Magnetotransport properties of an individual single-crystalline Bi nanowire grown by a stress induced method

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The magnetotransport properties of an individual crystalline Bi nanowire have been investigated in the range of 2–300 K using four-point measurements. *I-V* measurements show that the contacts were Ohmic at both 2 and 300 K, corresponding to resistivities of 1.0×10^{-4} and 8.2×10^{-5} Ω cm, respectively. The transverse magnetoresistance (MR) (2496% at 110 K) and longitudinal MR (−38% at 2 K) for the Bi nanowire were found to be larger than any values reported in the literature, demonstrating that the Bi nanowires grown by a stress induced method are high-quality single crystalline. The observed transverse and longitudinal MR behaviors in the Bi nanowire are consistent with variations in carrier concentrations as well as electronic structures, such as Fermi level and band overlap, based on simple two band model. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2980277]

There have been numerous studies[1–13] of semimetallic bismuth (Bi) with unusual transport properties over the last decade. The studies have involved both fundamental transport researches and possible thermoelectric applications. The great interest in Bi nanowires lies in the opportunity for exploring novel low-dimensional phenomena since the smallest effective mass of all known materials, $\sim 0.001 m_e$, makes it easy to observe the quantum confinement effect.[1–3] Realization of single-crystalline Bi nanowire devices, such as thermoelectric devices, would be a major development in thermoelectricity.[4]

However, to date, the electronic and magnetic transport properties of an individual single-crystalline Bi have not been studied because making electrical Ohmic contacts to Bi nanowires remains extremely difficult. This difficulty is due to a native 10-nm-thick Bi oxide layer that forms on the outer surface of the nanowire as well as its very low melting point (271.3 °C).[5] Although Cronin *et al.*[5] and Choi *et al.*[6] demonstrated four-point measurements of an individual nanowire using a focused ion beam to remove the oxide layer, they were limited in measurements of absolute resistivity without further fundamental transport properties such as magnetoresistance (MR), Shubnikov–de Haas (SdH) oscillations,[7] and gate effect.[7] Individual single-crystalline Bi nanowires are of particular interest in this context since they provide an ideal system for investigating the transport properties and electronic structures of Bi nanowires for use in thermoelectricity.

In the present work, we present the magnetotransport properties of an individual single-crystalline Bi nanowire grown by a stress induced method, investigating in the range of 2–300 K using four-point measurements. We find that the transverse MR (2496% at 110 K) and longitudinal MR (−38% at 2 K) for the Bi nanowire are the largest known values reported for Bi nanowires, indicative of the very long mean-free path and high-quality single crystalline of the nanowire. In order to clarify the MR behavior of the Bi nanowire, we also investigated temperature-dependent electronic structures and carrier concentrations of electrons and holes using a simple two band (STB) model.

In growing Bi nanowires, a Bi thin film was first deposited on a thermally oxidized Si (100) substrate in a dc/rf magnetron sputtering system with a basal pressure of 4 $\times 10^{-8}$ Torr. Interestingly, uniform straight Bi nanowires with high aspect ratios were found to be extruded from the surface of the as-grown films after heat treatment at 270 °C for 10 h. The Bi nanowires grown by our unique method were observed to be several hundred micrometers in length and a few tens of nanometers in diameter. The diameter and length of Bi nanowires were found to be tuned by controlling sputtering and annealing conditions. A detailed discussion of a stress induced method of Bi nanowires will be presented separately elswhere.[7] High-resolution transmission electron microscopy (HRTEM) studies revealed that a Bi nanowire is single crystalline and its axis is oriented along the trigonal direction [001] as shown in Fig. 1(a). A 10-nm-thick Bi oxide layer was also found to form on the outer surface of the nanowire. In order to make Ohmic contacts between Au electrodes and the nanowire, we employed a plasma etching technique to sputter away the oxide layer with Ar ions and then deposited Au electrodes by sputtering.[7] Both procedures

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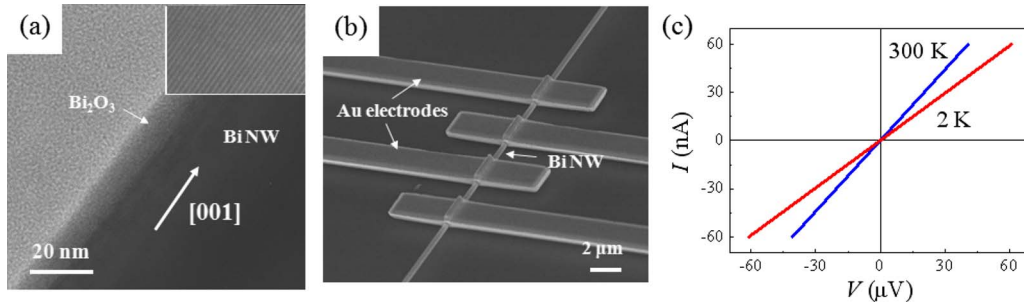b)Author to whom correspondence should be addressed. Electronic mail: wooyoung@yonsei.ac.kr.

FIG. 1. (Color online) (a) A HRTEM image of a Bi nanowire consisting of a single-crystalline Bi core and a 10-nm-thick amorphous Bi_2O_3 layer. The inset shows a HRTEM image of the Bi nanowire showing a perfect single-crystalline material without defects. (b) A SEM image showing an individual 400-nm-diameter Bi nanowire with four Au electrodes, deposited by sputtering after plasma etching to remove the oxide layer. (c) Four-point *I-V* curves taken at both 2 K and room temperature for the Bi nanowire device.

were done *in situ* without breaking vacuum in order to prevent further formation of an oxide layer. A combination of electron-beam lithography and a lift-off process was utilized to fabricate an individual 400-nm-diameter nanowire device as shown in Fig. 1(b). From *I-V* measurements, the contacts were observed to be Ohmic at both temperatures of 2 and 300 K, corresponding to resistivities ρ of 1.0×10^{-4} and 8.2×10^{-5} Ω cm, respectively [see Fig. 1(c)].

The temperature dependence of resistance $R(T)$ for the individual 400-nm-diameter Bi nanowire with and without magnetic fields in the temperature range of 2–300 K is shown in Fig. 2. In a zero magnetic field ($H=0$) for the Bi
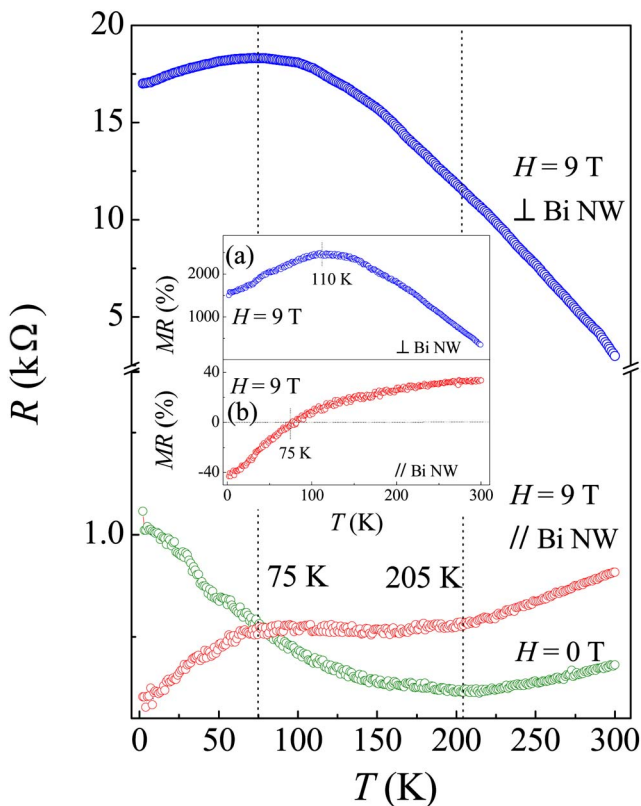

FIG. 2. (Color online) Temperature-dependent resistance for the 400-nm-diameter Bi nanowire, measured with and without a magnetic field of 9 T applied both perpendicular and parallel to the nanowire. The inset shows the temperature dependence of (a) transverse and (b) longitudinal MR ratios of the Bi nanowire with a magnetic field of 9 T.

nanowire, the temperature coefficient of resistance (TCR) was found to be positive (negative) above (below) 205 K, which was determined by the contribution of mobility (carrier concentration). TCR is negative in polycrystalline Bi nanowires since the contribution of the carrier concentration becomes dominant due to a decrease in the contribution of mobility caused by grain boundary scattering.[8,9] The observed behavior of $R(T)$ is believed to stem from the nature of the single-crystalline Bi nanowire, which will be further demonstrated by MR below.

Upon application of a magnetic field of 9 T, the variation in resistance with transverse fields (R_T) and longitudinal fields (R_L) to the axis of the nanowire has been investigated. MR is well known to be due to the bending of trajectories of carriers, for which the fundamental quantity is $w_c\tau$, where $w_c = eH/m^*$ and T are the cyclotron frequency and relaxation time, respectively, and m^* is the effective mass. We found that R_T at 9 T increased as T decreased from 300 to 75 K since mean-free path increased with decreasing T due to the reduction in phonon scattering. It was also found that R_T decreased with decreasing T to 2 K after reaching a maximum at 75 K. Meanwhile, there were three regimes in R_L: (I) R_L decreased when $205 < T < 300$ K, (II) R_L barely changed when $75 < T < 205$ K, and (III) R_L abruptly decreased when $2 < T < 75$ K as shown in Fig. 2. The reason for this will be addressed with calculated carrier concentrations as well as electronic structures such as Fermi level and band overlap.

The inset of Fig. 2 shows the variation in the (a) transverse and (b) longitudinal MR ratios in the temperature range of 2–300 K at 9 T for the Bi nanowire. The MR ratio is defined as $[R(H)-R(0)]/R(0)\times100$, where $R(0)$ is the zero-field resistance and $R(H)$ is the resistance at 9 T. In the present work, the largest transverse MR (2496%) was observed at 110 K as shown in the inset of Fig. 2(a), which is four times larger than the reported MR (35 K) of electrode-posited 400-nm-diameter Bi nanowire arrays grown using an anodic aluminum oxide template.[8,10] The magnitude of the MR effect is determined by w_cT. At a given value of H, the value of w_c is an intrinsic property of a given material. Such a large MR originates from a long relaxation time (T) and mean-free path (ℓ), supporting the view that Bi nanowires grown by our novel growth method[7] are the high-quality single crystalline.

On the other hand, the decreasing longitudinal MR with decreasing temperature at a high magnetic field, shown in the inset of Fig. 2(b), was observed in the temperature range of 2–300 K at 9 T for the Bi nanowire. This is attributed to the reduced wire boundary scattering for carriers associated with the classical size effect.[1,2] The wire boundary scattering effect arises from the reduction in the cyclotron radius, $r_c = (mv^2)/e(v \times H)$, caused by a high magnetic field parallel to the axes of cyclotron resonance.[1,2] The trajectories of the majority of electrons are helical between collisions with the boundary. In the plane normal to the wire axis, the projections of the electron trajectories are a circle when a magnetic field is applied parallel to the axis of the nanowire. With a high magnetic field, r_c gets smaller. Therefore, the effect of wire boundary scattering on the electrical resistance decreases with increasing H. Consequently, the electrical resistance of a nanowire will decrease as a magnetic field increases, giving rise to a negative MR. In addition, with decreasing T, mean-free path increases due to weaker electron-phonon scattering, further decreasing the electrical resistance of a nanowire. Therefore, the longitudinal MR decreased with decreasing T due to the reduced wire boundary scattering by the reduction in r_c. In our experiments, the largest longitudinal MR of −38% was observed at 2 K, indicating the strongest known wire boundary scattering effect in Bi nanowires reported in the literature.[1,2] Again, our results demonstrate that the Bi nanowire has the longest mean-free paths due to high-quality single crystalline. In fact, mean-free path for a 120-nm-diameter Bi nanowire was found to be 1.35 μm at room temperature, revealed from gate effect measurements.[7]

Figure 3 shows the (a) calculated Fermi energy level and band overlap in the temperature range of 0–300 K, (b) schematics of energy-band diagrams at both the L-point and T-point, and (c) calculated concentrations of total carriers (n_T), electrons, and holes of the Bi nanowire grown along the trigonal axis as a function of temperature. In order to clarify the behavior of MR in the Bi nanowire, we adopted a STB model.[14] Quantitatively, the variation in resistance upon a magnetic field can be expressed by

$$\text{MR} = 4(\omega_c \tau)^2 \left\{ \frac{n_e n_h/(n_e + n_h)^2}{1 + [\omega_c \tau (n_e - n_h)/(n_e + n_h)]^2} \right\}, \quad (1)$$

where n_e and n_h are the carrier concentrations of electrons and holes, respectively. Equation (1) shows that MR reaches a maximum at a certain H when the concentration of electrons and holes is equivalent, i.e., $n_e = n_h$, implying that the carrier concentration plays a critical role in determining MR of Bi since the number of electrons is known to be comparable to the number of holes in Bi nanowires.[4]

Since electron effective mass ($0.0052m_e$) is two orders of magnitude smaller than hole effective mass ($0.6340m_e$),[15] electrons contribute more to electrical transport than holes between 0–300 K. In particular, even in the temperature range of 205–300 K where the hole concentration is slightly larger than the electron concentration, $n_e < n_h$ [see Fig. 3(c)], electrons are still expected to be the dominant carrier due to their small effective mass by two orders of magnitude.
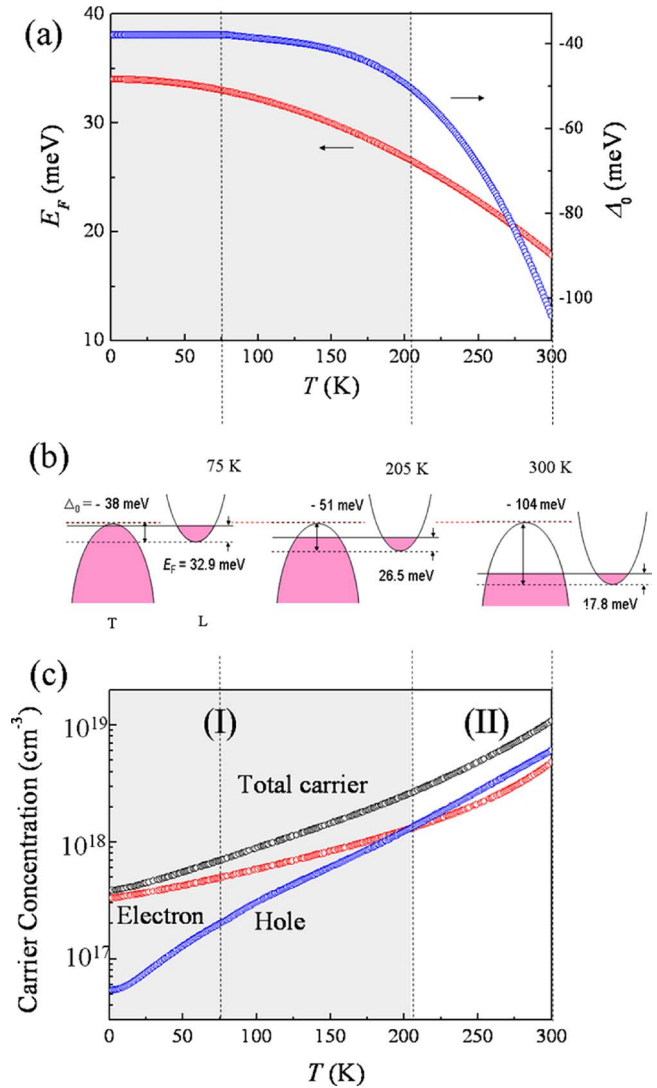

FIG. 3. (Color online) (a) Calculated Fermi energy level and band overlap of the Bi nanowire in the temperature range of 0–300 K at 9 T. (b) Schematics of energy-band diagrams at both the L-point and T-point with Fermi energy level at temperatures of 75, 205, and 300 K at 9 T. (c) Calculated carrier concentrations of electrons and holes of the Bi nanowire grown along the trigonal axis as a function of temperature at 9 T.

Therefore, electron effective mass is used in Eq. (1) to obtain the cyclotron frequency.

In free electron model,[11] the Fermi energy E_F is temperature dependent as described by

$$E_F = E_{F0} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_{F0}} \right)^2 \right], \quad (2)$$

where E_{F0} is the Fermi energy at 0 K and k is the Boltzmann constant. Taking into account that E_{F0} is dependent on the magnetic fields, it was found that E_{F0} ranged from 26.9 meV (at 0.1 T) to 29.0 meV (at 4.9 T) and increased dramatically over 5 T.[12] The variation in E_F ($\Delta E_{F,0–300 \text{ K}}$) in the temperature range of 0–300 K was calculated to be 16.2 meV [see Fig. 3(a)] using $E_{F0} = 34$ meV at 9 T.[12] These calculations are in good agreement with the following estimates of carrier density using the density of states of Bi [see Fig. 3(c)]. The value of $\Delta E_{F,0–300 \text{ K}} = 16.2$ meV is negligible in most semiconductors because ΔE_F is too small to compare with band

gap. However, ΔE_F (16.2 meV) should be considered in semimetallic Bi since it is comparable to the small band overlap (38 meV at 0 K). A further consideration is that the energy overlap of the bands [see Fig. 3(a)], Δ_0, varies with temperature as given by[4,13]

$$\Delta_0(T) = -(E_F^e + E_F^h), \qquad (3)$$

where E_F^e and E_F^h are the Fermi energies of the electrons and holes calculated from the edges of their bands, respectively. The calculated values of Δ_0 were found to be −38 meV at 75 K, −51 meV at 205 K, and −104 meV at 300 K, respectively, according to Eq. (3) of Ref. 13 as shown in Fig. 3(b). Our results demonstrate that E_F and Δ_0 vary with temperature in the range of 0–300 K, suggesting that n_e and n_h are temperature dependent. In order to confirm this, the concentration of total carriers, electrons, and holes of the Bi nanowire as a function of temperature has been investigated.

In order to quantitatively interpret temperature-dependent n_e and n_h, the concentration of total carriers, electrons, and holes of the Bi nanowire as a function of temperature has been investigated. The functional form of the density of states, $N(E)$, can be obtained from Bi band structure calculations as follows:[15]

$$N(E) = \frac{\sqrt{2}}{\pi^2 \hbar^3}(m_x m_y m_z)^{1/2} E^{1/2} \quad \text{for holes}, \qquad (4)$$

$$N(E) = \frac{3\sqrt{2}}{\pi^2 \hbar^3}(m_x m_y m_z)^{1/2}\left(\frac{E^2}{E_g} - E\right)^{1/2}\left(\frac{2E}{E_g} - 1\right)$$
$$\text{for electrons}, \qquad (5)$$

where m_x, m_y, and m_z are the carrier effective masses and E_g is the direct band gap at the L-point. Employing the effective mass for holes and electrons as well as E_g values,[4] we calculated n_e, n_h, and n_T, respectively, as shown in Fig. 3(c). In a previous study, total carrier concentrations in bulk Bi and Bi nanowires in the range of 0–300 K were calculated, but respective n_e and n_h values were not reported.[4] In Fig. 3(c), a crossover at which $n_e = n_h$ was found at $T = 205$ K, indicating that there are two regimes in carrier concentrations: (I) $n_e < n_h$, when $205 < T < 300$ K and (II) $n_e \gg n_h$, when $0 \le T < 205$ K. Our results are in good agreement with the qualitative n_e and n_h values estimated from variations in E_F and Δ_0 according to temperature as shown in Fig. 3(b).

The STB model[14] was utilized to clarify the correlations between the variations in R_T, R_L and n_e, n_h. As previously described, R_T increased with decreasing T to 75 K since mean-free path increased with decreasing T due to the reduction in phonon scattering. However, R_T begins to decrease after showing a maximum resistance at $T = 75$ K. Since mean-free path becomes less dominant at low T, carrier concentrations become more significant in determining R_T. Our calculation shows large differences in n_e and n_h when T is less than 75 K, which is attributable to the decrease in R_T according to Eq. (1). Therefore, our results support the speculation that $T_{\max}$ at low T stems from the delicate balance between T dependence of n (and p) and ℓ in a single-crystalline Bi thin film.[9]

On the other hand, R_L at 9 T decreased with decreasing T in the range of 205–300 K due to an increase in mean-free path. Then, R_L was found to no longer decrease with decreasing T in the range of $75 < T < 205$ K. The invariant resistance in the temperature range is attributable to the imbalance between n_e and n_h according to Eq. (1). R_L rapidly decreased with decreasing T to less than 75 K, attributed to the reduction in effective mass caused by $n_e \gg n_h$ as seen in Fig. 3(c) according to MR $\propto w_c \tau = (eH/m^*) \cdot (\ell/v_F)$. It should be noted that electron effective mass is two orders of magnitude smaller than the hole effective mass.[15]

In summary, we investigated the magnetotransport properties of an individual single-crystalline Bi nanowire grown by a stress induced method. We successfully fabricated a four-terminal device based on an individual 400-nm-diameter nanowire using a plasma etching technique to remove an oxide layer that formed on the outer surface of the nanowire. The transverse MR (2496% at 110 K) and longitudinal MR ratios (−38% at 2 K) for the Bi nanowire were found to be the largest known values reported for Bi nanowires. Our results demonstrate that the Bi nanowires grown by a stress induced method are the highest quality single crystalline ever reported in the literature. We found that the temperature dependences of Fermi energy (E_F) and band overlap (Δ_0) led to an imbalance between electron concentration (n_e) and hole concentration (n_h) in the Bi nanowire, which is in good agreement with the calculated n_e and n_h values from the respective densities of states $N(E)$ for electrons and holes, respectively. We also found that the imbalance of n_e and n_h played a crucial role in determining MR at $T < 75$ K for R_T and at $T < 205$ K for R_L while mean-free path was responsible for MR at $T > 75$ K for R_T and at $T > 205$ K for R_L. Further quantitative values, such as carrier concentration and mobility as well as mean-free path of an individual Bi nanowire through the observation of SdH oscillations and electrical gate effect, will be presented elsewhere.[7]

[1]J. Heremans, C. M. Thrush, Y. Lin, S. Cronin, Z. Zhang, M. S. Dresselhaus, and J. F. Mansfield, Phys. Rev. B **61**, 2921 (2000).
[2]Z. Zhang, X. Sun, M. S. Dresselhaus, J. Y. Ying, and J. Heremans, Phys. Rev. B **61**, 4850 (2000).
[3]Y. Lin, S. B. Cronin, J. Y. Ying, M. S. Dresselhaus, and J. Heremans, Appl. Phys. Lett. **76**, 3944 (2000).
[4]Y. M. Lin, X. Sun, and M. S. Dresselhaus, Phys. Rev. B **62**, 4610 (2000).
[5]S. B. Cronin, Y. Lin, O. Rabin, M. Black, J. Ying, M. Dresselhaus, P. Gai, J. Minet, and J. Issi, Nanotechnology **13**, 653 (2002).
[6]D. Choi, A. Balandin, M. Leung, G. Stupian, N. Presser, S. Chung, J.

Heath, A. Khitun, and K. Wang, Appl. Phys. Lett. **89**, 141503 (2006).

[7]W. Shim, J. Ham, K. Lee, W. Jeung, M. Johnson, and W. Lee (to be published).

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

[9]F. Y. Yang, K. Liu, K. Hong, D. H. Reich, P. C. Searson, and C. L. Chien, Science **284**, 1335 (1999).

[10]K. Liu, C. L. Chien, and P. C. Searson, Phys. Rev. B **58**, R14681 (1998).

[11]S. Kasap, *Principle of Electronic Materials and Devices* (McGraw-Hill, New York, 2002).

[12]M. Cankurtaran, M. Onder, H. Celik, and T. Alper, J. Phys. C **20**, 3875 (1987).

[13]C. Gallo, B. Chandrasekhar, and P. Sutter, J. Appl. Phys. **34**, 144 (1963).

[14]Y. Zhang, J. Small, M. Amori, and P. Kim, Phys. Rev. Lett. **94**, 176803 (2005).

[15]S. Cronin, Ph.D. thesis, Massachusetts Institute of Technology, 1999.