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# Ink-jet printing in micro-manufacturing: opportunities and limitations

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## Abstract

Ink-jet printing provides a family of mask-less digital processes for the controlled deposition of materials in liquid form. A wide range of materials, including metals, ceramics and polymers, can be deposited, and several process routes apart from direct additive deposition can be used. This review discusses methods by which the various classes of materials can be deposited, and their applications to micro-manufacturing. It is concluded that although much attention has so far been paid to thin-film products, the potential of ink-jet processes for the fabrication of 3-D products has yet to be developed.

**Keywords:** ink-jet printing, liquid drops, fabrication methods

## 1. Introduction

Ink-jet printing involves the controlled deposition of small droplets of liquid on to a substrate and is widely used for small-scale (home and small office) graphical and text printing. It is now being increasingly applied to commercial printing, and the process also offers a wide range of possibilities in micro-manufacturing. Several features make it particularly attractive for certain manufacturing applications.

First, it is a digital process. The location of each droplet of material can be predetermined on an x-y grid, and if necessary can in principle be changed in real time, for example to adjust for distortion or misalignment of the substrate, or to ensure that a certain height of final deposit is achieved. Because it is a digital process, each product in a sequence can easily be made different from every other, in small or even in major ways; bespoke products are generated just as readily as multiple replicas of the same design. Since the pattern to be printed is held as digital data, there may be significant cost savings over processes which involve the use of a physical mask or template.

Second, it is a non-contact method; the only forces which are applied to the substrate result from the impact of very small liquid drops. Thus fragile substrates can be processed which would not survive more conventional printing methods. Non-planar substrates can be printed, since the process can be operated with a stand-off distance of at least 1 mm.

Third, a wide range of materials can be deposited, and several different methods can be used to generate structures. Multiple combinations of materials can be used, and ink-jet printing can also be combined with other process steps, so that in principle complex heterogeneous and composite structures can be produced, with different materials distributed in all three dimensions.

The aim of this review is to explore the range of materials which can be deposited by ink-jet printing, the various methods by which ink-jet processes can be used for both additive and subtractive fabrication in micro-manufacturing, and the opportunities, but also the limitations, offered by these processes.

## 2. Principles of ink-jet printing

### 2.1 Drop generation

Two different methods are most commonly used to generate drops in ink-jet printing, termed continuous ink-jet (CIJ) and drop-on-demand (DOD). In CIJ a continuous stream of ink drops is generated from a nozzle by exciting the natural tendency of a continuous liquid jet to become unstable and break up into discrete drops under surface tension forces (Plateau-Rayleigh instability). Each drop is then individually electrically charged by induction from a nearby electrode, and steered (deflected) by electrostatic forces to write spots on the substrate. By varying the induced charge, the deflection experienced by the drop, and hence its final position on the substrate, can be controlled. Drops that are not charged in this way are fed into a gutter and recycled. Simple CIJ systems use single nozzles, but systems also exist with multiple nozzles.

In the DOD method an individual nozzle, usually within an array containing a large number of nozzles, is individually addressed to eject a single drop of ink on demand, by inducing a transient pressure pulse in a chamber behind the nozzle. The drop then travels in a straight line from the nozzle to form a deposit on the substrate.

A further method of drop generation uses an electric field to draw out liquid from a nozzle, forming a Taylor cone which then breaks up into a stream of very small droplets. This process, known as electro-spray, is not commonly employed in commercial ink-jet printing systems, although it is capable of producing very small drops (µm or even smaller) [1]. Although both electro-spray and CIJ methods have been investigated for some manufacturing applications, DOD processes can be used to deposit the widest range of materials and most research and commercial use of ink-jet methods for manufacturing has involved that technology. Further details of DOD and CIJ methods are available in [2, 3]. We shall focus on DOD printing here.

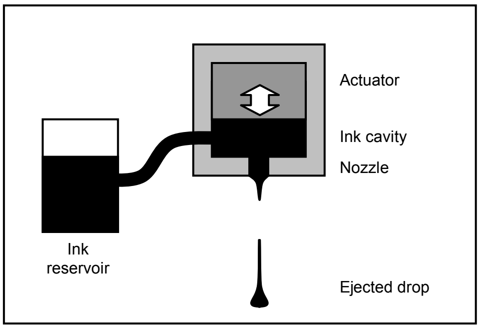

Figure 1. Schematic illustration of the principle of operation of a drop-on-demand printhead [2, 3].

In DOD printing the liquid is ejected from a cavity in the printhead in response to a trigger signal, as shown schematically in Figure 1, through the generation of a pressure pulse by an actuator. There are two common types of actuator. The thermal DOD (or bubble-jet) method is widely used in home and small-office printers; rapid transient heating of the ink by a small electrical heating element located in the ink cavity close to the nozzle creates a short-lived bubble of vapour which drives a jet of ink out of the nozzle. The bubble then collapses, drawing ink from the reservoir to refill the cavity, and the process can be repeated. More common in industrial ink-jet systems is the use of a piezoelectric element which changes the internal volume of the cavity on the application of an electric field, and generates pressure waves which in turn eject ink from the nozzle and then refill the cavity. Since thermal DOD involves the vaporisation of a small volume of the ink, this places significant restrictions on the materials which can be jetted by this method; they must be relatively volatile, or at least have a volatile component. There are no such restrictions for the piezoelectric DOD method. Printheads for both methods of DOD typically contain tens, hundreds or even thousands of separate nozzles, fed by a single ink manifold but each individually addressable.

Once the jet emerges from the nozzle, surface tension causes it to form a main drop followed by a fluid ligament which may collapse into one or more smaller satellite drops. These satellites may then combine with the main drop, or remain separate. In an ideal system the ink will have formed a single drop by the point at which it impacts the substrate, typically at a stand-off distance of 0.5-1 mm, but this is sometimes not achieved.

The diameter of the drop, which ultimately limits the resolution of the printing process, is similar to the diameter of the nozzle. Typically this is about 50 μm, corresponding to a drop volume of some 60 pL, although commercial printheads are available which produce drops as small as 1 pL (~10 μm diameter). By using a small nozzle and a complex drive waveform some second generation systems (‘grey-scale’ heads) can produce a stream of micro-drops which then merge into a single drop with controllable size before it strikes the substrate. Drop ejection velocities in DOD printing are typically 5 – 10 m/s, as shown in Table 1. The process of jet ejection and drop formation involves the sequential, discrete steps of fluid ejection and cavity replenishment, with a maximum frequency of operation governed by the timescale of these events. In a typical DOD system this results in a minimum drop spacing along the stream ejected from a single nozzle which is some 10 to 20 times the drop diameter.

Table 1
Comparison of performance and fluid mechanical parameters for typical commercial CIJ and DOD systems [3].

| Parameters | CIJ | DOD |
|---|---|---|
| Drop velocity m/s | 10 - 20 | 5 - 10 |
| Drop diameter μm | 10 – 150;<br>typically 120 | 10 – 150;<br>typically 50 |
| Drop volume pL | 0.5 - 2000 | 0.5 - 2000 |
| Fluid viscosity mPa s | 2 - 10 | 10 - 100 |
| Re (typical) | 100 - 1000 | 2 - 50 |
| We (typical) | 500 - 1500 | 50 – 150 |
| Oh (typical) | 0.03 – 0.2 | 0.1 - 1 |

The dominant forces which control the behaviour of liquid jets and drops arise from inertia, viscosity and surface tension. In comparing and analysing jetting and break-up phenomena, the conditions can be described in terms of appropriate dimensionless groups. The Reynolds number Re, defined by $Re = \rho DV/\eta$, describes the ratio between inertial and viscous forces in a fluid with dynamic viscosity $\eta$ and density $\rho$, at a velocity $V$ and a characteristic length $D$, usually taken to be the jet or drop diameter. The Weber number We, where $We = \rho DV^2/\sigma$ and $\sigma$ is the surface tension, describes the ratio between kinetic energy and surface energy: i.e. between inertial and surface forces. It is sometimes also useful to consider the value of the Ohnesorge number Oh which describes the relative importance of viscous and surface forces, where $Oh = We^{1/2}/Re = \eta/(\rho\sigma D)^{1/2}$. It has been suggested that DOD printing of a fluid is practical only if Oh lies within the range between about 0.1 and 1 [4], although there is some disagreement about the precise range of Oh for which fluids can be jetted from different designs of printhead. For Oh values above the upper limit, viscous dissipation in the fluid prevents drop ejection, while for values below the lower limit, multiple droplets form rather than a single well-defined drop. The criterion for 'jettability' of a fluid from a DOD system thus involves both its viscosity at the temperature of jetting, which must fall within the limits indicated in Table 1, and also the Ohnesorge number which should lie in the approximate range $1 > \mathrm{Oh} > 0.1$.

### *2.2 Drop impact*

A wide range of behaviour is possible when a liquid drop strikes a solid surface, as reviewed by Yarin [5]. For the conditions applicable to inkjet printing, both gravitational and fluid compressibility effects can be neglected. The dynamics of drop spreading can be characterized primarily by the Weber and Ohnesorge numbers, as shown in Figure 2. The value of We determines the origin of the driving force for spreading, while Oh describes the force that resists spreading. The conditions for ink-jet printing lie in a regime where, at least for the earlier stages of impact, inertial forces dominate and viscous forces are weak. As the spreading liquid comes to rest, however, capillary (surface tension) forces become more important.

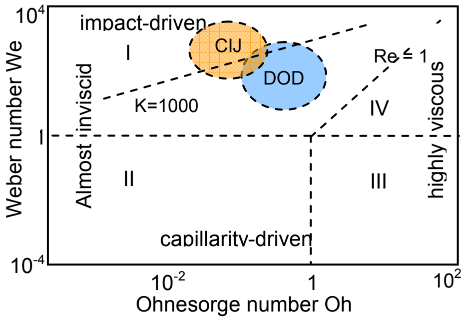

Figure 2. Schematic diagram showing four regimes of behaviour for a liquid drop on impact, based on the values of Weber and Ohnesorge numbers [3, 6]. The typical ranges of values for drop-on-demand (DOD) and continuous (CIJ) ink-jets is shown.

Splashing of the drop on impact is generally undesirable if precise placement and material deposition is required. The threshold for splashing to occur during impact depends on the condition of the surface (e.g. whether it is porous or not, its roughness, and the presence or absence of a liquid film), and can be expressed in terms of the dimensionless group $K = \mathrm{We}.\mathrm{Oh}^{-2/5}$. Although better models exist, an approximate condition for splashing for impact on to a non-porous surface is given by $K > 1000$, which is represented by a sloping line in Figure 2. Splashing will be favoured for conditions above this line, i.e. for a larger drop, higher impact velocity, lower fluid surface tension or lower viscosity. It will occur more readily on a rougher substrate, and under the usual conditions for CIJ printing than for DOD.

Figure 3 shows the four stages of development of the diameter of a liquid drop after impact on to a solid surface [7]. The three curves in the figure illustrate the behaviour for liquids which wet the surface well (top curve), and poorly (bottom curve); an intermediate case is also shown. The axes represent the diameter of the deposit in non-dimensional form $d^*$ (where $d^*$, often referred to as the spreading factor, is defined as the contact zone diameter divided by $D$), and the time after impact made non-dimensional by using the impact velocity $V$ and the initial drop diameter $D$ ($t^* = Vt/D$). Four phases can be identified. In the initial kinematic phase the drop has its initial spherical shape, truncated by the plane of the surface, and the contact circle increases according to a power law with $d^* \approx t^{*1/2}$. This phase of the impact is completely described by the impact velocity and initial diameter. In the next phase, beyond $t^* \approx 0.1$, the spreading depends most strongly on the viscosity of the liquid, with less effect of surface tension; less viscous liquids attain larger diameter drops than more viscous liquids, although towards the end of this phase (say for $t^* \approx 1$) the role of surface tension becomes more important. During the spreading phase the diameter is constantly increasing. After this phase (from $t^* \approx 2$) the effects of surface tension, and in particular of the contact angle between the liquid and the surface, play a major role. Depending on the wettability of the surface and the balance between inertial and viscous forces up to this point, the contact angle at the end of the spreading phase may be greater or less than the appropriate (advancing or receding) equilibrium value; the drop may therefore continue to expand, or retract, during the relaxation phase, as shown in Figure 10. For longer times ($t^* > \sim 10$) and if the surface is well wetted by the liquid, the drop continues to expand with a diameter proportional to $t^{*1/10}$ [8]. In practical applications of ink-jet printing, the first three stages of drop spreading shown in Figure 3 last only a few tens of microseconds. In order to achieve a well-localized deposit, a small final contact diameter is generally required, which in turn demands a small initial drop size and a relatively high contact angle. For a contact angle of 90°, where the equilibrium drop shape will be a hemisphere, the final value of $d^*$ will be 1.26.

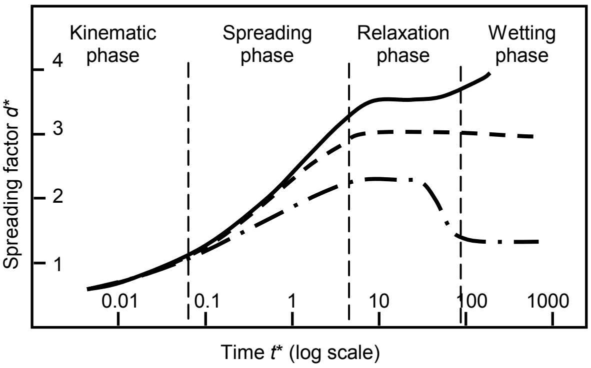

Figure 3. Schematic representation of the spreading of a liquid drop with time. The axes represent the non-dimensional diameter of the drop $d^*$ and the non-dimensional time $t^*$ after impact [after 7]. The labelling of the axes is approximate.

## 3. Materials

### *3.1 General remarks*

Inkjet technology has been used to deposit a very wide range of materials, including metals, ceramics and polymers for many different applications. Biological materials, including living cells, have also been successfully printed. The most important restriction is that the material being printed must be in liquid form (or contain small solid particles in a liquid medium) with appropriate rheological properties, at the point of printing. As discussed below, the material which is printed need not be the same as the final material required: several routes exist in which a precursor material is deposited.

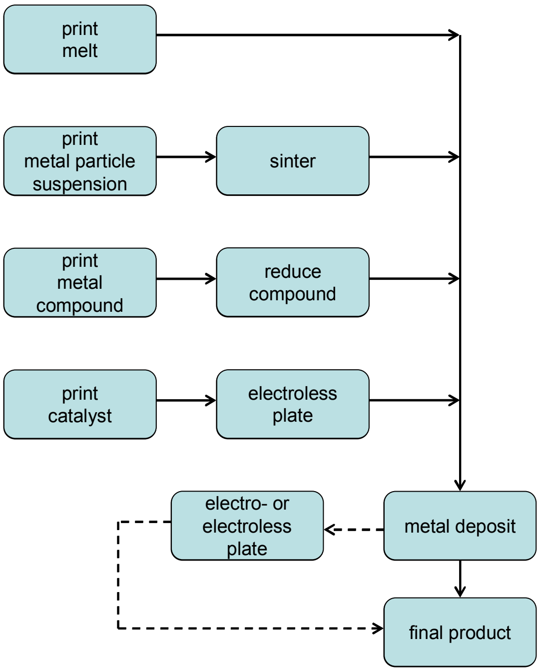

Figure 4. Process routes for the ink-jet deposition of metals

### *3.2 Deposition of metals*

Figure 4 illustrates several routes by which inkjet printing can be used to form metallic deposits: direct printing from a melt; printing a suspension of metallic particles which are then sintered to bond them together; printing a metal compound which is then chemically reduced to form the metal; and printing a suitable catalyst followed by electroless plating to deposit the metal. Any of these processes can in principle be combined with one or more secondary electroless or electro-plating steps to produce a thicker metallic deposit, which can even be of a different metal.

In principle, the simplest method is to print droplets of molten metal directly on to the substrate. An early application of the direct printing of liquid metal was to form solder droplets for chip connection bumps, via filling, connector tracks and rework on electronic printed circuits, and several researchers have reported the printing of lead-tin solder alloys by both CIJ and DOD methods [9, 10, 11]. Other metals with relatively low melting points such as indium, tin, lead and zinc have also been printed by CIJ and DOD [12, 13]. Alloys with higher melting points pose significant challenges for printhead design, and although piezoelectric drive may still be useful, precautions must be taken to isolate the transducer from the high melt temperature; other actuation methods have also been used, such as direct pneumatic ejection in DOD printing [13]. The deposition of aluminium, both pure and alloyed, has been demonstrated in a droplet-based net-form manufacturing process in which the drops are generated and deflected by piezoelectric CIJ technology, with drops 190 µm in diameter being generated at 17 kHz, corresponding to a mass throughput of 1.5 kg/h [14]. Deposition in an inert atmosphere is necessary to avoid oxidation of the molten droplets, and this requirement, together with the complications introduced by operating the printhead at high temperature, limits the attractiveness of the direct melt printing process for many metals.

Metallic particles suspended in a suitable fugitive liquid can be inkjet printed, and used for both structural and electrical applications. Small particles are generally favoured as the suspensions are more stable, i.e., the particles do not sediment, and nozzle clogging is avoided. Particles smaller than 1/10, and preferably smaller than 1/50 of the nozzle diameter are required to avoid blockage. A further very important advantage of small particle size is that the high surface to volume ratio leads to a lowered sintering temperature. There is considerable interest in the development of nanoparticle inks with good electrical properties, oxidation resistance and low sintering temperatures for printable electrical conductors [15]. Inks based on silver nanoparticles, typically 5 - 50 nm in size, for example can be sintered to form deposits of high electrical conductivity at temperatures below 300 °C, and even as low as 150 °C, which allows them to be used with some polymer substrates [16, 17]. Other nano-particulate metals which have been successfully printed include gold and copper [18]. Although prices are still high, several silver nano-particle inks are commercially available, and conductivities following sintering can be as high as 50% of bulk silver. Lowering the sintering temperature widens the range of possible substrates, and there is also interest in methods of sintering which do not involve bulk heating: examples include the use of a laser focused on the ink deposit or scanning rapidly over the surface, and microwave heating [19]. A novel process involving treatment with aqueous halide solution at room temperature has also been shown to produce conductivities similar to thermal sintering [20].

Conductive particulate inks in which the solvent does not evaporate but cures to form a binder will give lower conductivity, but this is sometimes desirable, an example being the use of carbon nanotubes in a polymer matrix for the in-situ fabrication of electrical resistors.

The third method of achieving a metallic deposit by ink-jet printing is to print a precursor: a solution of a compound of the metal, usually silver, which is then decomposed by heating. For example, inks based on silver nitrate and on organic silver compounds have been successfully printed and processed to yield conductive metallic deposits by CIJ [21] and DOD processes [22, 23]. Decomposition of the printed compound to form the silver deposit is usually achieved by heating, although photolytic processing by laser irradiation has also been reported [24]. It has been shown that the need for a separate decomposition step can be eliminated by printing an organometallic silver ink directly on to a substrate heated to 130 °C, a temperature compatible with the use of several common polymer substrates [25].

The final approach shown in Figure 4 is to print a non-conductive but chemically active deposit which is then subjected to a secondary treatment in a low-temperature electroless plating bath, typically to deposit copper or nickel. The printing process produces a template for the subsequent plating, and defines the area to be coated; the plating time can be varied to control the thickness of metal deposit. Excellent conductivity can be achieved in this way and the low process temperature is a significant advantage for some applications. As an example, silver nano-particle ink has been printed as a 'seed' layer, followed by electroless plating of nickel: final deposit heights up to 76 μm were reported [26].

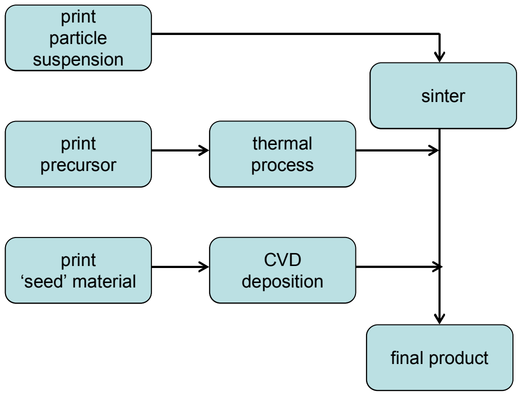

Figure 5. Process routes for the ink-jet deposition of ceramics

*3.3 Deposition of ceramics*

There are several different routes by which ceramic materials can be deposited by ink-jet printing, which are analogous to some of the methods used for metals and are illustrated in Figure 5.

Suspensions of fine ceramic particles can be directly jetted, provided that the viscosity and surface tension of the mixture lie within the correct range. Alumina particles with median sizes between 0.3 and 1.5 μm have been mixed with wax and kerosene to produce jettable suspensions containing up to 40% ceramic particles by volume, which were then sintered after deposition to produce a material with a final relative density of 80% [27]. A similar approach has been successfully used to deposit PZT (lead zirconate titanate) which was then sintered to effectively full density [4]. Thermal DOD has been used to print suspensions of 0.5 μm silicon nitride powder in an aqueous medium, and good mechanical properties have been claimed in the sintered product [28].

Chemical precursors can also be printed, and then transformed to the final ceramic product. One example is the dielectric ceramic, barium strontium titanate, which has been deposited by printing a metal-organic precursor on to a ceramic substrate, followed by pyrolysis and annealing, to form a capacitor structure [29]. Cerium oxide has been produced by ink-jet printing of precursor solutions on to a heated substrate, giving the desired crystalline deposit without any further heat treatment [30]. Several investigators have used sol-gel precursors followed by thermal treatment: for example, to deposit PZT [31] and barium titanate films [32].

A further method, which has been used to generate patterned deposits of nanocrystalline diamond, is to print a suspension of fine nanodiamond particles (4-5 nm in size) on to a silicon substrate and then to use these as 'seed' particles for the growth of a continuous diamond film by a conventional chemical vapour deposition (CVD) process. It has been suggested that this process may be developed to produce 3-D diamond structures by sequential ink-jet printing and CVD processing [33].

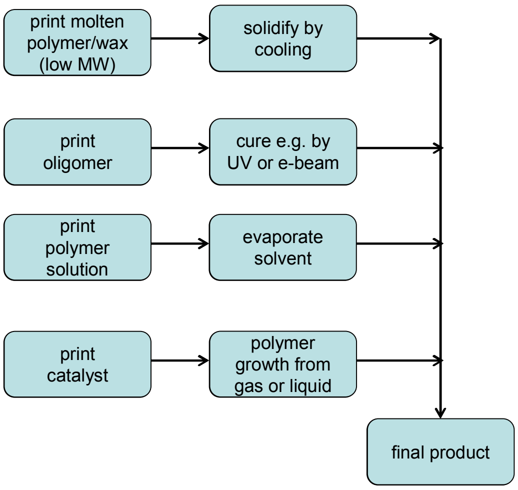

Figure 6. Process routes for the ink-jet deposition of polymers

*3.4 Deposition of polymers*

Figure 6 summarises the methods by which polymeric materials can be deposited. Waxes, and other relatively short-chain polymers with molecular weights of a few hundred Daltons, can form readily jettable melts, and can be used for some applications such as mask printing and rapid prototyping. Long-chain polymers, however, cannot be jetted directly since even as a melt their viscosity is usually too great, and alternative routes are needed to deposit these polymers by ink-jet printing [34]. They can be dissolved, or colloidally dispersed to form a latex, in suitable solvents, although even in solution the presence of a small concentration of high molecular weight polymer may introduce sufficient viscoelasticity to inhibit good droplet formation [35]. Electronically functional polymers, such as conductors (e.g. conjugated polymers such as PEDOT:PSS and polyaniline), semiconductors and polymer light-emitting diode (PLED) materials, can be DOD printed in solution. There is major commercial interest in printing organic semiconductors, for such applications as display backplanes, and also in fabricating large-area PLED displays [35].

For structural or optical applications or to achieve dielectric properties, thermoset polymers can be cross-linked in situ after printing, by thermal treatment, electron beam treatment, or by UV-curing a formulated ink containing a photo-initiator. UV curing is increasingly common in graphical printing applications, and can involve a brief ‘pinning’ exposure immediately after printing to arrest migration of the drop edge, followed by subsequent full curing, perhaps after further layers of material have been printed.

Finally, ink-jet printing of a suitable catalyst has been used to initiate local formation of conductive films of polyacetylene in subsequent gas-phase treatment [36].

## 4. Applications

A summary of possible process routes which employ ink-jet printing for micro-manufacturing is shown schematically in Figure 7. These routes are applicable in principle to any materials, although some have been little explored.

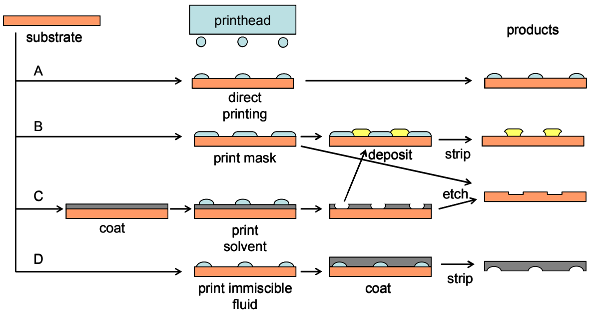

Figure 7. Process routes involving ink-jet printing for micro-manufacturing

### 4.1 Direct deposition

The process shown as route A in Figure 7, involving direct deposition of material on to a substrate in a digitally defined pattern (by any of the methods outlined in section 3), is the simplest process and has been widely exploited. Many manufacturing applications of ink-jet printing are to be found in the electronics industry, and involve products in the form of thin films. The printing of conducting tracks has been widely explored, and is currently the most important application of the inkjet printing of metals. Printing of silver nanoparticle ink followed by sintering, and the printing of a catalyst followed by electroless plating, can both give good electrical conductivity; circuit elements produced in these ways have been demonstrated, including UHF transmission lines and antennas [37], organic thin film transistors with silver electrodes [38], and metal-insulator-metal crossovers [17]. However, little attention has been paid to the possibility of depositing mechanical components by the printing of metal particle ink, although some examples have been provided by Fuller et al. [16], including thermal-expansion-driven actuators with features up to 1 mm tall, fabricated by multiple deposition (400 layers) of silver nanoparticle ink. Figure 8 shows an inductor fabricated with silver nano-particle ink by piezo-DOD printing [16].

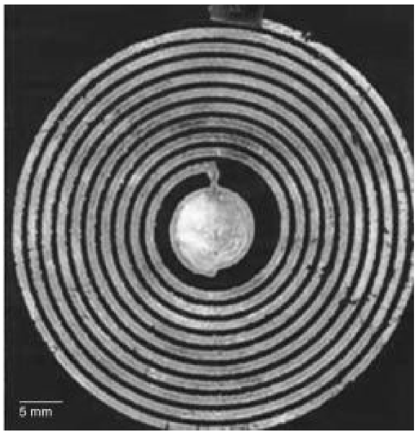

Figure 8. Inductor fabricated by ink-jet printing with silver particulate ink [16]

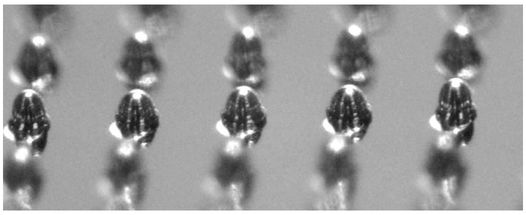

Figure 9. 100 μm solder bumps ink-jet printed on to 100 μm pads on 250 μm centres at a rate of 400 per second [39]

Direct printing of molten metal has been used to form solder bumps for electronics chip interconnection; the rapid heat transfer to the cooler surface leads to rapid solidification of the metal in contact with the substrate and thus to pinning of the spreading contact line, giving a well-defined smooth deposit with a high contact angle (Figure 9) [9, 39].

Repeated DOD deposition of liquid metal droplets has also been used to build vertical solder columns, up to a few mm in height corresponding to aspect ratios of about 20 [11], while macroscopic artefacts tens of mm in size have been fabricated by CIJ printing of liquid aluminium alloys [14].

Oxide ceramics in thin-film form have many potential applications, for example as dielectrics, piezoelectric materials and catalysts. Examples of their direct deposition by ink-jet processes have been given in section 3.3.

Thick deposits of ceramics can be built up by repeated printing of particulate suspensions, and the fabrication of 3-D artefacts by printing followed by sintering has been demonstrated for alumina [27], silicon nitride (as shown in Figure 10) [28], PZT and $TiO_2$ (Figure 11) [40]. Applications include mechanical components, piezoelectric transducers and photocatalysts.

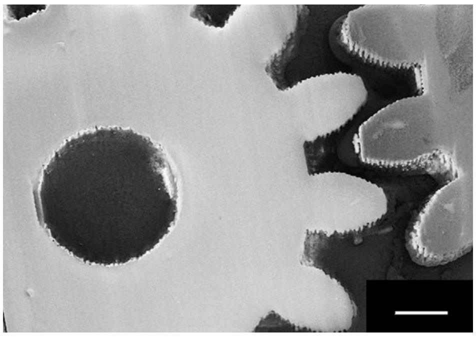

Figure 10. Sintered $Si_3N_4$ gearwheels fabricated by ink-jet printing and sintering [28] (scale bar 1 mm long).

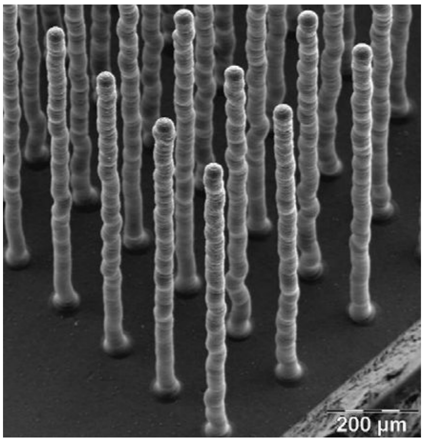

Figure 11. Ink-jet printed $TiO_2$ pillars [40]

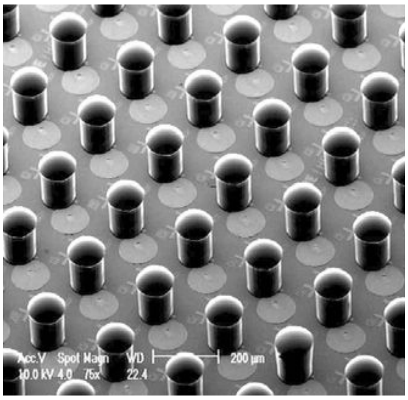

Figure 12 Epoxy resin microlenses printed on to 100 µm tall transparent pedestals for light collimation [39]

Thin films of polymers have wide application in electronics as dielectrics and conductors, and also as functional materials: for example as semiconductors and light-emitters. Polymers as well as ceramics provide materials for micro-scale sensors and actuators [41]. Processes discussed in section 3.4 have all been used to deposit polymer films. Thicker deposits have potential for optical applications, and inkjet printing has been used to form optical waveguides and small plano-convex lenses, as single lenses or as multiple lens arrays (Figure 12) [39, 42].

An important challenge in many applications in which droplets of suspensions or solutions are deposited, followed by evaporation of the solvent, is to achieve solid deposits which are as flat and even as possible. There is a natural tendency for solutes or particles to deposit from evaporating drops towards the rim of the drop where the contact line becomes pinned: the ‘coffee stain’ effect [43]. One explanation for this effect is that solvent close to the droplet edge evaporates more readily than from the centre, leading to a transport of material towards the boundary. In some applications special measures, e.g. through the use of mixed solvents, must be taken to reduce this effect, while in others it can be actively exploited to give a desirable variation in film thickness [44].

### *4.2 Ink-jet mask printing*

While direct deposition has been widely explored, it is by no means the only route by which ink-jet printing can be used to create digitally-defined structures. An alternative method (route B in Figure 7) is to print a mask, and then to use this to define areas to be etched, or on which a further material can be deposited (for example by electro-less or electro-plating). Direct ink-jet printing has been explored for masks for electronic printed circuit board production, but little work has been done on the wider application of ink-jet mask printing to the texturing of surfaces. CIJ has been used with a solvent-based polymer ink to deposit masks on to steel rolls for subsequent etch patterning; the deposited drop diameter was ~150 µm [45].

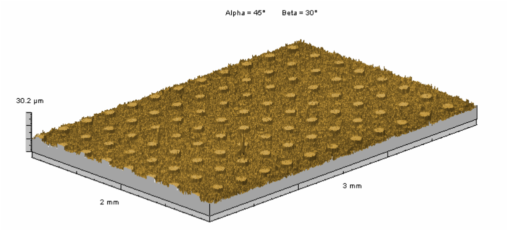

Figure 13. Steel surface patterned by ink-jet mask printing followed by etching [47].

More recently, several ink types were investigated for mask printing, and 120-150 µm features were printed on to metallic substrates with a UV-cured polymer ink [46]. An example of a steel substrate patterned by inkjet printing of a mask followed by acid etching is shown in Figure 13 [47]. The circular masked regions, formed with a solvent-based polymer ink, were 60 µm in diameter; the thinnest parallel gap which could be formed between mask lines was ~20 µm and the smallest square gap ~40 µm across. Solvent-based and UV-cured inks are not however generally designed for masking applications. Phase-change (e.g. wax-based) inks have been designed specifically as jettable etch-resists; they are printed at high temperature on to a cold substrate and give good edge definition as drop spreading is arrested once the drop begins to solidify. One major application of ink-jet mask printing is in photovoltaic solar cell fabrication.

### 4.3 Inkjet etching

Route C in Figure 7 is known as ‘inkjet etching’ and involves the printing of drops of solvent on to a suitable thin (usually polymeric) coating. Local dissolution of the coating, followed by evaporation of the solvent, leads to redistribution of the coating material at the edges of the crater (by the coffee-stain mechanism discussed in section 4.1) and thus to the formation of a hole in the coating. While there may still be some residual coating material at the centre of the crater after the first evaporation event, this can usually be removed by repeated printing of solvent drops. First explored as a process for making via holes in the fabrication of thin film transistors, inkjet etching has more recently been further investigated and shown to offer various possibilities of forming regular arrays of features, such as circular, rectangular holes and linear grooves, as illustrated in Figure 14 [48]. Patterning of polymer layers in this way has been proposed for the production of biochips and micro-patterned cell arrays, but it could also be used for mask fabrication, to be followed, as in direct mask printing, by subsequent etching of an underlying substrate or by deposition of a different material.

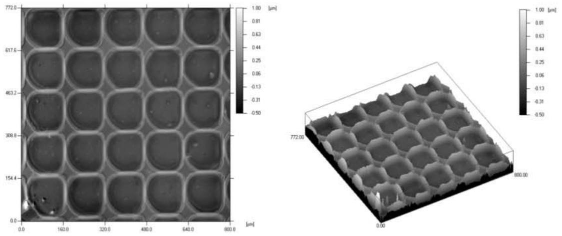

Figure 14. Array of rectangular holes etched in a polystyrene layer by inkjet printing of solvent [48]

Variations of the inkjet etching process have also been developed. For example, if small drops of solvent are printed on to a thick polymer substrate, they will evaporate leaving an array of smooth-surfaced craters which can either be used directly as micro-lenses, or as a template to form convex lenses by use of a suitable cast replicating material; the focal length of the lenses can be altered by varying the drop deposition sequence [49]. Ink-jet printing can also be used, not to remove a polymeric coating material, but to plasticise it so that an etchant can permeate through to attack the underlying substrate. The plasticisation can also be reversed, for example by heating the coating to drive off the plasticiser, creating a very versatile process for fabricating certain types of structure. It has been explored for forming openings in buried semiconductor layers in photovoltaic solar cells [50].

### 4.4 Inverse ink-jet printing

Route D in Figure 7 can be termed ‘inverse ink-jet printing’ since it forms holes or cavities in a solid material in the locations where the drops of ink are deposited. The process has been used to fabricate polymeric micro-sieves, by printing an array of sessile drops on to a substrate, applying a continuous film of a polymer which is immiscible with drops, curing it to solidify it, and then removing it from the substrate [51]. In this application the pore size in the sieve is controlled by the height of the printed drop and the thickness of the polymer layer, but the process could also be adapted, by using a thicker layer, to produce an array of concavities which could then be used either as concave lenses, or by replication, to generate an array of convex lenses.

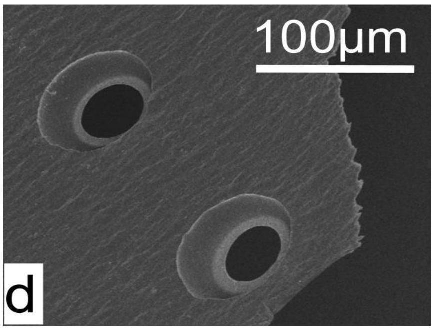

Figure 15. Area of polymer micro-sieve formed by inverse inkjet printing [51].

## 5. Potential and limitations

We have seen how ink-jet printing can in principle be used to deposit a very wide range of materials, singly or in combination, either directly or as a step in a more complex process route. It is already widely used industrially for printing of text and graphics, and is now being adopted for certain manufacturing processes where its ability to deposit precise volumes of material in well-defined locations under digital control offers special benefits. Examples include the deposition of organic LED materials in flat-screen displays, production of colour filter masks, and in the production of printed plastic electronics. However, there are important limitations to the use of ink-jet processes which must be borne in mind in considering new applications.

The resolution which can be achieved by ink-jet printing depends not only on the size of the final printed drop, after any solidification, drying or curing has occurred, but also on the precision with which the drop can be deposited on to the substrate. That precision is influenced by the accuracy of movement of the substrate or printhead, and also by inherent variability in the direction with which the jet leaves the printhead, on aerodynamic and electrostatic influences on the droplet in flight, which may themselves depend on the presence of other neighbouring drops, and other sources of process variability such as variation in drop size and velocity. In practice drop placement accuracy of better than several μm seem to be hard to achieve in direct inkjet printing on to a homogeneous substrate, and ~10 μm represents a current lower limit to the sizes of features (circular spots or line widths) which can be printed by DOD methods.

However, the final position of a liquid drop on a substrate can be controlled to some extent by using a heterogeneous substrate, in which different areas are wettable to different degrees by the printed drop. This approach has been very successful, for example, in printing thin film transistors, where laser, photolithographic or other methods have been used to pattern the surface energy of the substrate, and thus limit the movement of the deposited drop or steer it away from a hydrophobic region and towards a hydrophilic region [52]. Sub-micrometre features can be fabricated in such ways, and the edge definition which can be achieved is limited largely by the accuracy of the surface energy patterning process. In an ingenious extension of this approach, also used for transistor fabrication, the ink-jet printing of materials in sequence, so that the fluid in the second deposit is repelled by the first which is already on the substrate, can be used to generate extremely narrow channels between the two deposits: gaps of <100 nm have been demonstrated [53].

Most research and development on ink-jet printing for manufacturing purposes has been addressed to the formation of thin film deposits, often for electronics applications. These films may be tens, hundreds or even thousands of μm in lateral extent, but are often sub-μm in thickness, and are formed by the printing of small numbers of layers, or even only a single layer, of drops. Their electronic, rather than mechanical, properties have usually been optimised. In comparison there has been rather little attention, so far, to building 3-D deposits with aspect ratios of one or more for mechanical applications, with the exceptions of free-standing pillars of metals, ceramics and polymers. Surface energy control of liquid surface curvature has been used in forming optical components such as lenses and waveguides, and in depositing solder drops and bumps.

With the exception of some work on the overprinting of conductors and dielectrics as electronic circuit elements [17], there has so far been little attempt to address the challenges involved in sequential, or even simultaneous, deposition of the droplets of different materials which will be needed to fabricate complex 3-D structures from multiple materials. Careful control of surface energies and hence of relative wettabilities will be an essential component of this. Suspensions of small particles are widely used to print both metals and ceramics, but the volume fraction of solids which can be used in the fluid is generally low: there is scope for further development of more heavily-loaded colloidal fluids, which still have the rheological properties needed for printing, to extend the range of materials and products which can be achieved. Full exploitation of the undoubted potential of ink-jet printing for micro-manufacturing will require further research into all these aspects.

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