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Superconducting properties of lead nanowires fabricated by electrochemical deposition

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Abstract

Pb nanowires were fabricated by electrochemical deposition inside the nanopores of polycarbonate membranes. The diameter of fabricated nanowires ranged from 80 to 100 nm, and length is 5 μm on average. Temperature dependence of resistance was measured in magnetic fields by two-point contact method. It is found that the nanowires show a broad transition with higher critical fields compared with typical values of bulk Pb, and that the nanowires belong to Type II superconductors.

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Keywords: Lead; Superconducting nanowire; Electrochemical Deposition

1. Introduction

Since the discovery of high-T_c superconductors [1], new superconducting materials have been explored extensively. Recently, as the size of electronic devices has been miniaturized due to the development in fine processing technologies, many researchers have become more interested with nanometer size and fine-shaped superconducting materials, as well as high-T_c materials. New different phenomena are expected in such small size and low dimensional superconductors, as well as in metals and semiconductors. Understanding the physics of low dimensional superconductors, especially, nanowires and thin films, is very important to develop a new-generation of superconducting nanodevices. There have been some interesting theoretical predictions for the properties of superconducting

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nanowires, markedly the so-called ''phase slip'' in the superconducting order-parameter, which can be attributed to thermal or quantum phase slips [2]. Therefore further understanding will provide a possibility for the realization of superconducting nanodevices. In this study, we report on a fabrication method for Pb nanowires with a small diameter, and on their temperature dependence of resistance, which is measured in magnetic fields, as an example to study transport properties in small size superconductors.

2. Experimental

There are several methods to fabricate nanowires. Lithographic method followed by lift-off process can produce nanowires through mask and along patterns. Physical and chemical milling method can also be used with etching to reduce the dimension of the deposited materials. But such methods require a long processing time, even for the fabrication of only one nanowire. Electrochemical deposition is one of the most reasonable methods. It can produce large quantity of nanowires with uniform diameter and length simultaneously. Furthermore, diameter and length can be controlled by selecting templates with a desired size. Therefore, we selected for this work an electrochemical deposition technique for the fabrication of nanowires.

Lead nanowires are fabricated by electrochemical deposition inside nanopores of polycarbonate membranes. Commercially available membranes with thickness of 20 μm were used. The diameter of nanopores in the membranes was 50 nm, and their density was $3.13 \times 10^5\ \mathrm{mm}^{-2}$ (Fig. 1). The membrane was used as a working electrode in a three-electrode configuration system for the deposition. Carbon plate was used as a counter electrode, and Ag/AgCl electrode was used as a reference electrode in this system. Voltage was biased between the working electrode and the counter electrode keeping the potential of the working electrode at -0.5 V versus the reference electrode by a potentiostat. Electrolyte bath, in which the working and the counter electrodes were dipped, was filled with an aqueous solution of

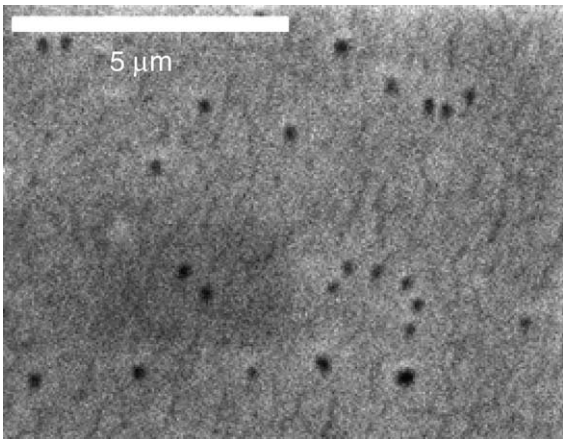

Fig. 1. SEM picture of polycarbonate surface after deposition of gold. The diameter of nanopores in the membranes was 50 nm, and their density was $3.13 \times 10^5\ \mathrm{mm}^{-2}$.

40.4 g/l $Pb(BF_4)_2$, 33.6 g/l HBF_4, and 15 g/l H_3BO_3. The other bath is filled with 3 M KCl solution, in which Ag/AgCl electrode was dipped, and was connected to the electrolyte bath via a salt bridge.

Before the electrochemical deposition, gold was deposited on both sides of the membrane by ion plating, and used as a working electrode, since polycarbonate was an insulator. Another purpose of depositing gold was to avoid etching of the membrane surface, as it was easy to melt in acids, such as aqueous solution in the electrolyte bath.

After filling Pb into the nanopores, Pb surged over the nanopores and covered the top surface of the membrane. It made the area of electrodeposition broader, and may have produced an increase in the deposition current. Even though there have been some reports that at the completion of nanopores filling-up it was possible to detect a sudden increase of current [3], such an increase could not be detected in our experiment. The current increased gradually, and saturated ultimately when the nanoporous were filled-up with Pb. The electrochemical deposition was stopped when the saturation of current was detected. Average current density was 2.05×10^{-2} $\mathrm{mA/mm^2}$ at the beginning of the electrochemical deposition, and 3.69×10^{-2} $\mathrm{mA/mm^2}$ at the end. Electrochemical deposition was carried out for

30 min on average. The electrochemical depositions were done several times by using the same aqueous solution in the bath. The concentration of the aqueous solution was changed as the number of depositions increased. The change of concentration influenced only the deposition time and current density.

In order to confirm the size and length of Pb nanowires inside the pores of membrane, the nanowires were retrieved from the membrane. Firstly the membrane was dissolved in chloroform at 60 °C and stirred at 200 rpm for 30 min. Then, the nanowires in this solution were dispersed onto Si substrates by spin coating, and observed by scanning electron microscope (SEM). X-ray diffraction (XRD) was also performed to characterize the crystal structure of the nanowires.

Electrical transport measurements were carried out to compare the property of nanowires with that of bulk samples. Temperature dependence of resistance in Pb nanowires was measured by using a liquid helium cryostat system at temperatures from 1.8 K to 10 K, applying magnetic fields up to 16 kOe. Two-point method with the electrodes on the top and bottom of the membrane was used in this work to measure Pb nanowires inside membranes. The contacts were put on both sides of the membrane by silver paste. All obtained data include the contact resistance between silver paste and lead. Thus a number of Pb nanowires is indeed connected to the silver paste. It means that a number of Pb nanowires inside the membrane were measured in parallel at the same time.

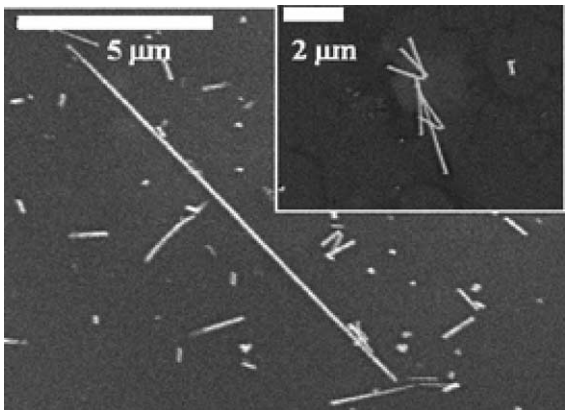

Fig. 2. SEM picture of Pb nanowires and clusters dispersed onto Si substrate after dissolution of polycarbonate membrane. The diameter of nanowires distributes from 80 nm to 100 nm, and the length is longer than 5 μm. The inset shows the nanowires connected with each other by spilled Pb from nanopores. They are connected with each other at the top or bottom by Pb layer made of spilled Pb from nanopores.

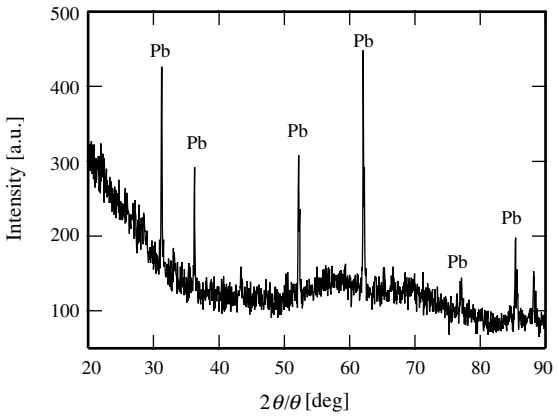

Fig. 3. XRD pattern of Pb nanowires and clusters. There are peaks originating from single crystal and background from amorphous. It is not certain that these peaks are attributed to Pb nanowires.

3. Results and discussion

The nanowires obtained by the electrochemical deposition are shown in Fig. 2. It includes a lot of short nanowires and residual Pb. XRD was measured to verify the composition of the nanowires and residual Pb as shown in Fig. 3. Some peaks are observed, and they can be attributed to Pb crystals. The nanowires and residual Pb do not contain oxidized Pb or other compounds. There is also a background in the diffraction pattern which originates from amorphous material. Further studies are needed to clarify the crystallinity of the nanowires, such as by transmission electron microscope. The diameter of Pb nanowires ranged from 80 to 100 nm, and most of Pb nanowires are about 90 nm. Even though the diameter of nanopores of the membrane was 50 nm, the diameter of Pb nanowires obtained was larger than that. It seems that the aqueous solution soaked into the nanopores and etched the inside of nanopores to

make the diameter larger. The length is larger than 5 μm, and the longest one was about 10 μm. When the membrane was melted, Pb nanowires in the chloroform were stirred to make the dissolution more effective. Most of Pb nanowires seem to break up in this process. Some clusters of Pb nanowires were also shown in the inset of Fig. 2. They were connected with each other at the top or bottom by a thin Pb layer made of spilled Pb from the nanopores.

Fig. 4 shows the temperature dependence of resistance in magnetic fields from 0 to 16 kOe. A decrease of resistance could be observed. This decrease is attributed to the superconducting transition of Pb, since this drop of resistance begin from near T_c of 7.2 K of bulk Pb. But the transition was broader to lower temperatures. Pb nanowires show superconductivity even at higher magnetic field up to 14 kOe at 1.8 K, while H_c of bulk value is 0.8 kOe at 0 K [4].

To confirm the superconductivity of Pb nanowires, we discuss the upper critical fields value below. A criterion was defined on the onset of superconducting transition to determine the upper critical field $H_{c2}(T)$. The Ginzburg–Landau coherence length $\xi_{GL}(T)$ was estimated from critical fields $H_{c2}(T)$. $\xi_{GL}(T)$ is related to H_{c2}(T) by the formula $H_{c2}(T) = \Phi_0/2\pi\xi^2(T)$ [5], where Φ_0 is the magnetic flux quantum. The obtained $\xi_{GL}(T)$ is plotted in Fig. 5. Furthermore, $\xi_{GL}(T)$ is related

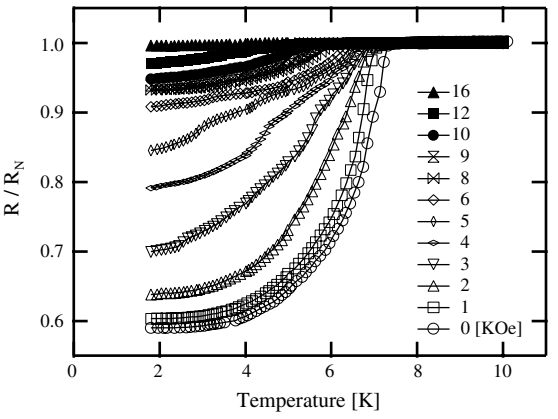

Fig. 4. Temperature dependence of resistance in magnetic fields. Large broadening can be seen below T_c. Increase of $H_{c2}(T)$ can also be seen.

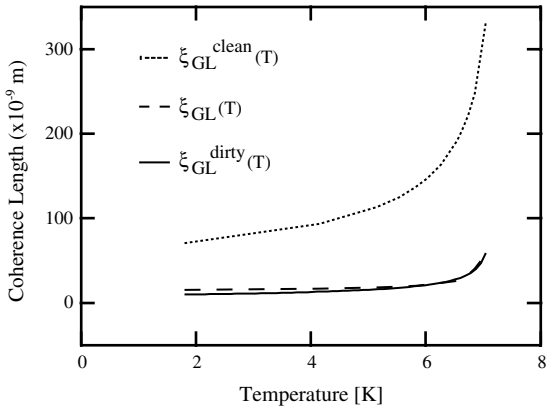

Fig. 5. Temperature dependence of coherence length. Dotted line shows $\xi_{GL}^{clean}(T)$, dashed line show $\xi_{GL}(T)$ and solid line shows $\xi_{GL}^{dirty}(T)$ respectively. $\xi_{GL}(T)$ shows good fitting for $\xi_{GL}^{dirty}(T)$ with a parameter l of 1.15 nm. Even though we tried to fit $\xi_{GL}^{clean}(T)$ to $\xi_{GL}(T)$, the parameter ξ_0 of coherence length obtained from fitting was 1152 nm. It is appropriate that nanowires seem to be in the dirty limit.

to the BCS coherence length ξ_0. In the clean limit ($l \gg \xi_0$), coherence length is expressed as $\xi_{GL}^{clean}(T) = 0.74\xi_0/(1 - T/T_c)^{1/2}$, and for dirty limit ($l \ll \xi_0$), expressed as $\xi_{GL}^{dirty}(T) = 0.86(\xi_0 l)^{1/2}/(1 - T/T_c)^{1/2}$ near T_c where l is the electron mean free path [5]. The ξ_0 of Pb was used as 87 nm [4]. The difference between $\xi_{GL}(T)$ and $\xi_{GL}^{clean}(T)$ is found to be large near T_c. Then, we tried to fit the formula $\xi_{GL}^{clean}(T)$ to $\xi_{GL}(T)$ obtained above with the parameter ξ_0. The ξ_0 obtained from the fitting was 1152 nm. Thus $\xi_{GL}^{clean}(T)$ formula is inadequate. It is appropriate that the nanowires used in this work are in the dirty limit. Then, $\xi_{GL}(T)$ obtained from the experiments is fitted by the formula of $\xi_{GL}^{dirty}(T)$ for dirty superconductor near T_c with parameter l. Obtained $\xi_{GL}^{dirty}(T)$ is shown as a solid curve in Fig. 5. As the result of this fitting, l was 1.15 nm. l is 10.43 nm for bulk Pb at 77 K, when l is estimated by using a Drude relaxation time of 0.57×10^{-14} s [6]. The l of nanowires obtained from fitting is much smaller than bulk value. This decrease of l seems to be attributed to disorder in the nanowires, such as granularity and defects.

For dirty superconductors, magnetic penetration depth $\lambda(T)$ is expressed as $\lambda(T) = \lambda_L(T)(1 + 0.75\xi_0/l)^{1/2}$ near T_c from the BCS theory [5], where

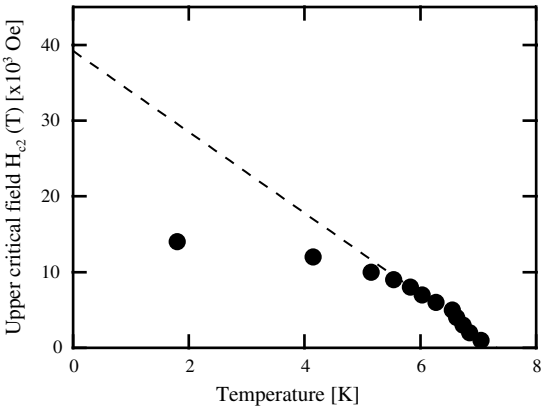

Fig. 6. Magnetic phase diagram of Pb nanowires obtained from magnetic transport measurements. Dots shows the upper critical field $H_{c2}(T)$ from transport measurements. Dashed line shows the gradient of $H_{c2}(T)$ obtained from fitting near T_c.

$\lambda_L(T)$ is the London penetration depth, and is expressed as $\lambda_L(T) \approx \lambda_L(0)[1 - (T/T_c)^4]^{-1/2}$. $\lambda_L(0)$ is 39 nm for bulk Pb [4]. The Ginzburg–Landau parameter is defined as $\kappa = \lambda(T)/\xi(T)$, and κ has a critical value of $\sqrt{2}/2$ [5]. Above this value, a superconductor belongs to Type II and below this value to Type I. The κ, estimated by using $\xi_{GL}(T)$ and l obtained above, shows much larger value than $\sqrt{2}/2$. Thus, nanowires in this work behave as Type II superconductors, even though the bulk is a Type I superconductor.

The DC current was biased to deposit Pb onto nanopores in this work, while there have been some report that single crystal nanowires were fabricated by applying AC current and polycrystal for DC current [7]. There is a high possibility that nanowires fabricated in this work were made of polycrystal and made electron mean free path l shorter. Therefore κ was enhanced and it is suggest that nanowires behave like Type II superconductor.

The upper critical field $H_{c2}(0)$ is given by the formula, $H_{c2}(0) = -0.6913(dH_{c2}/dT)$ near T_c for Type II superconductors in the dirty limit [8,9]. The value of dH_{c2}/dT is obtained from Fig. 6. As a result, $H_{c2}(0)$ of the Pb nanowires is determined to be 26.7 kOe. This value is close to the experimental value of $H_{c2}(0)$ as shown in Fig. 6.

4. Conclusion

Pb nanowires were fabricated by electrochemical deposition. The diameter of obtained nanowires distributes from 80 to 100 nm, and the length was more than 5 μm. Unusual behavior was observed in magnetic transport measurement below T_c. Transition was broadened widely below T_c and upper critical field $H_{c2}(T)$ was much larger than the value of bulk Pb.

The temperature dependence of coherence length was estimated from experiment, which seemed to deviate from that of clean limit. So nanowires were assumed to be in the dirty limit. The mean free path l obtained was 1.15 nm, which is much smaller than ξ_0 of bulk Pb. This small value of l seemed to enhance the value of κ to make Pb nanowires behave as Type II superconductor.

There are still unclear questions, for example, how dimensionality influences the superconducting property of Pb nanowire. Further experiments are needed, such as directional dependence of resistance on magnetic field.

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