

Surface Superconductivity in Thin Cylindrical Bi Nanowire

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ABSTRACT: The physical origin and the nature of superconductivity in nanostructured Bi remains puzzling. Here, we report transport measurements of individual cylindrical singlecrystal Bi nanowires, 20 and 32 nm in diameter. In contrast to nonsuperconducting Bi nanoribbons with two flat surfaces, cylindrical Bi nanowires show superconductivity below 1.3 K. However, their superconducting critical magnetic fields decrease with their diameter, which is the opposite of the expected behavior for thin superconducting wires. Quasiperiodic oscillations of magnetoresistance were observed in perpendicular fields but were not seen in the parallel orientation. These results can be understood by a model of



surface superconductivity with an enhanced surface-to-bulk volume in small diameter wires, where the superconductivity originates from the strained surface states of the nanowires due to the surface curvature-induced stress.

KEYWORDS: Bi nanowires, surface superconductivity, magnetoresistance, quantum oscillations

t has been known for a long time that rhombohedral bulk Bi at ambient pressure is a semimetal down to at least 50 mK.¹⁻³ Recent studies on this "old" material have uncovered a number of new phenomena,⁴⁻⁶ such as a quasi-one-dimensional (1D) topological metallic state at the (114) surface of a Bi crystal with a Fermi contour consisting of two closely separated, parallel lines of opposite spin direction, which resembles the 1D edge state in the quantum spin Hall effect (QSHE).⁴ Metallic surface states are a prerequisite for the formation of a topological insulator^{7,8} and have been found in bulk $Bi_{1-x}Sb_x$ with x = 0.07 - 0.22.⁹ In contrast to bulk Bi, single crystalline Bi nanowires have been predicted to be semiconducting when their diameter is below a critical value.¹⁰ However, there is also evidence that the transport behavior of Bi nanowires is dominated by surface effect.¹¹ The topology in Bi nanowires is quite interesting because it features a gapped bulk insulator while its surface supports a gapless metallic state. Recent experimental work on single crystal Bi nanoribbons,¹² thin films,¹³ and nanocontacts¹⁴ all highlight the topological nature of the surface state of crystalline Bi in confined geometries.

When the diameter of Bi nanowires is reduced down to 30 nm, Huber et al.¹⁵ found isotropic Shubnikov-de Haas (SdH) magnetoresistance (MR) oscillations above 1.8 K, which is in contrast to the ordinarily anisotropic SdH oscillations in bulk Bi. This led the authors to propose a scenario in which the 30 nm Bi nanowire is metallic in its entire volume with a spherical Fermi surface (FS), where the surface state dominates the

entire system and thus inhibits a semimetal to semiconductor transition.

Interestingly, we found granular Bi nanowires of 70 nm diameter with grain size of 10-15 nm show superconductivity with T_c of 7.2 or 8.3 K.^{16,17} In 72 nm diameter single-crystalline nanowires, two transitions were found near 1.3 and 0.69 K,¹⁸ lower than those observed in granular nanowires. Both the granular and single crystal nanowires we have studied showed a rhombohedral crystal structure, which is the same as that of semimetallic bulk Bi. The observation of superconductivity in granular and crystalline Bi nanowires allows us to conclude that the superconductivity in Bi nanowires arises from the grain boundary areas in granular wires or the interface between the amorphous oxidized surface and the crystalline core due to the structural distortion caused by internal stress. This assignment was confirmed by the observation of Little-Parks-like oscillations in 72 nm crystalline wires due to the fluxoid quantization for a superconducting cylindrical shell under a parallel magnetic field.¹⁸ Even so, the nature of the superconductivity in Bi nanostructures is not entirely clear, and one does not know whether this interfacial superconductivity is related to the surface state or the surface disordering of the wires due to surface oxidation.

This work explores the transport properties of ultrathin individual single-crystalline Bi nanowires of 20 and 32 nm

Received:September 3, 2014Revised:January 26, 2015Published:February 6, 2015

diameters at temperatures down to 50 mK. Compared with 72 nm Bi wire, four unusual features were observed: (1) the superconducting transition at 1.3 K was seen in both 20 and 32 nm cylindrical nanowires, but the 0.67 K phase observed in 72 nm wire does not appear; (2) the critical magnetic fields of the 1.3 K phase in both the parallel and perpendicular directions are unexpectedly smaller than those in 72 nm diameter wires; (3) no Little-Parks quantum oscillations under a parallel field (H_{\parallel}) and the SdH oscillations in perpendicular field (H_{\perp}) were seen; instead, quasiperiodic MR oscillations were found under H_{\downarrow} ; (4) the normal state resistivity of the thin nanowires was unexpectedly smaller than that of bulk Bi. These observations cannot be easily explained based on a bulk superconducting or metallic state but are understandable with surface superconducting or surface metallic states in these thin wires. The fact that the recent experiment on Bi nanoribbons with two flat surfaces did not show any superconductivity¹² suggests that the surface superconductivity observed here is related to the enhanced stress of the interfacial or surface layer in a cylindrical wire, and the effective thickness of the interfacial or surface superconducting layer increases as its diameter decreases.

The cylindrical Bi nanowires were fabricated by electrochemically depositing Bi into custom-made porous anodic aluminum oxide membranes as previously described.^{18,19} Figure 1a and the inset show the low magnification transmission



Figure 1. Transmission electron microscopic (TEM) image of randomly selected ~ 20 nm Bi nanowire (the inner core size). (a) Low magnification image of the wires; (b) high resolution image showing single crystalline morphology with a [11<u>2</u>0] growth direction.

electron microscopy (TEM) images of Bi nanowires. The high resolution TEM image of the wire in Figure 1b presents a single-crystalline morphology, verified by the fast Fourier transformation pattern (see the inset of Figure 1b). Further study on different wires indicated that the growth direction varies from wire to wire without a preferred orientation, and an oxide layer of approximately \sim 3.5 \pm 0.5 nm thickness is visible on the surface of the wire; thus, the quoted diameters, 20 and 32 nm, of the Bi nanowire represent the actual diameter of the Bi inner core without the oxidation layer. Although it is not possible to check all of the wires by TEM, the wires we randomly selected always show single-crystalline morphology. This is because the formation of the crystalline morphology in small diameter Bi wires is much easier than in large diameter wires based on the growth dynamics.²⁰ Compared with the 72 nm larger diameter wires, the small diameter wires do not show twinning structures, but this does not mean they are structural "perfect" uniform along their length. In most case, the wires

show variations of phase or thickness along its length due to the stress or the twisting. This is evident in the contrast variations in the TEM images along the wires. This structural inhomogeneity was found to have less effect on the superconductivity of the nanowires, which will be presented below.

Standard four-probe transport measurements were carried out on individual Bi nanowires with a physical property measurement system (PPMS) cryostat equipped with a dilution refrigerator insert and a 9 T superconducting magnet. Four Pt strips of 100 nm (width) \times 100 nm (thickness) were deposited onto the Bi nanowire as the electrodes using the focused-ion beam (FIB) technique. The ion beam current of the deposition was 10 pA under 30 kV acceleration voltage. The insulating Bi-O oxide layer covering the Bi was reliably penetrated by the deposition of Pt electrodes and an ohmic contact was obtained between the Pt lead and the Bi wire. The maximum spreading distance of Pt along the nanowires under these deposition parameters was found to be less than 300 nm beyond the intended position through a profile analysis of the TEM energy dispersive X-ray data.²¹ Because the Bi-O layer forms a protecting insulating surface layer over the Bi wire, the effect on the transport data due to the spreading of the Pt electrodes from the contact position is very likely to be much less than that along a conducting nanowire. For all samples we studied, the distance (L) between the inner edges of the two voltage electrodes was kept larger than 1.5 μ m.

Figure 2 shows the resistance (R) vs temperature (T) curves of 20, 32, and 72 nm samples at low temperatures, where the



Figure 2. R-T plot at H = 0 Oe for 20, 32, and 72 nm diameter Bi nanowires in the low T range, measured with a standard 4-probe technique by using FIB deposited Pt electrodes. The inset shows the data between 0.1 and 300 K.

distances, *L*, between the two voltage probing electrodes were 1.8, 2.5, and 2.35 μ m, respectively. The full range of *R*–*T* curves are shown in the inset of Figure 2. All three wires show a sharp resistance drop just below 1.3 K, independent of the diameters of the wires. Among the three wires, only the 72 nm diameter wire shows a resistance drop of nearly 4 orders of magnitude that reaches a value below the resolution of our measurements below 0.3 K. Though the additional shoulder at 0.67 K was seen in this large diameter wire, they were absent in the 20 and 32 nm small diameter wires. Instead, an almost temperature-independent finite resistance was observed below 0.67 K. Although the nature of the 0.67 K phase is still unclear, a possible origin is the FIB-induced weakening of the

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superconductivity near the Pt electrodes. This is because the FIB-deposition can damage the Bi wire at the contact areas, especially for 20 and 32 nm small diameter wires. The finite resistance of 0.2–0.3 k Ω below 0.67 K, which is about 2.2–4.0% of its normal state resistance, might be a consequence of the suppression of the superconductivity by the Pt contacts. This corresponds to 40–100 nm long part of the wire being nonsuperconducting, which is on the order of the width of the Pt electrodes. The fact that the 1.3 K phase of the three different diameter wires does not change significantly indicates that the FIB deposition has less effect on the superconductivity of the wire beyond the contacts.

Figure 3a and b, respectively, show the R-T curves of 20 and 32 nm wires under various perpendicular fields *H*. The



Figure 3. R-T curves at different perpendicular magnetic fields for 32 (a) and 20 nm (b) wires.

superconducting transitions were found to shift to lower temperatures with increasing *H*. An interesting feature is that the magneto-resistance curves show a temperature independent finite resistance at low temperatures and these low temperature resistance values increases with magnetic field continuously up to its normal state value, R_n . If the electrical conductivity is assumed to be from the entire wire, the resistivity of 20, 32, and 72 nm wires are, respectively, estimated to be 134, 202, and 584 $\mu\Omega$ ·cm at room temperature. The decrease in resistivity with decreasing wire diameter is opposite to the expectations for a thin Bi wire due to the size confinement effects.

Figure 4a, b and Figure 5a and b show, respectively, the *R* vs *H* curves measured with *H* aligned perpendicular and parallel to the wire axis. The nanowires exhibit anisotropic behavior with a broad phase transition from superconducting to normal state. If we define H_{cr} the critical field at which the resistance of the nanowire is restored to 97.5% of its normal state value, then the perpendicular critical fields at 0.1 K of 20 and 32 nm wires are, respectively, $H_{ct} \sim 33$ kOe and 27.6 kOe, which are on the order of $H_{ct} \sim 34$ kOe of the 72 nm wire. Under a parallel field,



Figure 4. (a) and (b) show R-H curves for 32 and 20 nm wires, respectively, at different temperatures under magnetic fields applied perpendicular to the wire axis. Dashed lines indicate the minima of the oscillations.



Figure 5. (a) and (b) show the R-H curves for 32 and 20 nm wires, respectively, at different temperatures under magnetic fields applied parallel to the wire axis.

 $H_{\rm cp}$ of both thin wires are, respectively, 56 kOe and 33.4 kOe. The values in these two thinner wires are smaller than that of the 72 nm wire with $H_{\rm cp} \sim 67$ kOe.¹⁸ The critical current, $I_{\rm c}$ of three diameter wires at 0.1 K were found to be respectively, 0.054 μ A for 20 nm wire, 0.18 μ A for 32 nm wire, and 0.14 μ A for 72 nm wire, which correspond to bulk critical current densities of $j_c \sim 1.7 \times 10^4$ A/cm², 2.2 $\times 10^4$ A/cm², and 0.34 $\times 10^4$ A/cm², respectively. Obviously, the smallest j_c found in the 72 nm wire is opposite to the expectation based on the critical magnetic field data shown above.

The fact that the 1.3 K superconducting transition is independent of the wire diameters and structural variations (the suppression of the superconductivity due to the size effect can be negligible) indicate the transition involves only the interfacial surface layer instead of the entire wire. The thickness variation of the superconducting surface layer is insufficient to tune the T_c but sensitively to H_c . Hence, the Ginzburg–Landau (G-L) theory is applicable to the thin cylindrical shells, where the parallel critical field H_{cp} in a thin film or cylinder is inversely proportional to the thickness, *t*, of the thin film (or diameter, *d*, of the cylinder), that, is, $H_{cp} \sim 1/t$ (or 1/d). This criterion has been confirmed previously in various superconducting thin films and wires.^{22–24} However, in our 20 and 32 nm Bi wires, the parallel critical field H_{cp} was unexpectedly lower than that in the 72 nm wire. These deviations again suggest that the conventional model of bulk superconductivity is not applicable for the superconducting Bi nanowires.

According to our previous model of the interfacial superconductivity between the Bi-oxide surface and the crystalline core of the Bi nanowires,¹⁸ such an anomaly is most likely the result of an increase of the thickness in the interfacial or surface superconducting layer when the wire diameter decreases. The thickness (t_2) of the superconducting interfacial shell in 20 and 32 nm wires can be roughly estimated as $t_2 = (H_{cp1}/H_{cp2})t_1$, where H_{cp1} and H_{cp2} are, respectively, the parallel critical fields of 72 and 20 nm (or 32 nm) wires, and t_1 and t_2 are the corresponding thicknesses of the superconducting interfacial layers. In a 72 nm wire, t_1 is estimated to be ~2.5 nm,¹⁸ we obtain $t_2 = 5$ nm in 20 nm wire and 3 nm in 32 nm wires, respectively. Therefore, the fraction of surface volume in both wires reaches about 52%, which is much larger than the ~13% fraction in 72 nm wires.

Based on the estimation of the thickness of surface superconducting layer, the conductivity of Bi nanowires above $T_{\rm c}$ should be dominated by metallic surface states. This is because the "bulk" Bi with a diameter of less than 65 nm is considered to be a true insulator due to the size confinement effect.¹⁰ This conclusion is confirmed recently in thin Bi film when the thickness is less than 90 nm.²⁵ As a result, the resistivity of the 20, 32, and 72 nm diameter nanowires at room temperature could be revised to 79.1, 106.8, and 79.0 $\mu\Omega$.cm, respectively, which are on the order of the 106 $\mu\Omega$ cm value for a bulk Bi (the surface contribution in a bulk Bi can be neglected completely because of the metallic nature of the entire system). Similarly, the critical current densities, i_c are then revised to be $\sim 4.1 \times 10^4 \text{A/cm}^2$ for 20 nm wire, $5.2 \times 10^4 \text{A/cm}^2$ for 32 nm wire, and $2.7 \times 10^4 \text{A/cm}^2$ for 72 nm wire, respectively. The fact that the resultant j_c are of the same order for the three wires supports our model of interfacial/surface superconductivity.

At first glance, it is puzzling that the Little–Parks-like oscillations observed in 72 nm wires were not seen in these smaller diameter wires under H_{\parallel} . Because the superconductivity in 20 and 32 nm wires has the same origin, that is, from the interfacial shell between the Bi–O oxide and the Bi inner core, then the periodicity, ΔH , of the LP oscillations in both wires under H_{\parallel} is expected to be around 134.5 kOe and 54.5 kOe, respectively, as given by the formula $\Delta H(\pi d^2/4) = \Phi_0$, where

 $\Phi_0 = 2.07 \times 10^7 \text{ G} \cdot \text{cm}^2$ and *d* is the diameter of the inner core of the cylinder. These values are much larger than the parallel critical fields, $H_{cp} \sim 56.3$ kOe and 33.4 kOe in 20 and 32 nm wires, respectively, above which both wires have been driven to normal states. This is the reason why Little–Parks oscillations are not seen in these two smaller diameter wires.

Compared with the data in a parallel field, the resistance oscillations in a perpendicular field (Figure 4) were clearly seen and the resistance oscillations show quasiperiodic behavior with H, instead of the SdH oscillations observed in the 72 nm wire. For T < 0.5 K, the quasiperiodic oscillations in the low field regime are not resolvable. The roughly recognized periods, ΔH , as indicated by the arrows in the R-H isotherms of Figure 4 are about 1.18 kOe for the 32 nm wire and 2.32 kOe for the 20 nm wire. A possible reason for the disappearance of the SdH oscillations in 20 and 32 nm thin wires under H_{\perp} might be that the magnetic length, ~ 10 nm of Bi at ultra quantum limit⁶ is already on the order of the radius of 20 and 32 nm wires.

Because the oscillations gradually disappear with increasing temperature and clearly absent above T_{c} , this allows us to conclude that the mechanism due to quantum interference of the normal electrons can be excluded. Although these quasiperiodic oscillations in the perpendicular field direction are poorly understood quantitatively, such phenomena are frequently observed in superconducting amorphous and granular nanowires^{26–28} or in single-crystal thin film nano-bridges.²⁹ For examples, in granular Sn nanowires,²⁶ the MR oscillations near the superconductor-insulator transition were interpreted as an effect of screening currents circulating around phase-coherent loops of weakly linked superconducting grains. In the case of amorphous indium oxide nanowires,²⁷ the oscillations below T_c were explained by Josephson weak linklike interference structures because the wires are not uniform in thickness. Xiao's group²⁸ reported MR oscillations near T_c in a polycrystalline niobium nitride nanowire with a diameter of ~650 nm. Their samples contained a high density of defects such as holes and gaps between grains. In single-crystal Pb nanobridges,²⁹ the magnetoresistance oscillations in H_{\perp} were interpreted as inhomogeneous superconductivity, that is, the presence of substantial normal regions in samples in the superconducting state.

In single-crystal Bi nanowires, the quasiperiodic oscillations in H_{\perp} may have similar origins to those observed in singlecrystal Pb-bridges. The interfacial superconductivity is rather inhomogeneous, coexisting with some weak spots or normal regions under H_{\perp} . If we assume that the length of the normal region is f_i and the width is equal to the wire diameter d_i we obtain *f* on the order of 446 and 548 nm in 20 and 32 nm wires, respectively, based on the formula $\Delta Hfd = \Phi_0$. Interestingly, f in both wires is much larger than the superconducting phase coherence length, 67 nm in both the 20 and 32 nm wires based on the formula $\xi(0) = \sqrt{3\Phi_0/\pi t H_c}$ (0) for a thin film. In other words, the vortex mechanism can be ruled out for these quasiperiodic oscillations. According to this scenario, the finite resistance of the R-T curves at low temperatures, which shows magnetic field dependent behavior, can be mainly attributed to the inhomogeneity of superconductivity in the surface layer, where the superconducting areas decrease with the increase of the field.

Finally, we will comment on the mechanism of interfacial or surface superconductivity in the Bi nanostructures. The fact that no surface superconductivity was seen in nanoribbons with two flat surfaces¹² suggests that oxidation-induced disordering

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or amorphization of the surface of Bi is not the crucial parameter. This conclusion is also consistent with the recent observation of superconductivity of Bi confined in an opal host without surface oxidation.³⁰ The superconductivity in cylindrical nanowires or particles is most likely related to the surface curvature-induced stress in the nanowires or nanoparticles. Such stress will give rise to considerable distortion or disordering in the surface states of the cylindrical nanowires. This is why the superconductivity is more easily seen in granular Bi film or wires and is very sensitive to slight changes in the surface environment. But the current data cannot pin down how the surface curvature or stress tunes the electronic structures of the wire. Theoretical studies on this may be revealing.

In conclusion, we report the observation of superconductivity in ultrathin 20 and 32 nm individual single-crystal Bi nanowires and find that their superconducting critical magnetic fields decrease with decreasing wire diameter. These results can be understood by a model of interfacial or surface superconductivity with an enhanced surface to volume fraction in small diameter wires. The superconductivity originates from the considerable distortion or disordering in the surface states of the nanowires due to surface curvature-induced stress.

ASSOCIATED CONTENT

Accession Codes

PACS number(s): 73.63.Nm, 73.90.+f, 74.78.Na

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Center for Nanoscale Science (Penn State MRSEC) funded by NSF under Grant No. DMR-0820404 and DMR-1420620 and by the National Basic Research Program of China (Grant Nos. 2011CBA00111, 2013CB934600, & 2012CB921300), the National Natural Science Foundation of China (Nos. 11174294, 11374302, U1432251, U1332209, U1332139, 11222434, & 11174007) and Scientific Research Grant of Hefei Science Center of CAS (SRG-HSC).

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