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Direct observation of the semimetal-to-semiconductor transition of individual single-crystal bismuth nanowires grown by on-film formation of nanowires

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Abstract

We have systematically investigated the semimetal-to-semiconductor transition of individual single-crystalline Bi nanowires. For this work, we developed a technique to reduce the diameter of Bi nanowires grown by our unique on-film formation of nanowires (OFF-ON) method. Cooling down the substrate temperature during Bi film deposition by use of liquid nitrogen, film structures with small-sized grains were obtained. Through thermal annealing of these fine-granular Bi films, single-crystalline Bi nanowires can be produced with minimum diameter of ∼20 nm. Elaborative nanofabrication techniques were employed to shape state-of-the-art four-probe devices based on the individual small diameter Bi nanowires. Diameter-dependent transport measurements on the individual Bi nanowires revealed that the semimetal-to-semiconductor transition really occurred at about $d_w = 63$ nm. Moreover, band structure calculations supported this occurrence of the semimetal-to-semiconductor transition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Bismuth (Bi) is well recognized as a semimetallic material in bulk with intriguing properties such as a highly anisotropic Fermi surface, low carrier concentration, and small electron effective mass (∼0.001 m_o) [1–5]. The transport properties of its nanowires have been widely investigated in search of novel quantum phenomena like wire-boundary scattering effects, quantum confinement effects, and semimetal-to-semiconductor transitions [1, 2]. A variety of growth methods have been investigated to obtain high quality Bi nanowires. Single-crystalline Bi nanowires are an excellent test-bed to investigate the unusual transport properties of Bi, as they make it possible to rule out defect-generated artifacts. Furthermore, the Bi nanowires with high single-crystallinity provide the potential for materializing nanowire-based thermoelectric devices with high thermoelectric figure-of-merit (ZT) values.

In a previous study, we grew single-crystalline Bi nanowires by our unique on-film formation of nanowires (OFF-ON) method [6]. The OFF-ON method is a stress-induced nanowire growth technique activated by the thermodynamic driving force that is caused by compressive stress accumulated in a film, arising from a difference in thermal expansion between a film and substrate. We found that the diameter of the Bi nanowire depends on the mean grain size in the as-grown film, which is determined by the thickness of the film. However, the smallest diameter of the Bi nanowire

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was 98 nm, which was attained by tuning the thickness of the Bi thin film grown at room temperature. Based on prior research, a semimetal-to-semiconductor transition appears in a Bi nanowire when the wire diameter shrinks to the critical diameter d_c, which depends on the crystallographic orientation of the wire [7]. This phenomenon is particularly important to thermoelectric applications because the thermoelectric degree of freedom could be increased, thereby ZT could be optimized once the nanowire converts to a semiconductor. However, it is difficult to reach the critical diameter of Bi nanowires with the normal OFF-ON method, mainly due to the limit in grain size reduction of the as-grown film. In this work, liquid nitrogen cooling was devised to grow a small diameter Bi nanowire to meet the critical diameter.

2. Experimental details

Bi films with a 50 nm thickness were deposited on a thermally oxidized Si(100) substrate, using a custom-made sputter, by a RF magnetron sputtering system at both 300 and 77 K. The sputter system was maintained in an ultrahigh vacuum (UHV) of 10^{-6} Torr before deposition, and sputtering was performed in Ar gas pressure of 2 mTorr for 12 s at a growth rate of 44 Å s^{-1}. For low temperature deposition, liquid nitrogen was forced through a substrate holder during the whole sputtering process. The Bi thin films were subsequently placed in a custom-made vacuum furnace for thermal annealing to grow nanowires by the OFF-ON method. Annealing was performed in a UHV of 10^{-6} Torr at 250 °C for 5 h. The Bi nanowires grown by this technique were characterized by TEM (FE-TEM JEOL 2100F), AFM (DI 9100 AFM with a Nanoscope IVa controller), and XRD. The nanowire measured diameters were 300–100 and 80–20 nm for nanowires grown from Bi films deposited at 300 and 77 K, respectively.

Four-probe devices based on individual Bi nanowires were fabricated in a step-wise manner. The first step is to remove the native oxide on the outer surface of the nanowire, which was performed by Ar plasma etching at room temperature for 3 min. DC sputtering of Cr/Au for contacts was next performed as the second step. The respective Cr and Au film thicknesses were 5 and 80 nm. These two steps were performed *in situ* without breaking the vacuum to prevent further oxide formation. In the final step, a four-probe device structure was shaped. For this purpose, a combination of E-beam lithography and a lift-off process was utilized: MMA (8.5) MAA EL9 resist was spin coated on the wafer with Bi nanowires at 1000/5000 RPM for 10/30 s, and then baked at 150 °C for 90 s. 950KA2 resist was spin coated on the same wafer at 1000/5000 RPM for 10/30 s, then baked at 180 °C for 90 s. After being exposed by an E-beam, the sample was developed for 15 s in PMMA and Copolymer DEVELOPER (Rohm and Hass Electronic Materials).

The temperature-dependent I–V characteristics were analyzed using a Keithley 236 Source-Measure Unit and 2182 Multimeter. The temperature was swept from 7 to 300 K with a cryostat (ARS DISPLEX DE 204 Closed Cycle Cryo-refrigerator), which is a closed cycle cryostat using high pressure helium gas to cool the system down to 4.2 K. The I–V characteristics were measured at each temperature after the temperature stabilized (fluctuation <0.01 K).

3. Results and discussion

Device fabrication and electric measurements on Bi nanowires were also a challenge due to their chemical instability, high fragility, and low melting point (∼271 °C). For this reason, two-point resistance measurements [8–14] were most widely performed on embedded nanowire arrays prepared in porous templates by various methods [13–15]. However, the numbers of nanowires under measurement were difficult to determine [16, 17]. Boukai *et al* [18] addressed this problem by engaging Bi-friendly nanofabrication steps into a device architecture used by Small *et al* [19], and Llaguno *et al* [20] for nanotube studies. However, their Bi nanowires, which were fabricated from evaporated Bi films by E-beam lithography, were polycrystalline. In this study, we fabricated four-probe devices based on individual single-crystalline Bi nanowires by applying our own nanofabrication steps to small diameter Bi nanowires grown by the OFF-ON method. A semimetal-to-semiconductor transition was observed for the first time in individual Bi nanowires with high quality single-crystallinity. The growth of semiconducting Bi nanowires with diameters smaller than d_c and the establishment of successful device fabrication techniques on individual Bi nanowires would allow for transport measurements on individual semiconducting Bi nanowires, which have never been previously explored.

Figures 1(a) and (c) schematically illustrate Bi nanowires grown by the OFF-ON method on Bi thin films with identical thicknesses, which were deposited at 300 and 77 K, respectively. Because the grain size of a Bi thin film depends on deposition temperature, Bi thin films deposited at the temperature of liquid nitrogen have smaller grains than those deposited at room temperature. The schematics indicate that Bi nanowires with large diameters ($d_w > 100$ nm) should grow on the thin film deposited at room temperature while Bi nanowires with smaller diameters ($d_w < 100$ nm) are favored for the film deposited at low temperature (77 K) after heat treatment. The films were characterized using atomic force microscopy (AFM) and x-ray diffraction (XRD). The insets in figures 1(b) and (d) show AFM images of the annealed Bi thin films grown at room temperature and liquid nitrogen temperature, respectively. The AFM images exhibit that the Bi films with the same 50 nm thickness are still polycrystalline, but have different grain sizes, even after being treated in vacuum at 250 °C for 5 h. The grain size of the inset to figure 1(d) is smaller than that of the inset to figure 1(b), reflecting that smaller diameter Bi nanowires are able to grow on the Bi thin film deposited at 77 K. In addition, the film grown at room temperature shows rougher peak-to-valley topography compared to the film grown at liquid nitrogen temperature.

To further study the structural differences of the two Bi films deposited at different temperatures, we performed XRD measurements on the annealed samples. As shown in figures 1(b) and (d), the grains of the Bi films grown at both room temperature and 77 K have preferred orientations

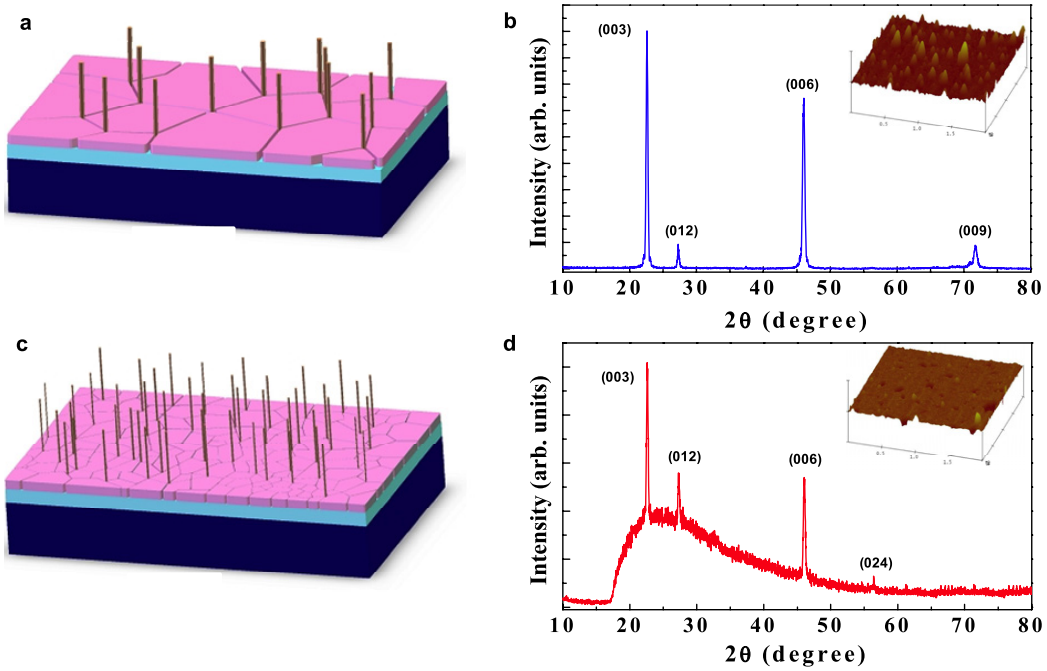

Figure 1. Thin film structures and XRD patterns for the growth of Bi nanowires: (a) and (c) are schematics for the growth of Bi thin film nanowires by OFF-ON from Bi thin films deposited at room temperature and 77 K, respectively, showing that the diameters of Bi nanowires depend on the grain size of the Bi thin films; (b) and (d) are x-ray diffraction (XRD) patterns of Bi films after heat treatment at 250 °C for 5 h. The Bi film grown at room temperature shows a straight baseline and strong peaks, while a curved baseline and weaker peaks appear for the 77 K-grown Bi film. AFM images for both films are included in (b) and (d).

of (003) and (006) after heat treatment. This implies that the preferred orientation of (00ℓ) is indispensable for Bi nanowires to grow on an annealed Bi thin film. Bi thin film grown at 77 K shows a curved baseline and weaker major peak intensities, as compared to Bi film deposited at room temperature. Considering the smoother surfaces for a 77 K-grown Bi film observed by AFM, these aspects indicate that the Bi film deposited at liquid nitrogen temperature consists of very small grains with much larger grain boundary areas, which hinder the constructive interference of the x-ray. In actuality, the grain size of the Bi film grown at 77 K was measured to be 10–20 nm, which is much smaller than its room temperature counterpart (50–60 nm). Furthermore, it was confirmed that Bi nanowires with very small diameters down to ∼20 nm could be grown from this 77 K-deposited Bi film.

A transmission electron microscopy (TEM) study was performed to investigate the crystal structure of the small diameter Bi nanowires thus grown. Figure 2(a) shows a TEM image of a Bi nanowire 32 nm in diameter. The Bi nanowires have a uniform diameter and smooth surface along the growth direction. It is found from figure 2(a) that a 5–7 nm thick oxide was formed on the nanowire outer surface. The reciprocal lattice peaks, which were obtained from two-dimensional Fourier transforms (2DFT) of the lattice-resolved images, can be indexed to the rhombohedral structure of Bi with the zone axes along the [001] direction (figure 2(b)). By this analysis, the growth front was assigned to (110) for the 32 nm diameter nanowire shown in figure 2(a). A cross-sectional high-resolution transmission electron microscopy (HR-TEM)

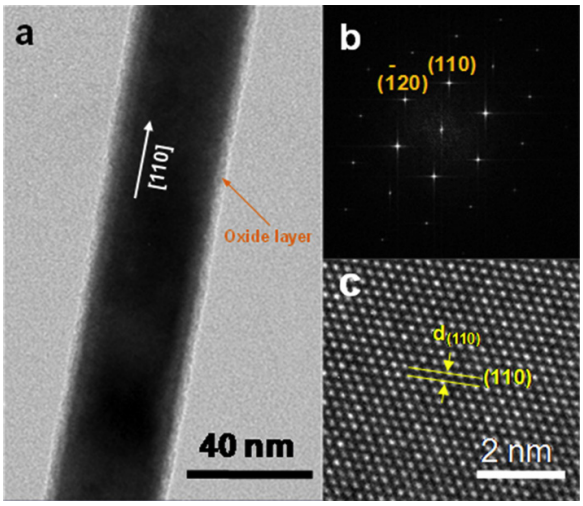

Figure 2. (a) A low-magnification TEM image of a 32 nm diameter Bi nanowire grown on a Bi thin film deposited using a liquid nitrogen cooling system; (b) a selected area electron diffraction (SAED) pattern of the nanowire along the [001] zone axis, indicating that the growth direction of the nanowire is [110]; (c) a high-resolution TEM image of the Bi nanowire, showing a perfect single-crystallinity.

image clearly demonstrates that the Bi nanowires are defect-free and high quality single-crystalline (figure 2(c)).

Since the diameter d_w of the Bi nanowires studied in this work was much smaller than the mean free path l_e of electrons in Bi, especially at low temperatures, the electrons would

experience quantum confinement effects, which is an important factor in determining the electrical transport properties of Bi nanowires. This confinement effect not only affects the carrier concentration in Bi nanowires, but also alters the band structure of the nanowires from bulk Bi. It has been reported that as the nanowire diameter d_w decreases, Bi nanowires undergo a semimetal-to-semiconductor transition when the wire diameter is reduced to less than the critical value d_c. In order to investigate this important phenomenon, we first calculated the effective band gap E_g as a function of wire diameter d_w for Bi nanowires with [110] crystal orientations, which is the case for our OFF-ON-grown nanowires.

Figure 3(a) shows the calculated subband energies for Bi nanowires and the corresponding band gap at 77 K as a function of the wire diameter. In this figure, the three L-point electron pockets in Bi are denoted as $L_e(A)$, $L_e(B)$, and $L_e(C)$. Likewise the three L-point hole pockets and a T-point hole pocket are represented by $L_h(A)$, $L_h(B)$, $L_h(C)$, and T holes. For the [110] wires, the L-point shows the same degeneracy as that for other major crystallographic orientations calculated by the Dresselhaus group [21], which causes two different groups of electron pockets, i.e., a single electron pocket $L_e(A)$ and two electron pockets $L_e(B, C)$. Since, according to our calculations, the $L_e(A)$ pocket has smaller mass components ($m_{x'}$, $m_{y'}$) in the direction perpendicular to the wire axis compared to the electron pockets $L_e(B, C)$, the $L_e(A)$ pocket forms a slightly higher conduction subband than the pockets $L_e(B, C)$. The lowest subband edge of the $L_e(B, C)$ electrons shifts up with decreasing wire diameter d_w, while the highest subband edges of the T-point and L-point holes move down with shrinking diameter. Consequently, the lowest L-point conduction subband edge crosses over the highest T-point valence subband edge at $d_c = 53.2$ nm, indicating the occurrence of the semimetal-to-semiconductor transition.

To clarify this result, we calculated the density of states (DOS) of a Bi nanowire 40 nm in thickness, which is below d_c described above. From figure 3(b), it is shown that the conduction and valence bands in the 40 nm diameter Bi nanowire are separated by a band gap of 16.6 meV, which is different from the bulk Bi that exhibits the conduction and valence bands overlap of 38 meV (see figure 3(a)), reflecting that the nanowire has undergone a semimetal-to-semiconductor transition.

The use of a four-probe device based on an individual Bi nanowire is important for measuring electrical transport properties. Reliable electrical Ohmic contacts to the nanowires are essential in fabricating such nanowire devices. A plasma etching technique was employed to remove an oxide layer that forms on the outer surface of the nanowire, and Cr (5 nm)/Au (80 nm) electrodes were deposited *in situ* by sputtering. A combination of E-beam lithography and a lift-off process was utilized to fabricate individual Bi nanowire devices. Figure 4(a) shows our four-probe device based on an individual Bi nanowire with $d_w = 42$ nm.

For four-point resistance measurements, the current–voltage (I–V) curves (figure 4(b)) were obtained. They exhibited good linearity in a temperature range from 7 to

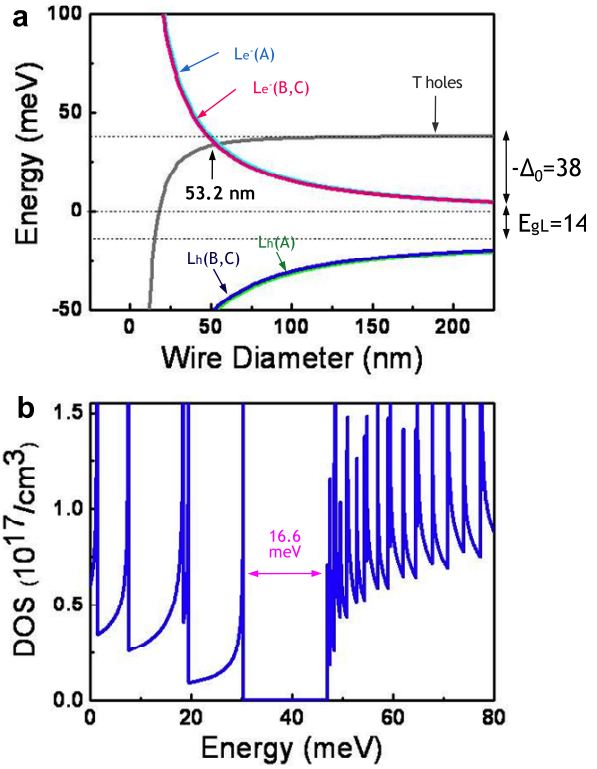

Figure 3. (a) The subband structure at 77 K of Bi quantum wires oriented along the [110] growth direction, showing the energies versus wire diameter of the highest subbands for the T-point and L-point hole carrier pockets as well as the lowest subbands for the L-point electron pockets (A, B and C). The zero energy refers to the conduction band edge in bulk Bi. As d_w decreases, the conduction subbands increase in energy, while the valence subbands decrease. At $d_c = 53.2$ nm, the lowest conduction subband edge formed by the $L(B, C)$ electrons exceeds the highest T-point valence subband edge, showing a semimetal–semiconductor transition; (b) one-dimensional density of states at 77 K of a 40 nm diameter Bi nanowire with a [110] crystalline orientation along the nanowire axis.

300 K, confirming good Ohmic contacts of the nanowires. The resistance was calculated from the slope rather than a single point I–V calculation to avoid possible influences from offset voltages. To our knowledge, temperature-dependent four-point measurements for individual single-crystalline Bi nanowires smaller than 70 nm with good Ohmic contacts have never been reported. From figure 4(b), the resistivities at 300 K are calculated to be 0.39, 0.54, 0.55, and 1.80 mΩ cm for 127, 63, 58, and 42 nm diameters, respectively, corresponding to 2.0, 2.7, 2.8, and 9.0 times that of bulk Bi. The increase of resistivity for smaller Bi nanowires reflects the greater contributions from boundary and surface scatterings. For comparison, a previous work on four-point measurement on a 70 nm diameter nanowire prepared by a template-assisted growth reported a resistivity six times larger than that of bulk Bi [17].

Temperature-dependent resistance is displayed in figure 5. The observed trends generally agree with those from two-point measurements on vapor-deposited Bi nanowire arrays [16]. The thickest wire ($d_w = 127$ nm) yields bulk-like semimetal

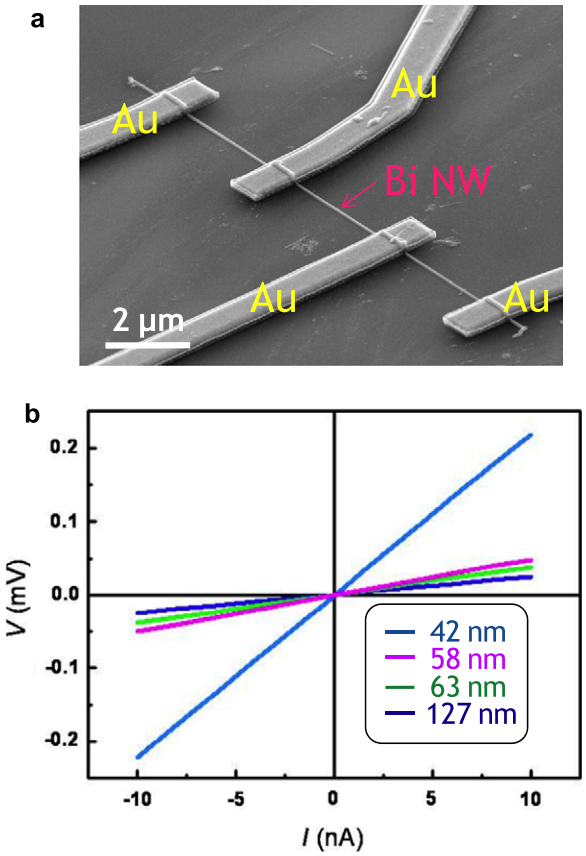

Figure 4. (a) SEM image of four-probe device based on an individual Bi nanowire to investigate its transport properties; (b) I–V curves showing good Ohmic contacts. The resistances at 300 K are 2.45, 3.83, 4.96, and 22.13 kΩ for 127, 63, 58, and 42 nm diameters, respectively.

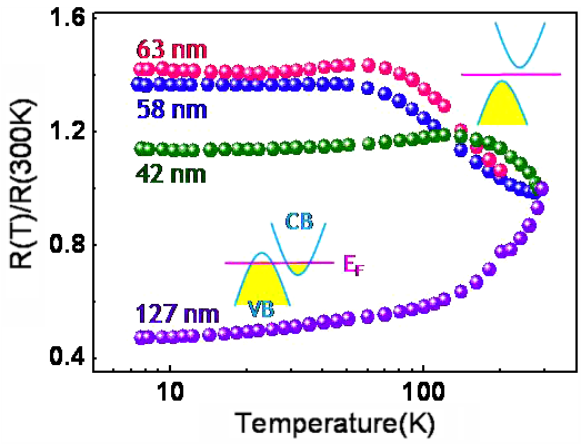

Figure 5. The temperature-dependent resistance of Bi nanowires, normalized to the resistance at 300 K. Each point in the plot is obtained by fitting a four-point I–V trace. The thickest wire ($d_w = 126$ nm) yields bulk-like semimetal behavior, while the resistance for the smallest three sets of wires ($d_w = 42$, 58, and 63 nm) increases with decreasing temperature.

behavior, while the resistance for the smallest three sets of nanowires ($d_w = 63$, 58, 42 nm) increases with decreasing temperature. From these trends, it is seen that the semimetal-to-semiconductor transition occurs near $d_w = 63$ nm, which is slightly larger than that predicted by theoretical calculation ($d_c = 53.2$ nm). This is the first direct observation of the phenomenon in an individual single-crystalline Bi nanowire. It is not clear why the resistance undergoes a slight decrease below 60 K. Temperature-dependent interplay between L-point electron and hole pockets and the T-point hole pocket might cause the indirect band gap to be slightly reduced in this temperature regime. In order to examine the semimetal-to-semiconductor transition of the small Bi nanowires in detail, more elaborate electrical transport measurements are under way on individual semiconducting Bi nanowires using gate effects, including temperature-dependent mobility and carrier concentration. The results will be published elsewhere [22].

4. Conclusions

In summary, we grew single-crystalline Bi nanowires with small diameters down to ∼20 nm by our unique OFF-ON method. The small diameters were achieved by diminishing the grain size of Bi thin films, which was enabled by liquid nitrogen cooling during Bi film deposition. Using selected area electron diffraction (SAED) analysis, the Bi nanowire growth direction was assigned to [110]. Based on these [110]-grown single-crystalline Bi nanowires, four-probe devices were successfully fabricated on an individual nanowire by the combined use of electron-beam lithography and a lift-off process. We observed a semimetal-to-semiconductor transition near $d_w = 63$ nm, which is slightly larger than the value expected from theoretical calculations. To our knowledge, this is the first direct observation of the phenomenon in individual single-crystalline Bi nanowires.

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