1

Introduction to Inkjet Printing for Manufacturing

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1.1 Introduction

The basic principles of conventional printing have remained the same for hundreds of years: the various different printing processes which we take for granted all involve the repeated reproduction of the same image or text many times. Usually, this is achieved by transferring a pattern of liquid or semi-liquid ink from some master pattern to the paper or other substrate through direct contact. Changes to the printed product can be achieved only by changing the master pattern, which involves making physical changes within the printing machine.

In contrast, the inkjet printer which is now ubiquitous in the modern home and office works on a fundamentally different principle. Each small droplet of ink, typically 10–100 μm in diameter, is created and deposited under digital control, so that each pattern printed in a sequence can just as readily be different from the others as it can be the same. The principles of inkjet printing were first developed commercially during the 1970s and 1980s, with the practical applications of marking products with dates and bar codes, and addressing bulk mail. As indicated in Figure 1.1, the technology used for these purposes, which demand high operating speeds but can tolerate quite low resolution in the printed text, is now fully mature: these printers, which use continuous inkjet (CIJ) technology, are widely used as standard equipment on production lines worldwide. The next development, from the mid-1980s onwards, involved drop-on-demand (DOD) printing which is capable of much higher resolution than the early coders and placed the

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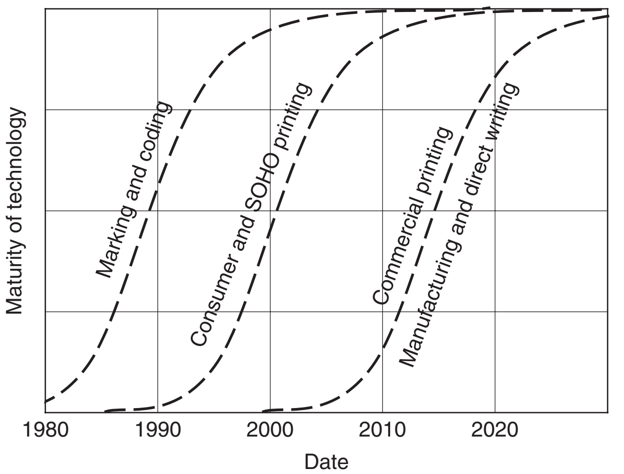


Figure 1.1 *The applications of inkjet technology have developed in three waves: initially for marking and coding, followed by desktop printing of text and graphics in the home and small office environment and, currently, increasing use in commercial printing and manufacturing.*

capability for digital reproduction of text and images, at low cost, into the domestic and small office environment. The principles of both the CIJ and DOD printing technologies are described in Chapter 2.

The subject of this book is the third wave of technology development shown in Figure 1.1; the use of inkjet printing as a manufacturing process. This advance, which is occurring in parallel with the use of inkjet for commercial printing in direct competition with such processes as offset lithography, employs the same basic principles of drop generation as the earlier applications, but with an emphasis on the features of reliability, accuracy, flexibility and robustness which are essential for successful industrial application. Many of the applications discussed in this volume are still under development, and there is undoubted scope for further innovation. Several features of inkjet printing make it particularly attractive for manufacturing.

Firstly, it is a digital process. The location of each droplet of ‘ink’ (i.e. the material being deposited) can be predetermined on a two-dimensional grid. If necessary the location can 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 in the form of digital data, there may be significant cost savings over processes which involve the use of a physical mask or template.

Secondly, 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. The substrate need not even be solid: we shall see examples in Chapter 13 where materials are printed into a liquid bath, and in Chapter 14 where the substrate is a bed of powder. Material can be deposited onto non-planar (rough or textured) substrates, since the process can be operated with a stand-off distance between the print-head and substrate of at least 1 mm. In conventional contact-based printing, the printed material may also be transferred by accidental contact, potentially causing poor quality or contamination; such problems are avoided in a non-contact process.

Thirdly, a wide range of materials can be deposited. By selection of an appropriate print-head, liquids with viscosities from 1 to 50 mPa s or higher can be printed. Several different methods can be used to generate printed structures. Multiple combinations of materials can be used, and inkjet 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.

A further benefit is that inkjet printing is modular and scalable. Multiple print-heads can be assembled to print in tandem, for example by placing them side-by-side to print a wider pattern, or one after the other to print different materials in sequence. These concepts are standard for graphical printing, where four or more colours are commonly used, but can also be readily extended to the manufacturing context.

In this introductory chapter, we shall briefly review the range of materials which can be deposited by inkjet printing and the various methods by which inkjet processes can be used for both additive and subtractive fabrication in manufacturing. The processes of jet and droplet formation, and the various types of print-heads, are introduced in Chapter 2. Later chapters describe the formulation of printable fluids and examine particular applications of inkjet printing in much more detail.

1.2 Materials and Their Deposition by Inkjet Printing

1.2.1 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; they are the subject of Chapters 12 and 13, and we shall not consider them further here. The most important restriction is that the substance 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 in Section 1.3, the material which is printed need not be the same as the final material required: there are several process routes in which a precursor material is deposited, followed by other steps to achieve the final product.

1.2.2 Deposition of Metals

Figure 1.2 illustrates several routes by which inkjet printing can be used to form metallic deposits. These involve 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 also be combined with one or more secondary electroless plating or electro-plating steps to produce a thicker metallic deposit, which can even be of a different metal.

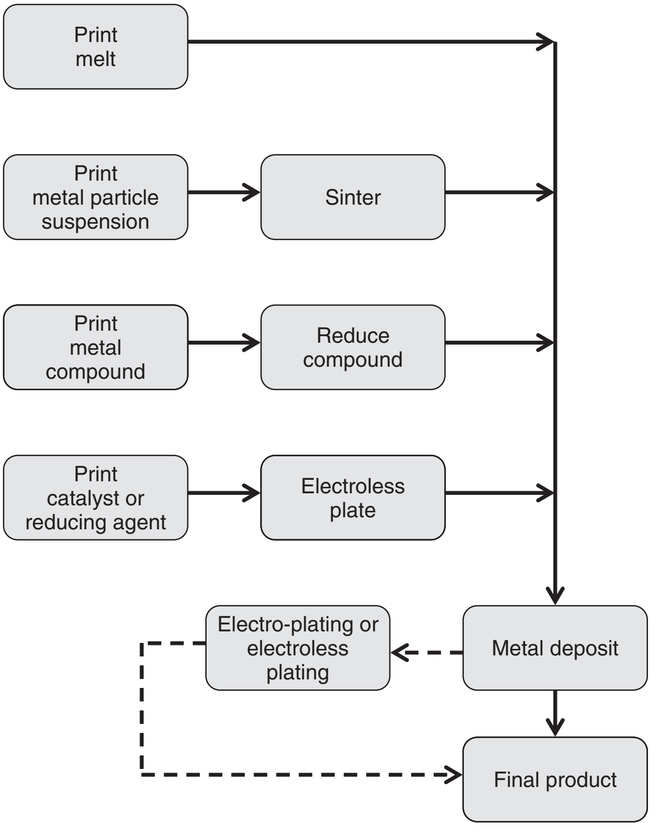


Figure 1.2 *Process routes by which inkjet printing can be used to deposit metals.*

In principle, the simplest method is to print droplets of molten metal directly onto 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 (Hayes, Wallace and Cox, 1999; Liu and Orme, 2001a; Lee *et al*., 2008). Other metals with relatively low melting points such as indium, tin, lead and zinc have also been printed by CIJ and DOD methods (Tseng, Lee and Zhao, 2001; Cheng, Li and Chandra, 2005). Alloys with higher melting points pose significant challenges for print-head design, and although piezoelectric drive (as described in Chapter 2) 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 (Cheng, Li and Chandra, 2005). 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 (Liu and Orme, 2001b). 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 print-head 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, that is, the particles do not sediment, and nozzle clogging is avoided. Industry rules of thumb suggest that particles smaller than 1/10 (and preferably smaller than 1/50) of the nozzle diameter are required to avoid blockage. Another very important advantage of small particle size, as discussed further in Chapter 7, 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 (Park *et al*., 2007). For example, inks based on silver nanoparticles, typically 5–50 nm in size, can be sintered to form deposits of high electrical conductivity at temperatures lower than 300 °C, and even as low as 150 °C, which allows them to be used with some polymer substrates (Fuller, Wilhelm and Jacobson, 2002; Sanchez-Romaguera, Madec and Yeates, 2008). Other nano-particulate metals which have been successfully printed include gold and copper (Park *et al*., 2007). Although prices are still high, several silver nano-particle inks are commercially available, and conductivities following sintering can be as high as 50% of that 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 that focuses on the ink deposit or scans rapidly over the surface, and microwave heating (Perelaer *et al*., 2008). A novel process involving treatment with aqueous halide solution at room temperature has also been shown to produce conductivities similar to those of thermal sintering (Zapka *et al*., 2008). 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 inkjet printing is to print a precursor: a solution of a compound of the metal, usually silver, which is then decomposed by heating. This is further discussed in Chapter 4. Inks based on silver nitrate and on organic silver compounds have been successfully printed and processed to yield conductive metallic deposits by CIJ (Mei, Lovell and Mickle, 2005) and DOD processes (Smith *et al*., 2006, 2008). 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 (Stringer, Xu and Derby, 2007). It has been shown that the need for a separate decomposition step can be eliminated by printing an organometallic silver ink directly onto a substrate heated to 130 °C, a temperature compatible with the use of several common polymer substrates (Perelaer *et al*., 2009).

The final approach shown in Figure 1.2 is to print a non-conductive but chemically active deposit (e.g. a catalyst or reducing agent) 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 nanoparticle ink has been printed as a 'seed' layer, followed by electroless plating of nickel: final deposit heights up to 76 μm were reported (Lok *et al*., 2007). A modification of this approach is to use inkjet printing to deposit a reducing agent and then subsequently a metal salt: this method has been used to form silver conductive tracks by printing ascorbic acid followed by silver nitrate solution (Bidoki, Nouri and Heidari, 2010).

1.2.3 Deposition of Ceramics

There are several different routes by which ceramic materials can be deposited by inkjet printing, which are analogous to some of the methods used for metals and are illustrated in Figure 1.3.

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% (Ainsley, Reis and Derby, 2002). A similar approach has been successfully used to deposit lead zirconate titanate (PZT) which was then sintered to effectively full density (Wang and Derby, 2005). Thermal DOD (defined in Chapter 2) 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 (Cappi *et al*., 2008).

Chemical precursors can also be printed and then transformed to the final ceramic product. One example is barium strontium titanate, a dielectric ceramic which has been deposited by printing a metal–organic precursor onto a ceramic substrate, followed by pyrolysis and annealing, to form a capacitor structure (Kaydanova *et al*., 2007). Cerium oxide has been produced by inkjet printing of precursor solutions onto a heated substrate, giving the desired crystalline deposit without any further heat treatment (Gallage *et al*., 2008). Several investigators have used sol–gel precursors followed by thermal treatment,

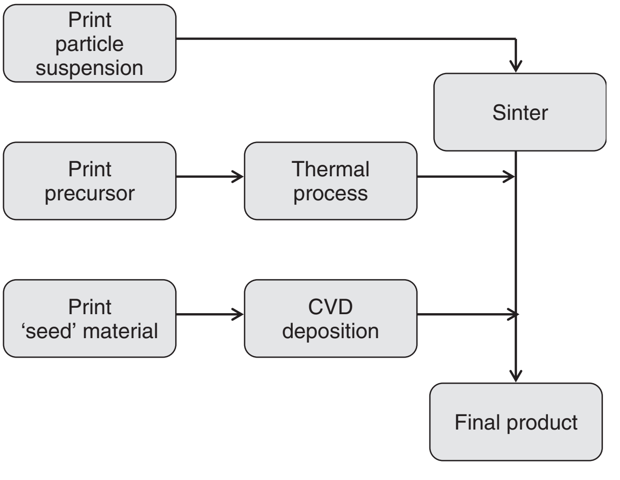


Figure 1.3 *Process routes by which inkjet printing can be used to deposit ceramics.*

for example to deposit PZT (Bathurst, Lee and Kim, 2008) and barium titanate films (Keat *et al*., 2007).

A further method, which has been used to generate patterned deposits of nano-crystalline diamond, is to print a suspension of fine nano-diamond particles (4–5 nm in size) onto 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 3D diamond structures by sequential inkjet printing and CVD processing (Chen, Tzeng and Cheng, 2009).

1.2.4 Deposition of Polymers

Figure 1.4 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 inkjet printing (Calvert, 2001). 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 (De Gans, Duineveld and Schubert, 2004). Electronically functional polymers, such as conductors (e.g. conjugated polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) poly(styrenesulphonate)(PSS), (PEDOT:PSS) and polyaniline), semiconductors and organic light-emitting diode (OLED) materials, can be printed in solution by

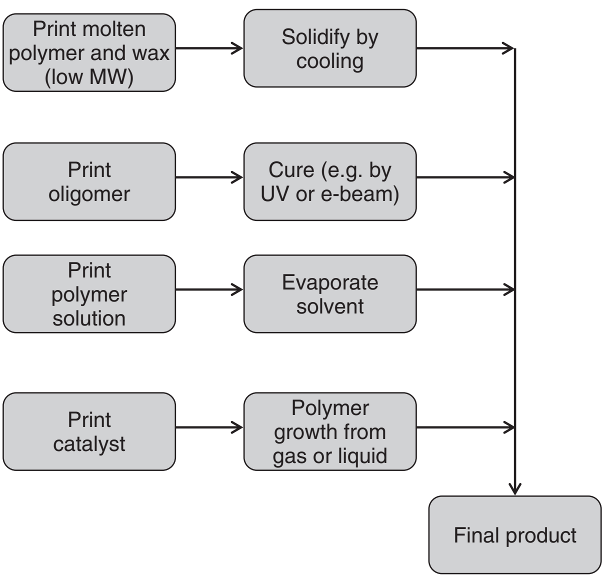


Figure 1.4 *Process routes by which inkjet printing can be used to deposit polymers.*

inkjet methods. There is major commercial interest in printing organic semiconductors for such applications as display backplanes, and also in fabricating large-area polymer light-emitting diode (PLED) displays, as discussed in Chapters 9 and 10.

For structural or optical applications or to achieve dielectric properties, thermoset polymers can be cross-linked *in situ* after printing, by thermal treatment, by 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. Chapter 4 contains further details.

Finally, inkjet printing of a suitable catalyst has been used to initiate local formation of conductive films of polyacetylene in subsequent gas-phase treatment (Huber, Amgoune and Mecking, 2008).

1.3 Applications to Manufacturing

A summary of possible process routes which employ inkjet printing for manufacturing is shown schematically in Figure 1.5. These routes are applicable in principle to any materials, although some have been explored rather little.

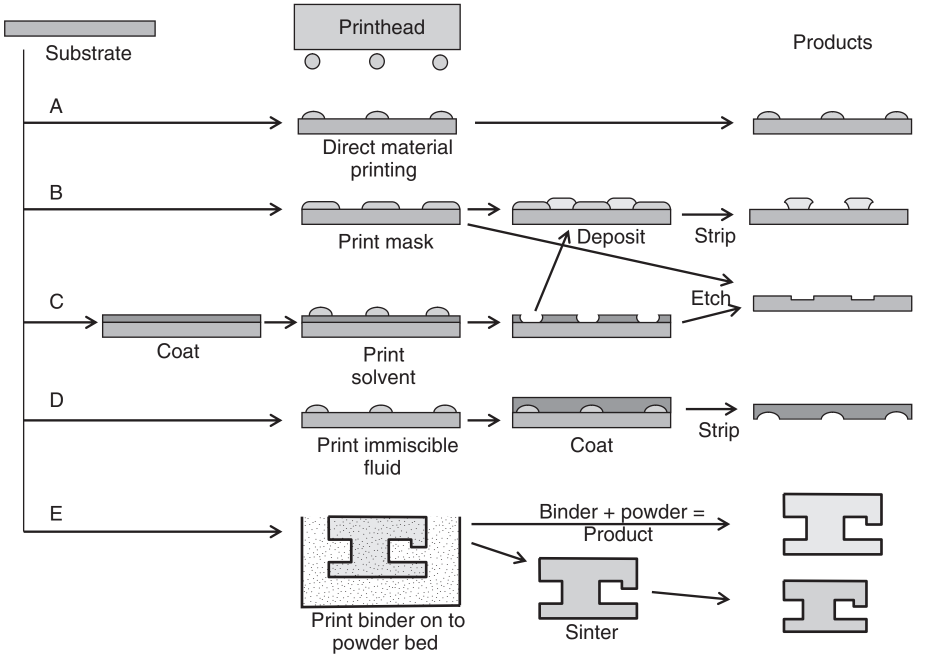


Figure 1.5 *Classification of process routes by which inkjet printing can be used to create structures: (A) direct material printing; (B) printing of a mask followed by material deposition or etching; (C) inkjet etching; (D) inverse inkjet printing and (E) printing onto a powder bed (See plate section for coloured version).*

1.3.1 Direct Deposition

The process shown as route A in Figure 1.5 involves the direct deposition of material onto a substrate in a digitally defined pattern (by any of the methods outlined in Section 1.2). This is the simplest process and has been widely exploited: it forms the basis of most of the examples discussed in other chapters of this book. Many manufacturing applications of inkjet 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. Both the printing of silver nanoparticle ink followed by sintering, as shown in Figure 1.6, and the printing of a catalyst followed by electroless plating can give good electrical conductivity; circuit elements produced in these ways have been demonstrated, including ultra-high frequency (UHF) transmission lines and antennae (Mäntysalo and Mansikkamäki, 2009), organic thin film transistors with silver electrodes (Kim *et al*., 2007) and metal–insulator–metal crossovers (Sanchez-Romaguera *et al*., 2008).

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, Wilhelm and Jacobson (2002), including thermal-expansion-driven actuators with features up to 1 mm tall, fabricated by multiple deposition (400 layers) of silver nanoparticle ink.

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 1.7) (Liu and Orme, 2001a; Wallace *et al*., 2006; Yokoyama *et al*., 2009).

Repeated DOD deposition of liquid metal droplets has also been used to build vertical solder columns up to a few millimetres in height, corresponding to aspect ratios of about 20 (Lee *et al*., 2008), while macroscopic artefacts tens of millimetres in size have been fabricated by CIJ printing of liquid aluminium alloys (Liu and Orme, 2001b).

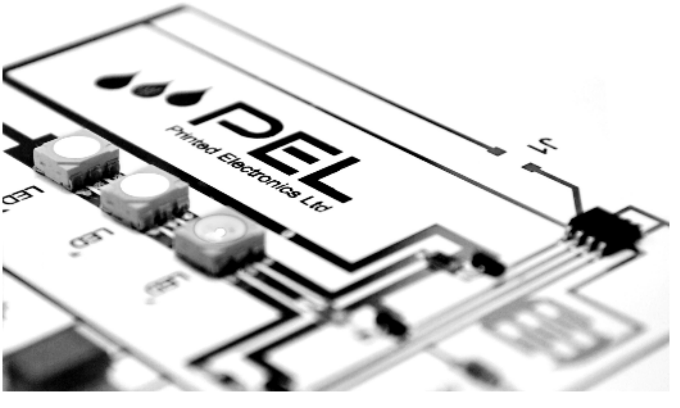
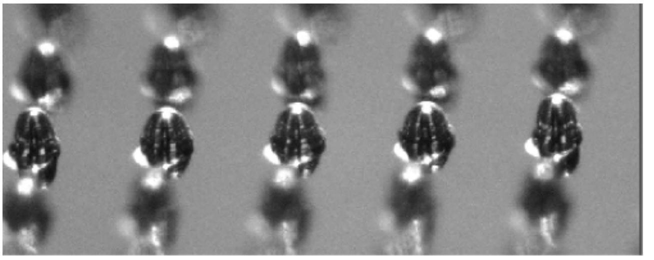
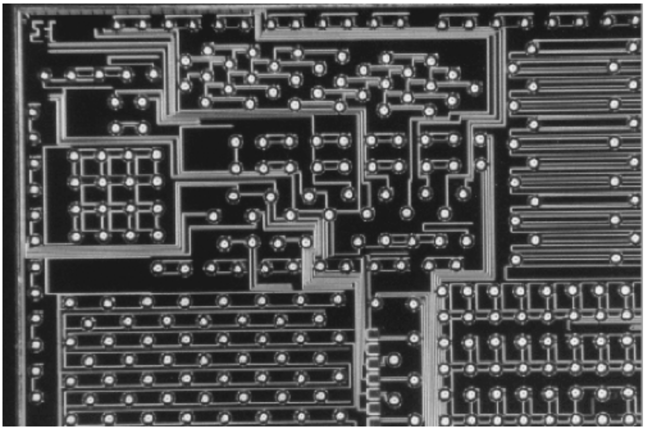


Figure 1.6 *Conducting tracks, 0.5 mm wide, made by drop-on-demand printing of silver nanoparticle ink onto a ceramic substrate, followed by thermal sintering (Courtesy of Printed Electronics Ltd.).*



(a)



(b)

Figure 1.7 *(a) Lead–tin solder bumps (100 µm diameter) printed by piezoelectric inkjet at 250 µm separation (centre-to-centre) and (b) multiple solder bumps (70 µm diameter) printed onto a test substrate (Reproduced with permission from Hayes* et al. *(1999) Copyright (1999) IMAPS Courtesy of MicroFab).*

Oxide ceramics in thin film form have many potential applications, for example as dielectrics, piezoelectric materials and catalysts. Examples of their direct deposition by inkjet processes have been given in Section 1.2.3. Thick deposits of ceramics can be built up by repeated printing of particulate suspensions, and the fabrication of 3D artefacts by printing followed by sintering has been demonstrated for alumina (Ainsley, Reis and Derby, 2002), silicon nitride (as shown in Figure 1.8) (Cappi *et al*., 2008), PZT and titania (Figure 1.9) (Lejeune *et al*., 2009). Applications include mechanical components, piezoelectric transducers and photocatalysts.

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 (Wilson *et al*., 2007). Processes discussed in Section 1.2.4 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, as discussed in Chapter 6 and illustrated in Figure 1.10 (Wallace *et al*., 2006; Chen *et al*., 2008).

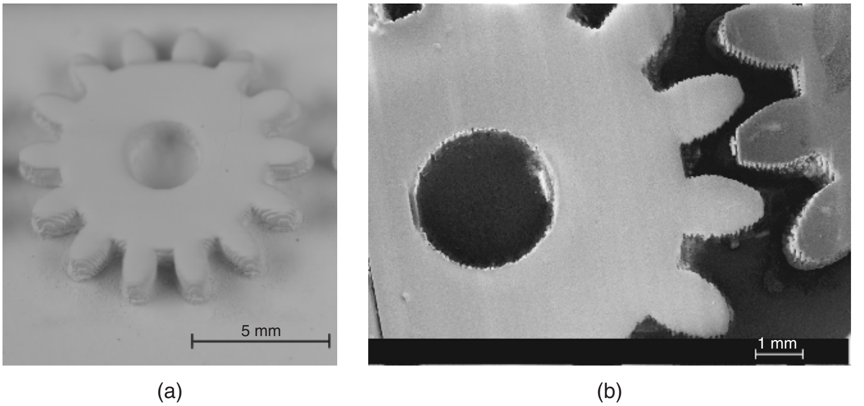


Figure 1.8 *Silicon nitride gearwheels printed by thermal drop-on-demand inkjet: (a) green (as-printed, unsintered) and (b) sintered components (Reproduced with permission from Cappi* et al. *(2008) Copyright (2008) Elsevier Ltd.).*

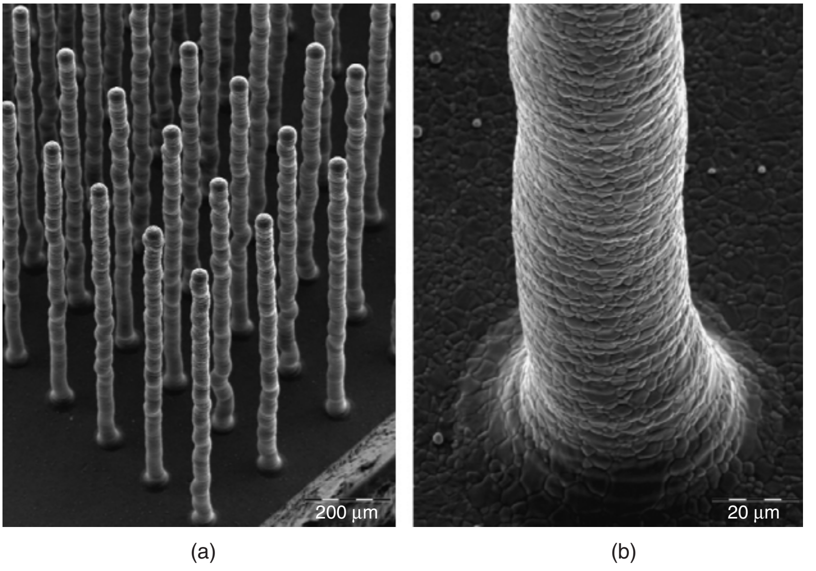


Figure 1.9 *(a,b) Sintered titania pillars formed by inkjet printing (Reproduced with permission from Lejeune* et al. *(2009) Copyright (2009) Elsevier Ltd.).*

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: this is the 'coffee stain' effect discussed further in Chapter 5 (Tekin, Smith and Schubert, 2008). One explanation for this effect is that solvent close to the droplet edge evaporates more readily than from the centre, leading to transport

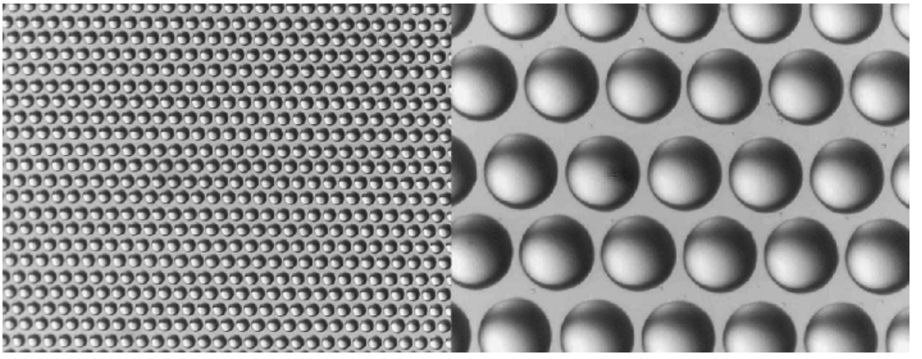


Figure 1.10 *(a,b) Portion of array of 200 000 polymer lenses, each 104 µm diameter, formed by inkjet printing (Reproduced with permission from Wallace* et al. *(2006). Copyright (2006) SMTA Courtesy of MicroFab).*

of suspended material towards the boundary. In some applications special measures, for example 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 (Lu, Chen and Lee, 2009).

A variant of the direct deposition process involves printing drops of liquid into another liquid: that is, the substrate is also a liquid. If the two liquids are immiscible and each printed drop adheres to the previously deposited material, then at least in principle this provides a potential method to manufacture fragile products, which are supported by the liquid bath as they grow. A method can also be used in which the printed liquid reacts with the liquid bath on contact to form a solid material. This type of approach, in which sodium alginate solution is printed into a bath of calcium chloride solution to form regions of hydrogel, has been used by Nakamura and colleagues to produce scaffolds and cell-containing structures for biological applications. It is discussed in detail in Chapter 13.

1.3.2 Inkjet Mask Printing

While direct deposition has been widely explored, it is by no means the only route by which inkjet printing can be used to create digitally defined structures. An alternative method (route B in Figure 1.5) is to print a mask, and then to use this to define areas to be etched, or onto which a further material can be deposited (e.g. by electroless plating or electro-plating). Direct inkjet printing of masks has been explored for electronic printed circuit board production (the application discussed in detail in Chapter 8), but little work has been done on the wider application of inkjet mask printing to the texturing of surfaces. CIJ has been used with a solvent-based polymer ink to deposit masks onto steel rolls for subsequent etch patterning; the deposited drop diameter was ~150 µm (Muhl and Alder, 1995).

More recently, several ink types were investigated for mask printing, and 120–150 µm features were printed onto metallic substrates with a UV-cured polymer

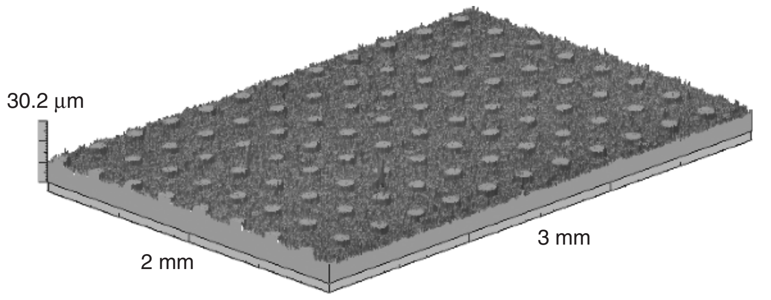


Figure 1.11 Steel surface patterned by inkjet masking followed by etching. The circular masked regions are 60 μm in diameter (Reproduced with permission from Costa and Hutchings (2008). Copyright (2008) Society for Imaging Science and Technology).

ink (James, 2004). An example of a steel substrate patterned by inkjet printing of a mask followed by acid etching is shown in Figure 1.11 (Costa and Hutchings, 2008). 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 onto a cold substrate and give good edge definition as drop spreading is arrested once the drop begins to solidify. One major application of inkjet mask printing is in photovoltaic solar cell fabrication.

1.3.3 Inkjet Etching

Route C in Figure 1.5 is known as inkjet etching and involves the printing of drops of solvent onto 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 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 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 or rectangular holes and linear grooves, as illustrated in Figure 1.12 (De Gans, Hoeppner and Schubert, 2007). 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.

Variations of the inkjet etching process have also been developed. For example, if small drops of solvent are printed onto a thick polymer substrate, they will evaporate leaving an array of smooth-surfaced craters which can be used either 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

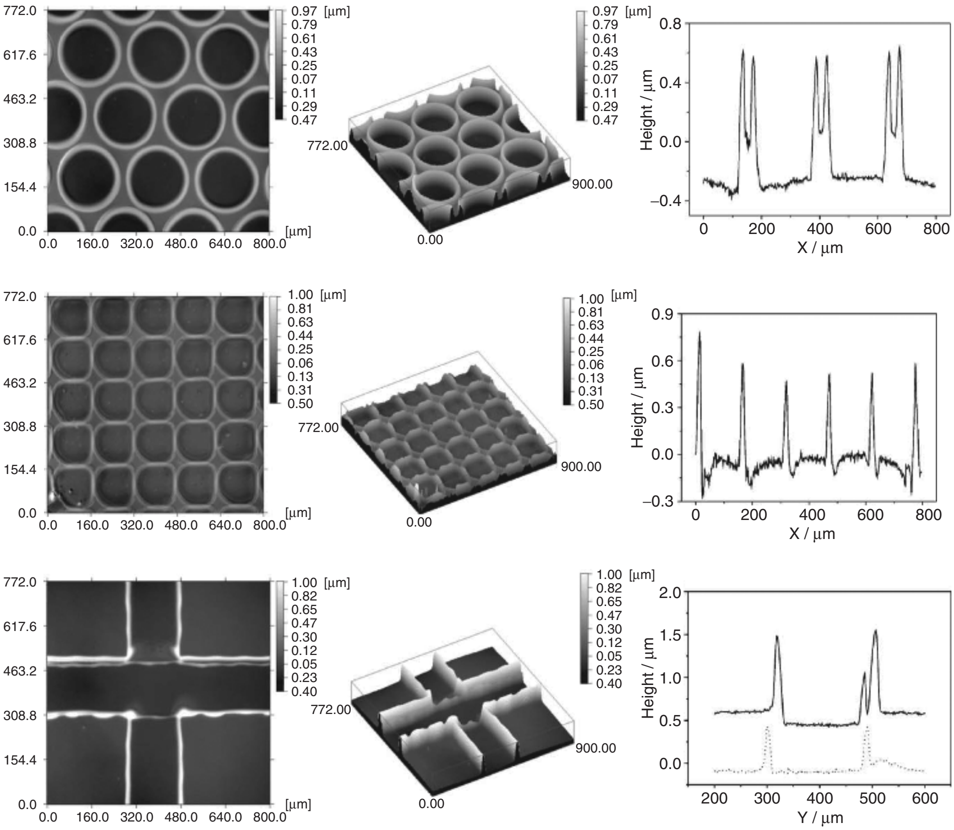


Figure 1.12 *Examples of features etched into a polymer surface (polystyrene) by inkjet printing of solvent droplets (Reproduced with permission from De Gans* et al. *(2007). Copyright (2007) Royal Society of Chemistry).*

sequence (Periccet-Camar *et al*., 2007). Inkjet printing can also be used, not to remove a polymeric coating material but to plasticise it so that an etchant can permeate it 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. This has been explored for forming openings in buried semiconductor layers in photovoltaic solar cells (Lennon *et al*., 2008).

1.3.4 Inverse Inkjet Printing

Route D in Figure 1.5 can be termed inverse inkjet 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 onto a substrate, applying a continuous film of a polymer which is immiscible with the drops, curing it to solidify it and then removing it from the substrate, as shown in Figure 1.13 (Jahn *et al*., 2009). In this application the pore size in the sieve is controlled

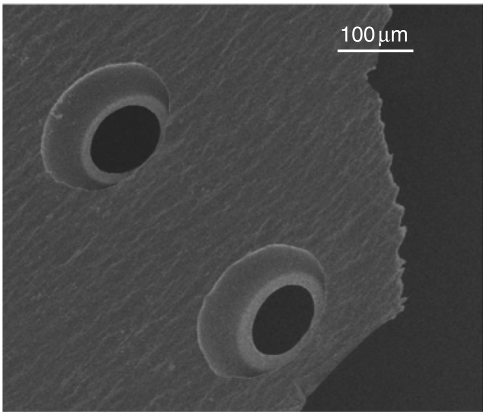


Figure 1.13 Example of polymer micro-sieve made by inverse inkjet printing (Reproduced with permission from Jahn et al. (2009). Copyright (2009) American Chemical Society).

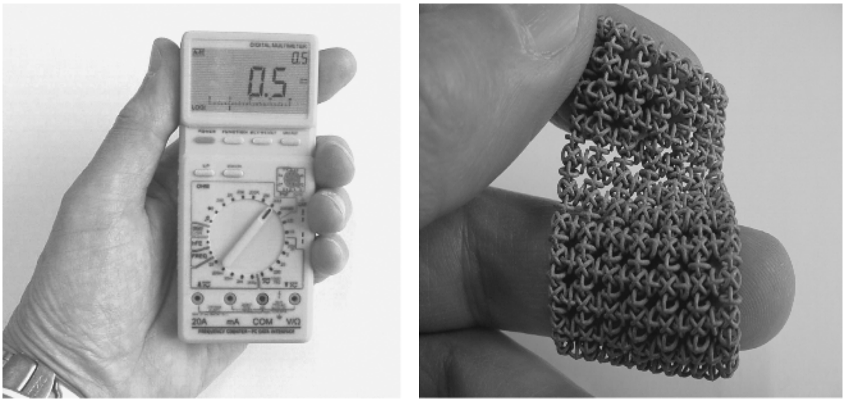
by the height of the printed drop and the thickness of the polymer layer, but the process could also be adapted, by using a thicker layer, to produce an array of concavities which could then be used either as concave mirrors or, by replication, to generate an array of convex lenses.

1.3.5 Printing onto a Powder Bed

The final process sequence, shown as route E in Figure 1.5, involves using inkjet printing to deposit drops of a liquid binder material (e.g. a UV-curable polymer) in a pattern onto a flat bed of a solid powder. This forms the basis for an important group of 3D printing processes and is discussed in detail in Chapter 14. After the binder has cured or dried, a thin layer of fresh powder is spread evenly over the surface of the bed and the process is repeated. If a suitable series of 2D patterns is printed in this way, a 3D object is created within the powder bed, consisting of powder particles bonded by the printed ink. This can then be removed and either used as it is (although it may have rather low strength) or processed further (e.g. by sintering or infiltration) to produce the final product. There are several commercial processes based on this principle. Figure 1.14 shows two examples of objects made in this way: a fully coloured model made by printing with water-based inks onto a plaster powder in which hydration of the plaster causes the particles to bond, and a stainless steel mesh which was heated to sinter the particles and thus densify the product after printing. Infiltration of the bonded product with a second liquid, which is drawn into the spaces between the powder particles by capillary action, provides a further potential method of post-treatment.

1.4 Potential and Limitations

We have seen how inkjet 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



(a) (b)

Figure 1.14 *Examples of parts made by printing onto a powder bed: (a) model of an electronic multimeter, made by printing binder onto ceramic powder by the Z-Corp™ process, and (b) stainless steel mesh, sintered after printing onto metal powder by the fcubic™ process.*

process route. It is already widely used industrially for printing 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. However, there are important limitations to the use of inkjet processes which must be borne in mind in considering new applications.

The resolution which can be achieved by inkjet 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 onto the substrate. That precision is influenced by the accuracy of movement of the substrate or print-head, by inherent variability in the direction in which the drop leaves the print-head, by aerodynamic and electrostatic influences on the drop in flight, which may themselves depend on the presence of other neighbouring drops, and by other sources of process variability such as variation in drop size and velocity. In practice, drop placement accuracy of better than several micrometres is hard to achieve in direct inkjet printing onto a homogeneous substrate, and $\sim 10\,\mu m$ 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 (Wang *et al*., 2004). 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 inkjet 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 (Sele *et al*., 2005).

Most research and development on inkjet printing for manufacturing purposes has addressed the formation of thin film deposits, often for electronics applications (Perelaer *et al*., 2010). These films may be tens, hundreds or even thousands of micrometres in lateral extent, but are often sub-micrometre 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 limited attention, so far, to building 3D deposits with aspect ratios of one or more by direct material deposition 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 (e.g. Sanchez-Romaguera, Madec and Yeates, 2008), 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 3D 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 inkjet printing for digital fabrication will require further research into all these aspects.

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