APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 25 21 JUNE 2004

Metallic contacts with individual Ru nanowires prepared by electrochemical deposition and the suppression of superconductivity in ultrasmall Ru grains

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(Received 5 February 2004; accepted 29 April 2004; published online 10 June 2004)

Nanowires of Ru are a promising candidate for studying the intrinsic behavior of individual one-dimensional superconducting wires. We have prepared Ru nanowires by electrochemical deposition in porous polycarbonate membranes and characterized them structurally by high-resolution transmission electron microscopy and electron diffraction. Ru wires with diameters of 50 and 100 nm were found to be polycrystalline, consisting of ultrasmall Ru grains with a typical size of 2 nm. Metallic contacts to arrays of Ru nanowire as well as individual wires were made. Electrical transport measurements showed that these wires were metallic, but not superconducting down to 0.3 K. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1763982]

Superconductivity in nanowires is a subject of fundamental interest. Experimentally, In wires made by step-edge lithography,[1] Pb wires prepared by combining e-beam lithography and quench deposition,[2] and MoGe wires grown on carbon nanotube substrates[3] were explored earlier. However, all these superconducting nanowires were polycrystalline, or amorphous, with potential of having structural defects that might lead to weak links.[4] Recently superconducting single-crystal Pb and Sn wires were prepared by electrochemical deposition in porous media,[5] raising the possibility that intrinsic properties of superconducting nanowires can be measured without the complications of structural defects.

However, electrical transport measurements on all superconducting nanowires prepared by electrochemical deposition have been limited to arrays of nanowires embedded in the host medium in a two-point configuration.[5–8] If the wires are taken out of the host medium, an insulating oxide layer forms quickly, making it difficult to prepare electrical contacts. So far no electrical transport measurements on individual superconducting nanowires prepared by electrochemical deposition have been published. Ru, an elemental superconductor with a transition temperature (T_c) of 0.5 K, may provide an opportunity to circumvent this problem because Ru oxide is itself conducting.

Nanowires of Ru were grown in commercial, track-etched polycarbonate membranes with a nominal pore diameter of 30 and 50 nm, respectively. Membrane thickness is 6 μm and the pore density is 6×10^8 cm^{-2}. The pores in the membrane are separated straight channels and are perpendicular to the face of the membrane within ±17°. The electrolyte used for electrochemical deposition was commercially available Ru plating solution (purity 99.9%, Technic Inc.). Prior to the electrochemical deposition, a 200 nm layer of Ag or Au was evaporated onto one side of the membrane as the cathode. A 0.8-mm-diam Pt wire was used as the anode. The electrochemical deposition was done under a constant voltage of 2.2 V. After depositing Ru, a layer of Ag or Au, used as the counter-electrode, was prepared on the finishing side of the membrane either by electrochemical deposition or thermal evaporation.

Electrical transport measurements on arrays of Ru wires in the membrane were carried out by attaching two Cu wires on the top and two on the bottom of a membrane containing Ru nanowires using Ag epoxy, forming essentially a two-point probe. To avoid electrical shorts, the Au or Ag films on the edge of the membrane surfaces were removed carefully using dry cotton swabs or cotton swabs with ethanol before attaching the leads. Electrical transport measurements were done in either ^{4}He or ^{3}He cryostat using a dc current source and a nanovoltmeter. The base temperature of the ^{3}He cryostat, equipped with a superconducting magnet up to 8 T, is 0.3 K. All leads entering the measurement space were filtered for rf interferences.

To measure individual Ru nanowires, the polycarbonate membrane was dissolved by dichloromethane. Drops of dichloromethane solution containing Ru nanowires were placed on Si wafers (coated with a 200 Å oxide layer) and blown dry. $Au_{0.9}In_{0.1}$ leads with good adhesion to the substrate were prepared by a standard lift-off process in photolithography. The resulting structure was inspected using either a high-magnification optical microscope or an atomic force microscope. Electrical connections were made to pairs of leads with individual Ru nanowires attached.

Structural characterization of the Ru nanowires was carried out by high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), and energy-dispersive x-ray spectrum in a JEOL 2010 F field-emission transmission electron microscope. Figures 1(a) and 1(b) show the TEM images of free-standing Ru nanowires obtained from membranes with quoted nominal pore diameters of 30 nm. The actual diameter is around 50 nm. The wires are uniform in long segment. The inset of Fig. 1(b) shows a typical ED pattern of a selected spot on a 50 nm-diam Ru nanowire,

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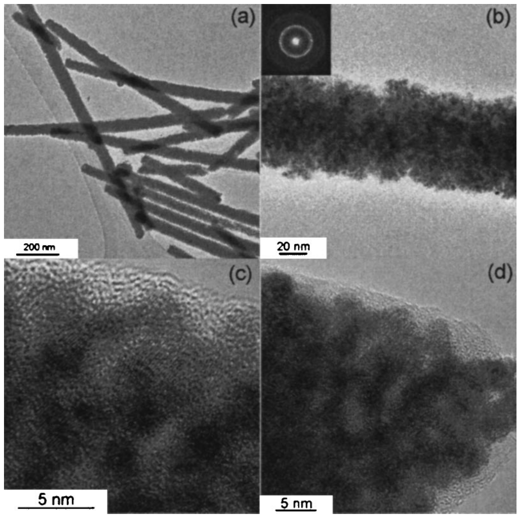

FIG. 1. (a) and (b) Bright field TEM images of free-standing 50-nm-diam Ru nanowires at two different scales. Inset: Typical electron diffraction pattern on a selected spot of the wire; (c) HRTEM image of a 50-nm-diam Ru nanowire; (d) HRTEM image of a 100-nm-diam Ru nanowire.

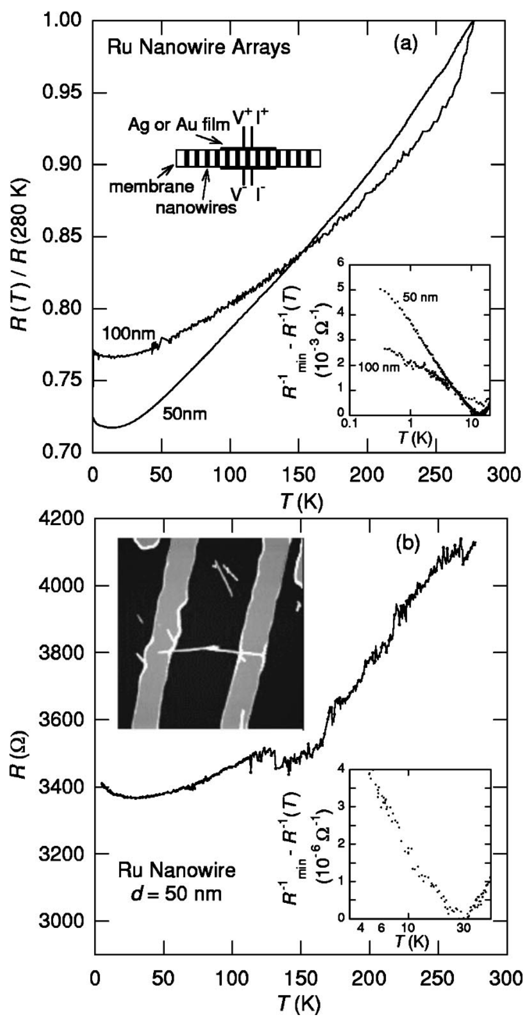

FIG. 2. (a) Normalized resistance as functions of temperature for two Ru arrays. Insets show a schematic of the sample configuration (upper) and ln T behavior of the conductance at low temperatures (lower); (b) resistance as function of temperature for two individual Ru nanowires in series. Insets show an AFM image of the sample (upper) and ln T behavior of the conductance at low temperatures (lower).

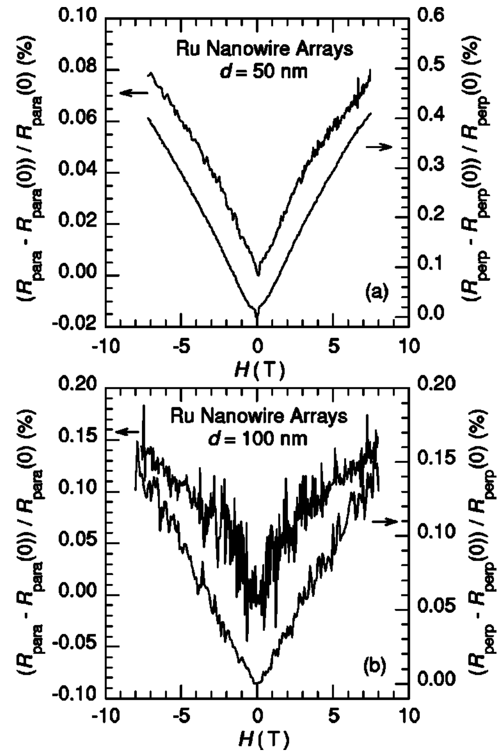

FIG. 3. Magnetoresistance at $T=0.3$ K measured on two arrays of 50- (a) and 100-nm-diam (b) Ru nanowires. The field orientations are as indicated.

showing that the wire is polycrystalline. Figures 1(c) and 1(d) give HRTEM images of the edges of the nanowires with diameters 50 and 100 nm, respectively. The dark clusters in the image of the wire were identified as ultrasmall grains with a diameter around 2 nm. Amorphous regions surrounding Ru grains (corresponding to RuO_2) could also be identified. Ru wires grown in membranes with quoted nominal pore diameter of 50 nm were found to have an actual diameter around 100 nm and an essentially identical structure.

Figure 2(a) shows the normalized resistance as function of temperature T for arrays of Ru nanowires of 50 and 100 nm diameters. Similar results on two individual 50 nm-diameter Ru nanowires connected in series are shown in Fig. 2(b). Although a small negative dR/dT is seen at low temperatures, these Ru nanowires are clearly metallic. In this low-T regime, the temperature dependence of the conductance change, $R_{\min}^{-1}-R^{-1}(T)$, was found to follow ln T behavior [insets to Figs. 2(a) and 2(b)]. No superconductivity was found down to 0.3 K, well below the bulk T_c of Ru, T_c $=0.5$ K.

Are individual Ru grains superconducting? If they were but the nanowire was not, the magnetoresistance (MR) of the wire should be large. We carried out MR measurements up to 8 T on the array samples (Fig. 3), with the field aligned both parallel and perpendicular to the Ru nanowires. For both field orientations, the MR was found to be small, a few tenths of percents at maximum, comparable with that of a typical normal elemental metal. The MR data therefore suggest that superconductivity is suppressed even in individual Ru grains. The linear MR and the ln T behavior shown in the insets of Figs. 2(a) and 2(b) are not expected in the one- or three-dimensional weak localization, or interaction theories.[9] The physical origins of the observed behaviors are yet to be determined.

The suppression of superconductivity in these Ru wires up to 100 nm in diameter is surprising. Polycrystalline Pb wires of small diameters (40 and 44 nm) were found to be nonsuperconducting down to 4.2 K but 100-nm-diameter ones were superconducting with a T_c close to that in the bulk.[7] The impurity level of the nanowires is low (less than 0.1%). Therefore superconductivity in Ru nanowires could not have been suppressed by impurities. For thin Pb nanowires, insulating oxide layer covering Pb grains tends to confine electrons. The discreteness of energy levels of confined electrons is known to lead to the suppression of superconductivity when the average level spacing becomes comparable or larger than the bulk superconducting energy gap.[10] For typical metal, this corresponds to a grain diameter around 10 nm.[11] Alternatively, the spatial confinement of electrons will lead to fluctuation in the phase of the order parameter, again suppressing superconductivity.[12] Neither mechanism seems to be applicable to Ru nanowires in which electrons are not confined.

We proposed that superconductivity is suppressed in the Ru nanowires because of the change of electron–phonon interaction in ultrasmall Ru grains embedded in amorphous RuO_2. It is known that RuO_2 in single-crystal form is a good metal, but nonsuperconducting. Amorphous RuO_2 formed in our Ru nanowires appears to retain its metallic behavior. However, given the small size of the Ru grain, the electronic states, and therefore, the electron–phonon interaction, can be strongly modified. Alternatively, even if the modified electron–phonon interaction still leads to the formation of Cooper pairs, the strong fluctuation in the amplitude of superconducting order parameter on ultrasmall grains embedded in a normal-metal matrix may suppress superconductivity.[13]

In conclusion, even though superconductivity was not observed in these Ru nanowires, metallic contacts and two-point electrical transport measurements on individual nanowires of an elemental superconductor prepared by electrochemical deposition were accomplished. It will be of interest if the superconducting Ru nanowires can be prepared so that electrical transport measurements on individual superconducing nanowires could be made.

This work is supported by NSF through Grant Nos. DMR-0080019 (the Penn State MRSEC) and DMR-0202534.

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