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Three-Dimensional and Multilayer Nanostructures Formed by Nanotransfer Printing

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ABSTRACT

This letter describes the use of nanotransfer printing (nTP) for forming three-dimensional (3D) structures with feature sizes between tens of nanometers and tens of microns over areas of several square millimeters. We demonstrate three different approaches–deep etching through printed hard masks, direct transfer of three-dimensional structures, and purely additive fabrication of multilayer stacks–for using nTP to fabricate a range of complex 3D nanostructures, including closed channels, suspended beams, and nanochannel stacks, that would be difficult or impossible to build with other methods.

Established methods for nanofabrication−scanning probe techniques, electron beam lithography, and deep ultraviolet projection mode photolithography−are exceptionally well suited for building two-dimensional (2D) structures on flat surfaces. Newer techniques based on molding,[1,2] printing,[3] and embossing[4] provide similar patterning capabilities with simple, low cost tools (i.e., molds, stamps, and presses) that avoid many limitations of conventional methods. More importantly, these new techniques can also generate certain types of three-dimensional (3D) structures (e.g., molded patterns with multiple levels of relief,[2,5] printed structures on nonplanar surfaces[5−7]) that can be useful for applications in photonics, microelectromechanical systems, and electronics. In this paper we show how a recently developed contact printing technique, which we refer to as nanotransfer printing (nTP),[8−11] can be used to build a range of complex 3D structures with feature sizes between tens of microns and tens of nanometers. Techniques similar to nanotransfer printing are being pursued independently by Schmid et al.[12] and Kim et al.[13] Here we describe the general approach for 3D nTP and illustrate its use for fabricating classes of nanostructures that would be difficult or impossible to generate with other methods.

The nTP technique uses high-resolution stamps coated with thin solid layers of 'inks'. Surface chemical bonding interactions between the substrate and the ink layer enable its efficient transfer from the stamp to the substrate by contact printing. The top frames of Figure 1a illustrate the nTP process for forming patterns of Au on GaAs substrates with a 1,8-octanedithiol monolayer to facilitate the transfer[10,11] from high-resolution poly(dimethylsiloxane) (PDMS) stamps. In the simplest approach to 3D, the two-dimensional patterns that result from the usual form of nTP serve as hard masks for deep etching of the underlying substrate, as shown in the bottom left frames of Figure 1a. Although it is possible to fabricate similar hard masks by multiple process steps using conventional techniques, nTP has unique capabilities that enable other routes to 3D. One of these relies on 3D conformal metal coatings instead of the 2D discontinuous layers on the raised and recessed regions of the stamp in the usual process. Figure 1b shows, as an example, a stamp with sloping sidewalls that lead to a continuous metal layer when gold is deposited onto the stamp surface. These 3D metal layers (which can also be thought of as nanostructured metal foils) can be transferred in a single step using the same nTP chemistries that work for 2D patterning. Furthermore, the purely additive nature of nTP allows these 2D and 3D printing steps to be performed many times to build up multilayer stacks. Figure 1b illustrates this approach, where cold welding[13,14] controls the transfer of the second printed Au layer to the first. By combining these procedures (deep

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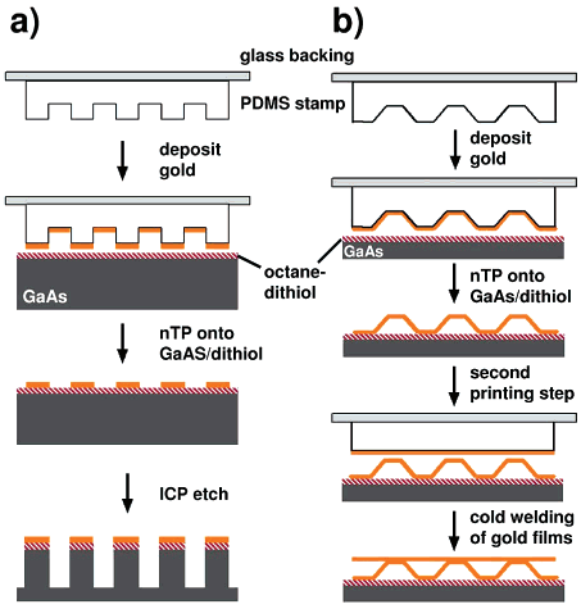

Figure 1. Schematic illustration of routes to three-dimensional structures by nanotransfer printing. Depending on the profile of the stamp, two-dimensional (a) or three-dimensional (b) Au films can be transferred onto the substrate (GaAs/octanedithiol). These structures can then serve as hard masks for deep etching or as substrates for additional printing steps, respectively.

etching, conformal ink and multilayer printing) it is possible to produce complex multilayer 3D nanostructures that would be difficult to fabricate using other means.

The following experimentally demonstrates these capabilities with the Au, 1,8-octanedithiol (Aldrich), and GaAs (orientation (110) or (100), semi-insulating or n-doped, Xtal Technologies Ltd.) system of Figure 1. The stamps consist of 50 μm thin layers of 'hard' PDMS (Gelest Inc.) on top of thick backings of 'soft' PDMS (Sylgard 184, Dow Corning Inc.)[15,16] formed by casting and curing against 'masters' with appropriate relief. Mounting these composite stamps onto glass slides before electron beam evaporation of Au (10 to 40 nm thick at 1 nm/s) allows them to be manipulated without introducing cracks that can arise from directly handling the stamps. Prior to printing, the GaAs wafers are cleaned and the native oxide layer removed by etching in ammonium hydroxide. Soaking for 12 h in a 10 mM ethanolic solution of octanedithiol generates densely packed dithiol monolayers on GaAs.[10,11,17] The raised regions on the stamp are pulled into conformal contact with the substrate by van der Waals forces, without the application of external pressure. Within seconds after this contact is established, the free thiol groups react with the Au on the stamp to form covalent bonds that are stronger than the adhesion of the Au to the PDMS. Removing the stamp from the substrate leaves the Au behind. Since the cohesion of the Au is also stronger than its adhesion to the PDMS, even those parts of a continuous Au film that are not in contact with the substrate effectively transfer (for some ranges of film thicknesses and relief geometries) to form free-standing structures, as illustrated in Figure 1b.

Figure 2a shows field emission scanning electron micrographs (SEMs) of Au lines (300 nm wide and ~20 nm thick)

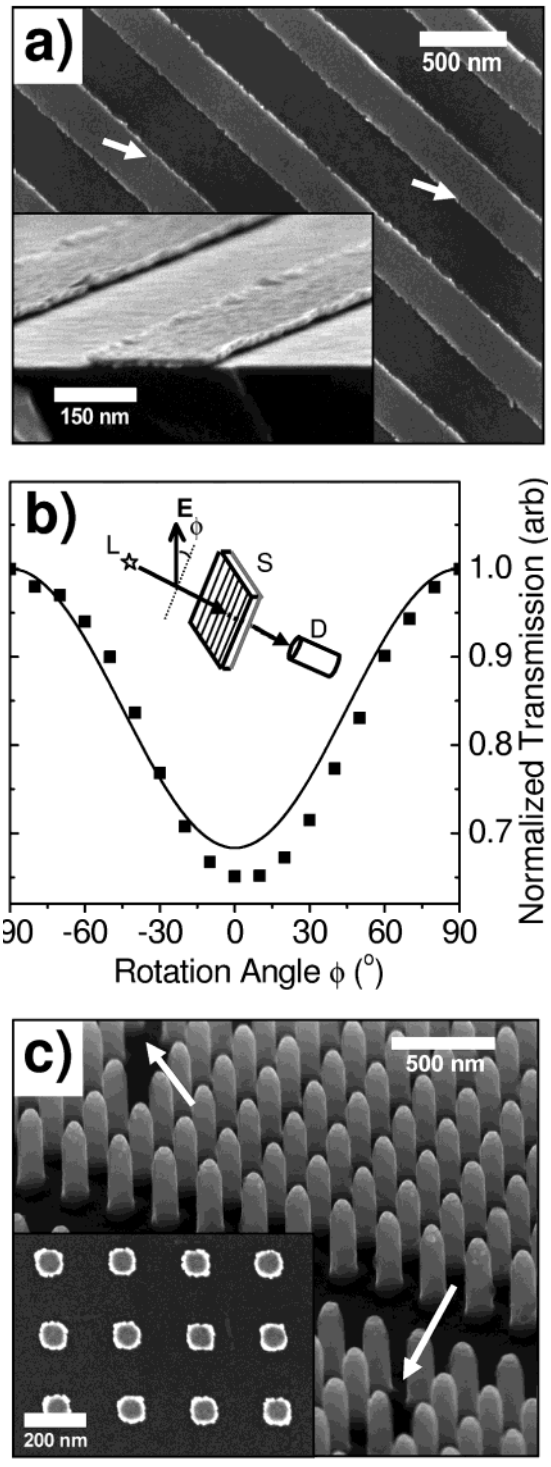

Figure 2. (a) SEM of Au lines (20 nm thick, 300 nm wide) produced by nTP. The arrows highlight nanocracks, which represent the most common type of defects in these structures. The inset shows a cross-sectional view. (b) Transmission of polarized infrared laser light (wavelength 1.55 μm) through a GaAs (110) sample with printed 300 nm wide Au lines (thickness 40 nm) as a function of rotation angle (squares: experimental data, solid line: RCWA simulation). (c) SEM image (tilted 60°) of ICP-etched GaAs posts formed by using nanotransfer printed dots of gold (10 nm thick, 100 nm diameter) as etch masks (note the remaining gold on top of the posts). The height and diameter of these posts are ~700 nm and ~120 nm, respectively. The inset shows a top view of the nanotransfer printed gold dots before etching. The arrows indicate areas where no dots were transferred.

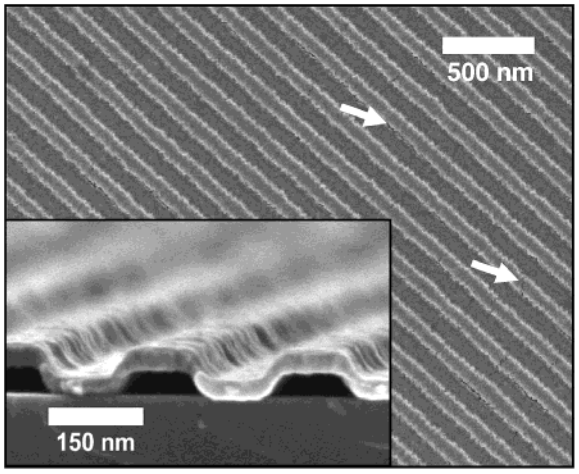

Figure 3. SEM of Au (25 nm thick) nanochannels (outer width 100 nm, outer height 80 nm) generated by nTP. The inset shows a cross-sectional view of the channels. The arrows highlight nanocracks, which are also present in this structure.

formed by nTP using a stamp with the geometry illustrated in Figure 1a. The inset of Figure 2a presents a cross-sectional view that shows slightly curved edges on the lines. This feature is due mainly to the slightly curved corners of etched relief in the SiO_2/Si master that was used for the stamps in this case.

These and the other structures described below exist over areas of several square millimeters, limited only by the size of the stamps. The film transfer is usually complete except for those areas of the stamp that cannot come into conformal contact with the substrate due to dust particles or rough edges of the stamp. The most common form of defect is nanocracking in the Au (highlighted by arrows in Figure 2a and Figure 3. The density and lengths of these cracks sensitively depend on the Au deposition conditions and the surface properties of the PDMS. Treating the PDMS with an ultrathin layer of Ti (~0.5 nm) or exposing its surface to a short oxygen plasma before coating with Au reduced the cracking significantly. High deposition rates avoid larger cracks owing to heating and expansion of the stamp during evaporation. These and other strategies for completely eliminating this type of defect will be described in detail in a separate paper.[18]

As a simple means to quantify this and other defects over large areas, we measured the transmission of linearly polarized infrared laser light (1.55 μm wavelength; beam diameter 250 μm) through an array of printed 300 nm Au lines (thickness 40 nm, periodicity 630 nm) similar to those illustrated in Figure 2a. The transmission as shown in Figure 2b (squares) is higher when the polarization is perpendicular to the lines, with a polarization contrast of 35% (extinction ratio 1.54). A simulation[19] based on rigorous coupled wave analysis (RCWA),[20] which includes the thickness, width and periodicity of the lines and optical properties of Au and GaAs, yields the curve shown in Figure 2b (solid line). The good agreement of the theoretical values with the experimental data attests to the high quality and large-scale uniformity of the structure made by nTP.

These printed 2D metal patterns can be used as hard masks to generate 3D structures by deep etching. Figure 2c shows

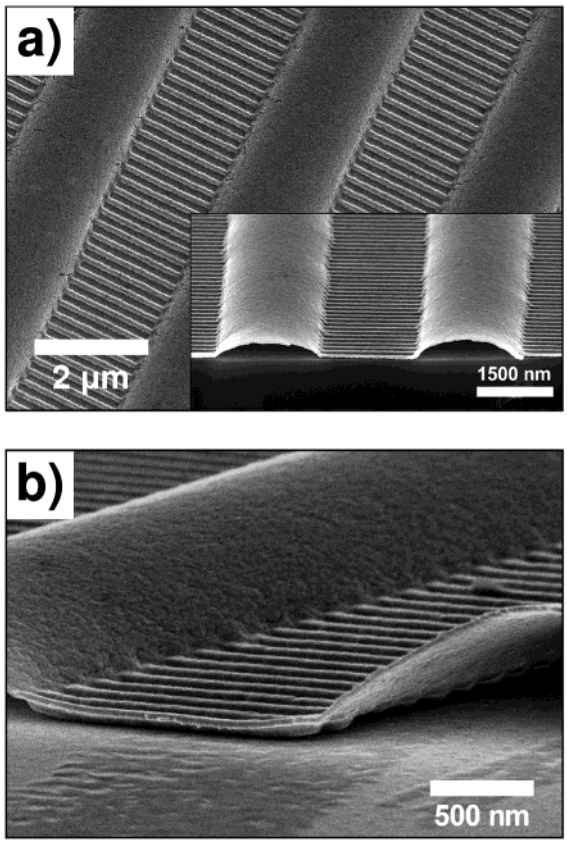

Figure 4. SEM images of continuously curved Au (20 nm thick) microchannels (width 2 μm, height 0.5 μm) connected by arrays of orthogonally aligned nanochannels (width 100 nm, height 80 nm). This structure was fabricated in a single step by nanotransfer printing. (a) Top and cross-sectional (inset) views; (b) angled view that illustrates the connection of the microchannels to the nanochannels.

tall posts formed by inductively coupled plasma etching (ICP; Surface Technology Systems etcher, 200 W ICP power, 50 W coil power, pressure 12 mTorr, 38 sccm chlorine, 12 sccm methane, 5 sccm argon; etching time 1.5 min) of the underlying GaAs (110) using 100 nm gold dots (thickness 10 nm; inset Figure 2c)) formed by nTP as etch masks. The posts are about 700 nm high and have a diameter of about 120 nm (note the remaining gold on top of the posts). Conventional methods can define such hard masks, too, but only through multiple processing steps.

Another route to 3D with nTP uses the transfer of conformal ink layers, as illustrated in Figure 1b. Figure 3 shows Au nanochannels generated with a stamp with tilted sidewalls. The outer height (80 nm) and width (100 nm) of the channels reflect the relief of the corresponding master (InP etched through a photoresist mask defined by laser interference lithography). The rough edges of the Au nanochannels are present in this master; they are faithfully reproduced by nTP. In this structure, cracks predominantly occur at the sides of the channels due to mechanical stress when the stamp is removed from the substrate.

This approach can also yield much more complex structures. To demonstrate some of the possibilities, we photolithographically patterned 2 μm wide lines of resist (Shipley

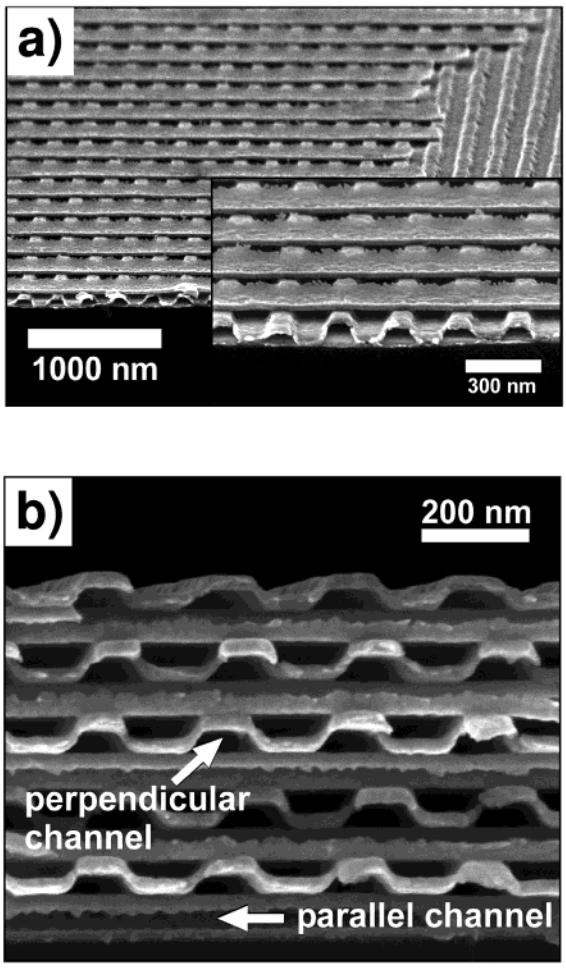

Figure 5. (a) SEM of printed Au (20 nm thick, 300 nm wide) lines on top of Au nanochannels. (b) SEM image of a cross section of a sample with 10 consecutively printed layers of 100 nm gold channels. For each step the stamps were rotated 90° with respect to the direction of the channels of the underlying layer. In both structures, the first layer adheres to the GaAs substrate through covalent bonds to the dithiol monolayer. Cold welding bonds the subsequent Au layers to each other.

1818, Microchem Inc.) perpendicular to the ~100 nm etched lines on the InP master that we used for the nanochannels. Reflowing the resist at 160 °C formed curved lines of resist with a height of 0.5 μm. nTP with stamps made from this master produced structures, such as the one shown in Figure 4, in a single printing step. Here, continuously curved Au microchannels (Au thickness 25 nm) connect to arrays of orthogonally aligned Au nanochannels. This structure incorporates a wide range of dimensions, relief heights, and profiles that would be very difficult to achieve with other techniques.

Performing 3D or 2D printing multiple times on a single substrate yields complex multilayer stacks. The 'soft' van der Waals contact of the PDMS stamps and the structural integrity of the printed layers are crucial for this process. Figure 5a shows lines of Au (300 nm wide, 20 nm thick) printed directly on top of printed nanochannel structures. Cold welding of the Au bonds the lines to the underlying channels. Between the tops of the channels, the lines are freely suspended. Figure 5b shows another example: a cross-sectional view of a multilayer lattice structure that was formed by consecutively printing 10 layers of nanochannels. For each step the stamps were rotated 90° with respect to the direction of the channels of the underlying layer. We did not observe any effects (i.e., structure collapse, poor transfer, etc.) that might limit such a structure to ten layers. Through additional printing steps, many more layers should be possible.

As demonstrated in this letter, nTP is capable of generating complex micro- and nanoscale three-dimensional metal structures on suitable substrates over large areas. The process is fast and simple and does not require pressure or elevated temperatures. The printed structures are mechanically robust to the 'soft' printing conditions of nTP with PDMS stamps, so they can serve as substrates for subsequent printing steps to generate multilayer assemblies. 3D nTP will be useful for a wide variety of devices, from electronic components that call for airbridges as circuit elements, to nanoelectromechanical systems that use suspended beam resonators, to nanofluidic networks that benefit from simply fabricated nanochannels, to photonic and plasmonic structures that use multilayer nanostructured lattices. These and other areas represent potential applications where nTP provides significant advantages in fabrication compared to conventional techniques.

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