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# New developments in inkjet of deposits carried out under localized extraction or helium

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## ABSTRACT

This paper presents the first results obtained by mounting on an ink-jet print head two first systems which through injection of a helium flow, allow faster ink-jet evaporation rates and higher resolution or increased droplet velocity without modifying the droplet diameter. A third type of system features extraction specifically located at the impact of the droplets onto the substrate. This avoids contamination of the machine environment while significantly improving printing resolution. In all cases, these systems allow printing at much lower temperatures and the use of inks with high-boiling point solvents.

**Keywords:** ink-jet printing, helium flow, localized extraction, low temperature deposition

## 1. INTRODUCTION

The ink-jet deposition technology has been undergoing development for almost twenty years [1], showing the difficulty of this technique which is now extensively used in graphics industries. Indeed more than 3,000 patents have been filed between 1989 and 2000. This technique which seems highly appealing when considered from the point of view of its principle nevertheless poses new problems in micro and nanotechnology applications, such as the safety issue of inks with nanoparticles, the clogging of ejection nozzles when low-boiling point solvents are employed and resolution problems associated with the print head fabrication technology and with deposition parameters. Line width can be predicted based on the well-known relationship reported in the literature [2]; and it is explained by the following equation:

$$\omega^2 = \frac{\frac{\pi d^3}{6p}}{\frac{\theta}{4\sin^2 \theta} \frac{\cos \theta}{4\sin \theta}}$$

where  $\omega$  is the as-printed track width,  $d$  is the drop diameter,  $\theta$  is the contact angle,  $p$  is the spacing of adjacent droplets. This function takes account of the contact angle, the droplet diameter and spacing between two droplets. As a first approximation, to increase resolution, one has to

increase the contact angle or spacing between two droplets. However, this entails inherent limitations as it cannot be repeated indefinitely. Beyond a certain point the printed line becomes unstable [3, 4]. Another solution consists in diminishing the droplet diameter; the latter depending on the nozzle diameter; in this case one is limited by the nozzle fabrication technology. However a number of methods have been studied to produce smaller droplets than the ejection nozzle hole diameter [5], but the implementation is sometimes difficult to address.

In this paper, three types of systems for which patents have been filed are presented. The first system based on helium flow injection allows the substrate temperature to be decreased during printing and to improve line resolution. A second system features a helium flow injected through use of a venturi-like design. It exhibits the same performance as the first system with the additional advantage of increasing droplet velocity without increasing the droplet diameter. The third system with localized extraction absorbs the gas emitted during solvent evaporation as well as the solid particles likely to be generated during evaporation. This system is equally used to enhance resolution.

## 2. EXPERIMENTAL RESULTS

To validate our equipment, we used an ethylene glycol-based ink with ZnO nanoparticles (10% in weight). Ethylene glycol was selected because of its high boiling point (198°C) which allows synthesis of inks which will not easily dry at the end of the ejection nozzle and therefore will not cause clogging during stop phases. But the disadvantage of working with a solvent at high boiling point involves a low writing velocity in order to allow the evaporation of solvent; in our case, the writing speed was fixed for all the operations at  $0,4 \cdot 10^{-3}$  m/sec. To achieve suspension of ZnO nanoparticles in ethylene glycol, there is no need to add a surfactant. Thus a deposition containing mainly pure ZnO is obtained following drying, supporting the fabrication of devices like gas sensors [6,7]. An Altatech equipment fitted out with a single nozzle from MicroFab is used.

### 2.1 Use of a system without droplet acceleration

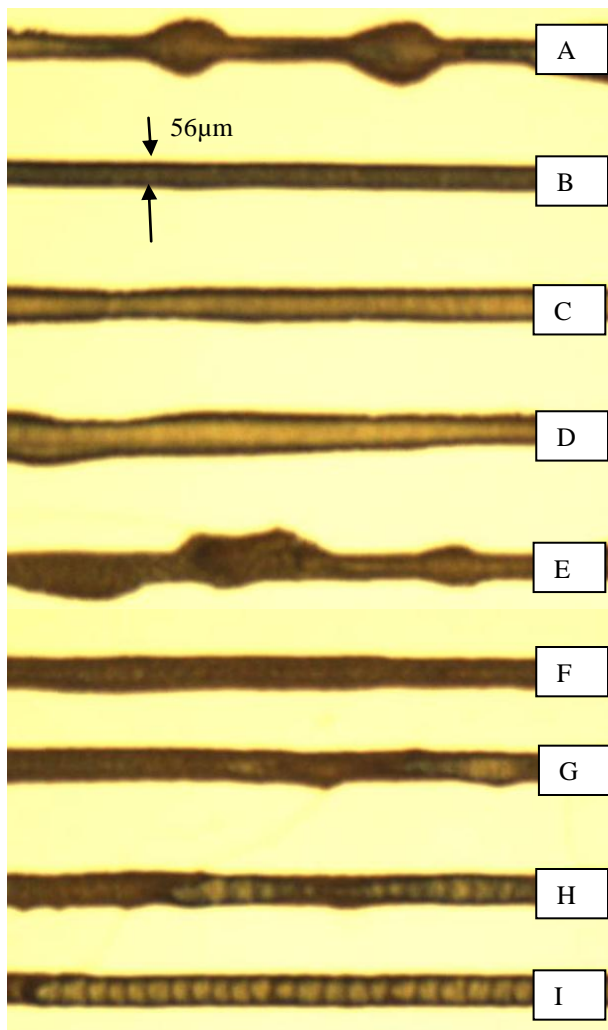


Figure 1: Optical picture of ZnO nanoparticles deposited on gold layer at different temperatures. Contact angle  $40^\circ$ ; diameter of the nozzle  $50\mu\text{m}$ ; distance between two droplets  $50\mu\text{m}$ .

The helium flow is injected at a rate of 300ml to 1,100ml per minute. Below 280ml per minute, the benefit of helium disappears. Between 300ml and 1,100ml per minute no improvement in terms of resolution, drying temperature or printing instability can be noticed. Figure 1 shows the resolution obtained with ZnO deposited on a substrate heated at  $65^\circ\text{C}$ : (A) without helium injection; (B) with helium injection (370ml/min); (C) with injection of nitrogen (370ml/min). Note that the line printed in (C) is thinner than in (A), but wider than in (B). In (B) the diffusion rate of the ethylene glycol vapour under helium atmosphere occurs faster than in air or nitrogen, leading to a higher evaporation rate.

The phenomenon associated with evaporation has been investigated and reported in the literature [8]. Starting from lines (D) to (I), the helium flow has been suppressed while

the substrate temperature was gradually increased; (D: $70^\circ\text{C}$ ); (E: $85^\circ\text{C}$ ); (F: $90^\circ\text{C}$ ); (G : $95^\circ\text{C}$ ); (H : $100^\circ\text{C}$ ). Up to line F, it can be noticed with the observation camera fitted onto our machine that ethylene glycol evaporates within a few seconds following deposition. In H, nothing occurs; in I ( $105^\circ\text{C}$ ), the annular structure of the deposition is typical of a rapid evaporation featuring deposition inhomogeneity. It can be considered that lines G and H best correspond to the aspect of line B, although the particle distribution seems less good. In this example, the temperature gain obtained with the use of helium is between  $30^\circ\text{C}$  and  $35^\circ\text{C}$ .

## 2.2 Use of a venturi-type system with droplet acceleration

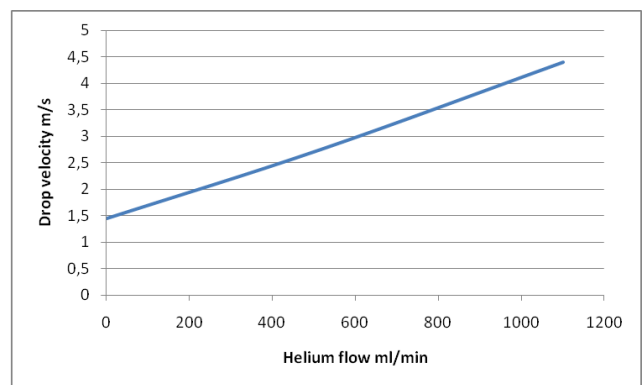


Figure 2: Droplet velocity vs helium flow with the venturi system.

A venturi-type system has been added at the outlet of the ejection nozzle. The results in terms of temperature or resolution are identical to those given by the previous system. On the other hand, we can increase the droplet velocity by increasing the helium output as shown in Figure 2. Thus this system enables us to increase droplet velocity without increasing the diameter as in the case of a voltage increase in the piezoelectric actuator. This is well accounted for in the literature [2].

The benefit of a higher velocity lies in having more spacing between the ejection nozzle and the substrate with no loss of resolution, and being able to print on high-aspect ratio substrates.

In our example of Fig. 3 for a 20 Volt excitation voltage of the piezoelectric actuator the droplet diameter is  $51\mu\text{m}$  with a velocity of 1.5m/s. To obtain a velocity of 4.5m/s, a 40 Volt excitation is needed. In this case a droplet with a  $60\mu\text{m}$  diameter will be obtained. With the use of the venturi system, one can keep an excitation voltage of 25 Volts and get a velocity of 4.5 m/s with a helium output of 1,100ml/min.

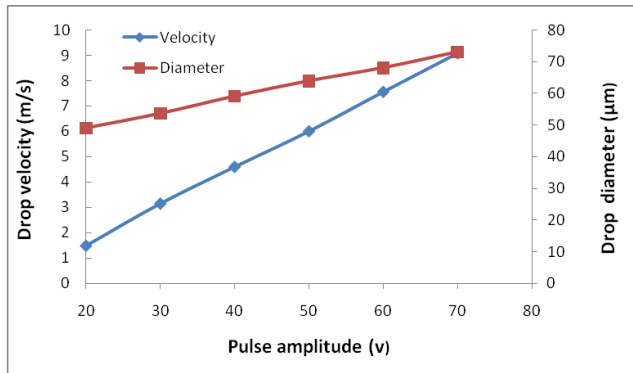


Figure 3: Drop velocity and diameter as a function of piezoelectric excitation voltage for an ink-jet 50µm dia. nozzle.

### 2.3 System with gas extraction

Extraction occurs at the outlet of the nozzle or in an annular fashion. Output may range from 500ml/min to 1,000ml/min. The advantage of this system lies in the extraction of gas or solid particles at the time of evaporation preventing the latter particles from settling in the machine environment. Given the high scan on the substrate, evaporation occurs more quickly than without suction; the major output can create a vacuum locally which promotes evaporation. Also a significant gain is achieved in terms of resolution as can be seen in Fig 4 where the three printing methods have been compared.

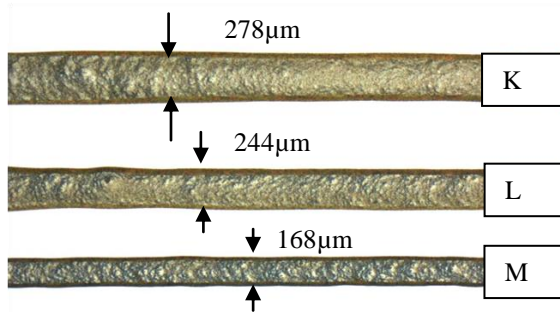


Figure 4: Comparison between the 3 methods. ZnO nanoparticles deposited on Silicon substrate at 65°C; nozzle diameter 50µm; more spacing between two droplets: 50µm; contact angle 17°.

(K) without injection of helium and without vacuum; (L) with suction; (M) with injection of helium. In this experimental case, the line width decreases from 278µm for a deposition without any system to 244µm for a system equipped with localized extraction (D) to 168µm for a system fitted out with helium injection.

Helium injection remains more efficient in terms of resolution.

## 3. CONCLUSIONS

These new systems, particularly those with helium injection, offer advantages relative to the other systems devoid of such improvements. The print resolution is greatly improved (up to 40% in certain cases). Printing can be performed at a lower temperature and high boiling-point solvents can be employed. Their use can be made compatible with biological molecules or substrates that cannot withstand high temperatures. With the venturi system, one can print with more spacing between the source and the substrate.

Additionally, these improvements greatly simplify the design of these machines. Although the system equipped with an extraction facility does not offer the same resolution performance as systems with a helium injection, it offers the advantage of efficiency protecting operators.

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