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Y-branched Bi nanowires with metal–semiconductor junction behavior

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Y-branched Bi nanowires (NWs) embedded in anodic aluminum oxide templates were synthesized by electrochemical deposition. Transmission electron microscope observations revealed that the "stem" and the "branches" of the Y-branched Bi NWs are about 80 and 50 nm in diameter, respectively. Selected area electron diffraction studies showed that both the stem and the branches are single crystalline. Current–voltage measurement revealed that the parallel Y-branched Bi NWs have characteristics of conventional metal–semiconductor junctions. Our approach to produce one-dimensional metal–semiconductor junctions using Y-branched NWs consisting of only one kind of semimetal and without any external doping can be exploited to create metal–semiconductor junctions of other semimetals, which may find various applications in nanodevices. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1779956]

Quasi-one-dimensional (1D) nanostructures have become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanodevices. They provide a good system to study the dependence of electronic and thermal transport or mechanical properties on dimensional reduction, and play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical nanodevices.[1,2] Longitudinal heterojunctions within 1D nanostructures are important to electronic and optoelectronic nanodevices. Until now, segmented heterojunctions in individual 1D nanostructures, such as carbon nanotubes (CNTs) and Si nanowires (NWs),[3] single-walled CNTs and carbide NWs,[4] *n*-*p* junction Si NWs,[5] *n*-*p* junction InP NWs,[5] *p*-*n* junction GaN NWs,[6] InAs–InP junction NWs,[7–9] ZnO–ZnMgO junction NWs,[10] and superlattice NWs of GaAs/GaP,[5] and Si/SiGe,[11,12] have been synthesized. Although these randomly oriented intramolecular 1D heterojunctions can be used as building blocks for nanodevices and device fabrication, however, the device fabrication involves dispersing, manipulating, and assembling, and is still very complicated and unreliable for practical application. If segmented heterojunctions in 1D nanostructures are synthesized within a template, then nanodevices consisting of 1D heterostructures can be realized simply by adding electrodes on the two opposite sides of the templates. This will also provide a convenient approach to study the transport properties of 1D heterojunction nanostructures. Segmented 1D heterojunction in straight nanochannels of an anodic aluminum oxide (AAO) template, such as, multimetal NWs,[13] metal–CdSe–metal NWs,[14] Ag–Si NWs and Ni–CNTs junctions,[15] Pt_6Si_5-Si NWs[16] and *p*-*n* ZnO NW junctions,[17] have been fabricated. Furthermore, Y-junction CNT heterostructures embedded in AAO template were also fabricated, and showed intrinsic nonlinear transport and rectifying behavior at room temperature.[18,19]

Bismuth (Bi) is a semimetal with unusual electronic properties that result from its highly anisotropic Fermi surface, low carrier concentration, small effective mass, and long mean-free path of the carriers.[20] Transport properties of Bi NWs have attracted a great deal of interest,[21–23] and the investigation results[21–23] revealed that a semimetal-to-semiconductor transition takes place as the diameter of Bi NWs decreases. When the diameter of Bi NWs is reduced to about 50 nm and smaller, the Bi NWs are found to be semiconducting, while Bi NWs with a diameter of 70 nm and larger are metallic. Our previous studies on the transport properties of straight Bi NWs revealed similar results.[24] We have now synthesized metal–semiconductor junctions in Y-branched Bi NWs using only one kind of semimetal (Bi) and without any external doping. This was made possible as the Y-branched Bi NWs in AAO template have large-diameter "stem" segments which are metallic, and small-

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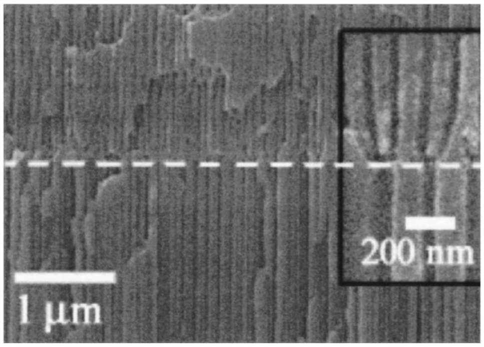

FIG. 1. A SEM image of the AAO template with Y-branched nanochannels, the inset shows the close-up of the Y-branched nanochannels. The dashed line shows where the Y branches start to grow.

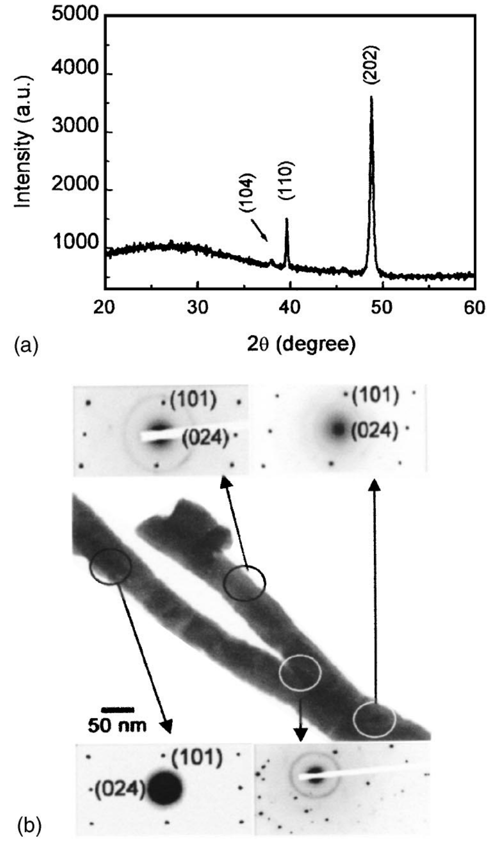

FIG. 2. (a) XRD pattern taken from Y-branched Bi NWs embedded in AAO template. (b) TEM image of a single Y-branched Bi NW. The four SAED patterns were taken from the two branches, the stem, and the branch near the branching point, respectively.

diameter "branched" segments which are semiconducting. In this letter, we report the fabrication of Y-branched Bi NWs, and the characteristics of their electronic transport properties.

AAO templates with Y-branched nanochannels were fabricated by using a similar method reported previously:[18] High-purity Al foils were anodized in 0.3 M oxalic acid solution at 50 V_{DC} for 4 h. After chemically removing the original film in a mixed solution of phosphoric acid (6 wt %) and chromic acid (1.8 wt %) at 60 °C for 6 h, a second anodization was performed under the same conditions for 4 h. The anodization voltage was then reduced to 35 V_{DC} (by a factor of $1/\sqrt{2}$), and another anodization was performed for 4 h. This will lead to nearly all large diameter channels (formed at 50 V) branched into two smaller-diameter channels (formed at 35 V).[18] After the remaining Al was removed in a saturated $SnCl_4$ solution, the templates were immersed in a 5 wt % phosphoric acid solution at 30 °C for 90 min to remove the barrier layer, and to widen the nanochannels homogeneously over the entire pore length.[12] Figure 1 is a scanning electron microscope (SEM) image of the cross section of the AAO template with Y-branched nanochannels. The inset of Fig. 1 shows the close-up of the region between stems and branches. The resulting AAO template consists of Y-branched nanochannels with stems and branches about 80 and 50 nm in diameter, respectively.

The electrochemical deposition of Bi into the Y-branched nanochannels of AAO template was carried out using a similar method to the one previously reported.[24,25] A gold layer was sputtered onto the bottom side (with branched channels) of the AAO template serving as the working electrode in a three-electrode electrochemical cell. The electrolyte contained 75 g/l $Bi(NO_3)_3 \cdot 5H_2O$, 65 g/l KOH, 50 g/l tartaric acid, and 125 g/l glycerol. The electrolyte was buffered to pH=0.9 with HNO_3 solution. The electrodeposition was performed under −30 mV relative to the Ag^+/AgCl reference electrode. X-ray diffraction (XRD) pattern [Fig. 2(a)] taken from the Y-branched Bi NWs embedded in AAO template shows that all peaks are located very close to the peak positions of bulk Bi, revealing that the rhombohedral lattice structure of bulk Bi is reserved in the Y-branched NWs. It should also be noted that the strongest peak of the Y-branched Bi NWs is (202), while other peaks are weak, indicating that most of the Bi NWs are oriented perpendicular to the (202) lattice plane. After dissolving the AAO template in a 5 wt % NaOH olution, transmission electron microscope (TEM) observation of a single Y-branched Bi NW [Fig. 2(b)] reveals that the stem of the NW is about 80 nm in dameter and the branches are about 50 nm in diameter, in agreement with those of the Y-branched nanochannels in the template. Selected area electron diffraction (SAED) patterns taken from both the branches and the stem [Fig. 2(b)] reveal that the rhombohedral lattice structure is preserved in the Bi NWs, in agreement with XRD results. Along the axes of both the stem and the branches, the diffraction patterns are identical, revealing that both the branches and the stem are essentially single crystalline, and the Bi NWs preferentially grow along the (101) stacking face. However, the diffraction pattern taken from the branch near the branching point [Fig. 2(b)] is not regular, indicating that this domain is polycrystalline, which may be caused by variations in the growth orientation of the branches.

The current–voltage ($I-V$) characteristic of the parallel Y-branched Bi NWs embedded in AAO template was measured at room temperature, as illustrated in Fig. 3(a) (inset). The result reveals that the $I-V$ curve [Fig. 3(a)] is nonlinear and asymmetrical about zero bias. This characteristic is analogous to Schottky junction between a metal and a degenerate n-type semiconductor.[26] The possible energy diagram for the device is shown in Fig. 3(b) (inset). The observed characteristics can be explained by assuming that the semiconductor is degenerate at room temperature with conduction electrons available from the bottom of the conduction band E_c to the Fermi energy E_F. The $I-V$ curve shows a kink close to zero bias on the positive side. This is highlighted on the conductance curve, which was derived from the $I-V$ curve by numerical differentiation [Fig. 3(b)]. The conductance

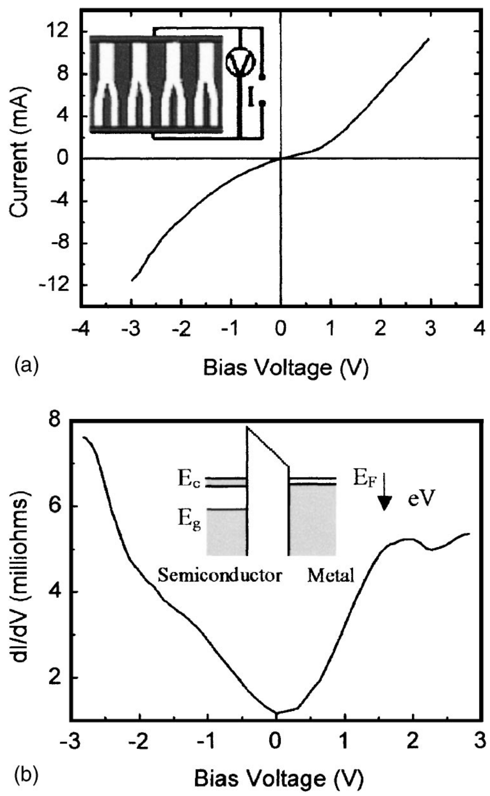

FIG. 3. (a) $I-V$ characteristics of parallel Y-branched Bi NWs embedded in AAO template. The inset is a schematic illustration of the $I-V$ measurement for the Y-branched Bi NWs. (b) Conductance curve, showing a minimum at about 110 meV, which is the Fermi-level energy difference, measured from the conduction-band edge of the semiconductor. (Inset) Energy band diagram of the semimetal and degenerate semiconducting Bi NW.

curve goes through a minimum at around 110 meV. This energy is then the difference between E_c and E_F. The forward bias region up to 1.4 eV is characteristic of carrier injection processes, as the metal crosses the forbidden energy gap in the semiconductor. The actual band gap of the semiconductor channel is complicated to extract, given the fact that the tunneling barrier shape changes due to image charges. Other factors to be considered are surface charging at the interface. The curve shows a peak at 1.9 eV suggesting the unavailability of additional conduction states with increase in bias. The reverse bias is dominated by electron tunneling from the semimetal Bi into the conduction band of the degenerate semiconductor Bi NW channel. The kink at −1.9 eV in the reverse bias region of the conductance is notable, as it indicates variation in conduction states in the metallic part of the NW, which may be responsible for the small peak at 1.9 eV. Previous studies revealed that semimetal-to-semiconductor transition is calculated to occur as the diameter of the Bi NW decreases below about 65 nm,[21] and experimental results showed that Bi NWs with diameters larger than 70 nm are metallic, while Bi NWs with diameters about 50 nm or smaller are semiconductor.[23,24] Our Y-branched Bi NWs with diameters of about 80 and 50 nm for the stem and the branches respectively, show metal–semiconductor junction properties without any external doping.

In conclusion, we have synthesized Y-branched Bi NWs by electrochemical deposition in the Y-branched nanochannels of AAO templates. The stem and the branches of the Y-branched Bi NWs are about 80 and 50 nm in diameter, respectively. $I-V$ measurement revealed that the parallel Y-branched Bi NWs have characteristics of conventional metal–semiconductor junctions. Our result showed that 1D metal–semiconductor junctions could be realized by Y-branched NWs consisting of only one kind of semimetal (Bi) and without any external doping, accordingly other semimetals should be considered for creating metal–semiconductor junctions with Y-branched NWs. These semimetal Y-branched NWs with metal–semiconductor junction characteristics may find various applications in nanodevices.

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