Microchannel Networks for Nanowire Patterning

Benjamin Messer, Jae Hee Song, and Peidong Yang*

*Department of Chemistry
University of California
Berkeley, California 94720*

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One-dimensional (1D) nanostructures, such as nanowires, nanotubes, and molecular wires are currently being investigated in great detail for their unique electronic and mechanical properties and their potential implementation as devices.[1−4] Integration of the nanotubes and nanowires into useful devices requires placing them in specific positions with desired configurations reproducibly.[1,4] This, however, remains to be a major challenge in the field. We describe a strategy for aligning and patterning conductive $[Mo_3Se_3^-]_\infty$ nanowires on substrates using microchannel networks.[5] This strategy relies on the solvent evaporation induced self-assembly of $[Mo_3Se_3^-]_\infty$ infinite chains within the microchannels. Aligned $[Mo_3Se_3^-]_\infty$ wires[6,7] as thin as several nanometers can be readily patterned using micrometer-sized channels. Multilevel cross-bar junction configurations and nano-to-macroscale connections were also demonstrated. Optical microscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) studies, and electrical measurements show that these wires are highly oriented, crystalline, and conductive.

The current process in constructing and measuring nanotube or other nanowire devices has been mainly involved the deposition on prefabricated electrodes in hope of getting tubes/wires at the right place and configuration.[1] Atomic force microscope (AFM) has also been used to push or deposit nanotubes into desired configurations.[8,9] Unfortunately, these device fabrication methods have the intrinsic limitations of being highly serendipitous or time-consuming. We wish to develop simple and parallel methods for this purpose using soft lithography. Soft lithography has been extensively used to create microstructures with lateral dimensions of 30 nm to 500 μm.[5] The patterned materials include metals, polymers, colloids, proteins,[10] and ceramics.[5,11] Generally, the patterned feature size reflects the actual dimension of the surface features on the micromolds. Here we show $[Mo_3Se_3^-]_\infty$ molecular wires can be patterned on a nanometer scale using micromolds having micrometer-sized channel network.

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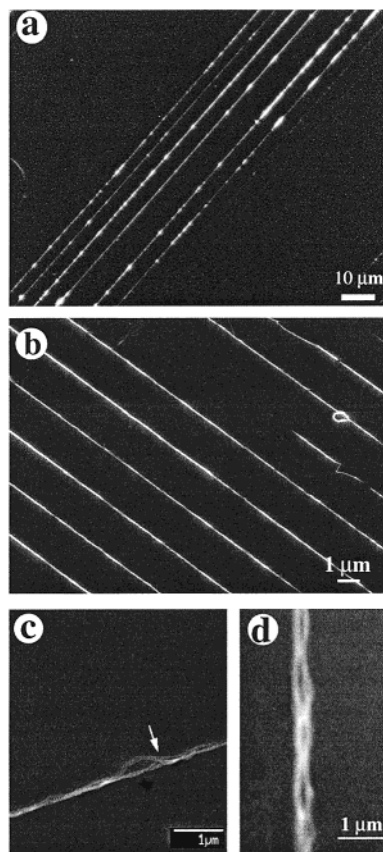

Figure 1. (a) Cross-polarized optical image of nanowire patterns on glass substrate. (b−d) FESEM images of wire arrays on silicon substrate. Arrow in c indicates the thinner wires are pulling together to form a thicker bundle.

$[Mo_3Se_3^-]_\infty$ molecular wires, 6 Å in diameter, are infinite chains of polycondensed Mo_6Se_8 polyhedra.[7] They have been experimentally determined to be highly conductive with a resistivity of $10^{-2}−10^{-4}$ Ω·cm at room temperature.[6,12] Individual $[Mo_3Se_3^-]_\infty$ molecular wires can be obtained as a solution ($10^{-4}−10^{-6}$ M) by dissolving single crystals of $LiMo_3Se_3$ in the polar solvent dimethyl sulfoxide or *N*-methylformamide.[7] Microchannel networks were formed between a poly(dimethylsiloxane) (PDMS) micromold and a silicon/glass substrate. The microchannels have variable height of 1−4 μm, width of 1−10 μm, and length of 5−10 mm. A droplet ($\sim$0.1−10 μL) of the wire solution was placed at the open end of the microchannels, and the channels were filled within minutes via capillary action. The solution-filled microchannel network was placed in a vacuum to evaporate the solvent.

We found that molecular wires tend to form nanowire bundles and align along the corners of the microchannels upon solvent evaporation and PDMS micromold removal, leaving an otherwise clean contact area. Cross-polarized optical microscopy studies indicate the wires are continuous up to several millimeters and are well aligned (Figure 1a). FESEM studies (Figure 1b−d) show the width of nanowires varies from 10 to 200 nm, which is largely determined by the molecular wire solution concentration and the microchannel volume. This feature size is significantly smaller than the microchannel size. Each nanowire generally consists of several thinner wires with diameter of $\sim$10 nm or less (Figure 1c). Double helix formation between these nanowires was

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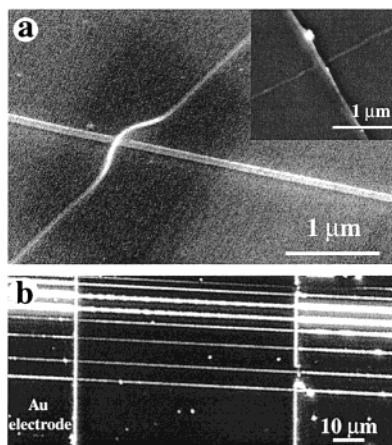
Figure 2. (a) FESEM image of a nanowire cross-junction. The sample is tilted during imaging. A cross-junction made of thinner wires is shown in inset. (b) Dark field optical image of wire arrays bridging two Au electrodes.

Figure 3. Schematic illustration for receding of liquid front within a microchannel, which eventually confines the nanowires in two corners.

frequently observed (Figure 1d). By scaling down the solution concentration and microchannel volume, we are able to further decrease the feature size to $1-3$ nm, which is close to the diameter of individual molecular wires. X-ray diffraction and TEM studies indicate these nanowires consist of highly crystalline $[Mo_3Se_3^-]_\infty$ units.[13]

After patterning the first layer of nanowires, the process can be repeated to deposit multilayer nanowire devices and complex networks. By rotating the micromold 90° during the second application, we are able to fabricate arrays of nanowire junctions in a well-controlled and reproducible fashion. A network of $[Mo_3Se_3^-]_\infty$ nanowires in a cross-bar configuration can be obtained. Figure 2a shows such a cross-junction between two nanowires with diameters of ~40 and 60 nm. When the size of the nanowires is smaller than 30 nm, no visible bending contour is observed as in Figure 2a. Instead, junctions with conformal contact are formed as seen for two wires with diameters of 20 and 30 nm in the Figure 2a inset. Excellent electrical connection for these junctions is also reflected by the small junction resistance.[14]

Significantly, it is further possible to pattern the nanowires on top of prefabricated devices. Figure 2b shows dark field optical microscope image of nanowires patterned on two lithographically fabricated 100 nm thick Au electrodes. Four-probe measurements on these patterned nanowires yield a resistivity of $\sim 5 \times 10^{-3}$ $\Omega \cdot$cm at room temperature.[15] These results demonstrate that the soft PDMS micromolds can be locally deformed and form conformal contact with both the substrate and protruded Au electrodes, which effectively confines the molecular wires within the microchannel and prevents them from leaking into the contact area or neighboring channels. This capability of direct patterning nanowires on prefabricated devices suggests that our process is capable of being integrated with current nano- and micro-fabrication technology and bridging the nanoscale or even molecular world with the macroscopic world.

The fact that the nanowires are self-organized only along the corners of the microchannel can be rationalized considering the process of the solvent-evaporation induced molecular wire self-assembly within a microchannel network. Upon solvent evaporation, the meniscus of the liquid front recedes into the two corners of the channels (Figure 3). The solution becomes concentrated, and $[Mo_3Se_3^-]_\infty$ chains self-organize into bundles through inter-molecular forces (electrostatic interaction between charged $[Mo_3Se_3^-]_\infty$ wires and counter cation Li) and align along the channel edge.

In summary, we have explored the self-assembly behaviors of molecular wires within a microchannel network and demonstrated nanowire alignment, patterning and cross-junction formation with a parallel approach. The $[Mo_3Se_3^-]_\infty$ molecular wires used in this study are highly conductive and have been found to exhibit Luttinger liquid behavior at low temperature;[6] thus, the current process may have direct implications for making nanoscale and molecular-scale electronic devices.[1,2,4] In addition, we expect this process can be readily extended to other systems including conducting polymers such as polythiophene[16] as well as func-tionalized nanotubes and nanowires.[17−19]

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(13) Exposing the nanowire pattern in air for several hours could cause the oxidation and decomposition of nanowires. However, this problem can be partially alleviated by using surfactant capped hydrophobic $[Mo_3Se_3^-]_\infty$ molecular wires (Messer, B.; Song, J. H.; Huang, M.; Wu, Y.; Kim, F.; Yang, P. *Adv. Mater.* In press).

(14) Junction resistance as low as several kΩ was measured using a two-terminal configuration (B. Messer, P. Yang, Unpublished results).

(15) Conductivity of the nanowires was measured on patterned nanowire arrays. Cross section of the nanowires was estimated on the basis of the FESEM and AFM studies.
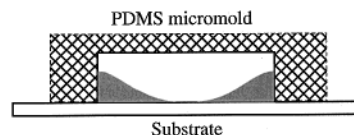
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