'Ink Jet for in-vacuum pattern printing and deposition - a look at the feasibility'

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Abstract

Currently the world of electronics is working hard to make better use of ink jet printing techniques to produce a variety of electronics. Many of these processes are aimed at being used to deposit onto web-based substrates. The developments are aimed at producing finer line-widths as well as depositing the structures at line-speeds compatible with other processes. Ink jets can deposit not only inks but monomers, filled sols or even molten metals. Thus, with a little imagination, one can envision multilayer coatings being produced on webs with different patterns overlayed and with mixtures of materials.

Currently, in vacuum the most widely used patterning process uses either direct or offset gravure coating. Thus if you want to change patterns it requires the gravure roll to be changed and hence requiring a break in vacuum. Using Ink Jet printing would only require a change in the software signal & so different patterns could be done on the same roll without breaking vacuum. Either by successive ink jet print heads or by winding the web backwards & forwards it would be possible to start building up mixed polymer/metal circuits.

Ink jet printing for fine line printing, 'drop-on-demand' (DoD) or continuous jet printing most commonly uses piezoelectric technology. An enclosed volume of ink has a piezoelectric crystal connected to a flexible end plate. As this end plate deforms the volume is reduced forcing a drop out of the nozzle. If the piezoelectric crystal is pulsed a stream of drops can be produced. If the drops as they leave the nozzle they will be charged up and the drops can then be guided.

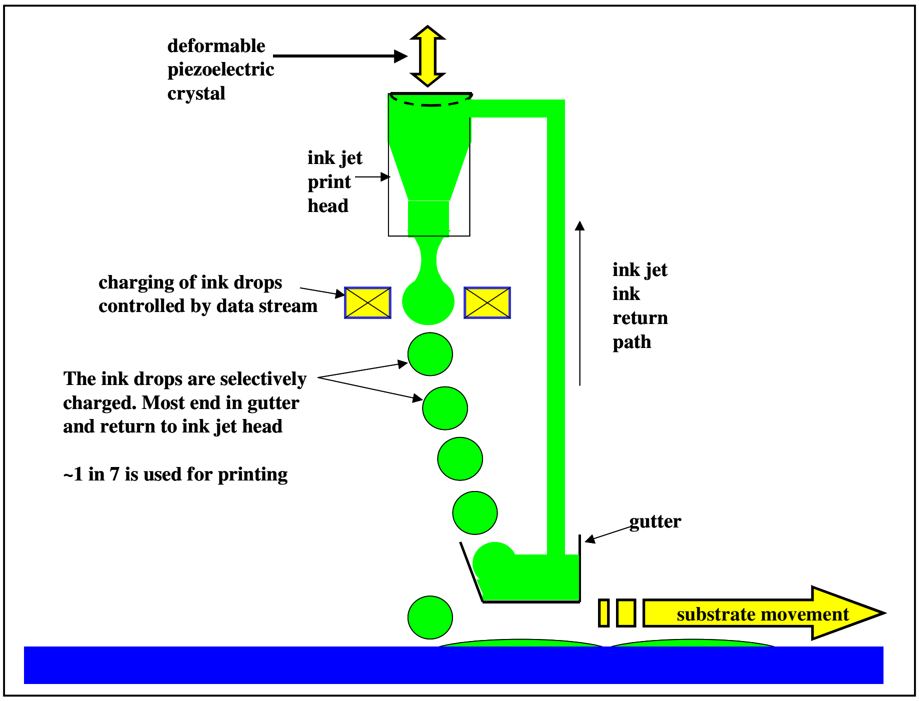


Figure 1.

Traditionally this charging was used so that most drops were directed to a gutter and the ink recycled back to the ink reservoir with only something like 1 in 7 drops used for printing as shown in Figure 1. Developments in the technology have made it possible to use every drop for printing, if required, this increasing the printing speed. Once the printing process reaches the point of being able to use every drop there is no purpose in having the electrostatic charging and the more simple ink jet head design can be used. Then the electrical signal can be controlled to space the drops to provide the desired pattern and thus the term 'drop on demand' as shown schematically in Figure 2.

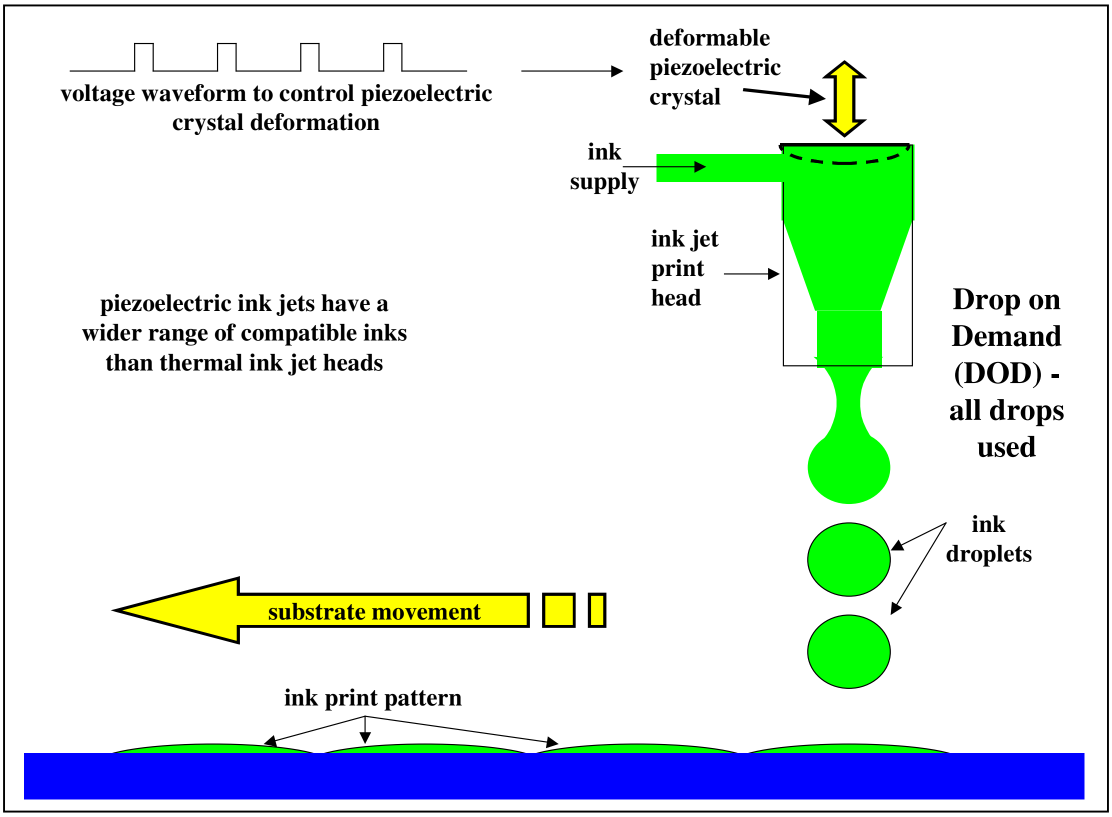


Figure 2.

One critical factor that affect the printing speed is the ink composition and the resultant viscosity. The higher the viscosity the larger the drop size needs to be. If the ink composition can be arranged to have a high surface tension the drop size can be reduced. The drop size governs the printed spot diameter with a rule of thumb that the printed diameter being approximately twice the drop diameter.

There are many options for the basic composition of the ink jet material the main three classes are as follows;

Liquids
- Aqueous inks
- Solvent based inks
- Monomers/polymers
- metallo-organic inks
- molten metals

Intermediates
Binders + particles
Nanoparticle colloids

Powders

Inks are rarely single component materials. There are many additives that can be included. Where colouration is required dyes or pigments can be added, if the ink jet is to be charged it may be necessary to change the conductivity of the ink, water and alcohol or glycol may be added as a viscosity modifier. Similarly there are options of adding preservatives to prevent bacterial decomposition and adding a binder to assist the ink adhesion.

Component	**Purpose**	**Required or not**
dye or pigment	**colouration**	**no**
liquid phase	**carrier for dye & binder**	**probably not**
binder	**assist ink adhesion**	**possibly**
water + alcohol	**viscosity modifier (CS) prevents nozzle clogging**	**different composition**
water + glycol	**viscosity modifier (DOD) prevents nozzle clogging**	**different composition**
charge generation additives	**enhances the charging capability of the ink**	**possibly not – aim is to use all ink drops**
preservatives	**prevents bacterial decomposition**	**optional**

Table 1. A summary of some ink components and what the requirement might be for inks that are used in vacuum.

Drop on demand – DOD **2 orders magnitude slower than CS**
5x better resolution than CS
1000 nozzles / head = 10M drops/s

Continuous jet – CS

Standard Ink-jet printers ~ 24hrs continuous use = clogged nozzle
(and this is for relatively large nozzle sizes)

Industrial Ink-jets - up to 30,000 nozzles / print head
40,000 drops/second - continuous use
(robust designs would require none of 30,000 nozzles block)

Figure 3. Some facts about Ink Jet print heads

Not only does the drop size affect the printed line size but also the way the printed drops overlap as shown in Figure 4. If the printed spots overlap by a minimal amount the edges of any line will be wavy but the line width will be a minimum. If the printed spots overlap by more than the drop radius then the line will have smooth edges but because of the extra volume of liquid the line width and height will be significantly increased.

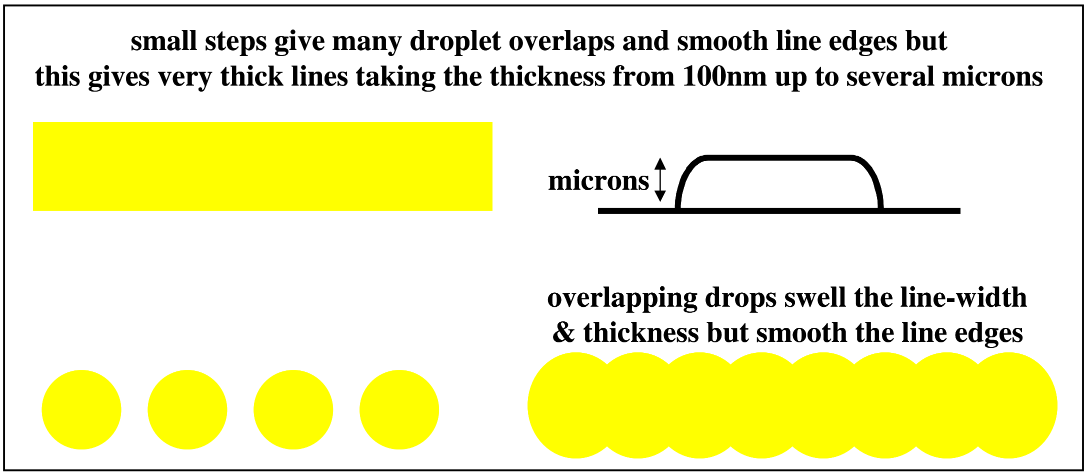


Figure 4. A schematic of how drops from lines of different quality.

One concern that frequently is raised is what happens when a drop of liquid hits a moving surface. The concern is how the liquid drop deforms, into what shape before it solidifies and will it fragment and splash. One piece of research has shown that, in a vacuum, drops hitting a surface do not splash.

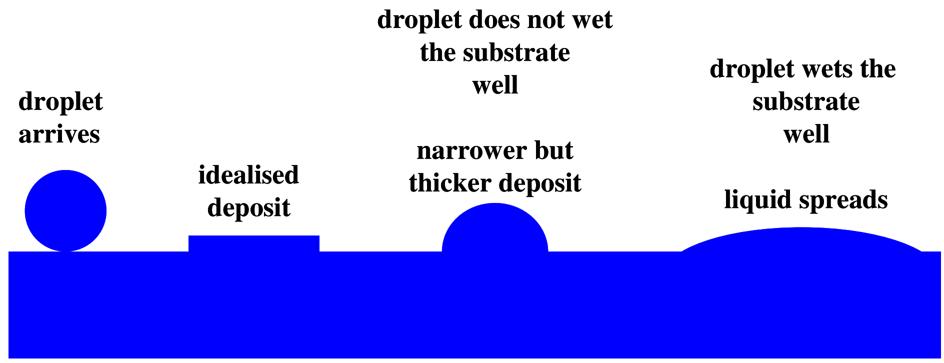
The most widely values for line with and line spacing would suggest that printing features of less than 20 microns with a line spacing of less than 10 microns and a printed height of 100nm or greater is possible. This fine line printing requires a ink drop volume somewhere in the range of 2 – 150 picolitres and this uses ink with a viscosity of somewhere around 1 - <5 mPascals. The ink drops can be produced at the rate of 1 million drops/s which equates to a dorp velocity of 50 m/s.These values are typical of the current practical and available fine line print available. However this is vastly different from the best that has been reported. The smallest droplet size that I have found was reported by the Nanotechnology Research Institute of the National Institute of Advanced Industrial Science and Technology (AIST) using ink from Harima Chemicals Inc. of Japan. They have shown examples of printing with a line width of 3.6 microns and a 1.4 micron spacing which was achieved using sub-femtolitre (attolitre) droplet size. This represents a reduction in droplet size by over three orders of magnitude over the more commonly available technology. The examples they showed were of conducting tracks where the inks contained conducting inorganic particles of approximately 5 nm diameter.

The speed of printing does depend on the technology with DoD being a couple of orders of magnitude slower than continuous ink jet printing. DoD does have five times better resolution than continuous ink jet printing. To compensate for the slower printing speed the number of nozzles/head can be increased and it is typical to have 1000 nozzles/head thus giving 10 million drops/s. For gross ink jet printing of coarse features as many as 30,000 nozzles/head have been produced.

Printing features **< 20 microns**
(~2.5 microns with laser cure)
Gap between lines **< 10 microns**
Thickness **< 100 nm and upwards**
Droplet volume **2 – 150 picolitres (pL) (typical)**
1 pl = 1 x 10^{-12} litres = < 10 ng
<1 femtolitre (attolitres) being developed
1fl = 1 x 10^{-15} litres
1al = 1 x 10^{-18} litres
Ink viscosity **~ 1 - < 5 mPas**
Droplet velocity **up to 50 m/s (1,000,000 drops/s)**

Figure 5. A summary of what can be expected in fine line ink jet printing.

When the drop arrives at the substrate surface there is the next technology challenge. One of the usual requirements is for the printed material to have good adhesion. In the same way that any vacuum coating process that requires good adhesion for printed material the surface energy of the substrate surface along with the precise chemical composition becomes important. If the substrate surface is flame, corona or plasma treated to increase the surface energy to improve the wetting of the coating that is deposited it will have two different effects. The first is that the surface having been increased in surface energy the depositing material will have improved wetting and improved adhesion. The second critical effect for the printed ink is that the wetting not only increases the adhesion but has a negative effect on the line width in that the improved wetting will significantly increase the printed line width. The idealised aim would be to convert the spherical drop into a parallel disc of printing. This would produce a minimised line width and height combination. The reality is something else. If the drop does not wet the substrate surface the drop will convert to a hemisphere, or worse. If the drop does wet the surface the drop will spread out and produce a drop considerably larger than the twice the drop diameter that is used as a rule of thumb. The higher the surface energy the greater the wetting and the larger the minimum line width will become. Thus the minimum line width will become dependant upon the combination of ink and substrate and any surface treatment used as shown in Figure 6.



Q. Is it better to plasma treat to improve adhesion but have the droplets spread?

thinner + wider **or** **thicker + narrower**

Figure 6. A schematic of the effect differing surface energy could have on printing.

One method of recovering the fine line width is to use a laser to cure the printed material and to wash off the excess material. This sounds easy but obviously the fine ink jet printing has to then have the laser writing in-register with the centre of the printed material as shown in Figure 7.

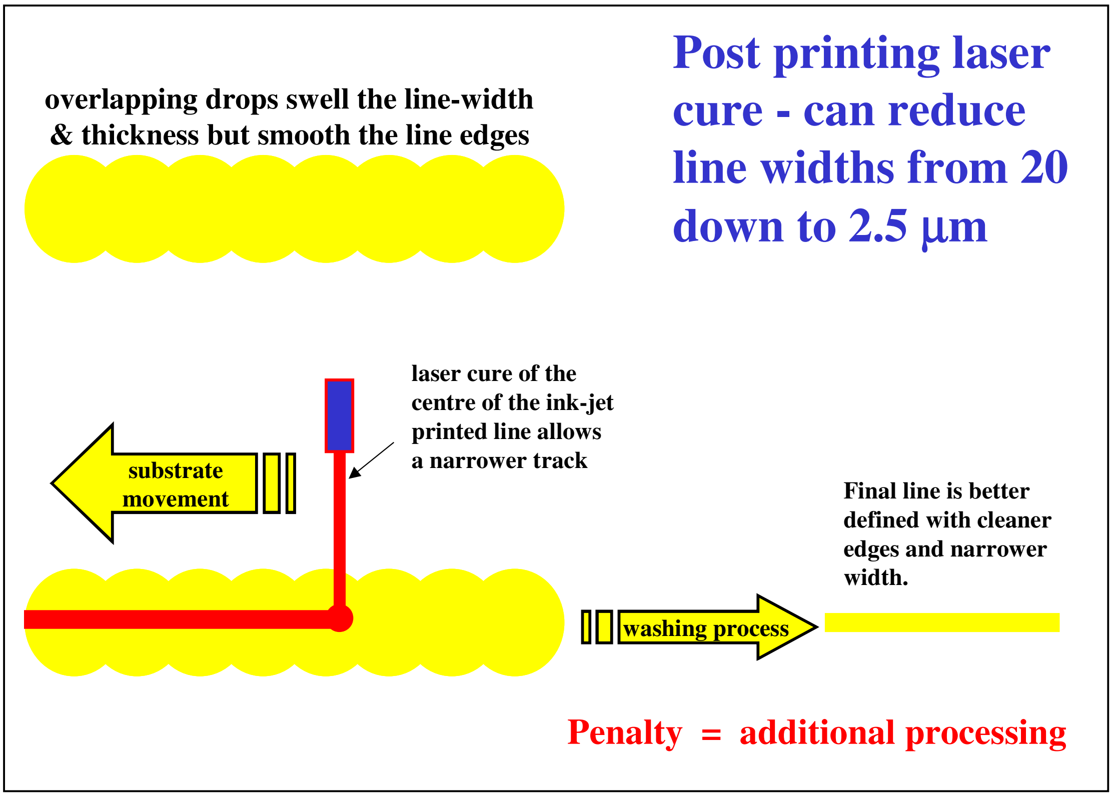


Figure 7. A schematic of the use of laser writing to refine the line width produced by ink jet printing.

This also requires that the ink composition is modified to remain liquid until laser cured and that there is the option of being able to wash off the excess material following the laser cure. Where the intention is of adding further layers also in vacuum this washing process may not be convenient.   This technology takes the line with down from 20 microns to around 2.5 microns. In theory if the ink jet printing is used to produce lines that overlap, that initially show as solid blocks of print, the laser writing can produce not only finer lines but also then write lines closer together than could be printed directly.

Conclusions.

Research has shown that ink jet printing in-vacuum is possible. Also since presenting this work it has come to my notice that one company has been developing thick copper deposition by molten ink jet printing in vacuum for flex circuit applications. This copper deposition produced copper tracks in the thickness range 75 microns down to15 microns. I would surmise that the track widths were similarly large.

Thus we have at least two data points, one that conventional ink jet can be used and does not splash in the way it does at atmospheric pressure and the second that molten metals can be printed in vacuum.

So the process is entirely feasible it is now just a matter of if the current state of the art atmospheric line widths can be translated to being produced in vacuum.

The state of the art ink jet printing at atmospheric pressure can produce 3 micron lines and 3 micron spacing and the writing speed, using multiple nozzles and heads, is in the same ball park as some of the slower vacuum deposition techniques such as sputtering.

There is still much work to be done to optimise the surface treatment to give the best compromise between adhesion and wetting and this is likely to be very system specific. I would expect that changing any of the ink, print head manufacturer or substrate would require the process to have to be re-optimised.

Allowing that this development work still has to be done it looks to be feasible to be able to print regular arrays of dots, a criss-cross of lines or a variety of other patterns suitable for controlling nucleation as well as making a variety of devices.

Thus we have one more technology available for exponents of vacuum coating to use for product differentiation.