Patterning Techniques

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One-Step Patterning of Aligned Nanowire Arrays by Programmed Dip Coating**

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A fundamental step in the construction of nanowire devices is transfer of the nanowires from their stock to the substrate on top of which the device will be built. Therefore, alignment and controlled positioning of the nanowires are highly desirable, especially for the large-scale (e.g., on a 4-inch (10-cm) wafer) fabrication of parallel device arrays. Nanowires are normally synthesized and processed in solution.[1] Therefore, any subsequent patterning technique would inevitably involve a dewetting step. Herein we show that nanowires can be aligned and selectively deposited at the edge of a drying droplet as a result of evaporation-induced capillary flow. This contact-line deposition can be regulated with a simple dip-coating setup to create massive nanowire arrays with predefined spacing and tunable wire density. It also enables the selective placement of the nanowire arrays directly onto prefabricated electrode arrays, thus providing a facile and inexpensive method for the large-scale fabrication of nanowire-based devices.

Although it is possible to integrate nanowires directly into some specific device platforms during synthesis,[2,3] it is more common to make nanowire devices starting from a nanowire suspension with a subsequent patterning process. A few methods have been developed to make aligned nanowire arrays on a substrate, for example, Langmuir–Blodgett,[4,5] microfluidic,[6,7] electric-field-assisted assembly,[8,9] and optical trapping.[10] For all these patterning processes, nanowires are either made or processed within a solvent. As a result, any such technique would eventually encounter solvent evaporation before the final dried nanowire pattern is obtained. Therefore, it should be of great interest and technological importance to explore the full extent of the dewetting process for assembling nanostructures.[11,12] Herein we report our observation of contact-line deposition and alignment of nanowires in an evaporating droplet. These findings are then employed and tailored for large-scale patterning of nanowires by dip coating.

Ring-shaped stains are often observed when a droplet of colloidal solution (e.g., coffee) is dried. An outward capillary flow of the solvent is necessary to compensate the loss of solvent at the perimeter, which also carries the dispersed materials to the solvent–substrate contact line[13] and leads to highly selective deposition along the perimeter of the droplet.[14] We have discovered that in a drying droplet containing nanowires, this capillary flow also sorts the nanowires along the radial direction (Figure 1 a), especially when the solvent is volatile (e.g., methylene chloride or chloroform). Figure 1 b shows a typical ring-shaped stain obtained from drying a droplet of nanowire dispersion in methylene

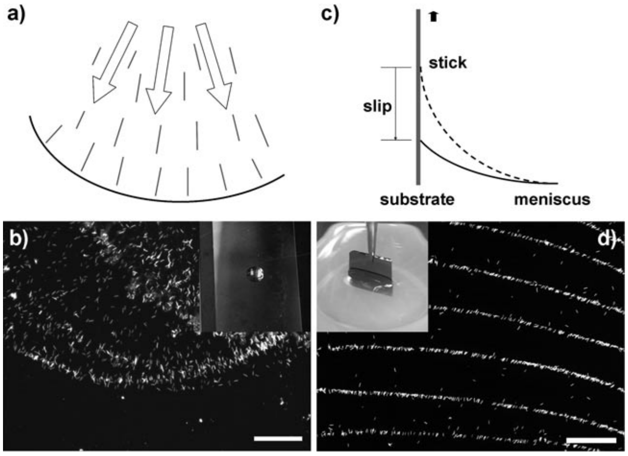

Figure 1. Evaporation-induced deposition and alignment of nanowires at the solvent–substrate contact line. a) Schematic illustration of the deposition of aligned nanowires at the edge of a drying droplet on a horizontal substrate. The pinning of the contact line (black line) induces an outwards capillary flow (block arrows) to compensate for the loss of solvent at the perimeter by evaporation. This flow aligns the nanowires (gray lines) and carries them towards the contact line, which leads to the final ring-shaped stain. b) Optical microscopy image showing a "coffee-ring stain" pattern of Ag nanowires formed upon drying a 10-μL droplet of a dispersion in methylene chloride onto a hydrophilic glass slide (inset). c) Schematic illustration showing the discontinuous stick–slip motion of the solvent meniscus on a vertical substrate during dip coating with pulling speed about 0.5 mm min^{-1} (see inset in (d)). d) Optical microscopy image showing well-spaced, parallel arrays of aligned nanowires collected through deposition of nanowires at each sticking event. The nanowires are aligned in the pulling/dewetting direction, except at the edges where the meniscus was bent (right-hand side). The solvent-phobic nature of the substrate helps to limit nanowire deposition in between the arrays. Scale bars: 100 μm.

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chloride. Methylene chloride beads up on the glass slide (Figure 1 b, inset) and is pinned during evaporation. A few seconds later, a ring shaped pattern is obtained. Although the overall ring pattern is rather disordered owing to the uncontrolled evaporation speed and dewetting direction, a radially aligned nanowire array is deposited along the initial edge of the droplet (Figure 1 b). This result suggests the possibility of making more-ordered nanowire patterns if the contact-line deposition and dewetting can be regulated.

The shape of the contact line is determined by how the solvent and the substrate intersect. Ideally, a droplet on a horizontal substrate forms a ring and a vertical substrate dipped into the solvent should form a line (Figure 1 d, inset). Therefore, a line of vertically aligned nanowires should be obtained when they deposit along the contact line in this vertical geometry. To form a relatively sharp meniscus, a solvent-phobic substrate is preferred. Methylene chloride was used as the solvent because of its low boiling point (leading to fast evaporation and fast deposition), and silicon wafers were treated with oxygen plasma to make their surfaces completely hydrophilic, which limit their wettability towards the hydrophobic methylene chloride. In a typical dip-coating experiment, the substrate is immersed into a dispersion of nanowires in methylene chloride and withdrawn continuously to collect the nanowires. There are a few unique features of dip coating for contact-line deposition. First, the contact line is straight, except at the edges, where the meniscus is bent. Second, the substrate is raised in a controllable manner; therefore, the dewetting speed and direction is uniform across the entire contact line. Third, the pinned meniscus is dragged by the rising substrate and becomes stretched. Eventually it will break and recede to a new pinning site on the substrate (Figure 1 c). This discontinuous stick–slip motion leads to well-spaced, parallel nanowire arrays (Figure 1 d). Each array is deposited during a "stick" event and the spacing results from the "slip" of the meniscus. The nanowires are aligned along the dewetting direction, which is the vertical pulling direction except at the edge.

Evidently, for a nanowire dispersion of given concentration, the density of the nanowire array depends on how long the meniscus sticks. The spacing between the neighboring arrays is determined by the slipping distance (Figure 1 c). If the stick and slip events can be controlled independently, the nanowire patterns can then be arbitrarily tuned. By using a programmable mechanical dipper, the sticking time and the slipping distance can be programmed accordingly by choosing appropriate pulling speeds and stopping durations. A high pulling speed (e.g., 100 $\mu m\,s^{-1}$) is used in this case to avoid nanowire deposition in between the desired deposition lines. In this way, arrays of aligned nanowires can be readily "printed" on a substrate in a line-by-line fashion over a large area. Figure 2 a shows a silicon wafer after a programmed dip coating. Uniform line patterns can be seen covering the entire 4-inch wafer. The patterns are composed of repeated sets of parallel lines (Figure 2 b, magnified view). Four lines can be seen in each set (Figure 2 c–f) from top to bottom, corresponding to the reduced sticking time of 20, 15, 10, and 5 seconds, respectively. The longer the sticking time, the denser the arrays (Figure 2 g). With even longer sticking time, multilayers of nanowires start to form. Although the length and the orientation of the nanowires vary, their upper ends start from the same straight line where the meniscus was.

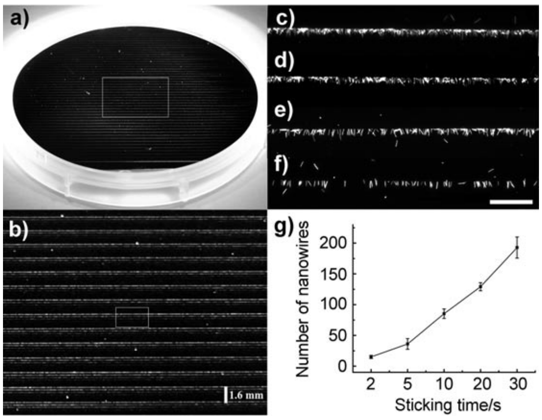

Figure 2. Large-scale patterning of nanowire arrays by programmed stick–slip motion. a) Nanowire arrays with tunable density and arbitrary spacing over an entire 4-inch wafer "printed" by programmed dip coating. b) A magnified view of (a) showing that each repeating set of nanowires is composed of four equally spaced arrays with decreased nanowire density as shown in the optical microscopy images (c–f, corresponding to sticking times of 20, 15, 10, and 5 s, respectively; Scale bar: 50 μm). g) Nanowire density as function of sticking time. The nanowire density is counted from images taken in areas the same size as those shown in (c–f) from a separate experiment.

Both the substrate and the deposited nanowires contribute to the pinning of the contact line. When the meniscus is stretched by the rising substrate, depinning occurs when the surface tension exceeds the pinning force (i.e. the substrate cannot "grab" the meniscus any more) or reaches its maximal value (i.e. the meniscus can not be stretched further). This suggests that there is a lower limit of the distance between neighboring arrays. Indeed, we have encountered this minimal array spacing in our experiments. Figure S1 (see the Supporting Information) shows the nanowire arrays obtained with the array distances programmed to be 30, 20, and 5 μm, respectively. However, the actual distances obtained are about 30, 20, and 20 μm, respectively. When the programmed slipping distance is too small, several slipping events are needed to break the meniscus, leading to a much larger array separation than expected. Above this minimal spacing, there is evidently no upper limit in programming the distance between the arrays.

One straightforward way to make nanowire devices is to use photolithography to define patterns of electrical contacts such as those shown in Figure 3 a. In this way, wafer-scale nanowire resistors or transistors can be obtained in high yield. However, nanowires of many materials may not be compatible with photolithography steps. Therefore, a more flexible method is to utilize the programming capability of our dip-coating technique to place nanowire arrays selectively on the prefabricated electrodes. We carried out a proof-of-concept experiment. Figure 3 a and b shows a 6 × 6 array of four-probe electrodes before and after nanowire deposition, respectively. After dip coating, 6 lines of nanowire arrays can be seen deposited precisely on the electrodes. This deposition was

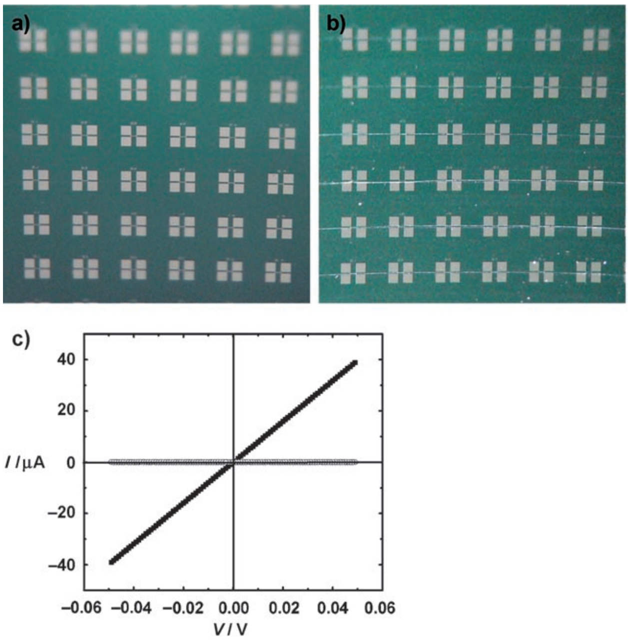

Figure 3. A proof-of-concept demonstration of selective positioning and addressing of nanowire arrays on prefabricated electrodes by programmed dip coating. a) Optical microscopy image showing a 6×6 array of Cr/Pt electrodes on a SiO_2/Si wafer. b) After selective nanowire deposition, the 6 parallel nanowire arrays can be seen lying across the electrodes. The center-to-center distance between the neighboring electrodes is 1 mm. c) *I–V* measurement of a thus-made device showing the successful addressing of the nanowire arrays. ○: before; ■: after nanowire deposition.

achieved by aligning the contact line with the electrodes by using a set of optical lens. Again, the nanowire arrays are bent at the edges owing to the shape of the meniscus. However, this would not be a problem in large-scale fabrication (see Figure 2). In potential industrial-scale fabrication, the registry (see Figure S2 in the Supporting Information) could be guaranteed by using a photoalignment setup similar to that used in standard microfabrication processes. The optical microscopy image in Figure S2 b shows a nanowire array lying across a sample electrode set. Its *I–V* curve (Figure 3 c) demonstrates that the nanowire arrays have been successfully addressed by the electrodes.

The facile dip-coating method reported herein can assemble nanowires directly from a dispersion, thus significantly decreasing the processing steps required for making nanowire devices. Deegan et al. note that contact-line deposition is a very general phenomenon with only three requirements:[13–15] that the solvent has a nonzero contact angle (partially wettable), that the contact line can be pinned, and that the solvent can evaporate. These requirements are met with most commonly used solvents and substrates. We recommend a simple "droplet test" to determine whether a solvent is suitable for making nanowire arrays by dip coating (see Figure S3 in the Supporting Information). If the solvent droplet completely wets the substrate, it will not be able to form a well-defined, pinned contact line. For example, when a droplet of ethanol containing nanowires is placed on an oxygen-plasma-treated glass slide, it readily spreads out to form a thin film. The nanowires deposited completely over the area and their orientation was random. Random nanowire deposition was also obtained by dip coating. In contrast, solvents that bead on the substrate (Figure 1 b, inset) are generally suitable for making nanowire arrays.

In conclusion, we have developed a facile, scalable patterning technique to make arrays of aligned nanowires over large areas. By programming the stick–slip motion of the solvent contact line during dip coating, selective positioning of nanowire arrays with controllable density and spacing can be achieved. Among the patterning methods developed so far, dip coating is the most versatile. For example, Langmuir–Blodgett assembly of nanowires is equally scalable but requires the transfer of nanowires from a volatile organic solvent to a water surface. Therefore, the nanowires need to be compatible with both the organic solvent and water, which limits the nanowire materials that can be assembled by this technique. In contrast, the method we have described starts directly from a nanowire dispersion—the most common form of nanowire stocks. Another significant advantage is that the material consumption of dip coating is minimal. The nanowire dispersion can be readily reused for future deposition by adding more solvent to compensate for evaporation. The stick–slip patterning technique demonstrates the potential of controlled dewetting for patterning nanostructures.

Experimental Section

As Ag nanowires can be made in relatively high yields and uniformity, they are a very good model system for studying the patterning process.[5,16] The Ag nanowires were synthesized by a modified polyol process using $AgNO_3$ as the metal precursor, ethylene glycol as the reducing agent, and polyvinylpyrrolidone (PVP, $M_w = 55000$) as the dispersing agent. The yield and uniformity of the Ag nanowires were improved by density-gradient separation in ethylene glycol. The nanowires were purified, and then the solvent for dispersing the nanowires was changed to ethanol by centrifugation and redispersion. Finally the nanowire/ethanol dispersion was diluted to about 4–5 % with methylene chloride or chloroform. The nanowires used for this study have an average diameter of around 60 nm and a length greater than 10 µm. Other nanowires that have been successfully patterned include Si[17,18] and ZnO[19] nanowires.

To create partially wettable substrates by methylene chloride or chloroform, cleaned glass or silicon wafers were treated with oxygen plasma. The contact angles of methylene chloride and chloroform (5-µL droplets) on these substrates are around 26.5 and 15.5°, respectively. The wafers were dipped into the nanowire dispersion and withdrawn by using a mechanical motor with programmable pulling speeds (KDS210 syringe pump).

Digital images were taken with a Panasonic FZ20 digital camera under strong illumination. Optical microscopy images were taken in reflected, dark-field mode on a Nikon Optiphot microscope with a Roper Scientific CoolSnap Photometrics camera.

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