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Citation: Appl. Phys. Lett. **86**, 152510 (2005); doi: 10.1063/1.1900953
View online: http://dx.doi.org/10.1063/1.1900953
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v86/i15
Published by the American Institute of Physics.

Fabrication and physical properties of Pb/Cu multilayered superconducting nanowires

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(Received 27 July 2004; accepted 1 March 2005; published online 7 April 2005)

Using nanoporous media as templates for electrodeposition, we have fabricated multilayered Pb/Cu nanowires 50 nm in diameter and 20 μm long with Cu layer thicknesses as low as 10 nm. This was achieved by using a single-bath technique and a precise selection of the copper deposition potential to limit the redissolution of lead when the potential is raised to electrodeposit the more noble metal. Such superconductor/normal multilayered nanowires show interesting magnetoresistance properties at a low magnetic field that may be related to the proximity effect, which can therefore be investigated in a quasi-one-dimensional geometry.
 [DOI: 10.1063/1.1900953]

Studies of high-aspect-ratio nanowires synthesized by electrodeposition into templates have revealed very interesting behaviors associated with their reduced dimensionality. In particular, there has been a huge interest in the study of magnetic nanowires, in which the characteristic dimensions are comparable to the scaling lengths in magnetism or spin-polarized transport.[1] Recently, the template method has been also used to fabricate arrays of superconducting nanowires[2] whose diameter is comparable to the characteristic superconducting lengths, i.e. the magnetic penetration length λ and the coherence length ξ. Such nanowires are indeed of special interest for studying size effects on the superconducting-to-normal state transition,[3] on flux-line penetration in a confined geometry[4] or on phase-slip mechanisms.[5] This electrodeposition technique offers the advantage of allowing not only the fabrication of nanowires made from a single metal but also complex structures, such as multilayers. Indeed, nanowires consisting of alterning magnetic (cobalt) and nonmagnetic layers (copper) have been prepared and investigated.[6] Moreover, in the film geometry, heterostructures involving the combination of a superconductor and a normal metal (S/N), a ferromagnet, or another superconductor, have generated a lot of interest.[7] Here, we present a way to fabricate lead/copper (S/N) multilayered nanowires 50 nm in diameter and a few tens of microns long. Because their diameter is smaller than or comparable to λ and ξ at all temperatures, they can be viewed as one-dimensional heterostructures that may lead to interesting physical properties.

The Pb/Cu multilayered nanowires were prepared by a single-bath electrodeposition technique into nanopores of homemade track-etched polycarbonate membranes.[8] We used a 21 μm thick membrane with pore diameter of $\sim$50 nm and a pore density of $\sim 2\times 10^9$ cm^{-2}. Single-bath electrodeposition of multilayers can be performed by the use of a periodically varying current or potential.[9] We used the potentiostatic control, which is known to give a sharper concentration gradient at the interface than in the case of a galvanostatic control. However, contrary to the case of magnetic multilayers, such as Ni/Cu or Co/Cu (Ref. 1), Pb tends to dissolve completely at the usual potential corresponding to copper deposition. Therefore, we found that a precise selection of the potential for the deposition of Cu is needed to avoid the redissolution of Pb as much as possible.

The electrolyte consists of an aqueous solution with 0.85 mol/l of lead sulphamate $[Pb(NH_2SO_3)_2]$ and 2.4×10^{-3} mol/l of copper sulphamate $[Cu(NH_2SO_3)_2]$, obtained by the reaction of lead carbonate ($PbCO_3$) and copper hydroxide $[Cu(OH)_2]$ with sulphamic acid in excess. Under our conditions, Cu starts to deposit significantly at about -0.1 V versus an Ag/AgCl reference electrode, while Pb deposition begins at -0.372 V. Therefore, we used a potential of -0.45 V to deposit Pb at room temperature and without stirring. A range of potentials were tried to further deposit Cu on Pb layers. Figure 1 compares the cathode current transients resulting from potentiostatic pulses for two different deposition potentials for Cu (-0.35 V and -0.37 V), both not sufficiently negative to deposit Pb. As can be judged by the undershoot in current, while the redissolution effect is pronounced at -0.35 V, it is much less at -0.37 V; allowing the growth of Pb/Cu multilayered nanowires. Since Pb and

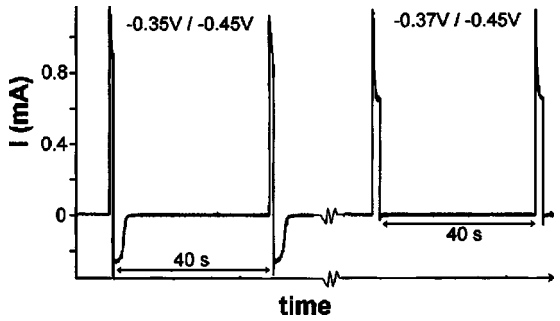

FIG. 1. Time evolution of the electrodeposition current when the potential vs Ag/AgCl reference electrode is switched between -0.35 V (or -0.37 V) for the Cu layer deposition and -0.45 V for the Pb layer deposition. Large current value (above 0.5 mA) corresponds to Pb deposition, small but positive value (~ 10 μA) of the current corresponds to Cu deposition and large negative value of the current corresponds to the dissolution of the previously deposited Pb layer during Cu deposition.

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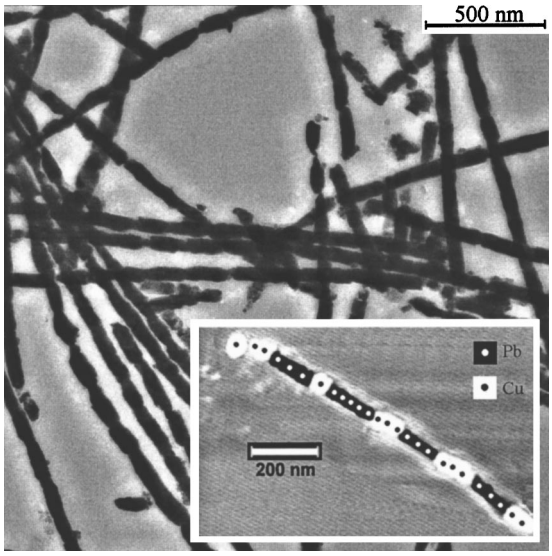

FIG. 2. TEM micrograph of Pb/Cu multilayered nanowire 50 nm in diameter. Inset: Schematic representation of such nanowire where dots indicate the location where EDX local chemical analysis was performed using spot size 20 nm in diameter.

Cu are not miscible, it is expected that this pulsed deposition technique leads to sharp interfaces when Pb is deposited on Cu, but when Cu is deposited on Pb this interface is certainly broader due to the slight dissolution. Characterization of multilayered nanowires is done by dissolving the host polymer membrane with dichloromethane. Energy dispersive x-ray spectroscopy (EDX) measurements in a scanning electron microscope performed on a large number of nanowires grown with this electrolyte at the constant potential of −0.45 V show that the Pb deposit contains less than 2 wt % of Cu. A small amount of Cu in the Pb layers is unavoidable with a single-bath technique; but is kept very small due to the low concentration of Cu ions in the electrolyte compared to the concentration of Pb. Transmission electron microscopy (TEM) was then used to characterize the morphology of the Pb/Cu multilayered nanowires. Figure 2 shows a TEM image of such Pb/Cu nanowires, while the inset of Fig. 2 shows schematically the multilayer structure. The nature of the layers was identified by EDX measurements done in the TEM with a spot size of about 20 nm in diameter; the location is represented by black or white dots in the inset. A series of such local chemical measurements along the wire allowed us to determine the average length of the Pb and Cu layers.

In order to make electrical transport measurements on single Pb/Cu multilayered nanowires, we used a self-contacting technique.[10] Indeed, in addition to the thick gold cathode from which the nanowires start to grow inside the pores, another contacting gold layer is deposited on the other side exposed to the electrolyte. This contacting layer is thin enough to ensure that it does not close the pores, so they can be filled by the electrolyte. As the nanowires do not grow at the same speed, the first emerging nanowire slows down the growth of the others by favoring the formation of a film on the contacting layer. This allows us to have a single nanowire in contact with the two gold layers to which electrical contact is made thereby facilitating two-wire transport measurements. Figure 3 shows the low-temperature resistance of two different single Pb/Cu multilayered nanowires. Sample A is

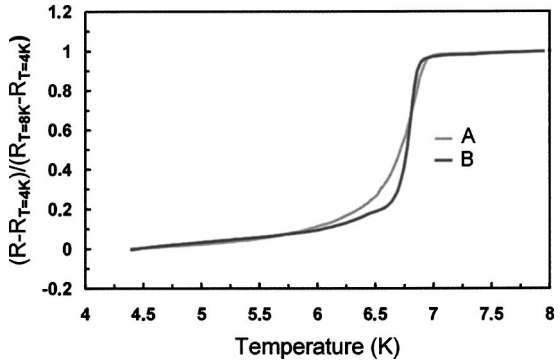

FIG. 3. Resistive transition of two Pb/Cu multilayered single nanowires 50 nm in diameter, 21 μm long measured with lock-in amplifier technique. Sample A is made of 15 bilayers (30 nm Cu/1370 nm Pb) and Sample B is made of 140 bilayers (10 nm Cu/140 nm Pb).

made of 15 bilayers with an average thickness of 30 nm for Cu layers and 1370 nm for Pb layers. Sample B contains about 140 Pb(140 nm)/Cu(10 nm) bilayers. One can see that the critical temperature is near the bulk T_c value of lead (7.2 K) and also that of pure Pb nanowires.[10] Though the relatively wide resistive transitions can be attributed to thermally activated phase slips,[11] part of the broadening is also certainly due to the small depression of T_c at the N/S boundaries in the limit of thick superconducting layers.[12] Figure 4 shows the magnetic field variation of the resistance $R(H)$ below T_c for Sample A (H is applied parallel to the wire axis). The overall dependence at 4.2 K [Fig. 4(a)] is symmetric and the critical field H_c is around 0.7 T, much larger than H_c for bulk Pb (0.055 T at 4.2 K). This is due to the incomplete Meissner effect as in the case of pure Pb nanowires of the same dimension.[3] As shown in Fig. 4(b), particular features appear at a low magnetic field in the superconducting state (which are not present above T_c). They could be attributed to the proximity effect (see, in particular, the negative magnetoresistance that appears for H around 0.03 T).

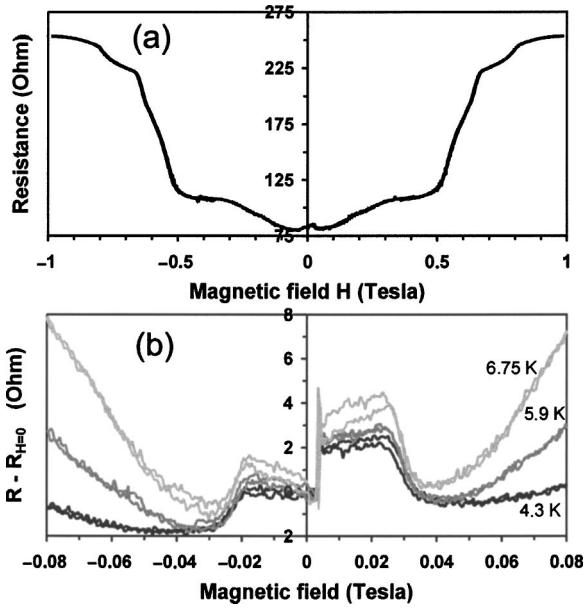

FIG. 4. (a) Resistance vs magnetic field at 4.2 K of a Pb/Cu multilayered single nanowire 50 nm in diameter, 21 μm long alternating 30 nm Cu and 1370 nm Pb layers. The magnetic field is applied parallel to the nanowire axis. (b) Zoom at a low magnetic field value for three different temperatures.

Indeed, within a thickness of the order of ξ at a N/S boundary, electrons and holes in N couple with the superconducting condensate by the mechanism of Andreev reflection,[13] and this region also becomes superconducting. Moreover, a quite small magnetic field (the breakdown field)[12] is usually sufficient to destroy this proximity effect. Sweeping the magnetic field, we observe in Fig. 4(b) an asymmetric behavior superposed on the negative magnetoresistance. As pointed out above, the Pb/Cu interfaces are broader than the Cu/Pb. Such structural dependence of the interfaces on the order in which N and S are deposited was also observed in some thin films prepared by evaporation.[12]

Moreover, the quality of interfaces is known to affect the electron transmission properties at these interfaces. These two classes of interfaces, being the only source of asymmetry, are believed to be source of the asymmetry in the transport properties with field direction. The negative magnetoresistance observed for both directions of the magnetic field slightly depends on the temperature in the temperature range investigated. This could be related to the small thickness of our Cu layer compared to the proximity characteristic length (typically of the order of 50 nm in the present sample). However, this interesting negative magnetoresistance effect is not yet fully understood and deserves more theoretical attention.

In conclusion, we showed that electrodeposition from a single bath allows the fabrication of Pb/Cu multilayered nanowires with a relatively good control of the geometrical parameters. Interesting magnetoresistance behavior is obtained at low magnetic field, likely due to the proximity effect. Further studies performed by varying the thicknesses of the individual Pb and Cu layers will provide a better understanding of the superconducting properties of these one-dimensional heterostructures.

The authors thank the "Laboratoire des Hauts Polymères" of the UCL for providing the polycarbonate membrane samples used in this study. One of the authors (S. M.) is a Research Fellow of the National Fund for Scientific Research (FNRS) Belgium. This work has been partly supported by the Belgian Interuniversity Attraction Pole Program (PAI-IUAP P5/1/1) and by the "Communauté Française de Belgique" through the Program "Actions de Recherches Concertées." The authors also thank the FRFC for the TEM equipment.

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