

Fabrication of nanoscale nozzle for electrostatic field induced inkjet head and test of drop-on-demand operation

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ABSTRACT

This paper presents the fabrication of microscale to nanoscale nozzle and patterning by means of electrostatic field induced drop-on-demand inkjet printing system. Typically using the nanoscale nozzle we could eject nanoscale droplets and show feasibility to form patterns ranging from micro scale to nano scale on large area substrates at high speed.

Keywords: electrostatic field induced inkjet, micro to nanoscale pattern, drop-on-demand

1 INTRODUCTION

Printing technology is considered to be a key technology even in the fields of electronics [1-3], materials processing, and biotechnology [4]. However, limited edge resolution, thickness homogeneity, and overlay problems still restrict the conventional printing approaches to applications. In general, these limitations have precluded printing patterns smaller than 20 μm , and it seems that, despite the great pressure on low-cost manufacturing, these applications have not been implemented yet. Although nanoscale high accuracy is achievable with soft lithography [5], alignment issues and low printing speed remain a great challenge. There is a genuine need for nano-to-macro integration technology for printing. This paper presents the fabrication of nanoscale nozzle and patterning by means of electrostatic field induced drop-on-demand inkjet printing system [6,7], to overcome the limitation and problem of conventional thermal and piezoelectric print heads described above.

When the meniscus of liquid is subject to strong electric field, electric charge is induced on the meniscus and electrostatic force elongates the liquid to form a droplet, as shown in Fig. 1. The electrostatic field induced inkjet printhead can generate very tiny droplet smaller than nozzle size because the droplet is detached from the tip of the meniscus. Therefore, a sub-microscale nozzle is expected to generate nanoscale droplets and write any dot, line, or geometries by controlling the ejection of the droplet.

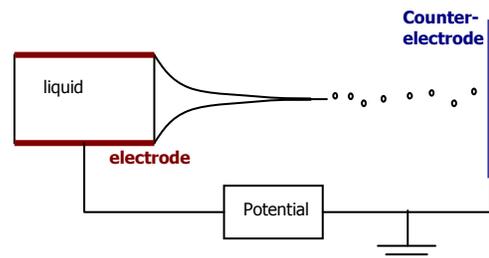


Figure 1 : Principle of electrostatic printing.

Current state-of-the-art electrostatic printing can reach to the resolution of hundreds nanometer [8]. To obtain such a high resolution the nozzle need to be placed as close to the substrate as the order of 100 μm . However, a very thin substrate is needed to get the support from a conductive backed layer. The substrate must be smooth to ensure a constant distance to the nozzle. Once the substrate is an insulator, the drop generation is influenced by suspended charged patterns. Therefore, high resolution electrostatic printing [8] requires either conductive substrates or a composition of a very thin insulator going with a conductive layer.

In this paper, microscale to nanoscale nozzles are fabricated and carry out patterning by means of electrostatic field induced drop-on-demand inkjet printing system. This system has ring-shaped electrode, which is able to focus the electric field at the centre and allow to fly the droplets through the hole and to deposit the following substrate

2 SIMULATION

A micro droplet is formed from the liquid meniscus due the induced electric field. The electric field is obtained by solving the following governing equations.

$$\nabla \cdot \epsilon \nabla \phi = -\rho \quad (1)$$

$$\vec{E} = -\nabla \phi \quad (2)$$

where \vec{E} denotes electric field vector, ϕ electric potential, ϵ the permittivity, and ρ charge density. These equations are solved by finite element solver, Comsol Multiphysics (Comsol Inc.) for an axi-symmetric 2 dimensional geometry.

In the direction of ejecting the micro droplet, the liquid meniscus is affected by two forces: an electric field force and a surface tension force [9]. We assumed that the shape of the meniscus is a sphere and the surface tension force f_1 and the electric force f_2 can be described as

$$f_1 = 2\pi r_c \sigma \quad (3)$$

$$f_2 = \int_0^{2\pi} \frac{1}{2} E \cos \theta \rho 2\pi r_d \sin \theta r_d d\theta \quad (4)$$

where E denotes electric field, σ is the fluid surface tension coefficient, ϵ_0 the permittivity of free space, r_c and r_d denote the radius of the nozzle and the droplet, respectively, and q denotes the net charge of the droplet.

E and ρ can be expressed by

$$E = \frac{q}{4\pi\epsilon_0 r_d^2} \quad (5)$$

$$\rho = \frac{q}{4\pi r_d^2} \quad (6)$$

If the electric field force is balanced by surface tension force, a critical electric field is obtained [9].

$$E = 2 \sqrt{\frac{\sigma r_c}{\epsilon_0 r_d^2}} \quad (7)$$

Equation (7) indicates that when the electric field on the liquid surface is larger than the critical electric field, the liquid meniscus on the tip of the nozzle will become unstable and the tiny droplet may be generated by the instability.

From this rough calculation, a threshold value of operating voltage for jetting can be estimated. If the droplet radius is 300 μm and 3 μm , the critical electric fields from Equation (7) is 7.39×10^6 V/m and 7.39×10^7 V/m, respectively. Table 1 and 2 show the values of the maximum electric fields, obtained from FEM simulations, on the liquid meniscus according to the various voltages applied to the electrode for cases of 300 μm and 3 μm radii. By comparing the maximum electric fields in Table 1 and 2 with the critical electric fields, the threshold voltage can be estimated as around 2.5 kV and around 250 V.

Table 1. Values of maximum electric field ($r_d=300\mu\text{m}$, $d=2$ mm)

Voltage (V)	2500	2800	3000
Max. E (V/m)	7.19×10^6	8.05×10^6	8.63×10^6

Table 2. Values of maximum electric field ($r_d=3\mu\text{m}$, $d=20$ μm)

Voltage (V)	100	200	300
Max. E (V/m)	2.88×10^7	5.75×10^7	8.63×10^7

3 EXPERIMENTAL METHOD

3.1 Fabrication of microscale and nanoscale nozzles

On the pursuit of high resolution drop-on-demand patterning, we have fabricated quartz nozzles with inner

diameters ranging from several micrometers down to sub-micrometer level. In order to prepare the nanoscale nozzle, a quartz capillary (ID. 700 μm) is pulled out to be extended and cut into micron or nano scale tip. Figure 2 shows a quartz tip with ID of 700 nm. Then, conductive material should be designed to be deposited on the surface of the capillary to enhance electrostatic force around the nozzle tip.

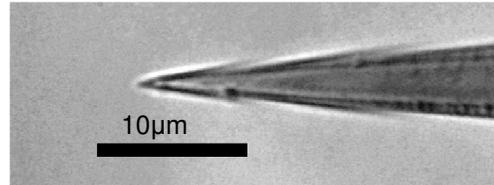


Figure 2 : A 700nm diameter quartz nozzle.

We tried to fabricate conductive nozzles by using three approaches. First, using e-beam evaporator (Thermionics), Au (150nm) layer is deposited on the outer surface of the nozzle, where NiCr (10nm) is coated to improve bonding strength between quartz and gold materials. Second approach is to fabricate a conductive layer in the quartz nozzle using silver nano-particle ink (TEC-IJ-010 from InkTec®). It is filled in the capillary nozzle and then is cured in the vacuum chamber under a temperature of 150 $^{\circ}\text{C}$ during 1 hour. Silver nano-particles are able to be sintered forming conductive wall inside the nozzle. Third, we used electroless plating [10]. For silver deposition, we prepared 0.2M silver nitrate (AgNO_3) in water, and 1.9M glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in a solution of 30 vol% methanol (CH_4O) and 70 vol% water as a reduction agent. Figure 3 shows the photographs of the coated nozzles.

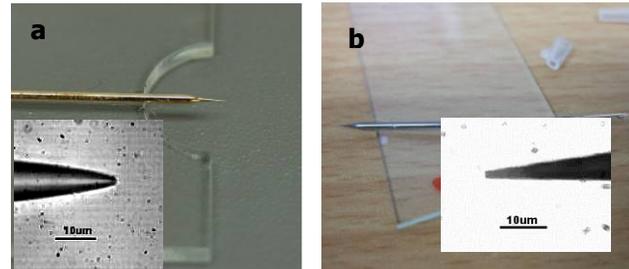


Figure 3 : Picture of tips coated with metal layer a) Au deposited outside b) Silver deposited inside the tips.

3.2 Experiment setup

To conduct a high resolution patterning experiment, a 2-dimensional x-y moving table is used. A conductive substrate is fixed on the moving table and the jetting system is located above the table. Metal ink (TEC-IJ-010 from InkTec®) is supplied through nozzle with flow rate ranging from 0.1 $\mu\text{L}/\text{min}$ to 1 $\mu\text{L}/\text{min}$ by a syringe pump. Negative potential that control drop-on-demand is provided by a function generator and high voltage amplifier, as shown in figure 4. The distance between the nozzle and the substrate is from 500 μm to 1000 μm . Small distance is favored in

terms of accuracy and operating-voltage-reduction. Nevertheless, reducing the distance increases the chance of electrical breakdown. A clearance ranges from 500 μm to 1000 μm is recognized as the best working distance in our experiment. Reaching of charge droplets to the substrate can be detected with a current measurer (Keithley 6485 picoammeter).

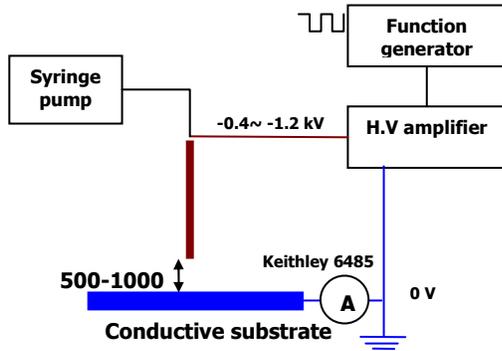


Figure 4 : Experiment setup for high precision patterning.

4 RESULTS AND DISCUSSIONS

4.1 Effects of deposition of metal layer

In this section, we examined the effects of gold exterior coated nozzle and silver interior deposited nozzle. For silver nozzle coated inside, we encounter difficulties from peeling off the silver materials near tip inside due to the electric stress. However, we have some successful jetting droplets and could decrease the operating voltage comparing with Au-coated tips outside. Figure 5 shows photographs of operating jets with the tips externally coated by Au (figure 8a) and internally coated by silver (figure 8b). While those two tips (ID 1 μm) are supplied with the same flow pressure and same distance between electrodes (1mm), the onset voltages are 800V for the tip coated with gold and 720V for the tip coated with silver. When the electrode is deposited outside of the tip, as shown in figure 5 (b), the liquid may be overflow and relatively large jet forms. Therefore, jetting characteristic depends much on the hydrophobic coating of the tip.

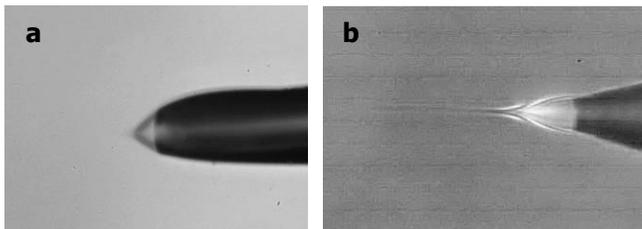


Figure 5 : Jetting images of tips coated (a) outside and (b) inside.

4.2 High resolution patterning experiments

For all patterning, we use nano silver ink (TEC-IJ-010, InkTec®) that contains nano silver particles. Figure 6 shows patterns of dots through a tip of 15 μm in diameter. The diameter of the droplets is around 20 μm , which is patterned on glass substrate. When we consider the hydrophilic surface of the substrate, the size of the droplet is estimated to be less than 10 μm .

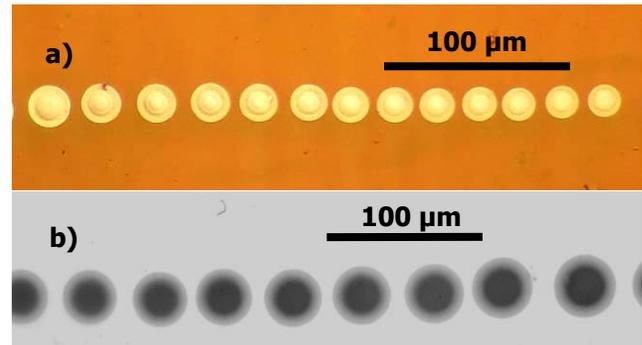


Figure 6 : Pattern dots through tip with 15 μm diameter, a) 10 Hz, and b) 5 Hz.

As the nozzle size scales down, the device is expected to generate fine droplets and offer higher resolution printing. However it is difficult to determine an optimal micro-dripping mode due to the lack of optical observation. Backing up with promising result that is up to 20 μm of resolution, we see the feasibility of scaling down the resolution to nano level as what have been obtained with the nozzle's size.

As the size of meniscus is getting smaller, the surface tension force that keeps the liquid in shape is also higher. When the meniscus breaks down to generate droplets under high electric field, the droplets are charged up with abundant amount of electric that surpasses the Rayleigh limit and are forced to divide into finer drops. Therefore we need further intensive study for investigating the optimal condition for micro-dripping mode. Figure 7 shows a line patterned by spray mode obtained from nozzle of 1 μm diameter. The drops are too fine to be spotted with optical range of our current device.

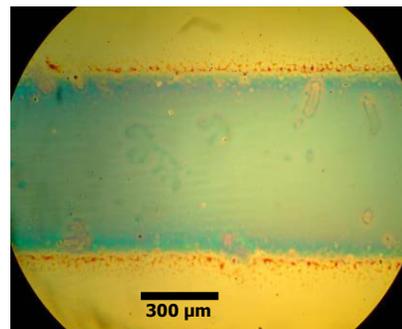


Figure 7. Pattern obtained from spray mode through nozzle of 1 μm in diameter.

In fact, jetting droplets and patterns may be unstable due to very small nozzle, liquid supply of small amount of liquid, alignment of nozzle and electrode. Furthermore, once the liquid is disconnected from the conductive edge of the tip, the edge can be stripped off under high electrostatic stress and lead to working failure. Even if a quartz tip is deposited with Au, high electric potential is applied to the deposit layer and breaks the bonding of metal layer and quartz tip. Therefore we need more researches for developing more stable coating technology and jetting devices.

5 CONCLUSION

In this paper, we show the feasibility of scaling down the nozzle for the electrostatic field induced inkjet head. Currently, we fabricated nozzle tips coated by metal inside or outside and examined high resolution printing. To utilize these tiny nozzles for nanoscale patterning, further examination need to be conducted to obtain the exact optimal working condition.

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REFERENCES

- [1] B.-J. de Gans, P. C. Duineveld, U. S. Schubert, *Adv. Mater.* 2004, 16, 203.
- [2] Arias, A. C.; Ready, S. E.; Lujan, R. A.; Wong, W. S.; Paul, K.; Chabinyk, M.; Salleo, A.; Street, R. A., *Applied Physics Letters* 2004, 85 (15), 3304.
- [3] Y. Young Noh, Ni Zhao, M. Caironi, H. Sirringhaus, *Nature Nanotechnology* 2007, 2, 784 – 789.
- [4] Maxim E. Kuil, J. P. Abrahams and J. C. M. Marijnissen, *Biotech. Journal* 2006, 1(9), 969-975.
- [5] John, A. Rogers, Ralph G. Nuzzo, *Materials Today*, February, 50-56, 2005
- [6] Sukhan Lee, Doyoung Byun, Daewon Jung, Jae Yong Choi, Yongjae Kim, Ji Hye Yang, Sang Uk Son, Bui Quang Tran Si, Han Seo Ko, *Sensors and Actuators, A*, Vol. 141, pp. 506-514, 2008.
- [7] J.Y. Choi, Y.J. Kim, S.U. Son, Y.M. Kim, S.H. Lee, D.Y. Byun, H.S. Ko, *Proceedings of NSTI-Nanotech 2007*, pp.403-406
- [8] J.U. Park, M. Hardy, S. J. Kang, K. Barton, K. Adair, D. Mukhopadhyay, C.Y. Lee, M. S. Strano, A.G. Alleyne, J.G. Georgiadis, P.M. Ferreira, and J.A. Rogers. High-resolution electrohydrodynamic jet printing, *Nature materials*, Vol. 6, pp. 782 – 789, 2007.
- [9] J. Xiong, Z. Zhou, X. Ye, X. Wang, and Y. Feng, *Research on electric field and electric breakdown*

- problems of a micro-colloid thruster, *Sensors and Actuators A*, Vol. 89, pp. 159–165, 2003.
- [10] N. Takeyasu, T. Tanaka, and S. Kawata, *Metal Deposition Deep into Microstructure by Electroless Plating*, *Japanese Journal of Applied Physics*, Vol. 44, No. 35, pp. L 1134– L 1137, 2005.