

Ink-Jet Printed Nanoparticle Microelectromechanical Systems

Sawyer B. Fuller, Eric J. Wilhelm, and Joseph M. Jacobson

Abstract—We report a method to additively build three-dimensional (3-D) microelectromechanical systems (MEMS) and electrical circuitry by ink-jet printing nanoparticle metal colloids. Fabricating metallic structures from nanoparticles avoids the extreme processing conditions required for standard lithographic fabrication and molten-metal-droplet deposition. Nanoparticles typically measure 1 to 100 nm in diameter and can be sintered at plastic-compatible temperatures as low as 300 °C to form material nearly indistinguishable from the bulk material. Multiple ink-jet print heads mounted to a computer-controlled 3-axis gantry deposit the 10% by weight metal colloid ink layer-by-layer onto a heated substrate to make two-dimensional (2-D) and 3-D structures. We report a high-Q resonant inductive coil, linear and rotary electrostatic-drive motors, and in-plane and vertical electrothermal actuators. The devices, printed in minutes with a 100 μm feature size, were made out of silver and gold material with high conductivity, and feature as many as 400 layers, insulators, 10 : 1 vertical aspect ratios, and etch-released mechanical structure. These results suggest a route to a desktop or large-area MEMS fabrication system characterized by many layers, low cost, and data-driven fabrication for rapid turn-around time, and represent the first use of ink-jet printing to build active MEMS. [657]

Index Terms—Colloid, electrostatic motor, heatuator, ink-jet printing, metal jet, nanocrystal, nanoparticle.

I. INTRODUCTION

MICROFABRICATION of electronic and mechanical structure at the submillimeter scale is typically a time-consuming and expensive process. Lithographic techniques for silicon micromachining, used to fabricate integrated circuits and MEMS, typically take several weeks to go from drawings to completed chips, and require expensive facilities and extreme processing conditions. An alternate approach in which multiple small volumes of metallic, semiconducting, or insulating material are deposited at computer-defined positions could enable the all-additive fabrication of such devices on a much faster and less expensive basis. Techniques that involve expelling small droplets of molten metal onto a substrate [1]–[5], however, have met with mixed success, primarily because of the difficulty of adhering droplets to previously solidified layers [2]. Other problems include oxidation of the liquid metal [1] and the difficulty of fabricating a droplet-expulsion mechanism compatible with the melting temperatures

of most high-quality metals beyond low-temperature solders [1], [2]. Other approaches for droplet deposition, called ink-jet printing, as a route to silicon-like device fabrication have included printing metallo-organic decomposition inks [6], [7], dry powders [8], organic light-emitting materials [9], [10], photonics and solders [1], and printing resin binders into successive layers of loose powder [11]. However, to date, such processes have been limited in terms of electrical conductivity, feature complexity and thickness, resolution, or material quality, and none have been able to fabricate active MEMS devices.

Previous work in our group has demonstrated high-mobility inorganic transistors fabricated by printing ink consisting of CdSe semiconducting nanoparticles dispersed in solvent [12]. Here, we propose and demonstrate a system in which an ink-jet print head deposits a nanoparticle colloid ink to print three-dimensional (3-D) metallic structures that circumvents the difficulties with depositing the materials in molten form [13]. Once printed, the nanoparticles in the patterns of ink are sintered to form material that is structurally and morphologically comparable to the bulk material. Because ink-jet printing is noncontact, nanoparticle material can be added layer-by-layer to form 3-D structures.

Nanoparticles typically measure 1 to 100 nm in diameter and consist of clusters of metallic, semiconducting, or insulating atoms. Because of their small size, nanoparticles exhibit a melting point as low as 1000 °C below the bulk material [14]. The lower melting point is a result of comparatively high surface-area-to-volume ratio in nanoparticles, which allows bonds to readily form between neighboring particles. Nanoparticles can be made into a colloid that can be printed like ink.

An ink-jet printer patterns material by expelling tiny droplets of liquid ink from an orifice one at a time as it is moved in two dimensions approximately 1 mm above a substrate. Each droplet takes ballistic trajectory to the substrate on command by a pressure impulse, often by a deformable piezo crystal, from within a small chamber attached to the orifice (Fig. 1) [15]. The pattern of droplets left behind on the substrate constitutes the printed output. Ink-jet printing is additive, reducing waste and processing steps compared to subtractive fabrication methods. It is data-driven, requiring no masks, reducing turnaround time over lithographic processes. Ink-jet printing is less limited by substrate composition and morphology, and can accommodate a greater number of layers and range of materials than can lithography and subsequent semiconductor-based batch processing. State of the art ink-jet print heads will allow minimum feature sizes lower than 20 μm [15]. In sum, ink-jet printing presents a number of advantages as a fabrication technology. Coupled with the novel use of nanoparticles as the building material, the process enables a practical route to a desktop fabrication system for electronic circuitry or MEMS.

Manuscript received January 2, 2001; revised September 14, 2001. This work was supported by Defense Advanced Research Project Agency Contract DABT63-99-C-0033 and by the Media Laboratory's Things That Think (TTT) consortium. Subject Editor R. S. Muller.

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Publisher Item Identifier S 1057-7157(02)00502-4.

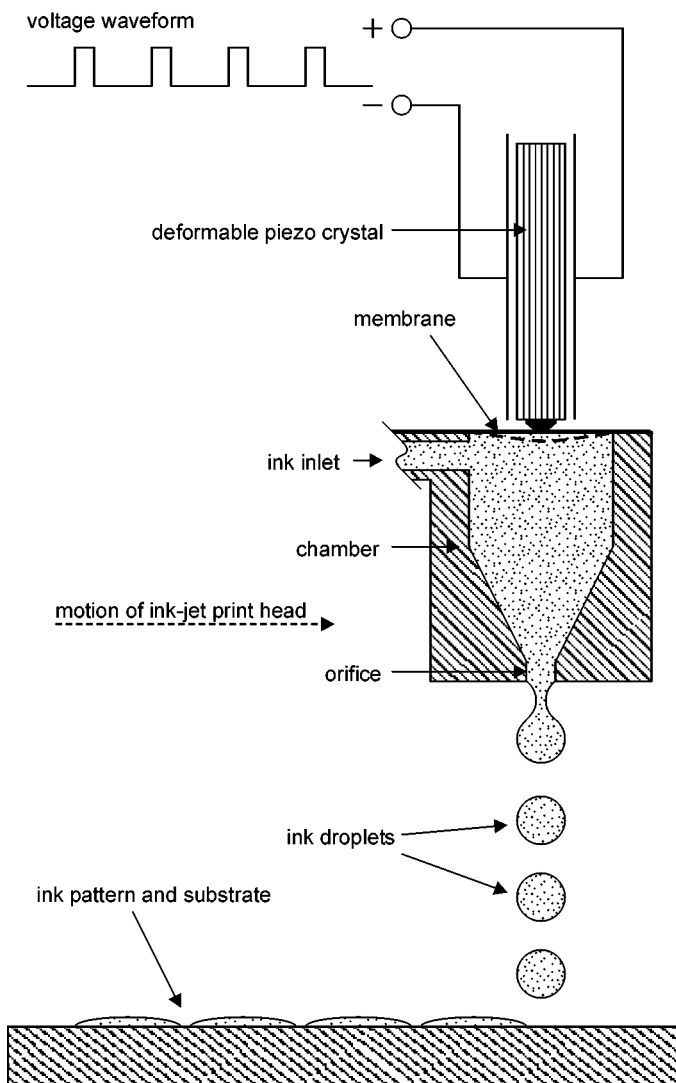


Fig. 1. Diagram of the piezo drop-on-demand ink-jet printing system. In the print head, a piezocrystal expands in response to an electrical driving signal, deforming a membrane, causing a pressure impulse within the ink chamber, expelling a single droplet from the orifice. The chamber is refilled through the inlet by capillary action at the orifice. Multiple droplets deposited onto the substrate leave the printed pattern.

We demonstrate the first known ink-jet printing of nanoparticles to build electrically and mechanically functional structures and the first active MEMS devices produced by this method.

II. APPARATUS

All of the ink-jet printed devices reported here were fabricated using a desktop piezo-driven ink-jet print head manufactured by Hitachi Koki Imaging Solutions, Inc. [16]. A piezo-based ink-jet print head offers a greater range of ink compatibility than thermal ink-jet heads, which are limited to water-based inks or require a new design for each different type of ink solvent. Continuous-mode print heads require higher priming volumes and have larger droplet placement irregularity, making them unsuitable for this work [15]. The print head was mounted onto a computer-controlled three-axis gantry system, and expelled droplets downward onto a horizontal substrate. The gantry system, manufactured by Aerotech, Inc.,

uses brushless linear motors for motion in the horizontal plane with a repeatability of $\pm 1 \mu\text{m}$ [17]. The gantry's motion is programmed in G-code using a PC-based software environment available from Aerotech.

Only a single nozzle from a given head was used at any time, which is a vector-based drawing approach, in contrast to the multiple-nozzle rasterization used by most desktop ink-jet printers. By relying on only a single nozzle, the system was simplified, and the arrangement was ideal for the simple but multilayered devices reported here. The nozzle was moved at 10 mm/s 1 mm above the substrate, expelling droplets continuously at 100 Hz, interrupted by or resumed by computer command.

The print heads were heated to 40 °C using power resistors to lower the ink viscosity to a range compatible with the print heads. Higher viscosity solvents with low evaporation rates were preferred. Solvents with high evaporation rates such as isopropyl alcohol typically printed for only a few minutes before the nozzle dried and clogged. The ink feed system contained enough to fill the reservoir inside the head, approximately 0.5 mL, and operate continuously for about an hour. The volume of each droplet ranged from 75 to 150 pL and depended on the strength of the driving pulse and the properties of the ink. The waveform to expel a single droplet was a +20 to +30 V pulse lasting 20 μs . Though not needed, the print head had the capability of expelling droplets at frequencies as high as 12 kHz.

The substrate was heated at 100 to 300 °C on a hotplate during the deposition process to improve deposit quality. By heating the substrate, the liquid in the droplets was flash-evaporated on contact, halving the feature size in comparison to room temperature printing. The rapid liquid evaporation also eliminated wetting problems, allowing multiple layers of multiple different materials to be rapidly added without intervention onto varying substrate materials and morphologies. Leaving the substrate at room temperature limited printing capability: surface tension caused lines and plates of ink to pinch and bulge, the ink wetted the surface unevenly in response to minute contamination, dust particles wicked the ink causing it to bridge gaps between neighboring lines, scratches in the surface of the substrate filled with ink by capillary action and caused unwanted conductivity, and multiple layers could not be added in rapid succession.

III. DEVICE FABRICATION AND RESULTS

Structural material was fabricated out of gold and silver colloidal nanoparticle inks consisting of 5–7 nm particles dispersed 10% by weight in α -terpineol [18]. Higher concentrations caused excessive clogging. When sintered at 300 °C, the conductivity of the nanoparticle gold or silver slowly increased over time. Devices were typically sintered for 10 min.

Other materials were ink-jet printed to complement the nanoparticle materials. A polyketone-based resin [20] designed to adhere to nonporous surfaces, dissolved 12% by weight in 50% ethyl lactate and 50% α -terpineol, acted as a printable

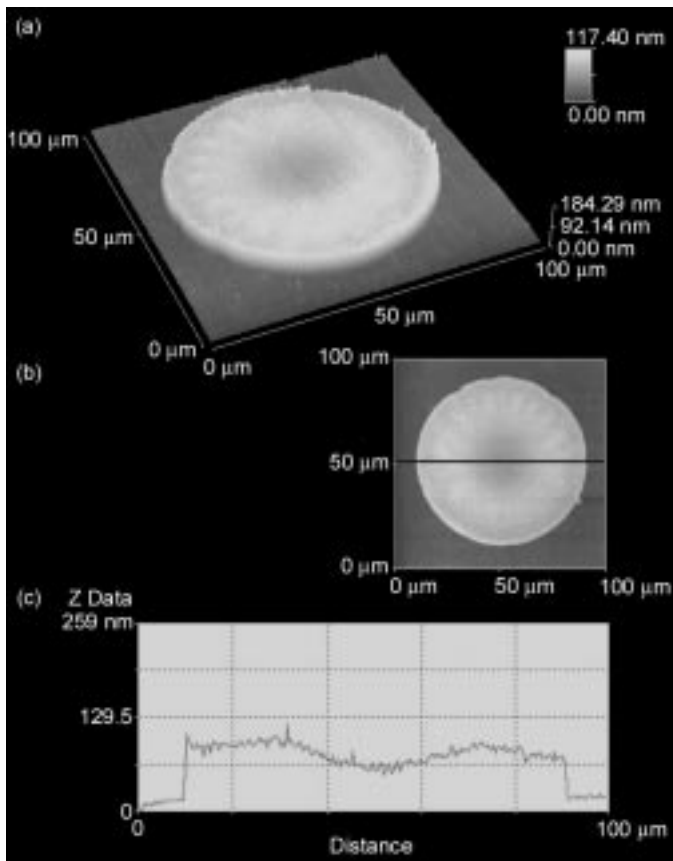


Fig. 2. An ink-jet printed droplet of nanoparticle silver on a glass slide after being sintered, imaged by atomic force microscope (AFM). (a) An isometric view, amplified by a factor of 80 in the vertical dimension. (b) An overhead view. (c) A cross-sectional profile.

insulator for the gold and silver nanoparticle ink [see Fig. 5(b)]. This material was able to withstand voltages as high as 700 V when patterned 40 μm thick (10 layers), though thinner layers can accommodate lower voltages. Spin-on-glass (Filmtronics 500FX, Butler, PA), diluted 50% in α -terpineol to meet viscosity and solids concentration requirements of the head, was printed by ink-jet but permanently clogged nozzles, and did not act as an insulator for the nanoparticle material after several attempts. Photoresist (Shipley Microposit FSC-L, Marlborough, MA) and polyimide film (Japanese Synthetic Rubber AL 3046) were printed by ink-jet but similarly failed to insulate.

With the substrate heated to 300 $^{\circ}\text{C}$, ink-jet droplets of the nanoparticle material, expelled at minimum driving voltage, left dots approximately 80–100 μm in diameter and 100 nm thick (see Fig. 2). Larger dots were achieved at lower substrate temperatures and higher driving voltages. Multiple drops were deposited to leave a conductive line or surface (see Fig. 3). The placement repeatability of individual drops was approximately $\pm 5 \mu\text{m}$, and gaps between lines of drops as low as 10 μm were repeatedly achievable.

If the substrate was heated to a lower temperature, such as 150 $^{\circ}\text{C}$, so that multiple droplets flowed together before solvent evaporation and sintering, a line with a very uniform cross section was achieved. An atomic-force microscope (AFM) was used to make a rough measurement of the cross-sectional area

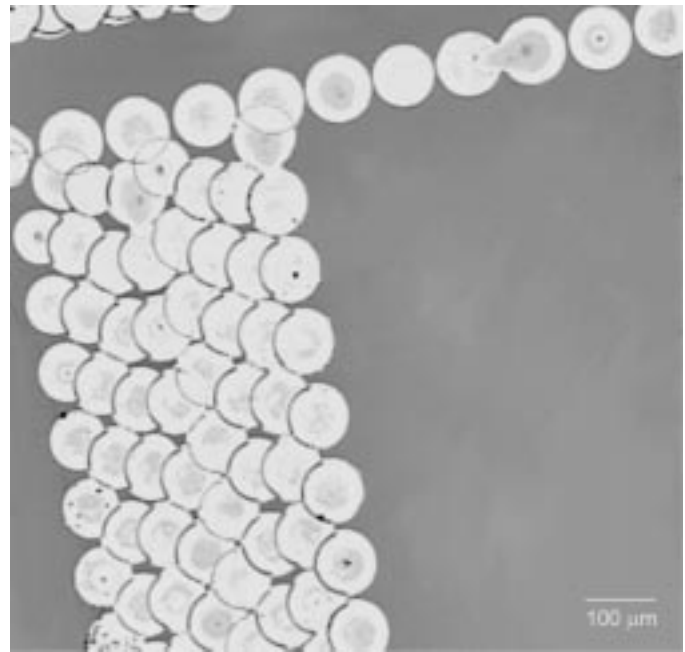


Fig. 3. Optical micrograph of an arrangement of sintered ink-jet printed nanoparticle gold droplets on plastic polyimide film. Electrically conductive lines and 3-D structure are fabricated by printing multiple layers of droplets.

of such a printed line to determine resistivity. Using the formula $\rho = RA/l$ on an 8 mm-long line, the printed silver was found to have a resistivity of approximately 3 $\mu\Omega \text{ cm}$, about twice that of bulk silver (1.6 $\mu\Omega \text{ cm}$). The limited conductivity is probably the result of organic solvent inclusions in the metal and/or incomplete sintering of the particles.

A. Resonant Inductive Coil

A resonant inductive coil (see Fig. 4) was printed in five layers of silver nanoparticle ink with 10 turns of a 1.3 mm wide coil arm. Capacitance with the air was sufficient to form a resonant LC circuit. The absorption quality of the coil was found using a radio-frequency vector network analyzer (Hewlett-Packard model 8753D) driving a reflective signal coil. In close proximity, the printed coil absorbed signals at 150 MHz with a quality factor Q of approximately 20. The electrical resistance from the center to the outside of the coil was 56 Ω . The high electrical conductivity suggests the applicability of the nanoparticle ink-jet printing process to fabricate remote-sensible radio-frequency identification (RFID) tags and/or electronic circuitry.

B. Electrostatic Drive Motors

An electrostatic drive motor with the ability to move small insulating objects was printed using gold or silver electrodes and polyketone resin [18] as an insulator [see Fig. 5(a)] onto polyimide plastic film [19]. The motor generated in-plane electrostatic forces on insulating objects such as dielectric glass balls or pieces of tissue paper. Force was caused by first capacitively generating localized areas of electrostatic charge on the object and then changing the electrostatic potentials of adjacent electrodes [21]. Three or more interdigitated electrodes, arranged

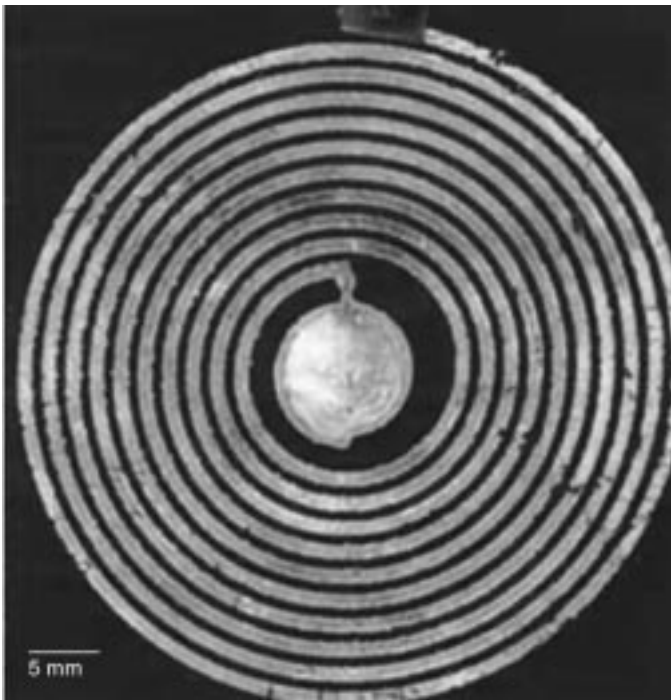


Fig. 4. Optical micrograph of an ink-jet printed resonant inductive coil.

in a repeating pattern, were sequentially pulsed at high voltage to carry the dielectric object in a chosen direction. The planar force can be purely linear, or, in the case of a rotary motor [see Fig. 5(a)], the electrodes were arranged radially to move the object in a rotary fashion around a central axis.

The motor was printed onto a 300 °C substrate using two ink-jet heads simultaneously. The second ink-jet head deposited polyketone resin insulator [20], a necessary component to keep the three electrodes electrically insulated from one another. First, the three metallic concentric circular electrode busses were printed in four layers. Next, ten layers of the insulator were printed over certain portions of one bus circle to make 40 - μ m-thick insulation deposits [see Fig. 5(b)]. Finally the radially oriented metallic electrodes were printed in two layers. The entire motor printed in 25 min and required no human intervention.

The drive waveform consisted of high-voltage (300–700 V) pulses to each electrode in turn, with each electrode grounded before the subsequent electrode's potential was raised. The pulse rate ranged from 5 to 20 electrodes per second. The arm, made of a small piece of tissue paper, was made to rotate the full arc many times about an axle fashioned from a probe tip. Only motors printed onto polyimide film were found to move the insulating object. Speeds up to 100° per second were recorded with a video camera. The device has functioned continuously for hours and the direction or speed was alterable without external intervention. A rough estimate for the energy required for a single rotation, found using a digital oscilloscope and a power resistor, was 2.5×10^{-3} J. Linear electrostatic motors with the ability to move dielectric glass spheres 250–500 μ m in diameter and small pieces of tissue paper were also fabricated.

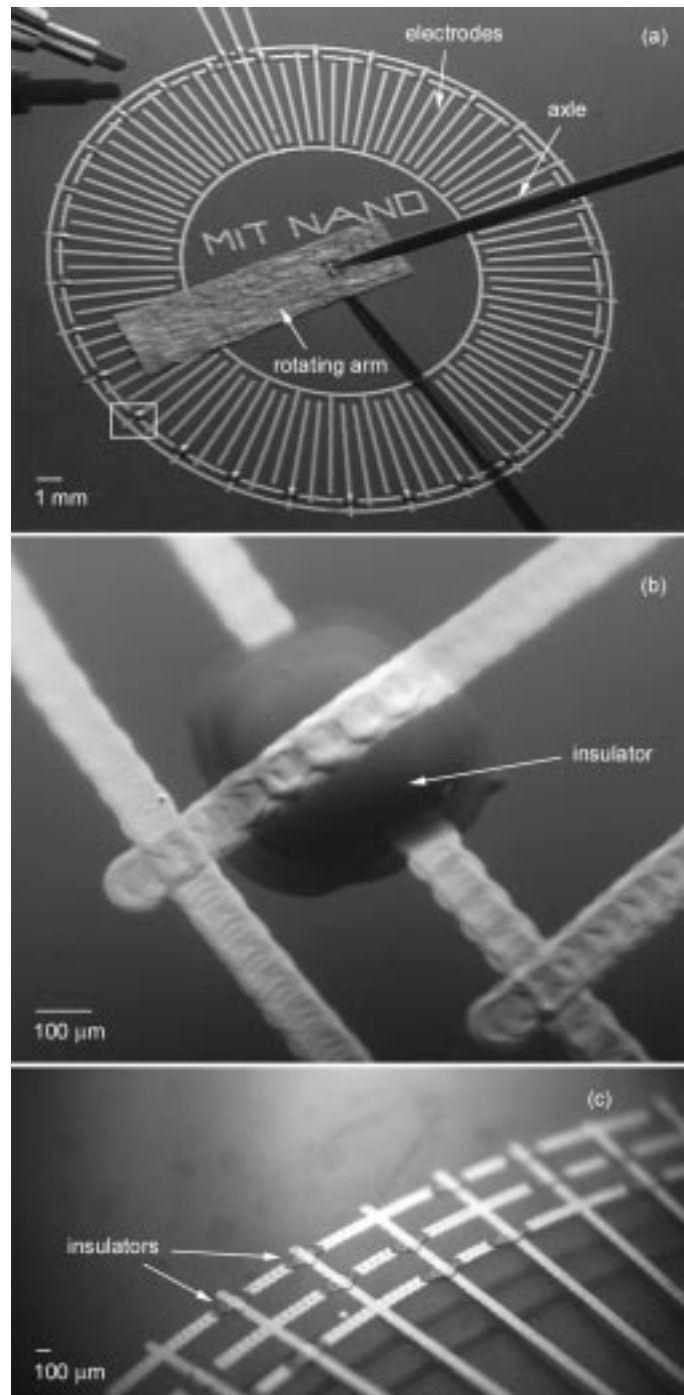


Fig. 5. Optical micrographs of rotary electrostatic drive motors. (a) Image of complete motor printed onto polyimide plastic film, including insulating tissue paper arm constrained to rotary motion about an axis fashioned from a probe tip. Signals to the three repeating interdigitated electrodes are received through the three bus lines extending beyond the top of the figure. The tip of a 0.7-mm mechanical pencil is included for scale. (b) Close-up of polyketone resin insulating structure, which electrically isolates the electrodes from each other. (c) A rotary electrostatic motor with a different bus arrangement.

C. Multiple-Layered Structures

Multiple layers of varying materials were printed to build 3-D structures. A structure consisting of a 40-layer stack of alternating gold and polyketone resin [20] layers was printed onto a wafer, cleaved in liquid nitrogen, and imaged with a scanning

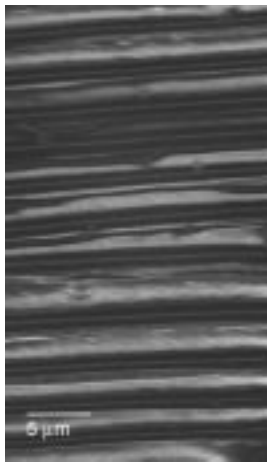


Fig. 6. A cross-sectional view of a 40-layer structure showing the presence of the internal structure of alternating nanoparticle gold and polyketone resin layers, imaged with scanning electron microscope (SEM).

electron microscope (SEM) to show the presence of the underlying layer structure (see Fig. 6).

D. Heatuators

A common MEMS actuator is a cantilevered structure that makes use of geometrical amplification of electrothermal expansion to generate motion [22], [23]. Such structures, called “heatuators,” are valuable for applications where low voltage and low substrate area are required [23]. Electrical current is passed from one anchor pad through the tip of the cantilever structure to the other anchor pad. The thinner “hot” half of the cantilever is resistively heated and expands more than the thicker “cold” side, moving the tip laterally. We present two different heatuators printed by nanoparticle ink-jet that demonstrate the ability of the process to build structures with functional mechanical structure and 3-D form.

1) *Vertical Heatuator*: Printing a large number of layers enables structures with high aspect ratios, such as a heatuator with the actuating cantilever portion oriented vertically away from the substrate [see Fig. 7(a)]. The 400-layer silver structure was printed onto a glass slide and stood approximately 1 mm tall. The thick “cold” side consisted of three joined pillars, while the thin “hot” side consisted of only a single pillar. Printing was carried out with the substrate at 300 °C and the print time was approximately 30 min. As drops were added to the towers they grew taller and thermal conductivity fell. Eventually the drops failed to fully evaporate before subsequent drops were added, ultimately mushrooming the liquid tops of the towers and causing them to join. However, it is believed that this means of wet-joining the towers was not necessary because printed overhangs have been achieved. Each 16-layer anchor pad was made large enough to contact with an electrical probe. The device was kept heated to 300 °C for an additional 30 min after printing to sinter the large bulb of material at the top of the cantilever.

At a driving voltage of 5 V, the actuator exhibited a small visible deflection when viewed through a low-magnification microscope. Higher voltages caused thermal breakdown.

2) *Planar Heatuator*: A planar, cantilevered heatuator was printed out of multiple layers of silver nanoparticles onto a glass

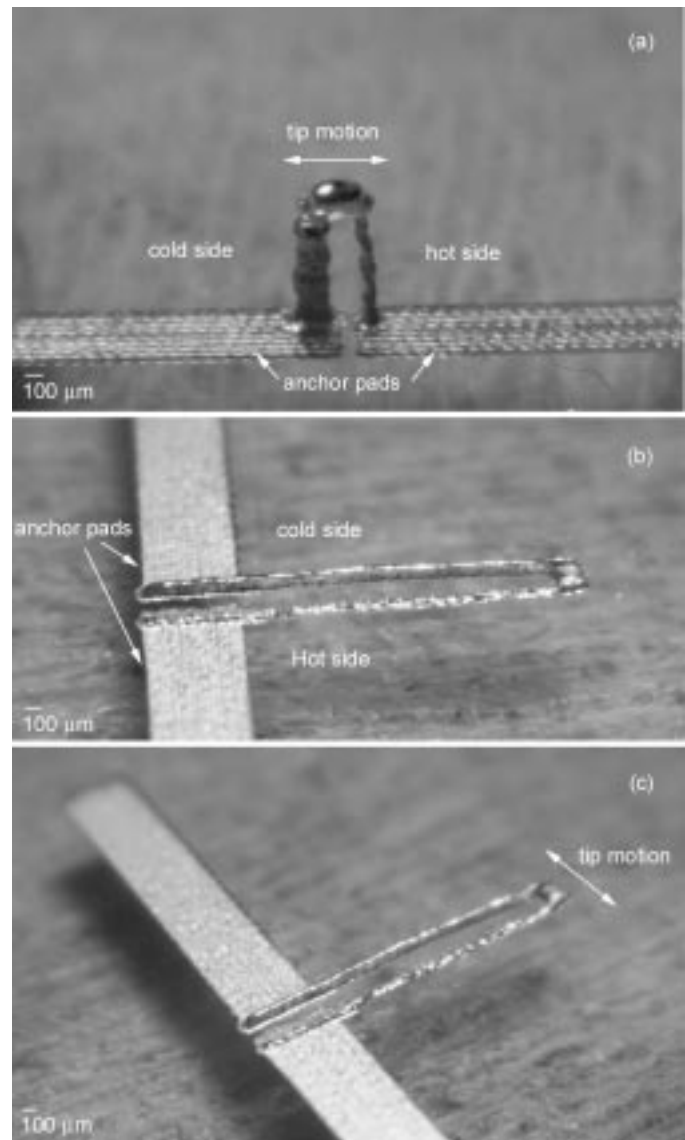


Fig. 7. Optical micrographs of heatuators printed on glass slides showing 3-D electrical and mechanical structure and a 100 μm feature size. (a) Heatuator printed with a vertical morphology. (b) Heatuator printed with a planar morphology and wet-etch released cantilever structure. (c) Alternate view of planar heatuator showing structural detail at the base.

slide and was released using a wet etch of polymethylmethacrylate (PMMA) [see Figs. 7(b) and (c) and 8]. PMMA was chosen because it retains solubility in acetone after the 300 °C printing step. The PMMA was dissolved 50% by weight into acetone and spread over a portion of glass slide using a draw-down bar suspended 100 μm above the slide and moving at 2 mm/s at room temperature. A thick layer of PMMA was required because it is slightly soluble in the nanoparticle ink solvent α -terpineol, which can penetrate the layer during printing. The slide was then positioned on the hotplate under the ink-jet print head so that only the cantilever portion of the heatuator pattern was deposited on top of the PMMA layer, leaving the anchor pads adhered to the glass slide. The thinner, “hot” side consisted of 40 layers of silver; the thicker, “cold” side 120 layers; and the anchor pads 16 layers. The ink-jet process was carried out with the substrate at 250 °C with a total print time of approximately

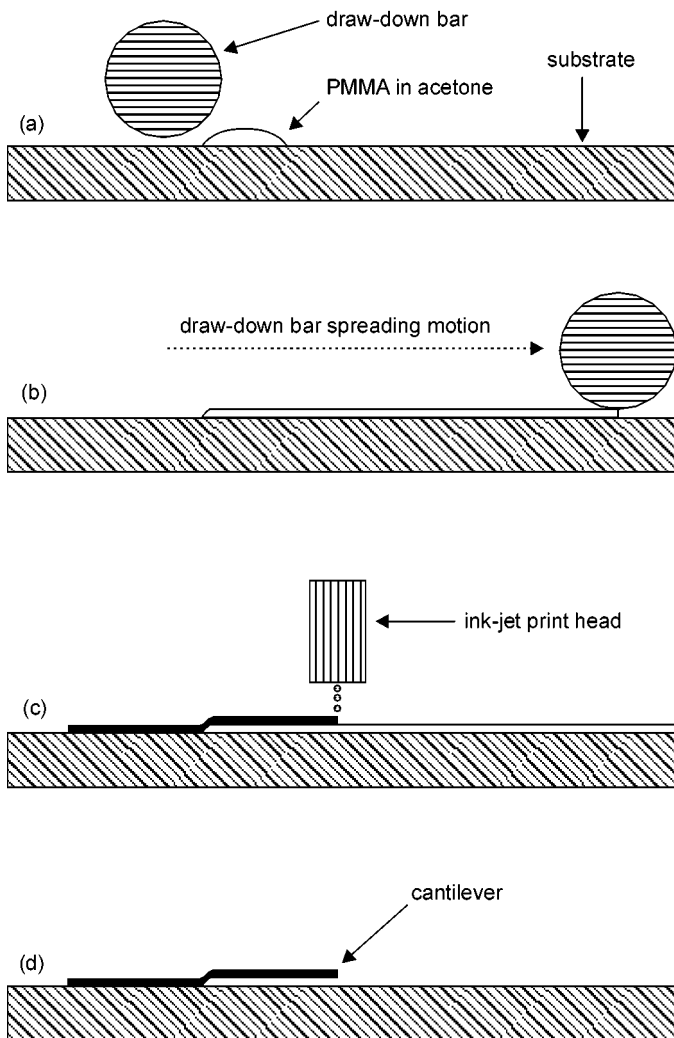


Fig. 8. The fabrication process for an ink-jet printed heatuator. (a) A liquid solution of PMMA in acetone is deposited onto a glass slide using a pipette at room temperature. (b) The PMMA is spread over a portion of the substrate using a draw-down bar suspended above the substrate. (c) The slide is placed onto a hotplate, and the heatuator is printed by ink-jet so that the cantilever is printed onto the portion of the slide covered by PMMA, and the anchor pads are printed directly onto the slide. After printing, the nanoparticle material is sintered for 10 min on the hotplate. (d) Sonication in acetone dissolves away sacrificial PMMA, releasing the cantilever.

30 min. Following a 10-min sinter at 300 °C, the structure was lightly sonicated in an acetone bath for 5 min to dissolve away the PMMA. The acetone had no effect on sintered nanoparticle material.

At 5 V, the planar heatuator generated 200 μm of motion at its tip, corresponding to 3° of rotation about an axis centered at its base. Power usage was 25 mW with thermal breakdown occurring at higher voltages. The time to move between fully actuated and fully neutral states was approximately 50 ms, measured using a video camera.

IV. CONCLUSION

We have presented several electrical and electromechanical devices that demonstrate the ability of ink-jet printing to build circuit-like devices and MEMS. Structures include a high- Q inductive resonant coil, linear and rotary electrostatic drive mo-

tors, and in-plane and vertical heatuators. The devices, printed in minutes with a 100- μm feature size, were made out of silver and gold material with high conductivity, and feature as many as 400 layers, insulators, 10:1 vertical aspect ratios, and etch-released mechanical structure. These results were made possible by the use of nanoparticles and represent the first known application of ink-jet printing to build active MEMS. With the exception of the draw-down step used to spread the etch layer for the planar heatuator, all fabrication was carried out in a data-driven fashion by ink-jet printing onto a substrate at plastic-compatible temperatures in ambient air. Microfabricating devices in this manner offers a potential cost savings over lithographic fabrication or molten-metal droplet deposition.

In light of results in our group in using printed nanoparticles to build the crystalline semiconductor structure of a field-effect transistor [12], we expect that a larger range of materials, including other nanoparticle metals, can be ink-jet printed to build more sophisticated devices such as transistors for integrated circuits or high-performance MEMS. Considering the versatility of nanoparticles and ink-jet printing, the results reported here represent a significant step toward realizing a desktop micro-fabrication system.

ACKNOWLEDGMENT

The authors wish to thank the members of the Molecular Machines Group at the MIT Media Laboratory and in particular, S. Griffith, B. Nivi, and J. Levitan for important contributions, C. Canida for constructive comments, and P. Linskey and R. Fletcher for contributions pertaining to the inductive coil.

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