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Parallel dip-pen nanolithography with arrays of individually addressable cantilevers

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In dip-pen nanolithography (DPN), nanoscale chemical patterns are created by directly transferring chemical molecules from the tip of an atomic force microscope probe to a surface. We report the development of a thermally actuated probe array for DPN applications. The array consists of ten thermal bimorph actuated probes, each 300 μm long, with a lateral spacing of 100 μm. The probes are actuated by passing dc current through a heater embedded in the probe base. The array is demonstrated by using it to simultaneously write ten different octadecanethiol patterns on a gold surface. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1644317]

Since the early development of scanning probe microscopy (SPM), many researchers have been interested in using such instruments to generate patterns on surfaces from microscopic to atomic scales. Most of the early techniques were high-resolution, single-probe, indirect forms of lithography, requiring the capture and placement of atoms on a surface or a monolayer resist to control the formation of nanoscale substrate features. As a result, these early SPM-based lithography approaches were too slow to be practical for most semiconductor and life science applications. Anodic oxidation methods, coupled with arrays of conducting probes, were a major step forward towards a parallel, direct-write methodology for nanoscale processing of semiconductor substrates.[1] However, anodic oxidation is limited to a narrow set of applications with regard to substrate and feature composition. In this regard, dip-pen nanolithography (DPN) is a significant departure from existing forms of scanning probe lithography in that it allows the direct deposition of most types of chemical or biological agents onto surfaces with nanoscale resolution and ultrahigh registration capabilities.[2] Since the patterning reagents are localized on the probe tip, one can envision ways of increasing throughput by using arrays of probes, each with the potential to deposit a different chemical ''ink.'' This is in contrast to micro- and nanocontact printing and stamping processes, in which registration and diffusion issues prohibit the precise loading of a large number of inks onto the stamp, or the precise alignment of a stamp with pre-existing surface structures. As a result, DPN is a powerful tool for making combinatorial libraries of nanostructures consisting of a diverse variety of materials, including oligonucleotides, proteins, catalysts, polymers, and solid-state materials.[3] However, a major roadblock to implementation remains. The throughput of DPN is low due to its serial deposition methodology. In this letter we report a major step towards increasing throughput with the development of a working parallel array of individually controllable cantilevers. The array has been demonstrated by using it to simultaneously generate ten different alkanethiol-based nanostructures at different locations on a surface.

To prepare an array with individually addressable cantilever probes, we considered several actuation approaches, including electrostatic and piezoelectric methods, before choosing thermal bimorph actuation. This method was chosen because (1) it can provide a large tip deflection or force in a robust, simple package and (2) the fabrication process is kept straightforward by avoiding difficult materials such as piezoelectric films. In this actuation mechanism, vertical tip motion results from the thermal strain mismatch in a heated, two-layer cantilever, as illustrated in Fig. 1. The probe array was fabricated through a combination of surface and bulk micromachining. First, a $\langle 100 \rangle$-oriented silicon wafer was oxidized, and the oxide was patterned into 8-μm-square silicon dioxide islands where each probe tip was to be located. The wafer was then anisotropically etched to form $\langle 111 \rangle$-defined silicon pyramids under each island. The tips were sharpened by using two rounds of thermal oxidation and oxide removal. Next, a 9300-Å-thick silicon nitride film was deposited by low-pressure chemical vapor deposition. This layer was patterned with tetrafluoromethane reactive ion

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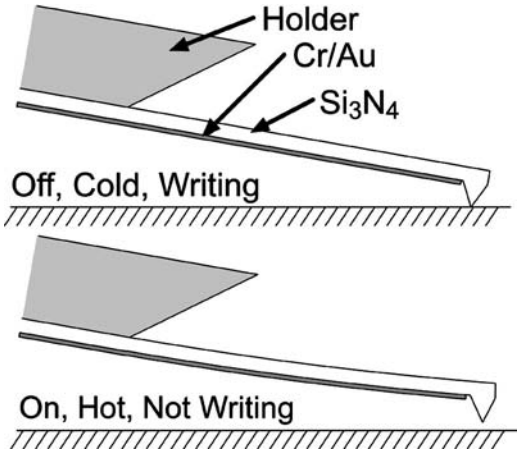

FIG. 1. The operating concept of a thermal bimorph actuated DPN probe. When heated with an embedded electrical heater, thermal mismatch strain between the two principal layers causes the probe to deflect away from the surface.

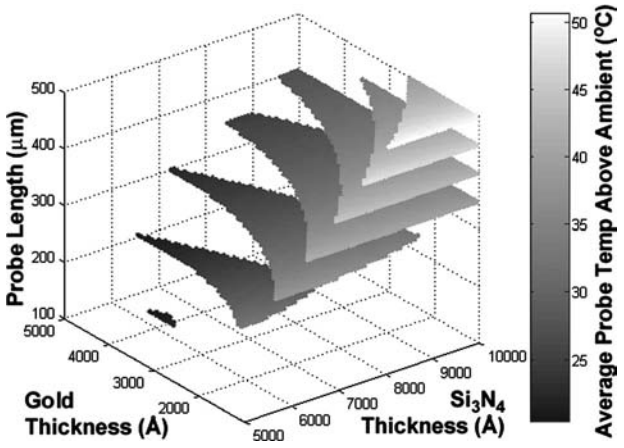

FIG. 3. Results of a 33 000 design feasibility study. Successful designs are plotted with respect to their dimensions. Shading is used to indicate the average temperature of each probe during operation.

etching to define the probe cantilevers and holder chips. Power leads, heaters, and actuators were created by thermally evaporating and patterning a 3600 Å gold thin film with a 250-Å-thick chromium adhesion layer on top of each cantilever. Finally, the probes were released from the substrate by undercutting them during a second anisotropic etch from the front side of the wafer. The resulting device is shown in Fig. 2.

By adding a separate actuator to each probe, adjacent probes can, in principle, generate different patterns while traveling the same overall path. Each of the ten probes in the array consists of two major compositional layers: gold [coefficient of thermal expansion (CTE) = 14.6 ppm/°C][4] and silicon nitride (CTE = 0.3 ppm/°C). Resistive heating causes the probe tip to move away from the substrate when deposition is not desired. The typical actuation current of 10 mA provides 2.1 mW of heating power to the probe and results in a tip displacement of 8 μm and an average probe temperature of 25 °C above ambient. Each probe is individually addressed by two wire leads, which are used for passing current through the resistive heater.

There are significant challenges to overcome when designing effective probe arrays for DPN. Several design parameters must be optimized, including the length, width, and thickness of the silicon nitride cantilevers and the geometries of the gold components that make up each actuator. The probe must provide enough lifting force to overcome surface adhesion and enough deflection to overcome array-to-surface misalignment. It must also remain soft enough to prevent surface scratching. Curvature resulting from intrinsic stress in the compositional layers must be minimized. Finally, all of these objectives must be achieved in a design that operates at low to moderate temperatures. To perform this optimization, a compact, analytical, thermomechanical probe model was created. The model is formulated for rapid evaluation[5] and forms the basis of a design-space evaluation algorithm. The algorithm iterates through a predefined set of potential layouts to identify acceptable designs.[5] In addition to the probe's heat transfer and mechanical characteristics, the algorithm accounts for tip–substrate mechanics, design issues related to the support hardware, and other user-defined limits. It evaluates and plots acceptable designs against the probe length and film thickness, as shown in Fig. 3.

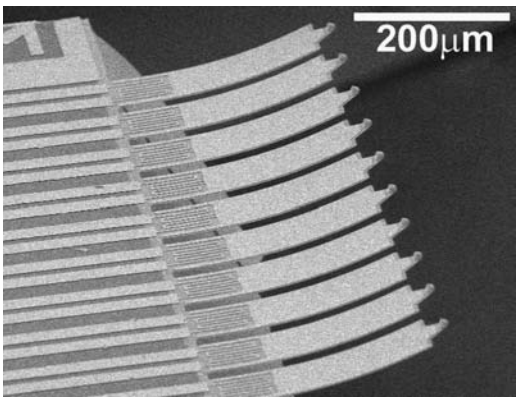

FIG. 2. An array of ten thermally actuated DPN probes showing the power lead and heater layout. Each probe is 300 μm long, 80 μm wide, and 1.3 μm thick.

The device in Fig. 2 is the final optimized design based on the optimization algorithm. The serpentine gold wire at the base acts as the ohmic heater, while the remaining gold acts with the silicon nitride beam as the bimorph thermal actuator. The probe tips are approximately 10 μm tall with a 960 nm radius of curvature. Tip-to-tip spacing is 100 μm, resulting in a 20 μm gap between individual probes.

The capabilities of this ten-pen array with individually addressable probes were studied using 1-octadecanethiol (ODT) as the ink and a substrate composed of a 20 nm evaporated gold film on an oxidized silicon wafer with a 5 nm Cr adhesion layer. ODT was chosen as an initial ink candidate because it has been extensively studied in the context of single-pen DPN.[2,6] Moreover, ODT can withstand temperatures up to 65 °C without degradation and it can be vapor deposited onto the array to avoid the problems associated with drying an array after solution immersion. All DPN writing was done with a Thermomicroscopes M5 AFM that was modified by the addition of a tip-tilt stage to the scan head and a custom DPN software interface. The stage allows the array to be precisely aligned with the substrate. The probe chip was mounted on a holder that allows it to be connected to an external control circuit.

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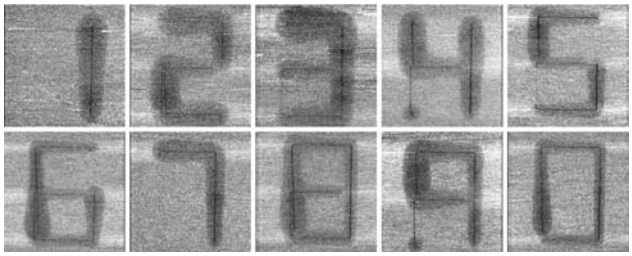

FIG. 4. LFM scans, 8 μm square, of ten simultaneously generated ODT patters on a gold surface. Each numeral is 6 μm tall, 4 μm wide, and was written at 1 μm/s.

An ideal experiment for demonstrating the parallel writing capabilities of the ten-probe array is to simultaneously write the numerals 0–9. After coating the array with ink and installing it in the AFM, the array was aligned with the gold substrate and passed through a figure-8 pattern. The figure-8 pattern was 6 μm tall and 4 μm wide, and was traversed at 1 μm/s. A different numeral was written with each probe by selectively actuating the probe to lift its tip off the surface to suspend deposition. After deposition, the patterns were imaged by lateral force microscopy (LFM) using a commercial silicon nitride contact-mode AFM probe. The ODT monolayer presents a lower surface friction than bare gold and is detectable by LFM. The ten 8 μm LFM scans are shown in Fig. 4. Each of the ten patterns exhibits a narrow line between 50 and 150 nm wide surrounded by a dim halo. The halos are believed to be caused by diffusing ODT where the surface density is not high enough to lead to a complete, well-packed monolayer.[7,8] The halo is partially a result of the relatively slow traversing speed required to accommodate manual switching of ten pens. The halo will be completely eliminated in future by using systems with automated switching and higher tip speeds.

The experiments described herein demonstrate the viability of doing parallel DPN with individually addressable cantilevers. This demonstration of the simultaneous creation of different numerals is particularly important. Indeed, if one can draw these ten independent features, in principle, one can generate almost any set of arbitrary patterns using this general approach. The fact that one can make such structures simultaneously is a major step towards parallel scanning-probe-based systems for increasing the throughput of DPN, and direct-write scanning probe lithographies in general.

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