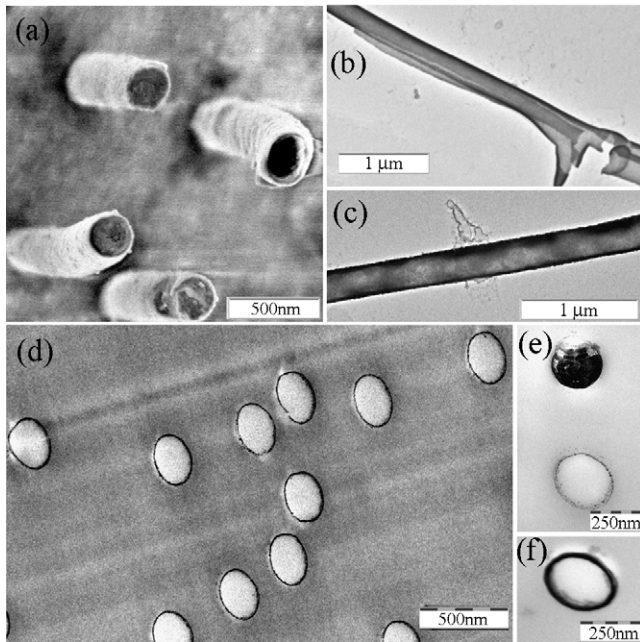


Figure 1. (a) SEM image of Pb nanotubes obtained after 2.5 min immersion in bath BH. (b)–(f) TEM micrographs. (b) and (c) Sn nanotubes obtained after 5 min immersion in baths BH and BSn, respectively. (d)–(f) Ultramicrotomy slice (95 nm thick) of a membrane filled with Sn nanotubes obtained after 10 min in bath BH. The wall thicknesses are 8 nm, 6 nm and 15 nm for the tubes shown in (d), (e) and (f) respectively. A filled cross-section is also shown at the top of (e).

The nanotubes were characterized by scanning electron microscopy (SEM) and TEM. Figure 1(a) shows a SEM micrograph of Pb nanotubes obtained after 2.5 min in bath BH. The membrane has been dissolved without removing the thick Pb layer. In order to get a better insight into the nanotube dimensions and regularity, TEM characterization was undertaken. At first, a dispersion of nanotubes on a grid was carried out after having dissolved the membrane. Nanotubes as long as 21 μm (i.e. the membrane thickness) have been observed. Tubular structures clearly appear in TEM, as evidenced by the darker regions that represent the thicker 2D tube projection of the wall, while the lighter regions indicate the hollow region of the tube. The nanotubes are usually regular, but they sometimes break during the dispersion or under the electron beam (see figures 1(b) and (c) showing Sn tubes obtained after 5 min in BH and BSn, respectively). Secondly, ultramicrotomy was used to measure the nanotube's inner diameter accurately. Slices of the nanocomposite (95 nm thick) were cut perpendicularly to the tube axis using a diamond knife. The sections of the tubes appear slightly distorted due to the cut, whose direction can be determined by the straight scratches left by the knife (figure 1(d)). As illustrated in figure 1(d), large parts of the membrane are uniformly filled with quasi-identical tubes (wall thickness ~8 nm). However, on the same sample we have also observed variations of the nanotube wall thickness (see figures 1(e) and (f)), sometimes leading to a completely filled cross-section. It is also worth mentioning that some pores remain empty, forming empty regions beside filled ones.

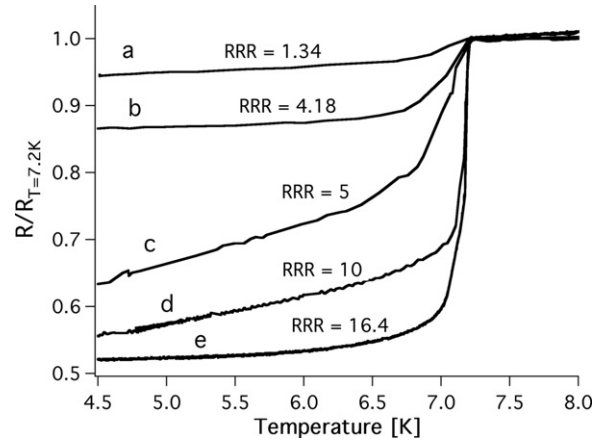


Figure 2. Normalized resistance versus temperature for different Pb nanotubes synthesized in the same electroless conditions considering two different polymer membranes. Samples a and c have an outer diameter of 250 nm and samples b, d and e have an outer diameter of 480 nm. The residual resistivity ratio (RRR) is also indicated.

In order to make electrical transport measurements, a thin contacting Au layer is deposited on the side of the membrane exposed to the electrolyte. This layer is thin enough to ensure that it does not cover the pores completely. After exposing the membrane to the bath BPb for 10 min to grow the tubes, an electrodeposition step is initiated by applying -0.5 V between the cathode (consisting of an array of Pb nanotubes vertically aligned on a thick Pb layer) and an Ag/AgCl reference electrode. The potential is applied for 10 s to establish a good electrical contact between a number of tubes and the thin contacting Au layer. It should be pointed out that under such electrodeposition conditions, a 10 s duration is much too short (by one order of magnitude) to grow solid wires along the entire nanopore length. Figure 2 shows the temperature variation of the resistance for some selected Pb nanotube samples. For all the samples, T_c is close to 7.2 K. A wide range of residual resistivity ratio RRR (defined as $RRR = R_{300 K}/R_{7.5 K}$) was found. From these values we can estimate the mean free path ℓ using the Sommerfeld approach [14]. The RRR values (1.3, 4.2, 5, 10 and 16.4) of samples a–e in figure 2 lead to $\ell = 0.9$ nm, 8 nm, 10 nm, 23 nm and 40 nm, respectively. When measuring electrodeposited solid wires, a simple calculation based on the RRR value and wire geometry leads to a rather good estimate of the number of wires contacted electrically. In our case, the large uncertainties in the nanotube inner diameter makes this estimation more difficult. In the following, we focus on the superconducting sample e (outer diameter: 480 nm), whose resistance is 20 Ω at 300 K. Assuming that the tube thickness roughly corresponds to ℓ (40 nm), we find that this particular sample consists of 4 tubes in parallel. Note that if a thicker tube wall is considered, the number of tubes contacted electrically would even be smaller. As all the samples of figure 2 were obtained under the same electroless conditions it is reasonable to think that the main differences between those samples originate from their wall thicknesses. Thinner tubes lead to smaller ℓ , thus tending to weaken the superconductivity, as revealed by a smaller drop in resistance at T_c and a broadening of the transition.

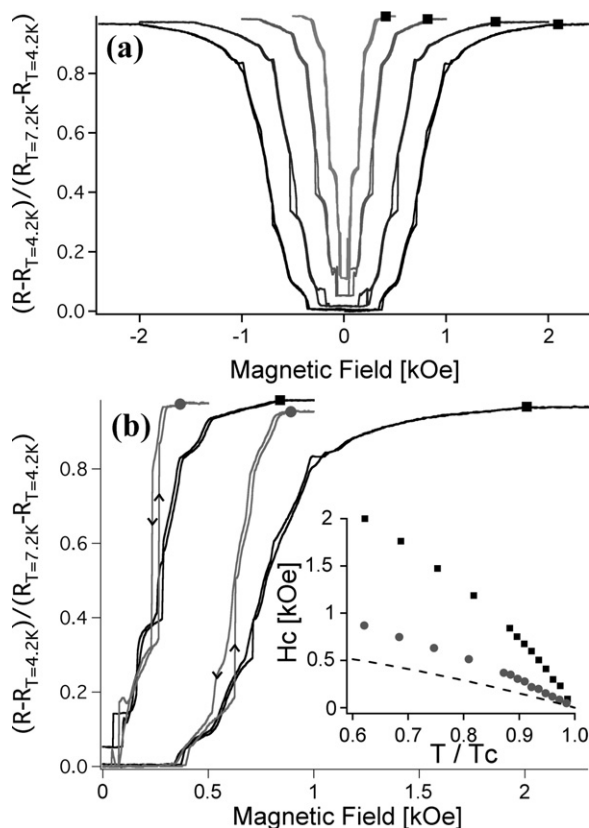


Figure 3. (a) Normalized resistance versus magnetic field at different temperatures for Pb nanotubes (sample e—480 nm outer diameter). Reduced temperatures T/T_c for the different curves are from left to right: 0.62, 0.75, 0.88 and 0.95. (b) Comparison of magnetoresistance curves between Pb tubes (sample e, in black) and Pb solid wires (in grey) having the same diameter at $T/T_c = 0.88$ (left) and 0.62 (right). The squares and dots mark the critical fields reported in the inset. Inset: critical field evolution with temperature for Pb tubes (sample e—squares) and solid wires (dots) compared to that of bulk material (dashed line). In (a) and (b), the magnetic field is applied parallel to the tube and wire axes.

The magnetoresistance of sample e is shown on figure 3(a) at different temperatures. The resistance was normalized by subtracting the resistance at 4.2 K and dividing by the resistance at 7.2 K. The magnetic field is applied parallel to the tube axis. The $R(H)$ characteristics are symmetrical. The first step (at about 0.4 kOe at $T/T_c = 0.62$) is attributed to the transition of the thick Pb layer located at the bottom of the membrane. A comparison between Pb nanotubes (in black) and electrodeposited solid wires (in grey) grown from same membrane is presented in figure 3(b) at two selected temperatures. The solid wire samples exhibit a RRR of 56, corresponding to a mean free path of 136 nm. The low field parts of the $R(H)$ characteristics are very similar, as expected since the samples have the same thick Pb bottom layer. The inset in figure 3(b) shows the temperature variation of the critical field H_c (defined as the field where superconductivity is completely destroyed) for the tubes (squares) and the solid wires (dots). The Pb bulk critical field is also represented (dashed line) for comparison. We can see that the H_c of the tubes is about twice that of the solid wires, which is also higher

than that of the bulk Pb material. This can be attributed to the incomplete Meissner effect, already present in the wire samples, and still more pronounced in the nanotube samples due to the small wall thickness. In figure 3(b) we observe hysteresis in the $R(H)$ characteristics both for tubes and wires. Such hysteresis can be associated with the presence of potential barriers to vortex entry/escape. The hysteresis is larger for the wires than for the tubes, which indicates higher energy barriers between the different magnetic states for the wires. While measuring tubes, we might expect to observe Little–Parks oscillations [15] for temperatures very close to T_c . However, the minimum oscillation period possible is estimated to be $\phi_0/S_{\max} = 114$ kOe, where ϕ_0 is the magnetic flux quantum and $S_{\max}$ is the maximal section considering the outer diameter of the tube. As the critical field of our sample is too small at temperatures where Little–Parks oscillations are supposed to show up, it is not surprising that no Little–Parks oscillations have been identified.

Recently, some measurements have been reported showing an apparent long-range proximity effect in nanowires electrodeposited using a thick cathode made of Pb or Sn [7, 8]. In [7], the T_c of a single Sn nanowire (21 μm long and 50 nm in diameter) in contact with Pb contacting layers was just below the T_c of bulk lead. Liu *et al* [8] showed similar results on Sn and Zn nanowires in contact with Pb or Sn layers. The Sn and Zn nanowires (60 μm long and 200 nm in diameter) also displayed the T_c of the contacting layers. The RRR values were in the range of 1.4–50, similar to those observed for our nanotubes fabricated by electroless deposition. We believe that these intriguing results might arise from this unexpected and spontaneous nanotube formation. The filamentary nanostructures measured in [7] and [8] could possibly be completely different from the ones expected. Instead, given the high growth rate observed here, they could consist of nanotubes having mostly the same composition as the massive bottom layer, serving as a cathode, with a limited inclusion of the metallic ions present in the initial electrolytic solution.

In conclusion, we synthesized superconducting lead and tin nanotubes by electroless deposition without using sensitization, activation or any specific compound, such as the reducing agent used in classical electroless processes. The precise growth mechanism is not yet clear, but the material must originate from the thick metallic layer closing the pores at the bottom side of the membrane. TEM characterization and transport measurements have revealed a certain dispersion in the geometrical and structural properties of these tubes. This spontaneous growth could explain the recent intriguing results showing apparent long-range proximity effects in nanowires.

Acknowledgments

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