High-Resolution Direct Patterning of Gold Nanoparticles by the Microfluidic Molding Process

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A novel microfluidic molding process was used to form microscale features of gold nanoparticles on polyimide, glass, and silicon substrates. This technique uses permeation pumping to pattern and concentrate a nanoparticle ink inside microfluidic channels created in a porous polymer template in contact with a substrate. The nanoparticle ink is self-concentrated in the microchannels, resulting in dense, close-packed nanoparticle features. The method allows for better control over the structure of printed features at a resolution that is comparable to inkjet printing, and is purely additive with no residual layers or etching required. The process uses low temperatures and pressures and takes place in an ambient environment. After patterning, the gold nanoparticles were sintered into continuous and conductive gold traces.

Introduction

Precise patterning of nanoparticles is critical for a number of different applications, including low temperature electrode deposition,1 optical coatings and photonics,2,3 biosensors,4 catalysts,5 and MEMS applications.6 Several methods are available for patterning nanoparticles, the most popular of which is inkjet printing.7,8 Inkjet printing is attractive due to its simplicity, high throughput, and low material loss. However, patterning with inkjet printing is limited to a resolution possible by adding complexity to the substrate prior to printing.9 Electrohydrodynamic printing has been proposed to increase the resolution beyond the limits of inkjet printing, achieving a line resolution as small as 700 nm.10 Both inkjet and electrohydrodynamic printing, however, do not allow precise control over the structure of the printed lines, often resulting in lines with scalloped edges or nonuniform width, and offer only limited control over the height of the printed features.11,12 Recently, nanoimprint lithography has been proposed as a means of decreasing the feature size of patterned nanoparticles while allowing more precise control over the structure of the printed lines.13–15 In this fabrication method, the nanoparticle inks are patterned by pressing with an elastomer mold and the particles dried into their final shape. While the resolution of this method is improved over inkjet printing, there exists a residual layer on the substrate that must be etched away after patterning, and control over the height of features can be frustrated by capillary interactions between the mold and the drying ink, especially along the length of longer features. As an alternative to nanoimprint lithography, nanoparticle self-assembly methods based on capillary filling of photoresist templates have been proposed.16 While these can produce high aspect ratio features with smooth edges, the photoresist must be etched away in subsequent processing steps without removing the particles themselves, which can be technically challenging or nonfeasible in some instances. Here, we demonstrate a nanoparticle patterning method based on permeation pumping17–19 that concentrates nanoparticles in selective regions inside a vapor-permeable polymer mold. This method is completely additive (no etching required) and allows for control over the structure of the patterned lines, including smooth edges and control over the height of the patterned features. The resolution obtained is comparable to that obtained with inkjet printing. Long, continuous lines of gold nanoparticles were patterned over large areas. After patterning, the gold nanoparticles were sintered into conductive traces. This method is compatible with the idea of ambient environment roll-to-roll processing and works on a wide variety of substrates with a wide variety of nanoparticle inks.

Experimental Method

Gold nanoparticles encapsulated in a hexanethiol monolayer were synthesized using a two-phase reduction method following the method of Brust et al. and subsequently encapsulated in a hexanethiol self-assembled monolayer and dispersed in an

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alpha-terpineol solvent. The specific nanoparticle synthesis method used here has been documented in previous publications. The ink was diluted to 3.5 wt % in alpha-terpineol. A master template was made using standard photolithography using SU8—2007 resist on a silicon wafer. The master template consisted of lines that are 15 μm in width, 9.5 μm in height, and 1 cm in length. PDMS (Sylgard 184 - Dow) prepolymer and cross-linker were mixed in a 10:1 ratio, poured over the silicon wafer and cured. After curing, the PDMS elastomer template was removed and cleaned by sonication in ethanol for 10 min and then dried. The resulting PDMS template was porous to solvent vapors. The nanoparticles were patterned on a substrate using the microfluidic molding self-assembly method, which is illustrated schematically in Figure 1. A polyimide, glass, or silicon substrate was placed in a custom-built press, coated with fresh solvent free of nanoparticles and positioned below the patterned PDMS elastomer template. The polymer template was placed on the top side of the press and the fresh solvent patterned by pressing. The pressure used was just enough to completely conform the elastomer mold to the substrate, and did not exceed 14 kPa. This filled the template channels completely with fluid, and excluded the fluid from all other areas. Any residual fluid trapped between the mold and substrate in areas without patterned features was simply evaporated through the porous polymer template in subsequent steps and, since this fluid contained no nanoparticles, left no residual layer. Next, the nanoparticle ink was added to designated filling ports at the ends of the channels. The temperature of the system was raised to 75 °C to evaporate the solvent through the porous polymer mold. The evaporating fluid drew the nanoparticle ink into the microfluidic channels, which replaced the fluid lost through evaporation. As the ink was brought into the channel, the solvent of the nanoparticle ink began to evaporate, self-concentrating the nanoparticles in the fluid. Eventually, the nanoparticle ink became so concentrated that the ink could no longer flow in the microchannel. At this point, the remaining solvent evaporated and the nanoparticles in the slurry began to close-pack. Some volume reduction of the nanoparticle features occurred at this point, as will be discussed later, but cohesion of the liquid in the solvent ensured that the nanoparticles remained in continuous traces, and the volume reduction occurred uniformly only in directions perpendicular to free surfaces. When the ink was completely dried in the microchannel, the system was cooled and the polymer template removed.

Following the nanoparticle patterning, the nanoparticles were sintered by heating in an oven. The nanoparticles were placed in an oven and the temperature increased to 220 °C for 8 h. The elevated temperature allows for oxidation of the hexanethiol monolayer and sintering of the gold nanoparticles. The long bake time was necessary to ensure the maximum conductivity of the gold, allowing the diffusion of the oxidized thiols from the interior of the gold traces.

Theoretical Calculations

The patterning of the nanoparticles in the microfluidic channels can be separated into two distinct stages: filling and drying. In the filling stage, the nanoparticle ink is drawn into the channel and self-concentrated by the evaporating solvent. This continues until the nanoparticle ink saturates at some point in the channel. After this point, part of the channel is saturated with nanoparticles and sustains no additional fluid flow, and part continues to allow fluid flow and self-concentration of the nanoparticle ink. The channel continues to fill with nanoparticles until the entire length of the channel is saturated with particles, at which time the nanoparticle patterning is complete. Each of the two stages was modeled by considering a one-dimensional channel. This model is appropriate as long as the length of the channel is much longer than the width and height of the channel to ensure that lateral diffusion across the channel is much stronger than diffusion along the length of the channel, causing a nearly uniform concentration at any given cross section. The velocity in the channel is approximated as a slug flow, and an effective diffusivity used to account for the Taylor dispersion due to the shear-enhanced diffusion of nanoparticles across streamlines in the parabolic velocity distribution. This one-dimensional channel is open to a reservoir of nanoparticle ink at a constant concentration at one end, and closed at the other.

For the filling stage, the velocity of the fluid in the channel is found by assuming a constant rate of evaporation of the solvent through the porous walls of the polymer template. This mass flux due to evaporation is represented by a volume flow rate per unit of surface area of the porous polymer template, \( q' \). To a first approximation, \( q' \) is assumed constant. This approximation ignores the dependence of the evaporation rate on the nanoparticle concentration, which is valid for a sufficiently low concentration of the nanoparticle ink and not valid for areas with highly concentrated ink toward the end of the channel. Given that the velocity of the fluid at the closed end of the channel must be zero, the velocity as a function of length along the channel is

\[
v(x) = \frac{q' P_p}{A} (L_0 - x)
\]

where \( P_p \) is the part of the perimeter of the microchannel consisting of the porous polymer, \( A \) is the cross sectional area of the one-dimensional channel, and \( L_0 \) is the total length of the channel. The equation for the velocity shows a characteristic length scale equal to the length of the channel, and a characteristic time scale given by \( t_s = A/(q' P_p) \). The dimensional variables are

\[

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nondimensionalized based on these characteristic scales, resulting in an equation for the velocity given by

$$v(\tau) = \frac{L_0}{t_s} (1 - \tau)$$

(2)

where the quantities with bars above are nondimensional equivalents of the corresponding dimensional variable without the bar above. An equation for the nanoparticle concentration $\phi(x,t)$ can be found by considering the flux of nanoparticles by both advection and diffusion. In one dimension, the advective diffusion equation is

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial x} (\phi v) = \frac{\partial}{\partial x} \left( D \frac{\partial \phi}{\partial x} \right)$$

(3)

where $D(x)$ is the effective diffusivity of the nanoparticles in the one-dimensional system, and will be discussed in detail later. Equation 3 is nondimensionalized based on the constant concentration of the ink in the reservoir $\phi_0$ and the length and time scales given above, and eq 2 is inserted. This results in

$$\frac{\partial \bar{\phi}}{\partial \bar{t}} = \bar{\phi} + (\bar{\tau} - 1) \frac{\partial \bar{\phi}}{\partial \bar{x}} + \frac{D_1}{L_0^2} \frac{\partial^2 \bar{\phi}}{\partial \bar{x}^2} + \frac{t_s}{L_0^2} \frac{D}{\partial \bar{t}} \frac{\partial \bar{\phi}}{\partial \bar{x}}$$

(4)

At $\bar{\tau} = 0$, the nanoparticle ink concentration is equal to the concentration of the ink in the reservoir ($\phi = 1$), which is taken to be a constant. The nanoparticle flux is zero at the end of the microcapillary, at $\bar{x} = 1$. At $\bar{t} = 0$, there are no nanoparticles in the channel, so $\bar{\phi} = 0$.

The magnitude of the diffusivity of nanoparticles in solvent can be estimated using the Einstein-Stokes equation for diffusion of spherical particles through a liquid with low Reynolds number. This equation is given by

$$D' = \frac{k_B T}{6\pi \eta r}$$

(5)

where $\eta$ is the fluid viscosity, $r$ is the particle radius, $k_B$ is the Boltzmann constant, and $T$ is the temperature. However, the value of the diffusivity must be modified to include shear-enhanced diffusion caused by velocity gradients perpendicular to the direction of the flow. These velocity gradients enhance the diffusion of nanoparticles as compared to the slug flow assumed here. A correction factor is therefore used to account for this enhanced diffusion

$$D(x) = \frac{1}{48} \frac{[v(x)r_b]^2}{D'}$$

(6)

where $r_b$ is the hydraulic radius of the microchannel.

The partial differential equation for the nanoparticle concentration was solved numerically using an explicit Euler method. Additionally, in the case where diffusion is negligible throughout the channel, the last two terms in eq 4 are negligible and an analytical solution to the above partial differential equation exists. This solution is given by

$$\bar{\phi}(\bar{\tau}, \bar{t}) = \frac{1}{1 - \bar{\tau}} u(1 - \exp(-\bar{t} - \bar{\tau}))$$

(7)

function of time was found to closely follow the analytical solution without diffusion given in eq 10. Note that, after a long time, the effective length of the channel approaches zero, and the entire channel fills uniformly with nanoparticles.

Results

To characterize the filling process, optical images were taken using a Canon 5D Mark II camera with a Canon EF 100 mm f/2.8 macro lens with a working distance of 8 cm. Continuous video was taken of the filling process, and the video was subsequently split up into individual frames for analysis. Images were analyzed using Matlab (MathWorks) to convert the images to grayscale and subtract the background from the images. ImageJ was used to analyze the average intensity of the light in the images along the microchannels. The light intensity in the images is proportional to the nanoparticle concentration, with darker areas containing more nanoparticles. Since the location of the maximum light intensity is easily tracked and corresponds identically to the location of the maximum nanoparticle concentration, the location of the maximum light intensity was tracked and plotted as a function of time and compared to the analytical model (see Figure 3). The time scale of the filling process was found by minimizing the least squared error between the theory and data. For the experimental data here, the time scale was found to be approximately \( t_s = 31 \text{ s} \).

Once the unsintered gold nanoparticles were successfully patterned, images of the resulting patterns were obtained. An optical microscope (Olympus BH-2) was used to confirm that the pattern was transferred over the entire area of the die. The optical image of the result for the glass and polyimide substrates are shown in Figure 4.

A scanning electron microscope (LEO 1550, Zeiss) was used to show the fine details of the resulting pattern and measure the final dimensions of the resulting printed features (see Figure 5). The width of the printed lines, measured using an SEM, were \( 11 \mu m \). The height of the printed lines were measured by imaging with a \( 90^\circ \) tilt, which showed a uniform height of approximately \( 6.5 \mu m \) over the entire area (see Figure 6a). Additionally, the features did show some sag in the center, known in the literature as the rabbit-ear effect (see Figure 6b). The volume reduction and resulting rabbit-ear height profile was to be expected. At the end of the filling stage, the nanoparticle ink becomes so concentrated that it can no longer flow in the channel, yet additional volume reduction results from further solvent evaporation and possibly some oxidation and removal of thiol groups on the gold nanoparticles. The nanoparticles pack densely together, leaving a gap between the particles and the top of the mold. The presence of this gap causes capillary adhesion between the remaining liquid solvent and the solid mold to form the rabbit-ear profile in the final dry structure. However, this effect is small, as the height of the sag in the center of the features was limited to approximately 15% of the total height of the feature.

Figure 3. Position of the maximum concentration in the channel as a function of time.

Figure 4. Optical micrograph of a nanoparticle pattern on (a) glass and (b) polyimide.

Figure 5. SEM image of the top of a line of patterned gold nanoparticles on a polyimide substrate.

Figure 6. SEM image of (a) the side of a patterned line of nanoparticles and (b) a cut cross-section of the patterned particle line showing a slight rabbit-ear effect.
The gold nanoparticles were then sintered, and the resulting
gold traces imaged (see Figure 7). The average height of the
sintered gold particles was approximately 2.5 \( \mu \text{m} \). The feature
heights exhibited a small amount of waviness over short distances,
but the average height of the traces was constant over the entire
area. The profile of the sintered gold traces was significantly
different from that of the unsintered particles. The reflow of the
gold during sintering changed the shape profile from having
rabbit-ears to having a dome shape. After the reflow, the average
line width was around 16 \( \mu \text{m} \).

The gold nanoparticles were then sintered, and the resulting
gold lines were electrically characterized. The resistance of the lines as a function of distance was measured (see
Figure 8). The resulting measurements were linear over large
distances, showing that the conductivity and the cross-sectional
area of the sintered gold are constant over the entire printed area.
This result further proves that the initial nanoparticle patterns
were uniform over large areas. The cross-sectional area of the gold
wires was approximated using a circular segment with the average
height and width of the patterned lines. Using the measured
resistance per unit length and the calculated cross-sectional area
of the gold traces, the average resistivity of the lines was measured
to be 6.7 \( \times 10^{-7} \) \( \Omega \text{m} \). The gold lines are approximately 4\% of
the conductivity of bulk gold. This value is slightly lower than
other values reported in the literature for thermally annealed
gold nanoparticles, which may be caused by the larger height
of the printed features and the corresponding difficulty for the
oxidized hexanethiol monolayer to migrate out of the sintered
gold.1,13,15,22–24

Conclusions

The proposed method for patterning nanoparticles allows for
excellent control over the structure of the printed features,
including both line widths and heights. In contrast to other
nanoimprint-based patterning methods, this process is designed
to form uniform nanoparticle patterns over large areas and leave
no residual layer that must be etched away later. Additionally, the
nanoparticles can be patterned at low temperatures and pressures
in an ambient environment. The process can be done very quickly
and the method is compatible with a roll-to-roll processing
methodology. Finally, the proposed technology has the potential
to be scaled down to achieve higher resolution, while retaining
control over the structure of the printed features.

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