APPLIED PHYSICS LETTERS **95**, 232107 (2009)

Shubnikov–de Haas oscillations in an individual single-crystalline bismuth nanowire grown by on-film formation of nanowires

Wooyoung Shim,[a] Jinhee Ham, Jungmin Kim, and Wooyoung Lee[b]
Department of Materials Science and Engineering, Yonsei University, 134 Shinchon, Seoul 120-749, Republic of Korea

(Received 30 August 2009; accepted 31 October 2009; published online 9 December 2009)

Shubnikov–de Haas (SdH) oscillations have been investigated in an individual Bi nanowire grown by on-film formation of nanowires that is a growth method producing extremely high-quality single-crystalline nanowires. The variation of observed SdH oscillations with transverse and longitudinal magnetic fields to the axis of the Bi nanowire is qualitatively consistent with the geometry of the highly anisotropic Fermi surfaces of Bi, and in turn, reveals the growth direction of the nanowires and demonstrates the high crystal quality. Our results demonstrate the vast potential of high-quality single-crystalline Bi nanowires for a variety of device applications and for fundamental investigations such as quantum transport. © *2009 American Institute of Physics*. [doi:10.1063/1.3267143]

The Shubnikov–de Haas (SdH) effect is an oscillatory magnetoresistance (MR) due to the profound changes in the density of state of the conduction electrons induced by the magnetic quantization of energy levels (Landau level). This effect has been widely used for investigating the Fermi surfaces (FSs) of metals,[1] semimetals,[2] and semiconductors[3] as well as two-dimensional (2D) electron gas[4] in heterostructures. The observation of these oscillations requires that the thermal energy and the scattering-induced energy broadening be smaller than the Landau level separation. Therefore, measurements must be performed at low temperatures where the scattering of electrons by phonons is suppressed, and the carrier mobility of a material needs to be relatively high. In this regard, SdH observation acts as an indicator of the crystal quality as well as a tool to provide insight into the geometry of the FS of high purity materials.[2]

Among the aforementioned materials, bismuth (Bi) is a semimetal that has been a favorable material for studying SdH oscillations because of (1) its extremely small FS (occupying 10^{-5} of the Brillouin zone)[5] and (2) a very long mean-free path (exceeding 2 μm at room temperature)[6] that enhances the signal in both period and amplitude, respectively. In fact, Bi was the first semimetal (or metal) whose FS was experimentally identified,[7] and continues to serve as a matrix to show novel physics that is driving the area of unexplored condensed matter physics.[8–10] Nevertheless, since the observation of SdH oscillations in bulk Bi,[11] SdH oscillations in Bi thin films (2D)[2] and one-dimensional (1D) Bi nanowire [12] arrays have been rarely studied. In particular, difficulties in observing the SdH oscillations in 1D arise from (1) the inability to grow high-quality single crystalline Bi nanowires with high aspect ratios and (2) the need for a reliable route to achieve an electrical Ohmic contact to the nanowire by removing an oxide layer on the surface of the nanowire. These limitations are a problem inherent to the field of nanowire synthesis and device fabrications in general. In an effort to overcome the aforementioned limits, Bi nanowire arrays have been fabricated by filling a porous alumina template with molten Bi (Ref. 13) and vapor-phase Bi,[12] thereby making single crystalline nanowires. However porous templates are not ideal as a measurement system for nanowires because it only provides a two-terminal device that does not allow one to obtain a quantitative picture about the electronic structures and the transport properties. Very few methods[14] offer the ability to fabricate an individual Bi nanowire device that allows one to perform a four-terminal measurement, however, these are limited in measurements of the absolute resistivity.

On-film formation of nanowires (OFF-ON) is a method that utilizes the thermal stress in a deposited polycrystalline thin film for growing single-crystalline nanowires, e.g., Bi (Ref. 15) and Bi_2Te_3,[16] as small as a few tens of nanometers in diameter and several hundreds of micrometers in length. In our previous studies,[15,17] we have shown that OFF-ON is capable of forming high-quality single-crystalline Bi nanowires through MR measurements in four-terminal devices fabricated using a plasma etching technique to routinely make Ohmic contacts. Fabrication of a reliable device based on an individual single-crystalline nanowire is driven by the need for a system that can be utilized in a variety of device applications as well as serves as a platform for fundamental transport studies. In the present work, we report the observation of SdH oscillations as well as large ordinary MR in four-terminal devices based on an individual Bi nanowire grown by OFF-ON. Plasma-assisted etching method has been used to achieve Ohmic contacts between electrodes and a nanowire, thereby demonstrating the utility of the OFF-ON and plasma etching method to overcome one of the major challenges in nanotechnology: the fabrication of a reliable device based on a high crystal quality nanowire. Importantly, the observed SdH oscillations with transverse and longitudinal magnetic fields to the axis of the Bi nanowire were found to be consistent with the geometry of the highly anisotropic FS of Bi. The correlations between the FS and resultant SdH oscillations are discussed.

In bismuth, the hole FS ellipsoid is aligned with the trigonal axis (**z**), while the three-electron FS ellipsoids, arranged symmetrically around the hole FS, are tilted by a small angle (~6.5°) out of the plane defined by the bisectrix

---

[a] Present address: Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108, USA.

[b] Author to whom correspondence should be addressed. Electronic mail: wooyoung@yonsei.ac.kr.

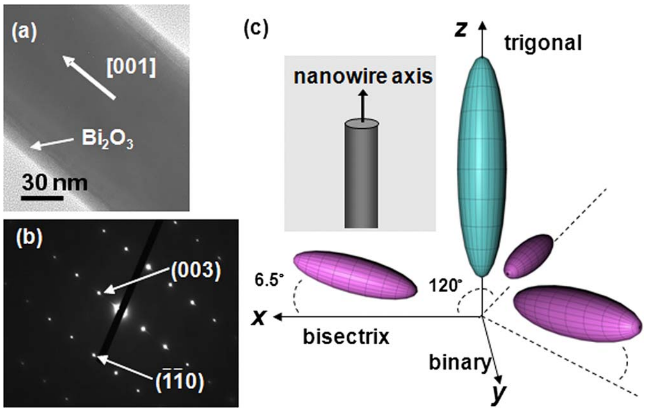

FIG. 1. (Color online) (a) A low-magnification TEM image of a Bi nanowire. (b) An ED pattern obtained in the direction perpendicular to the long axis of the nanowire was indexed to the hexagonal lattice of Bi ($a=4.574$, $c=11.80$) with the $[\bar{1}10]$ zone axis. (c) Schematic of the FS of Bi showing the hole ellipsoid along the trigonal axis and the three electron ellipsoids in a plane perpendicular to the trigonal axis.

(**x**) and binary (**y**) axes. Transmission electron microscopy (TEM) and electron diffraction (ED) pattern studies show that a Bi nanowire is single crystalline with a 10-nm-thick native oxide layer [Fig. 1(a)] and its axis is oriented along the trigonal direction [001] [Fig. 1(b)]. Therefore, the long axis of the nanowire is parallel to the hole FS ellipsoid and tilted to the three-electron FS by 6.5°, as shown in Fig. 1(c). This geometry of FS in the nanowire makes it a model system for investigating the dependence of a magnetic field on an applied direction for a highly anisotropic FS in 1D: a magnetic field applied parallel (perpendicular) to the axis of a nanowire is also parallel (perpendicular) to the hole FS ellipsoid. In making Ohmic contacts to the Bi nanowire, the oxide layer on the Bi surface was first sputtered selectively, where was predefined by electron beam lithography, by Ar ions, and then Au electrodes was deposited *in situ* without breaking vacuum.[15] A scanning electron microscope (SEM) image of a device based on a 400-nm-diameter Bi nanowire prepared using this technique is presented in Fig. 2(a). This device configuration based on an individual Bi nanowire allowed us to apply both transverse and longitudinal magnetic fields by rotating the sample with respect to the applied fields, as depicted in Fig. 2(b).

Figures 3(a) and 3(b) show the variation of the MR ratio with (a) transverse magnetic fields (T) and (b) longitudinal magnetic fields (L) to the axis of the 400-nm-diameter Bi nanowire in the temperature range 2–300 K. The largest value of MR ratio of 2496% (110 K) in the T geometry and −38% (2 K) in the L geometry was observed. The magnitude of MR is determined by the fundamental quantity of $\omega_c\tau$, where $\omega_c=eH/m^*$ and τ is the cyclotron frequency and relaxation time, respectively, and m^* is the effective mass. Since the value of ω_c is an intrinsic property of a given material at a given value of H, the increase in the MR as temperature (T) decreases, as shown in Figs. 3(a) and 3(b), is attributable to the increase in τ due to the reduction in phonon scattering. Meanwhile, at low T, scattering by phonons is negligible because the amplitudes of phonon oscillation are very small. In other words, the longer τ is expected in materials that have the lower impurity, resulting in the higher MR at a given T and magnetic field (H). In this work, the MR of 900% (at 5 K under 5 T) was observed, as shown in Fig. 3(a). Such a large MR compared to that of 280% (at 5 K under 5 T)[18] in large grain-containing polycrystalline 400-nm-diameter Bi nanowires indicates a long τ, thereby demonstrating the high-quality of Bi nanowires grown by OFF-ON. More details elucidating the behavior of MR in Bi nanowires are extensively discussed in previous works.[15,17]

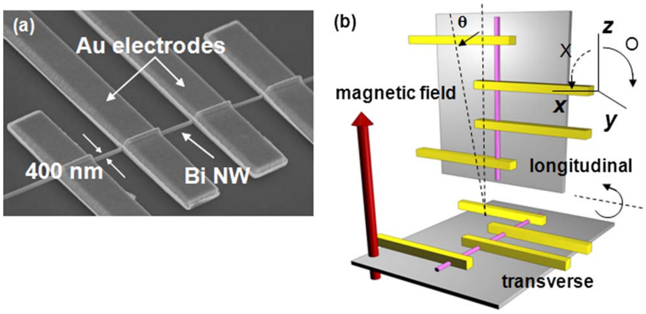

FIG. 2. (Color online) (a) A SEM image of a four-terminal device based on an individual Bi nanowire. (b) A schematic representation of two different device configurations (transverse and longitudinal) with respect to an applied field. The device is subject to rotate to the θ component only in the yz plane to switch from transverse to longitudinal configuration.

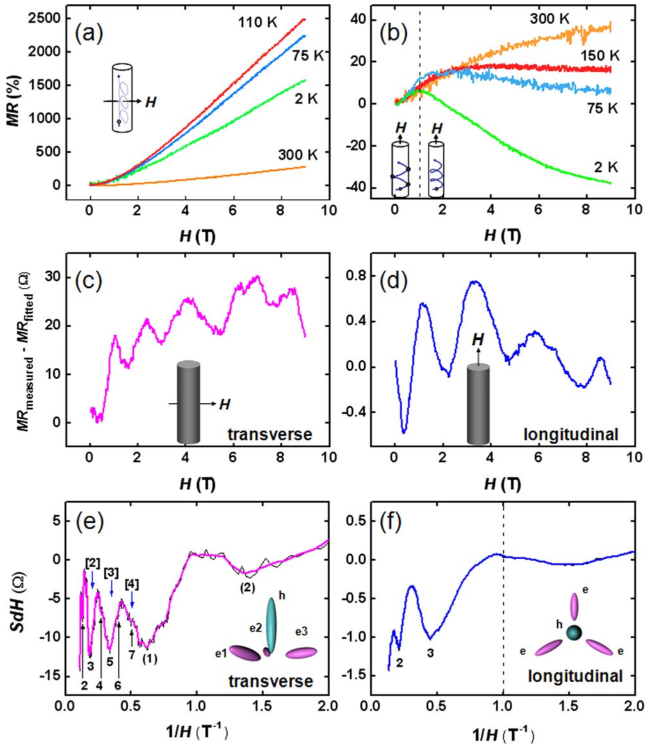

FIG. 3. (Color online) Ordinary MR ratios of the four-probe individual 400 nm diameter single-crystalline Bi nanowire in (a) transverse and (b) longitudinal geometries. The inset of (a) and (b) show schematics of curved trajectory of carriers in the magnetic field. SdH oscillations, displayed as MR(measured)-MR(fitted), vs a magnetic field H in (c) transverse and (d) longitudinal geometries at 2 K. The SdH oscillations were shown clearly by subtracting eight order polynomial fit from the T and L-MR. SdH oscillations of the same sample, shown in (c) and (d), vs an inverse magnetic field $1/H$ in (e) transverse and (f) longitudinal geometries at 2 K with the order n indicated. The insets of (e) and (f) show schematics of the FS of the Bi nanowire along the direction of an applied magnetic field.

Figures 3(c) and 3(d) show SdH oscillations that were superimposed on the T and L-MR at 2 K. The amplitude of the SdH oscillations is proportional to $\{[(2\pi^2m^*k_BT)/\hbar eH]/\sinh[(2\pi^2m^*k_BT)/\hbar eH]\}\exp(-\pi/w_c\tau)$,[19] where k_B is Boltzmann's constant and $\hbar$ is Plank's constant.

This relation suggests explains that the larger amplitude is expected in the lower defect materials at a given T and H due to the larger τ. This suggests that the SdH oscillations can act as an indicator of a high-quality, single-crystalline Bi nanowire. It should also be noted that the amplitude of the SdH oscillations is geometry dependent, as shown Figs. 3(c) and 3(d), that is, large for the T geometry and small for the L geometry. This is a reflection of the orientation dependence of the magnitude of the MR ratio.[2]

The periods of the transverse SdH (T-SdH) and longitudinal SdH (L-SdH) oscillations are also very different. This is due to the different extremal cross-sectional area (A) of the Bi Fermi surface normal to the direction of the magnetic field. The SdH oscillations are periodic in $1/H$ with a period of $\Delta(1/H)=2\pi e/\hbar cA$, because the separation of the Landau levels are the same in a given magnetic field. Figures 3(e) and 3(f) display the T-SdH and L-SdH oscillations versus $1/H$ at 2 K, respectively. It is clearly observed that the periods of the T-SdH oscillations are different from the L-SdH oscillations. However, we assume the possible locations of SdH minima in Figs. 3(e) and 3(f) according to reference periods from Bi thin films[2] and bulk Bi (Ref. 20) because it is difficult to assure the peak positions due to the small number and amplitude of the oscillations. With respect to A of the Fermi surface for the T geometry, it is expected that there are four extremal cross sections: $A_{T,h}$ from the holes, and $A_{T,e1}$, $A_{T,e2}$, and $A_{T,e3}$ from the electrons, where $A_{T,e1}$ is nearly equivalent to $A_{T,e3}$, as shown in the inset of Fig. 3(e). Their areas are in the order $A_{T,h}>A_{T,e1}>A_{T,e2}$, and hence the order of the periods is $\Delta(1/H)_{T,h}<\Delta(1/H)_{T,e1}<\Delta(1/H)_{T,e2}$. The hole ellipsoid has the shortest period and the electron ellipsoids of the smaller $A_{T,e2}$ have the longest period. In Fig. 3(e), the estimated minima from $A_{T,h}$ (n=2,3,4,5,6,7) and $A_{T,e1}$ (n=[2],[3],[4]) and $A_{T,e2}$ [n=(1),(2)] are in agreement with that of Bi thin films and bulk Bi, confirming highly anisotropic FS whose hole ellipsoid is parallel to the wire axis and tilted to the three-electron FS, as shown Fig. 1(c). In the L geometry, on the other hand, all three electron ellipsoids are equivalent, as shown in the inset of Fig. 3(f). Thus, there are only two extremal cross sections $A_{L,h}$ and $A_{L,e}$, and there can be two different periods of $\Delta(1/H)_{L,h}$ and $\Delta(1/H)_{L,e}$. The area of $A_{L,h}$ and $A_{L,e}$ are nearly the same,[2] resulting in only one observed period (n=2,3), as shown in Fig. 3(f). However, it should be noted that the estimated minima in the L geometry is not as clear as those observed in the T geometry.

These difficulties in observing clear oscillations in the nanowire system may arise from the fact that field-dependent oscillations are extremely sensitive to the alignment between the field and the wire axis, especially in the very thin wires. For example, it was claimed that a tilt in the sample in the measurement of MR may result in less precise value of cyclotron wave vector.[21] Yang *et al.* also suggested that the difference of the period $[\Delta(1/H)_{L,e}]$ between Bi thin film (0.20 T^{-1}) and Bi bulk (0.16 T^{-1}) in is most likely due to a small misalignment of the thin film sample with respect to the magnetic field.[2] In our device based on individual nanowire, aligning a magnetic field parallel to the axis of a nanowire is difficult because (1) T or L-geometry alignment is largely dependent on the manual setting of the device with respect to the magnetic field and (2) the sample holder (rotating puck) rotates to the θ component only in the yz plane [see Fig. 2(b)], leading to further deviations in the L geometry. As a consequence, we assume that the symmetry between the three electron and hole ellopsoids can be broken by the inevitable tilt of the nanowire axis in the xz plane. However, it is worth noting that the field-dependent oscillation was observed, demonstrating the anisotropic Fermi surface and high crystal quality of an individual Bi nanowire.

In summary, we have observed the oscillatory and nonoscillatory MR in an individual Bi nanowire with the transverse and longitudinal magnetic fields along the axis of the nanowire grown by OFF-ON. Although advances in making high-quality nanowires and fabricating the devices were made, a few aspects of device physics continue to challenge us. The precise alignment protocol for the nanowire with respect to an applied field and investigation of transport properties in sub-50-nm diameter individual Bi nanowire for quantum size effect must be addressed before the full potential of techniques is realized. Regardless of these challenges, our results demonstrate the type of the nanowire growth method and device fabrication technique that will maximize the capabilities of making devices for fundamental investigations and applications.

This work was supported by Priority Research Centers Program (2009-0093823) through the National Research Foundation of Korea (NRF), by a grant from “Center for Nanostructured Materials Technology” under “21st Century Frontier R&D Programs,” by Basic Science Research Program (Grant No. KRF-2007-314-C00107) through NRF and by Seoul Research and Business Development Program (10816).

[1] I. Thomas, V. Kabanov, and A. Alexandrov, Phys. Rev. B **77**, 075434 (2008).

[2] F. Y. Yang, K. Liu, K. Hong, D. H. Reich, P. C. Searson, C. L. Chien, Y. L. Wang, K. Y. Zhang, and K. Han, Phys. Rev. B **61**, 6631 (2000).

[3] Y. Sugama, T. Hayashi, H. Nakagawa, N. Miura, and V. Kulbachnskii, Physica B **298**, 531 (2001).

[4] T. Sedrakyan and M. Raikh, Phys. Rev. Lett. **100**, 106806 (2008).

[5] V. Édel’man, Adv. Phys. **25**, 555 (1976).

[6] A. Pippard and R. Chambers, Proc. Phys. Soc., London, Sect. A **65**, 955 (1952).

[7] D. Shoenberg, Proc. R. Soc. London, Ser. A **170**, 341 (1939).

[8] G. Sciaini, M. Harb, S. Kruglik, T. Payer, C. Hebeisen, F. Heringdorf, M. Yamaguchi, M. Hoegen, R. Ernstorfer, and R. Miller, Nature (London) **458**, 56 (2009).

[9] L. Li, J. Checkelsky, Y. Hor, C. Uher, A. Hebard, R. Cava, and N. Ong, Science **321**, 547 (2008).

[10] K. Behnia, L. Balicas, and Y. Kopelevich, Science **317**, 1729 (2007).

[11] R. Brown, Phys. Rev. B **2**, 928 (1970).

[12] J. Heremans and C. M. Thrush, Phys. Rev. B **59**, 12579 (1999).

[13] Y. Lin, S. Cronin, O. Rabin, J. Ying, and M. Dresselhaus, Appl. Phys. Lett. **79**, 677 (2001).

[14] S. B. Cronin, Y. M. Lin, O. Rabin, M. R. Black, J. Y. Ying, M. S. Dresselhaus, P. L. Gai, J. P. Minet, and J. P. Issi, Nanotechnology **13**, 653 (2002).

[15] W. Shim, J. Ham, K. Lee, W. Jeung, M. Johnson, and W. Lee, Nano Lett. **9**, 18 (2009).

[16] J. Ham, W. Shim, D. Kim, S. Lee, J. Roh, S. Sohn, K. Oh, P. Voorhees, and W. Lee, Nano Lett. **9**, 2867 (2009).

[17] W. Shim, D. Kim, K. I. Lee, K. J. Jeon, J. Ham, J. Chang, S. H. Han, W. Y. Jeung, M. Johnson, and W. Lee, J. Appl. Phys. **104**, 073715 (2008).

[18] K. Liu, C. L. Chien, P. C. Searson, and K. Zhang, Appl. Phys. Lett. **73**, 1436 (1998).

[19] J. Singh, *Physics of Semiconductors and Their Heterostuructures* (McGraw-Hill, New York, 1993).

[20] J. S. Dhillon and D. Shoenberg, Philos. Trans. R. Soc. London **248**, 1 (1955).

[21] J. Heremans, C. M. Thrush, Y. Lin, S. Cronin, Z. Zhang, M. S. Dresselhaus, and J. F. Mansfield, Phys. Rev. B **61**, 2921 (2000).