Dip Pen Nanolithography of Silver Nanoparticle-based Inks for Printed Electronics

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ABSTRACT

Here, we present liquid-ink based nanoscale deposition of commercially available silver nanoparticles onto defined locations on untreated silicon dioxide substrates. We monitor the flow of the ink from the cantilevers to the substrate using specially designed transparent cantilevers with a high spring constant (0.5 N/m) in an open geometry which prevents tip clogging that plagues both inkjet printing[10] and nanofountain probes[6, 11]. We discuss the deposition mechanism for the silver NP inks, including methods for creating nanoscale arrays, lines, as well as varying the size and shape nanostructures deposited with the silver NP based inks.

Keywords: dip pen nanolithography, nanoparticle, direct-write, nanoscale, ink

1 INTRODUCTION

Nanoparticles (NPs) offer a wide range of unique properties when compared with their bulk counterparts, including optical, electrical, catalytic and quantum properties. Metal nanoparticles' unique properties have lead to new applications in electronic circuits and waveguides[1]. The most common metals used in electronic devices are gold, copper and silver. A requirement for many metal nanoparticle applications is the controlled placement of the nanoparticles in the desired locations on a surface. Recently developed nanoparticle lithography approaches include the chemically directed assembly of nanoparticles on to locally modified surfaces [2, 3], the directed assembly of NPs using a meniscus and mask [4], direct printing of nanoparticle inks onto heated substrates by inkjet printing[5] and the direct deposition of liquid gold NP solutions onto a functionalized surface[6-8]. These additive approaches offer advantages over standard subtractive microfabrication techniques which require masks, larger volumes of material, expensive facilities and extreme processing conditions.

Of the additive techniques, dip pen nanolithography (DPN) offers several advantages including computer driven, maskfree lithography, ambient working conditions, inexpensive equipment, and compatibility of a variety of inks with various substrates.

Here, we present liquid-ink based nanoscale deposition of commercially available silver nanoparticles onto defined locations on untreated silicon dioxide and gold substrates. We monitor the flow of the ink from the cantilevers to the substrate using specially designed transparent cantilevers with a high spring constant (0.5 N/m) in an open geometry which prevents tip clogging that plagues both inkjet printing[10] and nanofountain pen probes[6, 11]. We discuss the deposition mechanism for the silver NP inks, including methods for creating nanoscale arrays, lines, as well as varying the size of dots deposited with the silver NP based inks.

2 LIQUID NANOPARTICLE INKS

Liquid inks involve the use of a transport medium (a "carrier" solvent) in which the nanoparticles are suspended and stabilized. Combined, this carrier solvent and nanoparticle source form the nanoparticle ink that is coated onto the outer surface of the cantilever. Many conditions must be met in the development of liquid inks DPN, because of the nature of the deposition mechanism. These factors result from the open tip geometry, ambient conditions, and nature of the ink and substrate, and may include:

1) a slow evaporation rate of the ink from the cantilever,
2) a homogeneous ink solution with a long shelf life,
3) uniform wetting and loading of the ink on the cantilever,
4) an affinity of the ink for the substrate, and
5) controlled transfer of ink from the cantilever to the substrate while writing.

Meeting all of these conditions often requires and multiple trials optimization, in particular if the ink is to perform in the same manner over many repetitions. Here, we present two inks optimized for DPN of silver NPs, one based on a glycerol carrier solvent and silver nanoparticles acquired from

NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8503-7 Vol. 1

P-Chem Associates, another based on heptadecane/α-terpineol mixture and a silver nanoparticle paste from Harima Chemicals.

Like in a macroscale fountain pen, the loading and wetting of the ink on the cantilever is key in determining written feature size, in addition to the nature of the ink itself. Controlled volumes of these inks are loaded onto the cantilevers using a microfluidic-based solvent delivery system, Universal Inkwells, and our newly developed transparent cantilevers.

3 ACCESSORIES FOR LIQUID INKS

In general, with contact mode cantilevers that are metal coated, investigation of the loading and wetting of the ink on the cantilever is accomplished by flipping the cantilever over and looking at it under an optical microscope. A thin, uniform & continuous film across the surface area of the cantilever indicates that it will write uniform feature shapes and sizes. The ability to investigate ink loading and wetting on the cantilever *in situ*, both immediately after loading and while writing, is of key importance in controlling feature size from experiment to experiment and tip to tip. To aid in the study of ink loading, wetting and flow, we use transparent cantilevers shown in Figure 1. The optical micrographs (a) show inking (inset), and resulting ink loading and wetting of transparent cantilevers with AgNP ink. Patterning from two different transparent cantilevers (b) shows a clear difference between properly & improperly inked cantilevers. The left has ideal ink loading and wetting resulting in good flow and small, uniform arrays, while the right has poor ink loading and wetting, and hence non-uniform flow from the cantilever and unreliable spot sizes.

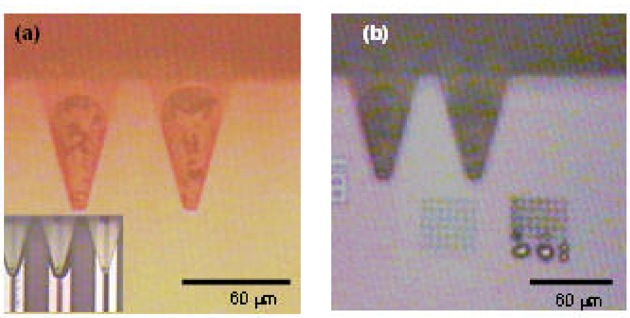

Figure 1: (a) Proper Ink loading and wetting on two cantilevers, (b) resulting pattern from properly loaded cantilever (left) and poorly loaded and wetted cantilever (right).

4 Patterning with Inks & Cantilevers

Once loaded with ink, the cantilevers are brought into contact with the surface, and then withdrawn to leave behind a droplet of ink. It is not necessary to align the laser on the back of the cantilever during this process because this process can be done without feedback. Indeed, this is in contrast to the diffusive inks, where feedback is needed during ink deposition. In fact, we observed that if we attempted to draw a feature without multiple withdrawals from the surface, the carrier solvent would deposit but the nanoparticles would remain on the cantilever; thus when curing the deposited droplets the carrier solvent evaporated and no particles remain behind. In this manner a dot-matrix like printing method was used to create both arrays and lines. After ink deposition, the substrates were annealed at between 300 – 500 ^{o}C to evaporate off the carrier solvent as well as to sinter the nanoparticles together into a continuous structure. The nanoscale alignment feature of InkCAD enabled AFM imaging of the deposited pattern after the substrate was removed from the system for annealing.

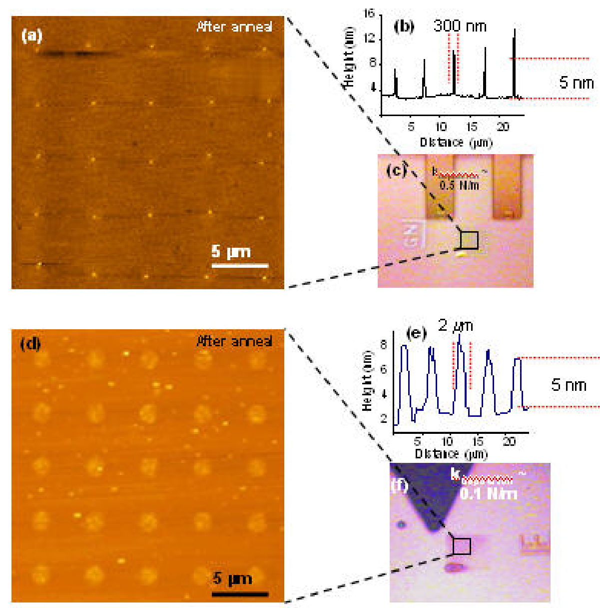

Figure 2: Patterning of dots with aqueous (*a*, *b* and *c*) and organic (*d*, *e* and *f*) silver nanoparticle inks.

Figure 2 shows the differences between features obtained by deposition of aqueous (*a*, *b* and *c*) and organic (*d*, *e* and *f*) silver nanoparticle inks. After deposition, an anneal at relatively low temperatures (300 – 500^{o}C) boils off the carrier solvent and sinters the metal nanoparticles into a solid feature. For the same tip-sample contact time of 0.01 ms, deposition of the organic silver nanoparticle ink resulted in ~2 micron sized features (*d*), whereas the aqueous silver nanoparticle ink yielded ~300 nm features (*a*),. We postulate that this difference is primarily due to differences in surface tension between the two inks. Since feature size is controlled by the size of the droplet deposited, a smaller droplet results in smaller features. Surface tension is an interfacial property that depends on the strength of intermolecular forces in a liquid. We postulate that our water based ink has more hydrogen bonding interactions between individual molecule than our organic ink. In addition to smaller droplet sizes, surface tension helps reduce feature sizes by drawing the nanoparticles towards the center of the feature. This pulling in of the nanoparticles takes place at the moving edge of the droplet as it boils off. Feature sizes are relatively uniform for the nanoscale silver features formed in this manner. Across 10 randomly selected dots in five separately written arrays, the average dot diameter is 287 nm with a standard deviation of about 35 nm.

Since ink is deposited when the cantilever withdraws from the surface, lines cannot be easily obtained by dragging the cantilever across the surface. Lines are realized, however, by close deposition of a line of spots of silver nanoparticle ink, as shown in Figure 3. Post annealing, the lines are between 300 and 800 nm wide and 5 nm tall. Continuous features are obtained as the nanoparticles are carried to the center of the feature by the evaporating solvent, before they sinter together.

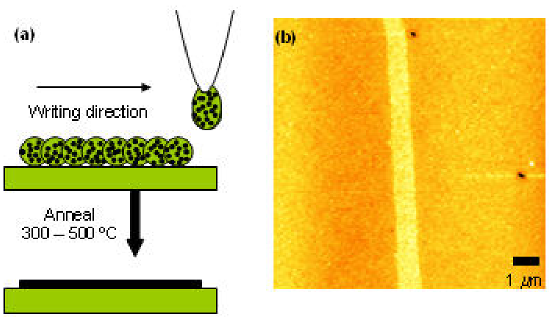

Figure 3: (a) Schematic showing fabrication of lines of silver by close deposition of AgNP ink and (b) topography image revealing continuous silver line on SiO2 after annealing at 300 – 500ºC.

We can control the dimensions of the nanoscale features deposited with the silver NP ink. With the liquid silver NP inks this is accomplished by repeatedly striking the tip in the same location on the sample, in order to deposit more ink to the surface. The results of such an experiment are shown in Figure 4, post anneal. The first spot (x1) was formed by repeatedly spotting at the same location 10 times, and is both taller and broader than the second (x2) which was formed by spotting five times, and the third (x3) spot formed by striking three times.

The ink remains on the surface with each subsequent cantilever strike because the adhesive forces between the sample surface and the NP suspension are stronger than the adhesive forces between the tip and the suspended NP solution. In all likelihood a dry cantilever would remove previously deposited ink while a wet cantilever allows the deposition of additional ink to the substrate.

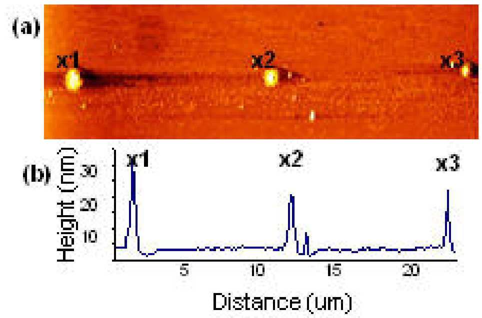

Figure 4: Variation in the size of the deposited material is accomplished by spotting

5 CONCLUSIONS

In conclusion, two types of silver nanoparticle ink (aqueous and organic) were developed to consistently obtain solid features on untreated SiO_2. Inks resulted in features that were about 2 μm in diameter, whereas nanoscale features were achieved using aqueous inks due to higher surface tension. Transparent cantilevers were used to investigate ink loading and wetting as well as the flow of ink from the cantilever to the substrate in real time. Methods for controlling the size and shape of the deposited nanostructures are discussed, both for dots and lines.

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