

Magnetic Alignment of Nanowires

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Spatial manipulation and ability to assemble and position nanostructures in a controlled manner so they are registered to lithographically defined contacts is a critical step toward scalable integration in high-density nanodevices. By integrating ferromagnetic ends on nanostructures and using the magnetic interaction between ferromagnetic ends and electrodes, we demonstrated assembling, positioning, and spatial manipulating of nanostructures on ferromagnetic contacts. Segmented nickel/gold/nickel (Ni/Au/Ni) and nickel/bismuth/nickel (Ni/Bi/Ni) nanowires with controlled dimensions were fabricated by template-directed electrodeposition. One hundred percent magnetic alignment of nanostructures to the imposed magnetic fields was achieved by applying a low external magnetic field of 200 Oe. In addition, directional controllability of the magnetic assembling technique was demonstrated by assembling nanostructures with angles from 45° to 135° with respect to the electrodes. This magnetic assembly technique was shown to have potential for high-density interconnects without registration and individually addressable nanostructures with the use of different substrate architectures for two-dimensional control of nanostructures placement.

Introduction

Nanowires and nanotubes are critically important building blocks of nanotechnology for two reasons. First, their high aspect ratios and quasi-one-dimensional features¹ are appealing for integration in high-density devices, giving rise to devices that are lighter, more compact, and portable. Second, nanostructures begin to exhibit unique properties that diverge from the bulk due to confinement effects. At this level semiconducting nanostructures enter a quantum confinement regime where the optical, optoelectrical, and electrical properties of the wire are dependent on its dimensions.² The effective band gap above bulk values has been shown to be linearly dependent on the inverse square diameter in nanowires.³ This translates to a band gap that can be customized for specific optoelectrical and electronic applications by controlling the diameter of nanostructures. However, exploiting the full potential of nanostructure materials and their characteristics has been limited by the inability to spatially manipulate and address these nanoentities.¹ Controlled assembly of nanowires into more complex networks is necessary to realize applications such as nanoelectronics, spintronics, optoelectronics, sensors, and thermoelectric devices. Previous efforts include during and postgrowth electric-field-assisted alignment,^{4–6} magnetic entrapment,^{7–9} Langmuir–Blodgett method,¹⁰ and microfluidic techniques.¹¹

In this paper, we focused on spatial manipulation and positioning of nanowires on prefabricated ferromagnetic contacts using magnetic interaction between contacts and nanowires with capped magnetic ends. Controlled placement of nanowires is demonstrated through design of ferromagnetic electrodes for array applications and individual addressability. Nanowire directionality is shown to be dominated by an external magnetic field with the percent of aligned nanowires being a function of the magnetic field strength. Finally, a novel and cost-effective method of making electrical contact is described and used for electrical characterization of Ni/Au/Ni nanowires.

This alignment technique utilizes nanowires with magnetic ends or caps that facilitates a functional midsection and is a self-assembly method based on inherent properties of ferromagnetic materials and their magnetic interaction. A gold midsection was used to demonstrate proof-of-concept but is interchangeable with a variety of materials by electrochemical means, including metals, metal oxides, alloys, semiconductors, and conducting polymers. Bismuth was used as an example of a functional midsection material and is unique in that it has a positive magnetoresistance and a high bulk thermoelectric figure-of-merit. Ballistic electron transport has also been shown to increase the thermoelectric power of Bi

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- (1) He, H.; Tao, N. J. *Encyclopedia of Nanoscience and Nanotechnology*; American Scientific Publishers: Stephenson Ranch, CA, 2004.
- (2) Sapra, S.; Sarma, D. D.; Sanvito, S.; Hill, N. A. *Nano Lett.* **2002**, *2*, 605.
- (3) Yu, H.; Li, J.; Loomis, R. A.; Wang, L. W.; Buhro, W. E. *Nat. Mater.* **2003**, *2*, 517.
- (4) Smith, P. A.; Nordquist, C. D.; Jackson, T. N.; Mayer, T. S.; Martin, B. R.; Mbindyo, J.; Mallouk, T. E. *Appl. Phys. Lett.* **2000**, *77*, 1399.

- (5) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature* **2001**, *409*, 66.
- (6) Kumar, M. S.; Kim, T. H.; Lee, S. H.; Song, S. M.; Yang, J. W.; Nahm, K. S.; Suh, E. K. *Chem. Phys. Letts.* **2004**, 383.
- (7) Tanase, M.; Silevitch, D. M.; Hultgren, A.; Bauer, L. A.; Searson, P. C.; Meyer, G. J.; Reich, D. H. *J. Appl. Phys.* **2002**, *91*, 8549.
- (8) Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1255.
- (9) Love, J. C.; Urbach, A. R.; Prentiss, M. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12696.
- (10) Huang, Y.; Duan, X.; Wei, Lieber, C. M. *Science* **2001**, *291*, 630.
- (11) Bentley, A. K.; Trethewey, J. S.; Ellis, A. B.; Crone, W. C. *Nano Lett.* **2004**, *4*, 487.

nanowires and is believed to have the potential for increasing its thermoelectric figure-of-merit.¹² Moreover, bismuth–antimony and bismuth–tellurium alloys are important room-temperature thermoelectric materials¹³

Experimental Section

Nanowires were synthesized using template-directed electrochemical deposition, an approach pioneered by Martin.^{14,15} This method uses a nanoporous membrane as a scaffold with a metallic seed layer on one side to serve as a cathode. The bulk of these studies used commercially available anodized aluminum oxide membranes, Whatman Anodisc 13, with a nominal pore diameter of 200 nm. Anodic alumina is a rigid material that can withstand temperatures in excess of 600 °C and harsh chemical environments and can be produced with pores as small as 5 nm in diameter.¹⁴ In addition, the high density, order, and aspect ratios of these membranes are ideal characteristics of nanowire templates. Since alumina nanotemplate with a pore size as small as 5 nm can be anodized, template-directed electrochemical deposition will allow fabricating nanowires with a diameter less than 10 nm.

Copper metallic seed layers (ca. 500 nm thick) were sputtered using an Emitech K550 tabletop sputter. The template was fixed to a glass support with the seed layer face down using double-sided conductive copper tape. Single-sided conductive copper tape was used as a lead to the glass support. The entire sample, except for the middle of the template and the end of the copper tape lead, was masked with a commercially available dielectric material (Microstop, Pyramid Plastics, Inc.).

The nanowires were deposited galvanostatically (i.e., constant current mode) with the template serving as the cathode. Nickel anodes were used in nickel electrodeposition, and platinum-coated titanium anodes were used as the inert electrodes for gold and bismuth electrodeposition. The nickel electrolyte composition was 0.91 M $\text{Ni}(\text{H}_2\text{NSO}_3)_2$ + 0.10 M H_3BO_3 + 30 ppm HCl and deposited using a current density of 5 mA/cm² at ambient conditions without agitation. The pH was kept constant at 4 using either sulfamic acid or NaOH. The gold segments were electrodeposited from a ready-to-use cyanide-free gold bath (Technic RTU-25) at 1 mA/cm², 50 °C, and agitation from a 1 in. stir bar in a 150 mL beaker at 240 rpm. Bismuth segments were deposited from two different solutions, an 8 mM $\text{Bi}(\text{NO}_3)_3$ + 1 M HNO_3 solution under ambient conditions with a 1 in. stir bar in a 150 mL beaker at 240 rpm and 0.127 M BiCl_2 , 1.20 M NaCl, 0.54 M glycerol, 0.66 M tartaric acid, and 1 M HCl solution at room temperature with no agitation. The applied current density was 5 mA cm⁻². All materials were electrodeposited using a multichannel EG&G PAR VMP2 potentio/galvanostat. The segmented nanowires with magnetic ends were constructed by depositing Ni, changing the electrolyte for deposition of the functional midsection, gold or bismuth, and switching back to a Ni bath. The lengths of different segments were controlled by adjusting deposition time at a given current density. The template electrodes were rinsed with Nanopure water between plating solutions to prevent cross-contamination.

The nanowire-embedded template was removed from the substrate by detaching the copper tape lead and sonicating the glass support in acetone for approximately 10 s. Alumina templates were sonicated again in clean acetone and then isopropyl alcohol for

another 10 s to remove the copper tape conductive adhesive residue from the backside of the template. The seed layer was removed from the template using either 50 mM CuCl_2 + 30% HCl or 10% HNO_3 etchant. The template was dissolved in 1 M NaOH solution for 8 h at 60 °C. The nanowires were washed with water and isopropyl alcohol three times each using a small ceramic magnet to collect the nanowires between washings. Finally, the nanowires were suspended in 1 mL of isopropyl alcohol and sonicated. The resulting nanowire suspension was highly concentrated and required a subsequent dilution of up to 1000-fold for alignment trials.

Three different microfabricated electrodes were used for aligning the nanowires. The I – V response was measured with Abtech IAME 0504-PT, and additional alignment studies were carried out with lithographically prepared nickel patterns on silicon substrates. The Abtech IAME contained four parallel microbands having a width and spacing of 5 μm and length of 3 mm. The microbands were platinum with a tungsten adhesion layer. These microelectrodes were fabricated with a dielectric mask that exposed only the microbands and contact pads, allowing for ease in plating of the microbands. The IAME was attached to an adapter, available from Abtech, with Krazy Glue. The IAME was electrically contacted to the adapter with indium melted by a solder gun. The resistance from the contact pad of each microband to its corresponding lead from the adapter was measured to be <8 Ω . The IAME microbands were plated with 1 μm of nickel using the same setup and operating conditions for nickel nanowire deposition as previously mentioned with the IAME serving as the working electrode or cathode. A 1- μm solder film was deposited on top of the nickel microbands using Technic 820 HS 60/40 (60Sn40Pb) at 10 mA cm⁻² in a 150 mL cell and agitation with a 1 in. stir bar at 240 rpm with a platinum counter electrode. The assembled electrode was tested again to ensure that the resistance from the contact pad to adapter lead was <8 Ω as well as to ensure the microbands were not shorted.

The silicon substrates with in-house-made nickel patterns were prepared by lift-off lithography. Each wafer contained multiple chips, which were composed of grids, parallel stripes, and arrays of microcircles in sizes ranging from 3 to 50 μm . The parallel Ni stripes were primarily used, but alignment with the other geometries was investigated as well. In addition to the bare Ni stripes used for alignment studies, grids were electrically contacted with SPI high-purity silver paint and plated with 1 μm of solder using a solution of Technic 820 HS 60/40 (60Sn40Pb) with the operating conditions described earlier. The silver paint was removed by sonicating the chip in acetone three times for 5 s in clean acetone each time followed by rinsing with isopropyl alcohol and Nanopure water.

The substrate, either the IAME or the in-house-made silicon chip, was placed between two small ceramic magnets with a field strength of 450 G, and 2 μL of the nanowire solution was dispensed on the substrate over the ferromagnetic pads and allowed to dry. The effect of external magnetic field on the magnetic alignment of nanostructures was determined by varying the external magnetic field. The external magnetic field was adjusted by controlling the gap distance between two ceramic magnets. The magnetic field was measured using a F. W. Bell model 9500 Gaussmeter. The substrate was examined visually for nanowire alignment under a Hirox KH-3000 digital optical microscope. Aligned nanowires on the IAME substrate were tested for electrical contact by measuring the I – V response with a EG&G PAR VMP2. The Abtech IAME samples were prepared for scanning electron microscope (SEM) imaging by sputtering a \sim 20 nm gold/palladium layer with an Emscope ES500. All SEM work was conducted on a Phillips XL30-FEG.

(12) Heremans, J. P.; Thrush, C. M.; Morelli, D. T.; Wu, M. C. *Phys. Rev. Lett.* **2002**, 88, 216801.

(13) Dresselhaus, M. S.; Lin, Y. M.; Rabin, O.; Jorio, A.; Souza Filho, A. G.; Pimenta, M. A.; Saito, R.; Samsonidze, G. G.; Dresselhaus, G. *Mater. Sci. Eng. C* **2003**, 23, 129.

(14) Martin, C. R. *Science* **1994**, 266, 1961.

(15) Martin, C. R. *Chem. Mater.* **1996**, 8, 1739.

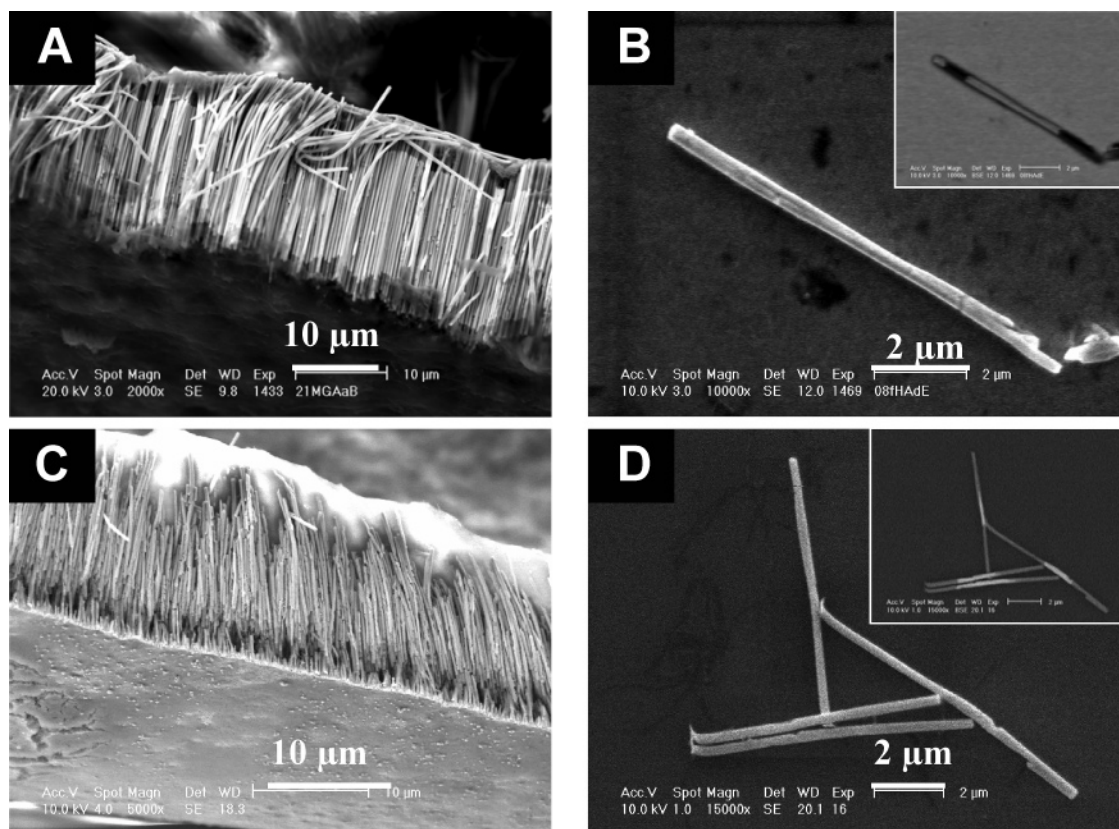


Figure 1. (A) Secondary electron (Se^-) SEM images of templated Ni/Au/Ni nanowires. (B) Se^- SEM image of a single Ni/Au/Ni nanowire and a backscattering electron (BSe^-) SEM image of the same nanowire (inset). (C) Se^- SEM image of templated Ni/Bi/Ni nanowires. (D) Se^- SEM image of a single Ni/Bi/Ni nanowire with the corresponding BSe^- image in the inset.

Results and Discussion

Figure 1 shows SEM images of Ni/Au/Ni and Ni/Bi/Ni nanowires in partially dissolved templates, capturing the high-density nature of template-directed nanowire fabrication. The different components of Ni/Au/Ni nanowires are shown to have a clear contrast between nickel and gold. Ni/Bi/Ni nanowires were not readily distinguishable with secondary electron (Se^-) SEM imaging (Figure 1C,D) but were differentiated using backscattering electron (BSe^-) SEM images (Figure 1D, inset). Segments of a single Ni/Au/Ni nanowire were also optically discerned with the Hirox KH-3000. Hirox images of Ni/Au/Ni nanowires show a color distinction between the two metals and were also used to verify the length of each component in the nanowires. The segments in the Ni/Bi/Ni nanowires did not show a sharp color contrast under the optical microscope but were visually characterized using only BSe^- SEM. The length of each segment in the multicomponent nanowires was varied to match the microbandwidth and pitch of the substrates they were aligned upon (Figure 2A,B).

Positioning of the nanowires on the substrate was dictated by the interactions between the ferromagnetic ends on the nanowire and the ferromagnetic contacts. The nanomagnets preferentially align adjacent to the Ni stripes as opposed to on top of them. Nanowires with nickel cap lengths equal to the ferromagnetic line width align between the lines as opposed to on top of them (Figure 2A). The nanowires with a total length equal to the separation distance and electrode width can be seen to align between the microbands in Figure

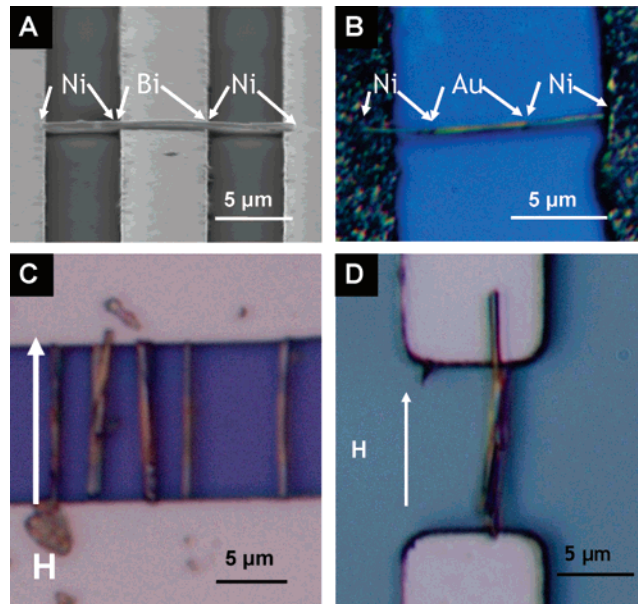


Figure 2. Alignment of (A) a single Ni/Bi/Ni nanowire on nickel lines and (B) an optical image of a single Ni/Au/Ni nanowire between solder-plated nickel electrodes. Magnetic alignment has also been demonstrated for (C) individually addressable with a single aligned Ni/Au/Ni nanowire and (D) high-density arrays achieved with multiple alignments of a dilute suspension.

2B. In this case the Ni ends of the nanowires are still adjacent to the microbands. Increasing the length of the midsection or the Ni ends on the nanowire will cause one Ni end to remain adjacent to the microelectrode with the other end aligned on top of a Ni stripe. The larger of the two nickel ends is usually positioned adjacent to the ferromagnetic pad

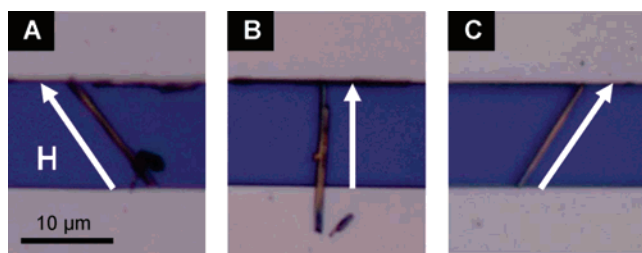


Figure 3. Optical images of magnetically aligned Ni/Au/Ni nanowires at (A) 45°, (B) 90°, and (C) 135° with respect to the ferromagnetic lines.

when the Ni ends have unequal lengths, with the smaller end on top of a parallel Ni electrodes (Figure 2D). In all instances the nanowire alignment maximizes the length of the Ni ends adjacent to or between the ferromagnetic pads, which is in agreement with magnetic trapping of nanowires.⁷ As the magnetic field travels between the two magnets the path of least resistance will restrict the field to the ferromagnetic electrodes in the *z*-direction, reducing the magnetic interactions with the nanowire and the top of the electrodes. As a result the electrodes behave as micromagnets with high magnetic fields emanating from the electrode edges for preferential alignment of the nanowires in plane and adjacent to the electrode edge. Therefore, by manipulating the electrode geometry to have a large perpendicular edge, such as interdigitated microbands, or a small perpendicular edge, such as centered fingers, magnetic alignment can be coordinated for array applications or individually addressable nanowires (Figure 2C).

High-density alignment of nanowires was achieved by sequential alignments with a dilute nanowire suspension in a fixed magnetic field and direction (Figure 2D), allowing the solution to dry before subsequent trials. The high-density arrays were produced with this technique and show particular potential for high-density interconnects without registration. This alignment platform can also give rise to more complex structures by allowing rotation of the substrate orientation with respect to the magnetic field. The magnetic field controls the nanowire directionality, achieving angles from 45° to 135° with respect to the electrodes as demonstrated in Figure 3A–C. A complete range of directions can be attained by lithographically patterning the electrodes perpendicular to one another and rotating the magnetic field appropriately. The full flexibility of the sequential alignment technique is demonstrated in Figure 4A and B, applying perpendicular fields that allow subsequent alignment without disrupting previously positioned nanowires. This feature, a quick and facile technique for precision control over directionality without disturbing previous efforts, is important for complex devices which will require a hierarchy of nanowire networks.

In addition to more complicated structures, the sequential alignment technique plays an important role in preventing chaining events. At higher concentrations the magnetic interactions between the nickel caps of separate nanowires leads to end-to-end alignment of nanowires, which can be seen to interfere with the placement in Figure 5A. This phenomenon occurs naturally when a magnetic field is imposed on the solution in the absence of a ferromagnetic pattern to direct assembly. Chaining is a function of separation length and has been previously modeled assuming

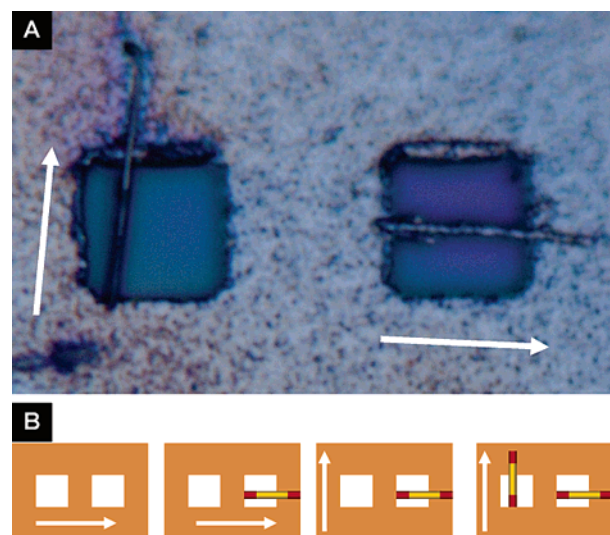


Figure 4. (A) Positioning of nanowires perpendicular to one another by sequential alignments without the loss of initial alignment efforts. (B) Schematic of the four-step processes.

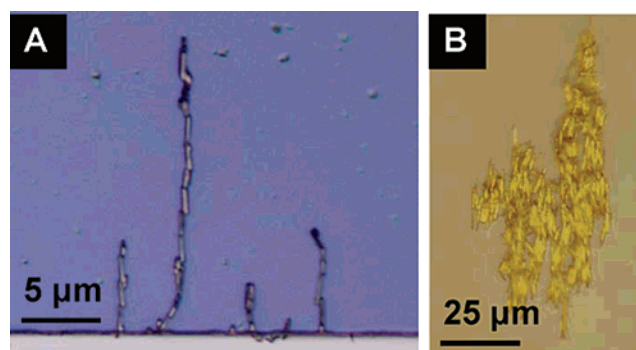


Figure 5. (A) At high concentrations directionality is maintained but placement of nanowires on the substrate is disrupted due to chaining interactions of the nickel caps. (B) At excess concentrations aggregation can occur in which directionality is lost.

viscous drag and magnetic dipole–dipole interactions as dominant forces.¹⁶ On a substrate with a ferromagnetic design strong magnetic forces between electrode edges and nanowire caps dominate magnetic dipole–dipole interaction between the nanowires, minimizing chaining, which can then be controlled by nanowire concentration and magnetic field strength. The upper limit of nanowire chaining concentrations is met with aggregation in which general directionality is kept but mass aggregates of nanowires are formed (Figure 5B). This occurs at excessive concentrations on the order of 10^{10} nanowires/mL or after settling when the nanowires are too entangled to be separated by sonicating.

Figure 6 shows the effect of external magnetic field on the alignment of Ni/Au/Ni segmented nanowires with dimensions of $3/4/3\ \mu\text{m}$. The concentration of segmented Ni/Au/Ni nanowires was 2.93×10^7 nanowires/mL, and the gap between patterns was $10\ \mu\text{m}$. The nanowires aligned parallel ($\pm 20^\circ$) to the imposed magnetic field of 450 Oe at a 100% success rate for straight Ni/Au/Ni nanowires. However, a field strength of 200 Oe was sufficient to achieve total alignment. Below this field strength the percent alignment of nanowires parallel to the applied magnetic field

(16) Tanase, M.; Bauer, L. A.; Hultgren, A.; Silevitch, D. M.; Sun, L.; Reich, D. H.; Searson, P. C.; Meyer, G. J. *Nano Lett.* **2001**, *1*, 155.

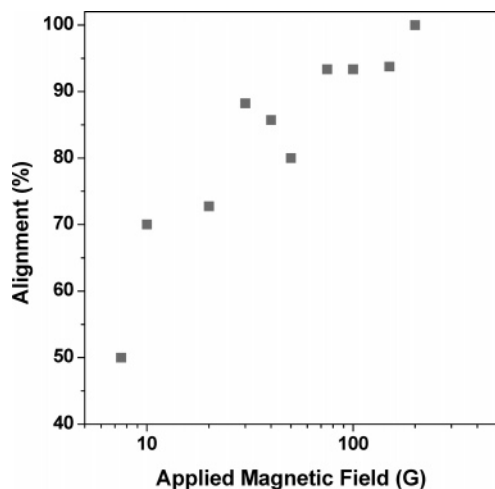


Figure 6. Alignment percent of nanowires vs. applied magnetic field strength.

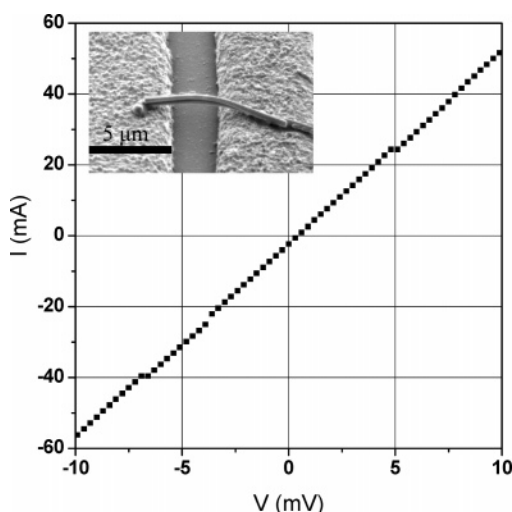


Figure 7. Current–voltage response from Ni/Au/Ni nanowires (inset) bridging two electrodes.

($\pm 20^\circ$) is shown to have a logarithmic dependence on magnetic field strength, with a 70% success rate at only 10 Oe.

The current–voltage (I – V) response for two nanowires aligned perpendicular to ferromagnetic pads (Figure 7) was

measured using an Abtech AIME plated with nickel followed by solder. The aligned nanowire was heated to 350 °C for 5 min to allow for reflow of the solder film to establish electrical contact. The nanowires were orientated in a manner to allow the gold midsection to bridge the microelectrodes. The resistance for the two nanowires was 175 Ω at 300 K for a resistivity of 2.2 m Ω /cm. This is one order of magnitude greater than the resistivity of bulk gold and may be attributed to the native oxide layer that forms on the solder electrodes.

Conclusion

Magnetic alignment with ferromagnetic caps has been demonstrated to achieve directionality with high success for straight and independent nanowires regardless of substrate orientation. Chaining, which was shown to interfere with nanowire placement, was controlled to a large extent by strong magnetic interactions between nanowires and the ferromagnetic substrate and then by proper dilutions, which determine the nanowire separation distance. The subsequent alignment technique was demonstrated to have potential for assembly of complex networks without disruption of initial alignments. The magnetic interactions between the nanowires and the ferromagnetic pads were shown to direct the placement of the nanowires on the substrate with the Ni caps aligning adjacent and in plane with the pads rather than on top of them. The nanowires were consequently observed to align between the microbands as opposed to bridging two separate microbands. The applicability of this assembly method lies in the nanowire synthesis technique, which can facilitate a variety of functional materials for the midsection for use in numerous devices. The versatility of this approach is owed to the high controllability achieved by magnetic field strength and substrate architecture, having potential for aligning both high-density interconnects without registration and individually addressable nanowires.

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