

## Electric-field assisted assembly and alignment of metallic nanowires

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This letter describes an electric-field assisted assembly technique used to position individual nanowires suspended in a dielectric medium between two electrodes defined lithographically on a SiO<sub>2</sub> substrate. During the assembly process, the forces that induce alignment are a result of nanowire polarization in the applied alternating electric field. This alignment approach has facilitated rapid electrical characterization of 350- and 70-nm-diameter Au nanowires, which had room-temperature resistivities of approximately 2.9 and  $4.5 \times 10^{-6} \Omega \text{ cm}$ . © 2000 American Institute of Physics. [S0003-6951(00)04735-5]

Recent interest in molecular-scale electronics as a means to fabricate extremely dense logic and memory circuits has led to the development of molecular diodes, switches, and negative differential resistance devices. Although devices based on donor-acceptor,<sup>1,2</sup> rotaxane,<sup>3</sup> and nitroaromatic molecules<sup>4</sup> may provide the necessary electronic building blocks, a molecular-scale interconnect technology is needed to fully utilize their extremely small dimensions. Present photolithographic techniques grow exponentially more expensive with decreasing feature size, and may never reach the dimensions required for this new technology. Based on these limitations, it has been suggested that future device integration may be based on alternative approaches that rely on assembly of nanometer-scale colloidal particles such as isotropic and anisotropic metallic particles<sup>5,6</sup> and carbon nanotubes.<sup>7</sup> Therefore, research has focused on developing new chemical and electric-field assisted assembly techniques to control the placement of these particles with the precision required to form well-ordered logic and memory circuits.

Following the pioneering work of Pohl,<sup>8,9</sup> nonuniform electric fields have been used to manipulate dielectric particles that are suspended in liquid media. While considerable effort has been devoted to separating biological particles,<sup>10</sup> dielectrophoresis has also been used recently to orient colloidal dispersions of nanometer-scale rod-shaped gold particles in an electro-optical cell<sup>11</sup> and to align carbon nanotubes between biased electrodes on a glass substrate.<sup>12</sup> In the second application, the nanotubes aligned randomly along the electrode edge with their length oriented in the direction of the electric field. In this letter, we describe an alternative approach that utilizes nonuniform alternating electric fields to precisely align metallic nanowires from a colloidal suspension between two lithographically defined metal pads. This alignment technique has permitted rapid electrical characterization of Au nanowires ranging from 70 to 350 nm in diameter.

The nanowires used in this work were fabricated using a process described by Martin *et al.*<sup>13</sup> where Au metal is elec-

trodeposited into a nanoporous alumina membrane. These metal replicas are then released into solution by dissolving the alumina membrane in an aqueous base and resuspending them in isopropyl alcohol (IPA), which served as the transport medium during the assembly process. Figure 1 shows an optical microscope image of 8  $\mu\text{m}$  long, 350-nm-diameter Au nanowires dispersed randomly from solution onto a silicon substrate.

Electric-field assisted assembly of the nanowires was studied using electrically isolated electrodes shown as a top view and cross section in Fig. 2(a). The metal electrodes consisted of an interdigitated finger pattern defined by metal liftoff of 50 nm Ti/150 nm Au on a silicon dioxide (SiO<sub>2</sub>) substrate, where the finger width and separation was 3 and 5  $\mu\text{m}$ . The electrodes were protected with 500 nm of silicon nitride (Si<sub>3</sub>N<sub>4</sub>) deposited by plasma enhanced chemical vapor deposition (PECVD) to prevent shorting of the electrodes by the metallic nanowires during the assembly process. As shown in Fig. 2(a), a 30- $\mu\text{m}$ -wide stripe of Si<sub>3</sub>N<sub>4</sub> immediately above the interdigitated fingers was thinned from 500 to 100 nm to increase the field strength in these areas relative to those covered by the thicker Si<sub>3</sub>N<sub>4</sub>.

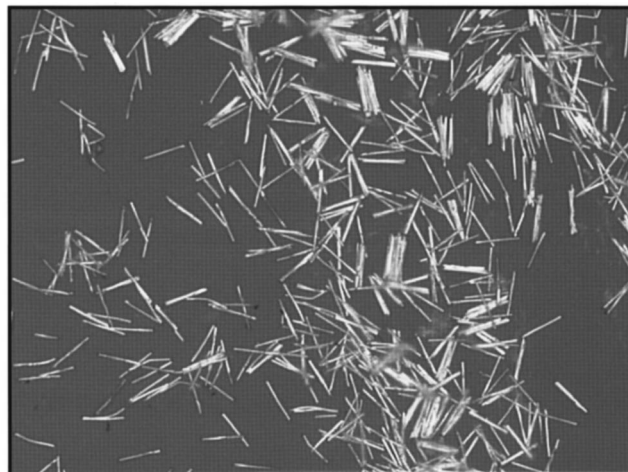


FIG. 1. Optical microscope image of electroplated 8  $\mu\text{m}$  long, 350-nm-diameter Au nanowires dispersed randomly onto a glass substrate.

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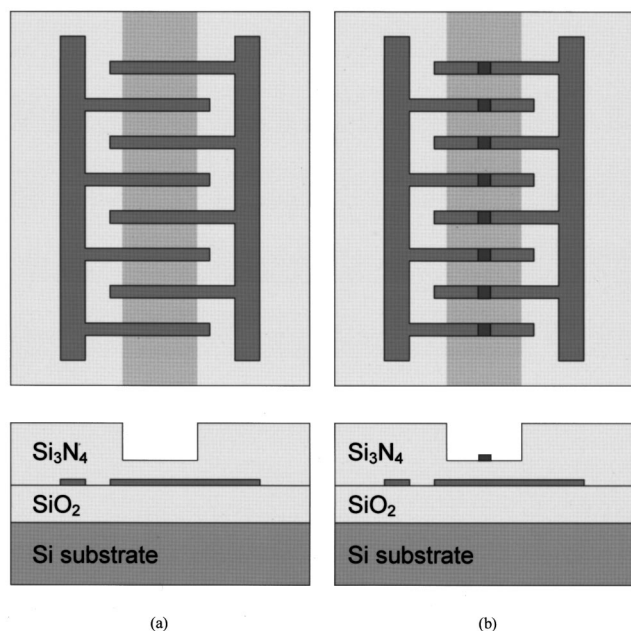


FIG. 2. Top- and cross-sectional views of the electrode structures used in the field assisted assembly experiments. (a) The  $3\text{-}\mu\text{m}$ -wide Ti/Au electrode fingers are spaced  $5\text{ }\mu\text{m}$  apart. The  $\text{Si}_3\text{N}_4$  is thinned over the fingers to enhance the electric field in that region. (b) The same electrode structure with  $4\times 4\text{ }\mu\text{m}^2$  top electrodes added to improve the alignment precision.

Assembly experiments were conducted by dispensing a dilute suspension of nanowires onto samples biased with alternating electrode voltages ranging from 5 to  $70\text{ V}_{\text{rms}}$ , which corresponds to electric field strengths of  $1.0\times 10^4\text{--}1.4\times 10^5\text{ V/cm}$ . An optical microscope image of  $5\text{ }\mu\text{m}$  long,  $200\text{-nm}$ -diameter Au nanowires that were aligned by applying a voltage of  $30\text{ V}_{\text{rms}}$  at a frequency of  $1\text{ kHz}$  to the left relative to the right grounded electrode is shown in Fig. 3(a). This demonstrates that the nanowires align perpendicular to the direction of the interdigitated electrode fingers in the high field regions covered with thin  $\text{Si}_3\text{N}_4$ . Although alignment is achieved, the nanowires are distributed randomly along the electrode fingers. Alignment was observed for electrode voltages exceeding  $25\text{ V}_{\text{rms}}$ , with

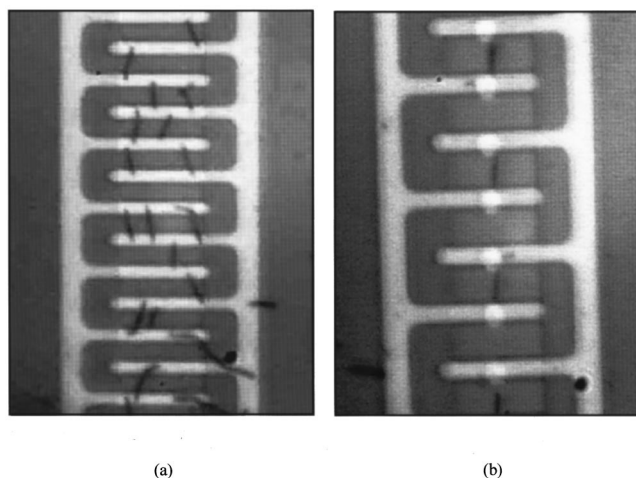


FIG. 3. Optical microscope image of  $5\text{ }\mu\text{m}$  long,  $200\text{-nm}$ -diameter Au nanowires aligned by applying a (a)  $30\text{ V}$ ,  $1\text{ kHz}$  voltage to the structure without upper field electrodes, and (b)  $20\text{ V}$ ,  $1\text{ kHz}$  voltage to the structure with upper field electrodes.

the length of time required for the nanowires to align decreasing from 9 to 5 s as the bias was increased from 25 to  $70\text{ V}_{\text{rms}}$ . Nanowires with diameters as small as  $35\text{ nm}$  aligned under similar conditions, suggesting that this technique may also be applied to align conductive carbon nanotubes.

This experiment indicates that alignment of the nanowires between the electrode fingers is due to forces that direct the nanowires toward regions of high field strength. The metallic nanowires polarize readily in the alternating electric field due to charge separation at the surface of the nanowire. Because the nanowires are more polarizable than the dielectric medium, they will experience a dielectrophoretic force that produces net movement in the direction of increasing field strength,<sup>8,9</sup> which occurs at the periphery of the electrode fingers. As the nanowires approach the electrodes with spacing approximately equal to the length of the nanowires, the electric field strength between the electrodes and nanowire tips increases proportionally to the inverse of the distance from the electrodes.<sup>14</sup> It is this large near-field force that results in alignment of the nanowires between two electrode fingers.

The random placement of nanowires within the thin  $\text{Si}_3\text{N}_4$  region can be accounted for by considering the variation of the electric field strength as a function of position along the electrode finger during the assembly process. Prior to assembly, the electric field strength at each point along the electrically isolated electrode finger is identical, making it equally probable that a nanowire will align anywhere on the electrode. After a nanowire aligns, the local electric field strength is reduced, which prevents additional nanowires from aligning in close proximity on the same and adjacent electrodes. Because the reduction in field strength is limited to a  $2\text{ }\mu\text{m}$  region surrounding the nanowires,<sup>14</sup> alignment of subsequent nanowires will continue in a random fashion until the nanowires are depleted from the solution.

The strength of the forces exerted on the nanowire are related to voltage and time dependencies of the alignment. At a constant frequency, the dielectrophoretic force that results in long range movement of the nanowire toward the electrodes is proportional to electric field strength. For this sample, the force exerted on the nanowires for voltages below  $25\text{ V}_{\text{rms}}$  was not sufficiently strong to cause alignment. As the electrode voltage was increased, the force on the nanowires increased, resulting in improved alignment and reduced alignment times.

To achieve alignment at fixed locations along the electrode fingers,  $4\times 4\text{ }\mu\text{m}^2$  metal electrodes were deposited on top of the thin  $\text{Si}_3\text{N}_4$  layer at the center of the electrode fingers as shown in the top view and cross section of Fig. 2(b). Capacitive coupling between the lower and upper electrodes results in an electric field strength that is much higher at the periphery of the top electrodes than in the surrounding areas along the lower electrode fingers.<sup>14</sup> Figure 3(b) shows an optical microscope image of  $5\text{ }\mu\text{m}$  long,  $200\text{-nm}$ -diameter Au nanowires that were aligned by applying a voltage of  $20\text{ V}_{\text{rms}}$  at a frequency of  $1\text{ kHz}$  to the lower electrodes. Under these conditions, the nanowires align to bridge alternating pairs of adjacent upper electrodes. For electrode voltages exceeding  $25\text{ V}_{\text{rms}}$ , additional nanowires begin to align

randomly along the electrode fingers as observed previously for the sample that did not contain electrically isolated top electrodes.

The additional degree of alignment obtained at low electrode voltages is due to the large electric field that is localized between adjacent top electrodes and the force that this field induces on the nanowires. When a nanowire bridges adjacent top electrodes, the electric field between them is eliminated, while the field between these and neighboring electrodes is reduced by a factor of two. The modified electric field distribution accounts for the observed tendency of single nanowires to align between alternating pairs of top electrodes.

The frequency dependence of nanowire alignment was studied by fixing the voltage between the bottom electrodes at 20 V<sub>rms</sub> and varying the frequency from 20 Hz to 20 kHz. Little field-induced movement of the nanowires was observed for frequencies below 200 Hz. As the frequency was increased to 1 kHz, the nanowires began to bridge the top electrodes. The alignment time decreased for frequencies greater than 1 kHz, with the fastest alignment of less than 1 s occurring at the highest frequency of 20 kHz.

The reduction in alignment time with increasing frequency suggests that at low frequencies, the polarization of the dielectric medium surrounding the nanowires also plays a role in the alignment process. At low frequencies, the polar molecules in the dielectric medium shield the charge separation on the nanowire leading to relatively low alignment forces.<sup>15</sup> As the frequency increases, the polar molecules are not able to reorient in the rapidly varying electric field due to their long relaxation times.<sup>15</sup> This results in greater net polarization of the nanowire tips and stronger alignment forces.

The electrical properties of 350-nm Au nanowires were investigated using an electrode pattern designed to allow integration of large-area pads for mechanical probing. Low-resistance electrical contacts were made to the tips of the aligned nanowires by metal liftoff of 10 nm Ti/500 nm Au that was deposited using thermal evaporation. Room temperature current–voltage (*I*–*V*) characteristics of the Au nanowires that were aligned and processed simultaneously were measured as a function of probe pad spacing using a four-point probe technique. The *I*–*V* characteristics of these nanowires were linear for current densities that were as high as  $3 \times 10^7$  A/cm<sup>2</sup>. The sum of the nanowire and contact resistance was determined from the slope of the *I*–*V* characteristics and plotted versus probe pad spacing in Fig. 4. From these data, the resistivity of the 350-nm-diameter Au nanowires was established from the product of the slope times the cross-sectional area of the nanowire and found to be  $\sim 2.9 \times 10^{-6}$  Ω cm, which is similar to that for bulk Au. Using this procedure, a room-temperature resistivity of  $\sim 4.5 \times 10^{-6}$  Ω cm was determined for 70-nm-diameter Au nanowires. Structural and temperature dependent electrical measurements are being performed to determine if the increase in nanowire resistivity with decreasing diameter is due to increased grain boundary scattering or surface scattering.

In conclusion, electric-field assisted assembly has been used to position individual Au nanowires from colloidal suspensions onto lithographically defined metal pads. The voltage and frequency dependence of the electric field assembly

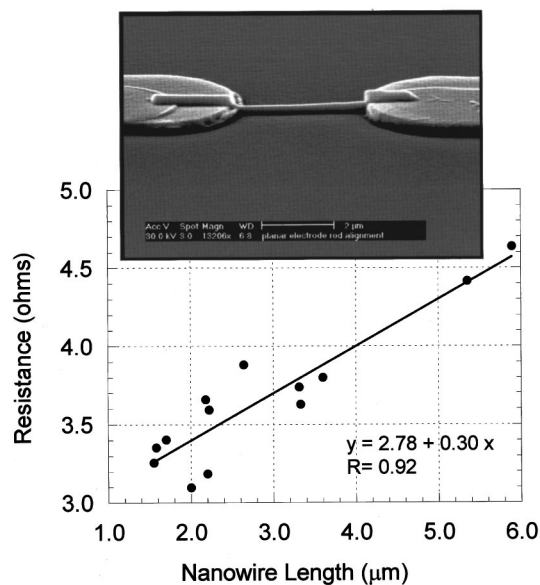


FIG. 4. Resistance vs nanowire length of 350-nm-diameter Au nanowires measured at room temperature. A resistivity of  $\sim 2.9 \times 10^{-6}$  Ω cm was determined from the product of the slope times the cross-sectional area of the nanowire. A scanning electron microscope image of a nanowire with top evaporated probe pads is shown as an inset.

process indicates that the alignment forces result from polarization of the nanowires in the alternating electric field. This technique has facilitated electrical characterization of Au nanowires by permitting integration of large-area probe pads. The room-temperature resistivity of the Au nanowires was found to increase from  $2.9$  to  $4.5 \times 10^{-6}$  Ω cm as the nanowire diameter was reduced from 350 to 70 nm. This research is currently being extended to investigate multimetal (Au–Pt–Au) nanowires where molecules with various device functions (e.g., diode, NDR, insulator) or terminal functionality (e.g., hydrophobic, electrostatic, DNA) are integrated onto a single nanowire using orthogonal self assembly.

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- <sup>1</sup>A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **29**, 277 (1974).
- <sup>2</sup>R. M. Metzger and C. A. Panetta, *J. Mol. Electron.* **5**, 1 (1989).
- <sup>3</sup>C. P. Collier, E. W. Wong, M. Belohradský, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, and J. R. Heath, *Science* **285**, 391 (1999).
- <sup>4</sup>J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, *Science* **286**, 1550 (1999).
- <sup>5</sup>V. P. Roychowdhury, D. B. Janes, and S. Bandyopadhyay, *Proc. IEEE* **85**, 574 (1997).
- <sup>6</sup>R. Service, *Science* **286**, 2442 (1999).
- <sup>7</sup>T. Hertel, R. Martel, and P. Avouris, *J. Phys. Chem. B* **102**, 910 (1998).
- <sup>8</sup>H. A. Pohl, *J. Appl. Phys.* **22**, 869 (1951).
- <sup>9</sup>H. A. Pohl, *Dielectrophoresis* (Cambridge University Press, London, 1978).
- <sup>10</sup>N. G. Green and H. Morgan, *J. Phys. D* **30**, L41 (1997).
- <sup>11</sup>B. M. I. van der Zande, G. J. M. Koper, and H. N. W. Lekkerkerker, *J. Phys. Chem. B* **103**, 5754 (1999).
- <sup>12</sup>J. S. Yamamoto, S. Akita, and Y. Nakayama, *J. Phys. D* **31**, L34 (1998).
- <sup>13</sup>B. R. Martin, D. J. Dermody, B. D. Reiss, M. Fang, L. A. Lyon, M. J. Natan, and T. E. Mallouk, *Adv. Mater.* **12**, 1021 (1999).
- <sup>14</sup>Field simulations performed using Maxwell 3-D, Ansoft Corp. (1999).
- <sup>15</sup>J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum, New York, 1970).