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Finite-size effects in bismuth nanowires

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Arrays of semimetallic Bi nanowires, fabricated by electrodeposition, exhibit strong finite-size effects in transport properties as the carrier mean-free path is limited by the wire dimensions. We have observed a resistivity enhancement, a very large positive magnetoresistance, and a resistance maximum that depends on the strength and orientation of the magnetic field and the nanowire diameter. These results demonstrate electrodeposited Bi nanowires as a new medium for studying the intricate physics in Bi nanostructures. [S0163-1829(98)52246-1]

Magnetic nanostructures, such as multilayers (e.g., Co/Cu) (Refs. 1–3) and granular solids (e.g., Co-Ag) (Refs. 4 and 5) with metallic constituents, have attracted a great deal of attention, due to the realization of new phenomena such as negative giant magnetoresistance (GMR) and interlayer coupling.[6] The effect size of GMR in magnetic nanostructures is generally on the order of a few to a few tens of percent, except in nearly perfect superlattices which show the largest GMR effect of about 150% at 4.2 K.[7] To date, the constituent materials in the overwhelming majority of magnetic nanostructures include transition metals, alloys, and noble metal elements.

Recently, we have successfully fabricated arrays of semimetallic Bi nanowires by electrodeposition,[8] in a new attempt to explore nanostructured semimetals. Semimetallic bismuth (Bi) is a material that exhibits interesting magnetoresistance (MR) characteristics[9] and finite-size effects. Pure bulk Bi is known to exhibit a large positive MR with a prescribed field dependence. The electronic properties of Bi are fundamentally different from those of common metals, due to the complex and highly anisotropic Fermi surface. The elongated pockets of holes and electrons with small effective masses lead to a large Fermi wavelength of about 400 Å, as opposed to a few Å in most metals.[10] The carrier mean-free path in Bi can be as much as a millimeter at 4.2 K, several orders of magnitude larger than those for most metals.[11] Due to the unusual electronic structure, Bi has been used to study both classical and quantum finite-size effects, for which the characteristic lengths are the carrier mean-free path and Fermi wavelength, respectively. The pursuit of quantum size effects, initiated by the observation of resistivity oscillations in Bi thin films as the thickness is varied,[12] has continued to attract attention since the 1960s.[10,13–15] Most of these studies involve Bi thin films, for which film thickness is a convenient variable.

To date, the fabrication of high quality Bi thin films has been limited to molecular beam epitaxy. Other traditional deposition techniques, such as sputtering, have been unsuccessful in preserving the intrinsic Bi properties in thin films, such as the large MR effect, due to the inferior film quality. There have also been early studies using the Taylor process to fabricate micron and submicron-size Bi wires.[16,17] The electrodeposited Bi nanowires we fabricated offer a new medium for studying the intricate physics as well as applications in Bi nanostructures.

The Bi nanowires were electrodeposited into nanometer-size cylindrical pores in polycarbonate membranes.[18] They are typically 10 μm in length, arranged in a parallel manner. Detailed electrodeposition conditions of the Bi nanowires have been published elsewhere.[8] In this work, nanowires with diameter of 2 μm, 1 μm, 400 nm, and 200 nm were fabricated, with a corresponding wire density of 2×10^4, 2×10^5, 1×10^6, and 3×10^6 wires/mm^2, respectively. Structural characterizations by x-ray diffraction, TEM and electron diffraction confirmed a polycrystalline rhombohedral structure. Typical Bi grains in the wires are elongated in shape, with the width comparable to, and the length up to 2–4 times, the wire diameter.

For transport measurements, two Au strip layers were patterned on the top and bottom surfaces of the membrane in order to make electrical contact to a smaller number of Bi nanowires.[19] A quasi-four-probe geometry was achieved by attaching a voltage lead and a current lead to each Au strip layer. The measured resistance is the sum of the Bi nanowire resistance and the contact resistance, the latter of which is negligible due to the much larger area in the current path. This method allows us to estimate the resistance of a single Bi wire from a group of wires connected in parallel.

Assuming all the Bi wires in the selected area contribute equally to the total resistance, then the resistance of a single Bi nanowire is rather large. For the case of 400-nm wires, the resistance per wire is over 1000 Ω in the temperature range of 5–300 K. This is much larger than the value of about 100–200 Ω expected using the resistivity of 115 $\mu\Omega$ cm for bulk Bi at 300 K, or the value of 200 $\mu\Omega$ cm for electrodeposited 1 μm-thick polycrystalline Bi film at 300 K. Electron microscopy shows that the vast majority of the nanowires have protruded above the membrane surface and are expected to make electrical contact with the Au layer. Therefore there is an enhancement of 5–10 times in the resistivity due to the nanowire geometry. Previously, similarly large resistivity enhancement has also been reported in multilay-

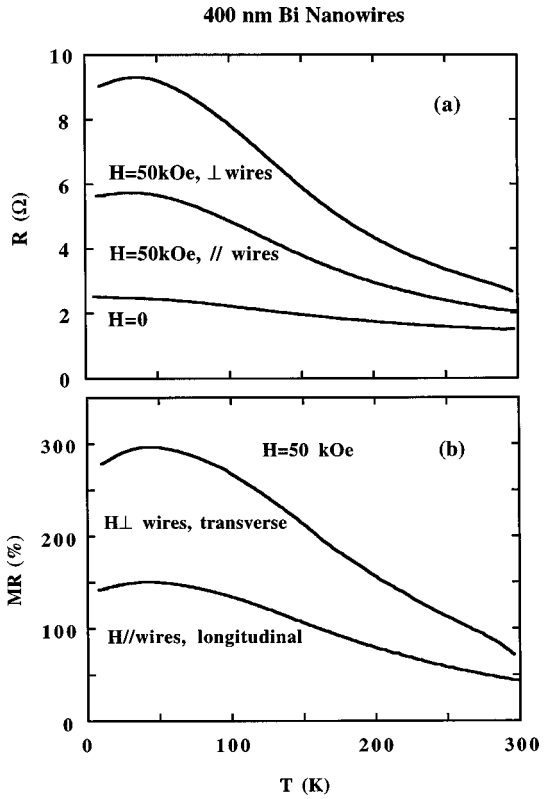

FIG. 1. Temperature dependence of (a) resistance and (b) magnetoresistance of the 400-nm Bi nanowires, with and without a magnetic field of 50 kOe applied perpendicular and parallel to the wires.

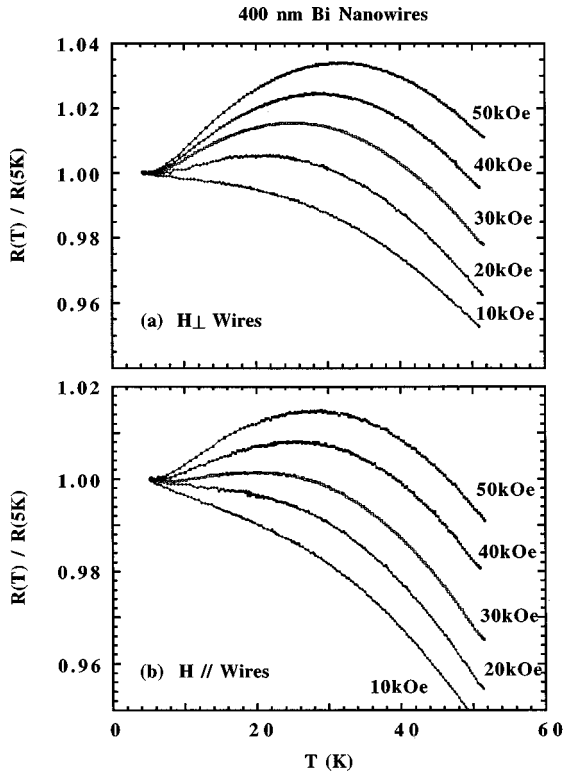

FIG. 2. Temperature dependence of resistance (normalized to the value at 5 K) of the 400-nm Bi wires showing resistance maximum at T_{max} for various values of (a) transverse and (b) longitudinal magnetic field.

ered Co/Cu nanowires.[19] Since the mean-free paths of Co and Cu are much smaller than the wire dimensions, the additional resistance is due mainly to scattering at the numerous Co/Cu interfaces, and, to a lesser extent, boundary scattering at the wire surface. In the present case of Bi wires, scattering at the wire surface and particularly grain boundaries is expected to be strong since the wire dimensions are much less than the bulk Bi mean-free path, which could reach mm scale at low temperatures. Therefore, the enhancement of resistivity in Bi nanowires can be ascribed to classical finite-size effects, as the mean-free path is effectively limited by the wire diameter. Further evidence of strong finite-size effect will be illustrated later.

We next describe the temperature and field dependence of the transport properties. The temperature dependence of the resistance of 400-nm Bi nanowires is shown in Fig. 1(a). In zero magnetic field, the resistance increases gradually with decreasing temperature. The ratio of resistance at 5 K and 293 K, $R(5\,\mathrm{K})/R(293\,\mathrm{K})$, is about 1.5. This negative temperature coefficient (TCR) is observed in all the Bi nanowire samples with different diameters. The TCR of Bi is determined by the relative contributions due to the carrier concentration and mobility, which have opposite temperature dependence. With increasing temperatures, the carrier concentration increases, whereas the carrier mobility decreases, leading to respectively a negative and a positive TCR. When the temperature dependence of the carrier mobility is suppressed by structural imperfections or finite-size effects, that of the carrier concentration dominates the TCR. In the present case of Bi nanowires, because of the polycrystalline nature of the material, and the smaller wire diameter in comparison with the mean-free path, the TCR is generally negative.

Upon the application of a magnetic field H, the resistance of the Bi wires increases for both field parallel (longitudinal) and perpendicular (transverse) to the wires, as shown in Fig. 1(a) for $H=50$ kOe. It is noted that the transverse MR in Bi nanowire is always larger than the longitudinal MR. Furthermore, the temperature dependence of the resistance shows a maximum at T_{max}, at about 40 K. The resistance maximum under a magnetic field observed in Bi wires resembles the resistance maximum in zero magnetic field in very thin single crystal-like Bi films (<60 nm).[10,13] In those previous studies, the value of T_{max} was found to shift to higher temperatures as the film thickness was reduced. In the Bi nanowires, such a maximum does not occur until a sufficiently large magnetic field is applied. The temperature dependence of the MR effect size is shown in Fig. 1(b). Because the resistance $R(0)$ at $H=0$ is weakly temperature dependent, the temperature dependence of the MR is essentially that of the resistance in the field $R(H)$, also exhibiting a maximum at low temperatures. In the case of 400-nm wires, the transverse and longitudinal MR are about 70% and 40% at room temperature, respectively, increasing to about 300% and 150% at around 40 K.

We have further examined the resistance maximum at low temperatures. Figure 2 shows the development of such a resistance maximum in transverse and longitudinal magnetic fields for the 400-nm wires. To illustrate this effect more clearly, the resistance has been normalized to the value at 5 K. In the transverse geometry [Fig. 2(a)], the maximum is

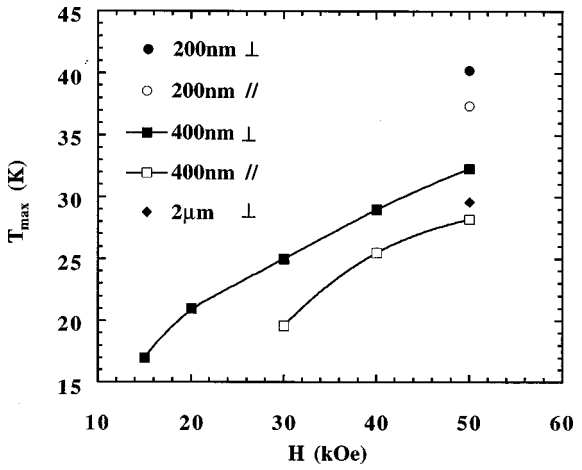

FIG. 3. The dependence of resistance maximum T_{max} on magnetic field for various wire diameters, where solid and open symbols stand for transverse ($\perp$) and longitudinal ($\parallel$) field geometry, respectively.

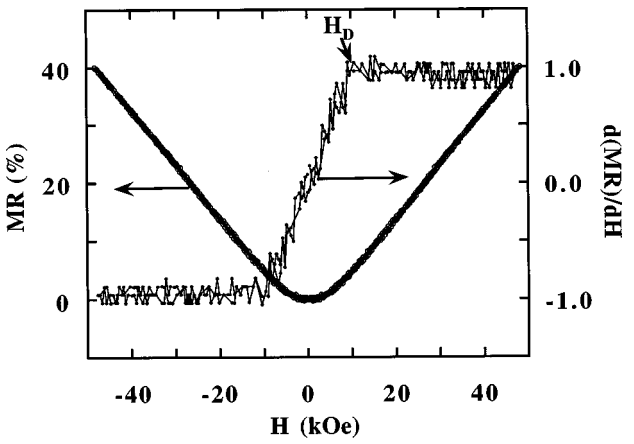

FIG. 4. Representative magnetic field dependence of (a) magnetoresistance and (b) d(MR)/dH for 400-nm Bi nanowires, with the deviation field H_D indicated.

not appreciable until the applied field is above 20 kOe, beyond which T_{max} is shifted to higher temperatures. A similar trend is observed in the longitudinal geometry [Fig. 2(b)], except that the threshold of the applied field is larger, about 30 kOe, in order to induce a maximum. The maximum in the transverse geometry always occurs at a higher temperature than that in the longitudinal case. The value of T_{max} also depends on the wire diameter. When the same magnetic field is applied in the same geometry, the value of T_{max} increases with decreasing wire diameter. The dependence of T_{max} on field strength, field orientation, and wire diameter is summarized in Fig. 3.

In very thin Bi films, the appearance of T_{max} was attributed to the rapid increase of mobility at low temperatures, a mechanism originated from the quantum size effect.[13] The size quantization decreases the number of available states, therefore restricts the electron-phonon scattering. Furthermore, at very low temperatures, there are no phonons capable of transferring electrons between the size-quantized sub-bands. The suppression of electron-phonon scattering effectively increased the mobility. In the present Bi nanowires, the size quantization may have come into play as the smallest wire diameter is already comparable to the Fermi wavelength. It was estimated that for 200-nm Bi wires, the quantum size effect should take place in $T<30-40$ K.[17] This effect results in the dependence of T_{max} on the wire diameter. The fact that no resistance maximum is observed in zero magnetic field, as in the case of thin single crystallike Bi films,[10,13] is due to the polycrystalline nature of the nanowires. Application of a strong magnetic field can introduce magnetic quantization. The phonon scattering processes are also impeded in the similar fashion by magnetic quantization at low temperatures,[9] especially in strong magnetic fields where the energy difference in adjacent magnetically quantized sub-bands becomes larger. The resultant increase of mobility at low temperatures gives rise to the resistance maximum. The dependence of T_{max} on field orientation is essentially a geometrical effect of the Lorentz force, when the magnetic field is applied parallel and perpendicular to the current.

The positive MR of Bi originates from the ordinary MR effect, which is the curving of the electron trajectory by a magnetic field. The characteristic quantity is $\omega_c\tau$, inversely proportional to the carrier density, where ω_c is the cyclotron frequency and τ is the relaxation time.[9] The ordinary MR in most metals is usually very small, less than a few percent, owing to the very small values of $\omega_c\tau$. However, in semimetallic Bi, due to the very low carrier concentration, several orders of magnitude smaller than those in most metals, the characteristic term $\omega_c\tau$ is much larger, leading to a large positive magnetoresistance. The fact that Bi is a compensated metal also enhances the MR because the Hall field cannot be set up to completely balance out the Lorentz force as in common metals.

The magnetic field dependence of the MR is represented in Fig. 4 for the 400-nm wires. At all temperatures, the MR is nonhysteretic, quadratic at low fields, and becomes linear at higher fields. The solution of the Boltzmann equation readily gives a H^2 dependence of MR for small fields. At higher fields, deviation from the H^2 dependence occurs at a certain field value H_D, defined as the deviation field. The location of H_D can be demonstrated in the derivative of MR, as shown in Fig. 4, where the H^2 dependence of the MR at $-H_D<H<H_D$ and the H dependence at $|H|>H_D$ are evident. It is more insightful to examine the deviation from the H^2 dependence in terms of the intrinsic quantity $\omega_c\tau$, which dictates the field dependence of MR. This term can also be expressed as $\mu H/c \sim lH$, where μ is the carrier mobility and l is the carrier mean-free path. When deviation occurs, the value of H_D may vary from one Bi sample to another. However, the intrinsic quantity $\mu H_D/c \sim lH_D$ is the same for all Bi samples, and thus serves as a reference point to gauge the carrier mobility or mean-free path in various Bi samples.[10,20]

We have determined the value of H_D at different temperatures for various nanowires, as shown in Fig. 5. In the 400-nm wires, H_D is 11 kOe at 300 K, and decreases to 9 kOe at 200 K and 5 kOe at 40 K. The reduction of H_D at lower temperature corresponds to an increasing carrier mean-free path and mobility. Since H_D only decreases by a factor of 2.2 from 300–40 K, the carrier mobility increases by the same factor. This is consistent with the suppression of the temperature dependence of the mobility discussed earlier. At the same temperature, narrower wires show a larger H_D, or

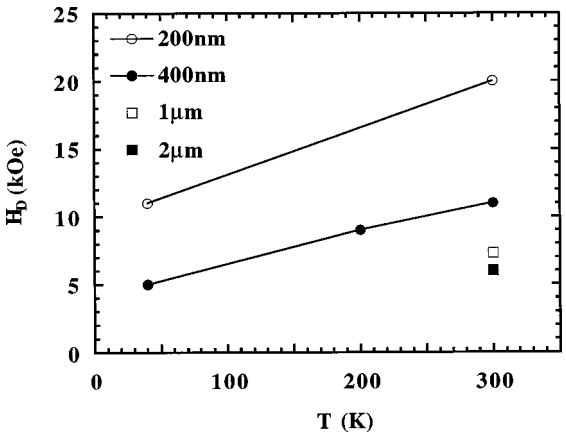

FIG. 5. Temperature dependence of the deviation field H_D for various wire diameters.

smaller mean-free path and mobility. For example, at 300 K, H_D is 20 kOe in 200-nm wires, 11 kOe in 400-nm wires, 7.3 kOe in 1-μm wires, and 6 kOe in 2-μm wires. In comparison, in bulk Bi single crystals, deviation from the quadratic field dependence occurs at a very small field of only 4 Oe at 4.2 K, relating to a very long mean-free path of about a millimeter.[20] In our Bi nanowires, H_D is several thousand Oe, even at very low temperatures. The large values of H_D indicate a reduction of mean-free path by over three orders of magnitude, to less than 1 μm, on the same scale as that of the nanowire diameter. As a crude estimate, relating a mean-free path of 1 mm to a deviation field of 4 Oe as in bulk Bi, one obtains a reduced mean-free path of 200 nm for the 200-nm wires, 360 nm for the 400-nm wires, 550 nm for the 1-μm wires, and 670 nm for the 2-μm wires. This estimate agrees very well with the simple argument made earlier of restricting the mean-free path to the nanowire diameter. It gives further credence to the conclusion that the enhanced resistivity in Bi nanowires is indeed due to the finite-size effects.

In summary, we have demonstrated that electrodeposited Bi nanowires provide a means for studying quasi-one-dimensional Bi nanostructures. Because of the unusual electronic properties of the semimetallic Bi and the nanowire geometry, we have observed strong finite-size effects in the transport properties, such as the resistivity enhancement, the resistance maximum, and the specific field dependence of the MR. Large positive magnetoresistance, 300% at low temperatures and 70% at room temperature, have also been observed. The one-dimensional nanostructures of semimetals show promise of a medium for fruitful explorations of interesting phenomena and technological applications.

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