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Printing Technologies for Nanomaterials

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1.1 Introduction

For centuries, printing of texts and graphics on flat (two-dimensional) substrates such as textiles and paper has been an essential enabling technology for the cultural development of mankind. Only recently has this technique been considered as a valuable tool for the processing of functional nanomaterials, for example, in the electronics and biomedical industries [1–6]. For electronics manufacturing, for example, printing has some decisive advantages compared with the more traditional approaches of semiconductor processing. First of all, printing is an additive process, meaning that functional materials are deposited only where needed and can be used much more efficiently than with subtractive techniques, which tend to produce a lot of waste [7, 8]. In addition, printing can be carried out at atmospheric pressure, making high-vacuum technologies obsolete, which also contributes to significant savings on production costs. A third advantage is the selectivity of printing, making multimaterial applications such as multicolor lighting [9–11] or printed thin-film transistors [12, 13] possible. Since in the graphics printing industry, many 2D printing technologies have already been developed toward roll-to-roll processing, commercial mass production of nanomaterial-based printed electronics devices in a continuous manufacturing mode is also within reach [14–16].

A wide variety of 2D printing technologies has been applied for the processing of functional nanomaterials, which can be subdivided into two different groups: noncontact or digital (maskless) printing technologies (without physical contact between printing equipment and substrate) and contact (mask-based) printing technologies (with physical contact). In noncontact printing, droplets or jets of the functional ink are generated at a (small) distance from the substrate and transferred onto it by a pressure pulse that propels them across the interspace. Contact printing typically makes use of a predetermined pattern, embedded as a mask in a drum or screen, which is repeatedly replicated on the substrate by directly touching it. Typical examples for noncontact techniques are inkjet printing (IJP) and laser-induced forward transfer (LIFT), and examples of contact technologies are offset, flexo, gravure, screen, and microcontact printing.

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In general, critical issues to be considered during the choice for a specific printing technology for functional nanomaterials are technical aspects such as resolution, feature definition, adhesion, process reliability and stability, manufacturing speed, and device performance. Also nontechnical process features such as production volume and cost, environmental impact, and operator and customer safety are important, since all of these combined will determine whether printing will be a technically and economically viable option for a specific type of device. Since functional electronic and biomedical devices are frequently composed of complex ultrathin stacks of various (nano)materials, some of which can be highly sensitive to mechanical pressure, contactless printing can be a decisive advantage [17]. The balance between design flexibility and the potential for mass manufacturing is another consideration. Digital printing technologies offer a lot of design freedom and easily allow for image adjustments to compensate for possible substrate deformations (for instance, in the case of flexible or stretchable substrates [18]). However, productivity should come from mass parallelization with the obvious challenges such as yield, stability, reproducibility, and durability.

By contrast, all contact printing techniques involve some kind of physical stencil that determines the printing pattern and needs to be adjusted every time a different image is to be produced. This feature, in combination with its potential for very-high-throughput production, makes many contact printing techniques especially suited for the production of large numbers of identical devices [15]. In mature industrial production processes, contact printing is therefore usually preferred, unless possible damage to the products by mechanically touching the surface prohibits its use. By contrast, noncontact processes are generally the technology of choice where small series are required, such as in many academic research laboratories and in early-stage industrial research and development. However, the potential for scalability or transfer to other processes, which are more adept for mass production, is required for the latter to be of any practical use.

In addition to nanomaterials' deposition in two dimensions on flat substrates, functional printing has recently also been applied for the construction of three-dimensional objects [6, 19, 20]. 3D printing or additive manufacturing (AM) is known as a layer-by-layer manufacturing technology to build 3D products. In analogy to 2D technologies, it is an enabling approach with numerous advantages compared with the conventional (subtractive) manufacturing technologies. AM enables the cost-effective manufacturing of complex, personalized, and customized products. It also offers the possibility to introduce multimaterial products or parts with material gradients [21]. AM integrates very well with design tools and computer-aided design (CAD) software and as a result, the AM approaches can significantly impact both time and cost savings, as well as inventory, supply chain management, assembly, weight, and maintenance. AM is seen as an enabling technology for many applications, such as embedded and smart integrated electronics (Internet of things, smart conformal and personalized electronics [22]), complex high-tech (sub)modules made of ceramic or metal with multimaterial or grading material properties [23], and human-centric products (e.g., dentures, prostheses, implants [6, 24]). While new materials and manufacturing technologies are introduced in the market, we see that for many applications the technology is still immature: product quality is inferior to that obtained with conventional methods, the choice of available materials is limited, yield is low by process-induced defects, manufacturing costs are high, and productions speeds are typically low [25].

3D printing comes in various embodiments. Selective deposition techniques, such as viscous jetting, fused deposition modeling, cladding, or wire feed are well-known technologies based on the consecutive deposition of a printable/processable (nano)material to build layer-by-layer the 3D product. The product definition is determined by the spatial deposition and the dimensional stability of the deposited material (the material needs to have fluidic properties during the release from the reservoir or nozzle to print but should have (rigid and) superior material properties in the final product), and the patterning resolution of the deposition heads. The other class of AM technologies is based on pattern definition with an external source (e.g., laser beam or E-beam) in a homogeneous layer of material. During each print step, a homogeneous layer of material is deposited, but only the fraction that constitutes the final product is fused to the part via a sintering process (selective laser sintering (SLS)), melting process (selective laser melting (SLM)), binder jetting process, or photopolymerization process (stereolithography (SLA), vat photopolymerization). This family of AM technologies comes often with a higher spatial resolution but frequently suffers from inferior material properties (porosity in SLS, defects in SLM, uncured monomers and inferior material properties in vat). Emerging technologies are combinations of these: two-photon, reactive jetting, conformal printing, and so on.

The current focus for metal AM is on monomaterial technology improvement to enable lightweight parts for space, aerospace, and automotive applications and customized parts for medical and high-tech. The currently utilized processes are mainly based on cladding or selective melting (with laser or e-beam) to make metallic parts from powder. Challenges include the avoidance of thermally induced stresses that give rise to warpage and mechanical deformation, homogeneity and purity of the printed part, and defectivity control (e.g., small defects might result in fatigue challenges).

The currently utilized technology for ceramics parts is selective sintering: the fusion of ceramics particles under the influence of heat or photopolymerization based on a polymer binder system, in which a ceramics powder is dispersed. In both cases, the final ceramic product is preferably 100% pure and does not comprise contaminants of the binder.

Nanomaterials are typically used in both 2D and 3D printing to add functionality to the polymer or multimaterial systems. Nanomaterials can be added to a polymer system to improve material properties (e.g., mechanical strength, color, flame-retardation ability, biocompatibility), or to create anisotropy (via fibers, filaments, nanotubes, etc.). Examples include the addition of clay particles to photoresins to improve the mechanical properties such as impact strength and biocompatibility for use in high-tech engineering. Another example is the addition of metal compounds, such as metal nanoparticles, to make conductive tracks in free-form electronics applications.

1.2 Ink Formulation Strategies

The core ingredient of an electronic or biomedical ink is the functional nanomaterial to be deposited. Since a detailed overview is presented in Chapters 7–14, here only a brief summary is given. A wide variety of nanomaterials with all kinds of properties and shapes have been formulated into inks and pastes. Examples include conductive [26], semiconductive (e.g., electroluminescent or photovoltaic [27]), or piezoelectric [28] as well as catalytically and biologically active materials [29]. Also the dimensions of the materials used cover the entire range defined for nanotechnology from the sub-nanometer regime up to fractions of a micrometer. "Zero-dimensional" objects such as nanoparticles of spherical, but also other shapes have been processed [26], as well as more complex shapes such as rods and wires [27], sheets [30, 31], and complex three-dimensional architectures [32, 33]. Apart from functional nanomaterials consisting of a single component, more complex nano-objects have also been reported as functional ink ingredients [34]. In accordance with this wide variety of materials and functionalities, the technical applications also represent the entire range of devices such as sensing, energy conversion, communication and logic, lighting, and catalysis. For specific examples, the reader is referred to Chapters 15–16 of this book.

Ink formulation requires a delicate balance between the desired functional properties in the device after deposition and postprocessing, and printability. To achieve good printability, precise control over a number of ink properties is necessary, such as viscosity, stability, wettability, and drying behavior.

In all ink formulations, the functional nanomaterials are dispersed in some kind of fluid carrier, which can be a pure solvent or a mixture and has the function to allow processing from the liquid state. The choice for a particular solvent system depends on a variety of considerations, such as compatibility with the nanomaterials and the intended substrate, envisioned processing conditions, and intended application. For large-scale production, cost, environmental, and health issues also need to be taken into account.

Pure dispersions of nanomaterials in liquids usually are not stable and thus cannot be properly deposited by printing technologies. For example, nanoparticles strongly tend to cluster, agglomerate, and precipitate, due to their high surface energies, which in turn leads to altered rheological properties, an uneven distribution of the material, or an increased surface roughness after printing. Dispersants are, therefore, typically used to stabilize the nanoparticles (see [35] for a theoretical study and [36–38] for practical examples). These compounds are typically neutral or electrically charged organic molecules or polymers. They cause reciprocal repulsion when adsorbed on the particle surfaces, thereby preventing the formation of larger aggregates. Also, pH and electrolyte concentration can influence the dispersion stability of the nanoparticles because of their influence on the zeta-potentials. pH can be controlled by the addition of a buffer system. For biological functional components, pH control is especially important, since proteins tend to denature upon pH changes, thereby losing their functionality [39].

Ink stability during storage is another demanding requirement. In addition to agglomeration and settling of particles, as described earlier, evaporation of solvents may lead to a change in ink composition and an increasing concentration of nanomaterials, which in turn impacts printability. Lifetime stability can be increased by high-boiling-point solvents. Another possibility is the addition of humectants, which bind the solvent components, thereby lowering their tendency to evaporate [40]. Typical examples are polymers with polar side groups, which attract polar solvents, especially water.

Ink rheology (e.g., viscosity or shear thinning behavior) impacts printability and needs to be adapted for each deposition technology. Ink viscosity can, for instance, vary from 2 mPa s (water-like inks typical for IJP) to above 300 Pa s (very thick pastes for screen printing). Ink viscosity can be controlled by concentration of the functional nanomaterials, viscosity of the carrier liquid, and additional ink ingredients. The optimum amount of dispersed particles is typically determined by the printing method. Viscosity modifiers such as high-molecular-weight polymers, gelators, or lower viscosity solvents can be added to achieve the desired viscosity, and some of them are also useful to induce shear thinning behavior by chain alignment or reversible network collapse under shear stress.

Controlling an ink's surface tension is another crucial step when formulating an ink. During the printing processes, the material will become deformed. This degree of deformation and the force necessary to achieve it are determined by several factors, one of which is surface tension. Lowering an ink's surface tension is usually rather easily achieved by the addition of small amounts of surface-active molecules, which tend to accumulate at the interfaces. A more extensive reformulation such as replacement of the main solvent is usually necessary if an ink's surface tension is too low.

In addition, the wetting behavior of an ink on a substrate after deposition is also influenced by its surface tension. A variety of substrate materials are used in functional printing, from glasses and semiconductor wafers to plastic foils, papers, and textiles. Accordingly, a wide range of varying surface properties is encountered, defined by the material and its surface chemistry and topology (e.g., roughness, porosity, possible anisotropy, prepatterning). In addition, surface chemistries can be tuned by the application of coatings and other surface treatment methods, such as exposure to reactive plasmas or ozone [41]. This wide range of surface properties needs to be taken into account during ink formulation, since only an appropriate combination of substrate and ink characteristics will result in the formation of well-defined printed patterns [42]: very strong repulsive interactions generally give rise to the formation of isolated droplets instead of continuous structures, whereas very strong attractive interactions will result in wide spreading, thereby limiting feature resolution. In order to print well-defined, fine, and continuous functional structures, usually a regime of intermediate wetting is preferred. Good or even complete wetting, however, can be useful when large areas need to be coated with a homogeneous continuous film of functional materials. Chemical compatibility with the substrate or coating material is also an important factor for the selection of ink ingredients, since chemical reactions between substrate and ink or the dissolution of the surface coating are usually undesired.

Postprocessing steps are typically applied to improve the functional performance of the deposited nanomaterials, for instance, exposure to heat to remove the solvents and additives. These steps can also be controlled by adjusting the ink composition. Especially, inks with low nanomaterial loads, high solvent contents, and low viscosities exhibit complex flow patterns during solvent evaporation, which tend to accumulate the solid functional nanomaterials at the edges of the structures, giving rise to the so-called “coffee ring effect”. These irregular height profiles can aggravate further processing and compromise device performance, for example, when very thin continuous films need to be deposited on top. This can be avoided by designing complex solvent mixtures composed of ingredients with different boiling points (and thus sequential evaporation), thereby causing continuous compositional changes in the ink, or by choosing appropriate drying conditions [43, 44].

Evaporation of the solvent may also lead to deterioration of the wetting properties of an ink. Although under special circumstances, this effect can be exploited to create well-defined, extremely thin lines with high aspect ratios [45], it is usually detrimental and therefore unwanted. The drying process can obviously be influenced by the choice of volatile components in the ink, but in addition, specific interactions between the various solvents and other ink ingredients need to be taken into account. Nonvolatile compounds with high affinity to one or several of the solvents, for example, added as humectants or dispersants, can retard evaporation, giving rise to different transient ink compositions during the drying process.

After treatment, proper functionality of an ink deposit is frequently closely related to its topology and internal structure. Solvent loss and the decomposition of organic components such as stabilizers usually result in a significant volume shrinkage, which can result in crack formation and a rough surface profile. Similar damage can also occur from mechanical stress when flexible or stretchable devices are prepared. These phenomena can cause partial material disintegration, structural defects, and incomplete adhesion of possible consecutive layers. Achieving good cohesion within a dried ink structure is, therefore, crucial for the ultimate device performance and can be achieved by the addition of binders, which keep the structures together. In the specific case of electrically conductive inks based on metal nanoparticles, special “sintering agents” have been added, promoting nanoparticle merging during the drying process [46].

Another aspect of ink functionality is its adhesion to the underlying surface, since delamination can seriously affect final device performances. Typically, nanomaterials do not exhibit good adhesion to common substrate materials such as glass or plastic foils. To improve binding properties, polymeric binders and specific bifunctional adhesion promoters can be added with high affinities to both substrate and functional ink components. Typical examples include molecules containing silane groups, which can easily bind to glass, and thiol groups, which have a strong affinity toward certain types of metals, which by themselves do not adhere well on glass [47, 48].

1.3 Printing Technologies

Noncontact printing technologies typically deposit the ink in the form of free flying droplets formed at some distance from the substrate. The two most important noncontact printing technologies are IJP [42] and LIFT [49]. Whereas IJP is a well-established technology, LIFT is a rather new development specifically aimed at high-resolution printing of high-viscous and solid materials. Aerosol patterning is another type of noncontact printing [50]. Heat is used to create airborne nanoparticles that are directed to a substrate via a confined jet. An annulus of air is used to control the dimensions of the deposited material.

As outlined earlier, noncontact printing combines the key advantages of being compatible with mechanically sensitive substrates and digital patterning. This means that both technologies offer a high flexibility of design, since an adjustment in the digital printing pattern will directly be reflected in a different printed structure. As a consequence, a freedom of design is achieved that is not easily equaled by other approaches and can be especially advantageous when batches of limited numbers of identical functional devices are produced.

1.3.1 Inkjet Printing

IJP is characterized by the formation of droplets by a sudden pressure pulse in the nozzle chamber. In order to leave the nozzle in a reliable manner and to allow fast droplet generation (high printing frequencies), inkjet inks generally have low viscosities (in the order of 2 – 50 mPa s) and rather low solid contents. At least two types of IJP are distinguished, depending on the manner of droplet formation and ejection, which can be achieved either by a heat pulse, inducing solvent boiling and thus a pressure pulse (thermal IJP), or by the shape change of a piezoelement integrated in the nozzle chamber walls (piezoelectric IJP) (Figure 1.1). In both cases, the pressure pulse is eventually the result of an electric voltage pulse, which can be modulated in terms of intensity, time duration, and voltage ramp in order to optimize the ejection process. Since the exact pulse shape will influence printing parameters such as reliability, droplet size, and speed and printing stability, this so-called waveform tuning is of crucial importance during printing parameter optimization [51 – 53].

Due to the surface tension of the ink, during flight, the formed jet will contract into a single spherical droplet or will break up into a number of individual droplets, some of which might merge into one main droplet, while others will remain as so-called satellite droplets (Figure 1.1) [54]. The latter ones are unwanted, because they tend to diminish the definition of the printed pattern by landing outside the designated area. An important part of waveform optimization is, therefore, to avoid satellite droplet formation.

A number of phenomena can occur when droplets hit the surface. First of all, the physical interactions between the substrate surface and the ink are important, which are governed by the ink composition, the physical properties of the substrate, and the impact velocity. An ink droplet hitting the surface at too high speed will splash and create a very ill-defined pattern. Waveform tuning can control impact velocity and avoid the occurrence of splashing. After deposition, the shape of ink droplets on a substrate is determined by the former's surface tension and the latter's surface free energy. A measure for this interaction is the contact angle, that is, the angle formed between the substrate and the ink droplet. Very high contact angles indicate unfavorable interactions and a high degree of repulsion. Under these conditions, it is usually difficult to obtain

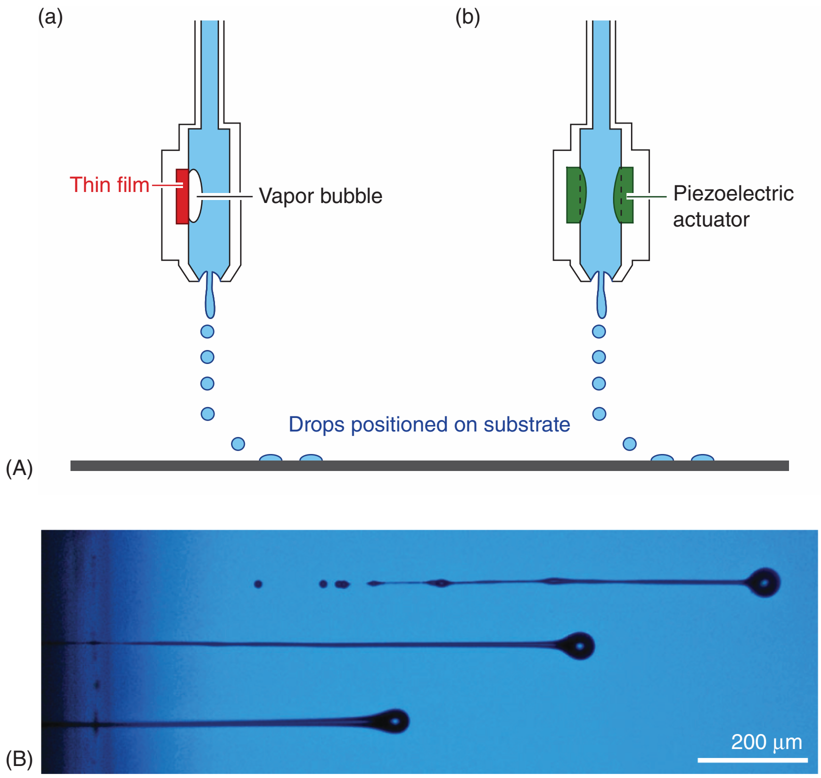

Figure 1.1 Operational principles of thermal and piezoelectric inkjet printing (A) and jet break up and satellite formation during the inkjet process (B). (Derby (2010) [42]. Reproduced with permission of Annual Reviews.)

continuous functional (e.g., electrically conductive) structures, since any printed line will have a high tendency to break up into individual, unconnected droplets (dewetting). On the contrary, very low contact angles lead to complete wetting, that is, there are strong attractive interactions between ink and substrate, and thus a high contact area between both is thermodynamically favored. Too strong wetting can lead to extreme spreading of the ink, thus preventing any fine details to be formed. For high-resolution functional patterns, an intermediate wetting regime is usually optimal. It can be achieved by either modifications to the ink formulation, for example, by lowering its surface tension, or by changing the surface chemistry of the substrates, for example, by coatings or plasma treatments [55, 56]. Furthermore, for a given ink–substrate combination, the quality of the printed features can be additionally controlled by adjusting the printing parameters such as substrate temperature, droplet spacing, and jetting frequency (Figure 1.2) [57].

The drying process has also a major influence on the final properties of an ink-jetted pattern. Because of the low viscosities and high solvent contents of inkjet inks, transport phenomena occur on a larger scale than in more paste-like functional inks.

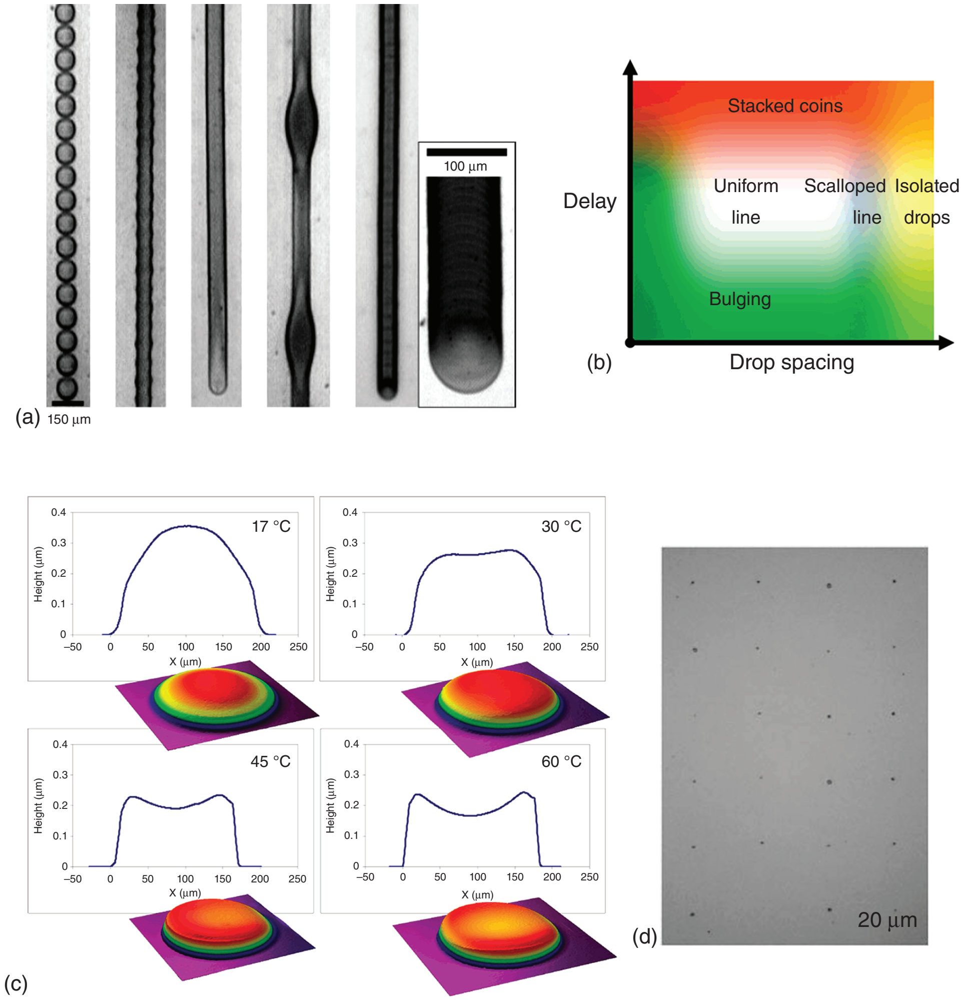

Figure 1.2 Effect of drop spacing and deposition delay on definition of inkjet-printed lines (a,b) and effect of drying temperature on surface profiles of inkjet-printed droplets (c). (Soltman and Subramanian (2008) [57]. Reproduced with permission of American Chemical Society.) Array of micrometer-sized droplets of a nickel nanoparticle ink deposited by electrostatic IJP (d). (Ishida *et al*. (2007) [58]. Reproduced with permission of Japan Society of Applied Physics.)

Due to wetting, line widths achievable by IJP are usually limited to a minimum of 20 µm, unless specific measures are taken such as prepatterning of the substrate surface. Also, it is possible to reduce the droplet sizes, but a reduced process speed is usually the consequence. The typically low solid contents of inkjet inks result in high volume shrinkage during drying, which means that (average) line thicknesses after processing are in the order of a few micrometers at most. Multiple layer printing offers a solution but has its own specific challenges, such as interlayer alignment, instabilities of multiple wet-stacked ink layers, or different wetting behavior of the ink on a predried layer than on the substrate. Another possibility is to increase the resolution, which means to increase the droplet density to be deposited, but this can also lead to a collapse of the high wet lines. In addition, both approaches to higher structures are directly related to a lower printing speed.

Electrostatic IJP is a variety of "classic" IJP, where the droplet is not produced by a pressure pulse but by an electric field between the nozzle tip and the substrate [59]. Very small droplet volumes can be achieved with this technology, allowing extremely fine structures to be deposited. Drop sizes on the substrate of below 1 μm have been demonstrated (Figure 1.2) [58]. In addition, the electric field also serves to guide the droplet toward the substrate, thereby limiting deviations and increasing positioning accuracy. This is especially important for small droplets, which tend to stray away more strongly from a straight trajectory than do larger droplets. In contrast to classic IJP, electrostatic IJP is also compatible with inks of higher viscosities. A major drawback for industrial mass production at current state is its incompatibility with high production speeds and large-area fabrication.

1.3.1.1 Toward 3D Printing

Viscous jetting technologies come in different embodiments. Material can be liquefied by heating it up to above the melting temperature to squeeze it through nozzles and to form voxels on the target substrate. Examples include thermal wax, polymer, and metal. Polymer systems can go to 300–400 °C, while metal printing can go well above the 1000–1500 °C range. The jetted materials reach the substrate in a molten or fluidic state, causing, in combination with the wetting properties of the surface and previously built layers/parts, the voxel to spread out, thereby limiting the resolution and pattern definition. A key advantage is the recovery of the material properties after solidification.

Different nozzle systems have been developed. TNO has developed a jetting system for high-viscous material systems. The technology is based on the Plateau–Rayleigh instability to create a steady stream of well-defined droplets. The instability is induced by the design of the nozzle in combination with a piezo perturbation [60]. The system showed the capability to create 40–50 μm voxels in the case of metal (Sn, Au, and Ag) and polymer systems. Several methods have been introduced for droplet on demand applications, for instance, by mechanical or electrical removal of the redundant droplets/voxels.

An image of the high-viscosity jetting head of TNO is given in Figure 1.3. Jetting systems are ideal for multimaterial applications, where different nozzles can feed different materials to the build. Challenges include material interface instability, material compatibility, and unwanted mixing.

A related application is the formation of monodisperse particles (powders) via well-defined cooling or drying of the dispersed droplets. The technology was successfully applied to the formation of metal powder (via immersion in a cooling liquid) and to the formation of milk powder and fine chemistry products (via conditioned cooling in air) [61]. A proof-of-concept study of a multinozzle system with internal filtration was executed by TNO. IJP was also applied for low-temperature 3D metal microstructure fabrication of metal nanoparticles [62]. Metal nanoparticle inks were successfully deposited via IJP to create

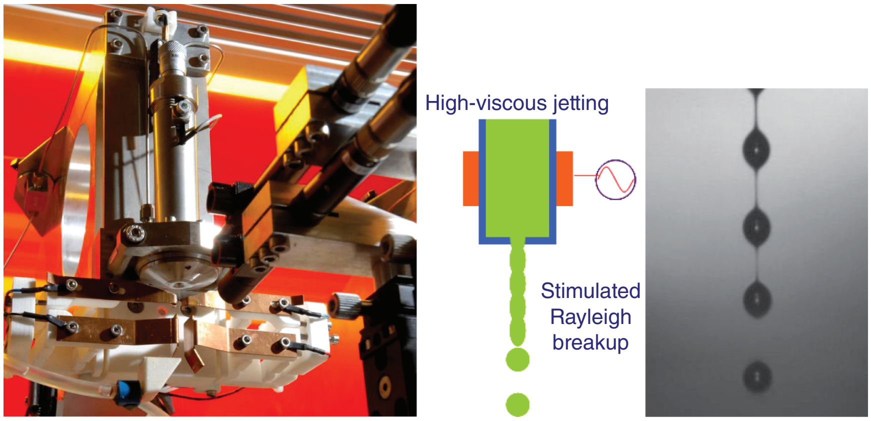

Figure 1.3 Image of a high-viscous inkjet system, schematic, and the resulting droplet shape.

3D metal microstructures, such as micro metal pillar arrays, helices, zigzag, and microbridges.

1.3.2 Laser-Induced Forward Transfer

LIFT is another digital printing technology [49]. LIFT differs from IJP especially in the manner of droplet formation. The source of the functional material is a donor sheet coated with a layer of ink or an evaporated or sputter-deposited solid film. This material is locally heated with a high-power, short-pulsed laser, released and transferred as a droplet onto an acceptor substrate located at some distance from the donor sheet. The release is either accomplished by direct heating of the functional material or by thermal or photochemical decomposition of a dynamic release layer located underneath the functional material. A schematic picture of the LIFT process is given in Figure 1.4.

A wide range of inks (from inkjet formulations to screen printing pastes) and even solid materials can be transferred using the LIFT process. The droplet formation and thereby printed spot size and spot definition are controlled by both the donor layer characteristics (composition and thickness) and by the laser parameters (fluence, wavelength, pulse length, and spot size). Optimizing laser pulse conditions is somewhat equivalent to waveform tuning in IJP [63, 64]. The optimization process is, therefore, a complex interplay between ink properties, donor layer thickness, and laser pulse parameters. Very high fluences can induce spray formation instead of well-defined jet formation or result in splashing droplets upon impact on the substrate (Figure 1.4). Donor layer thickness impacts the amount of transferred material, but changes made to this parameter usually require pulse parameter adjustment as well to remain optimal printing results. A homogenous and uniform layer thickness is a crucial prerequisite for reliable printing quality over larger areas.

Under optimized conditions, LIFT can produce well-defined narrow functional features with line widths in the order of a few micrometers [65]. Especially when high-viscous materials are transferred, high aspect ratio structures can be prepared, since there is hardly any spreading in these cases. In addition, certain

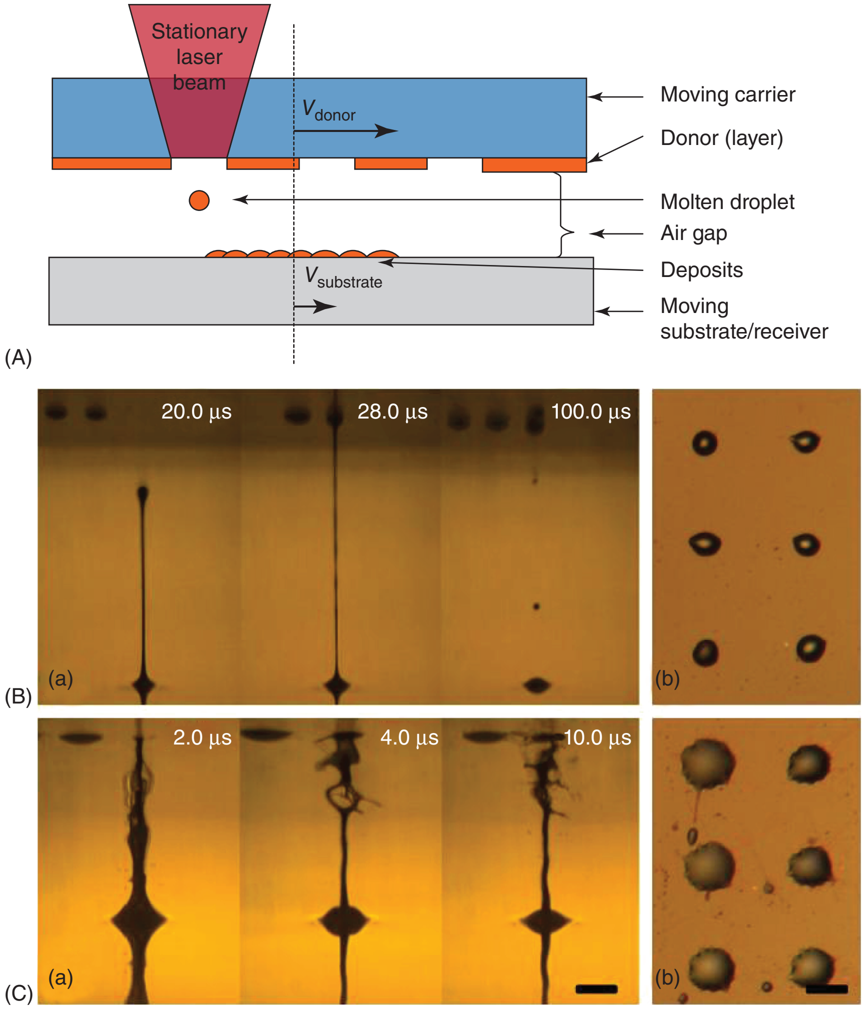

Figure 1.4 Principle of LIFT (A) and influence of laser fluence (100 (B) and 230 (C) mJ cm^{-2}) on jet formation and droplet size and definition of a silver nanoparticle ink [63]. Scale bars correspond to 50 µm. (Boutopoulos *et al*. (2014) [63]. Reproduced with permission of Springer.)

geometries such as very sharp turns with small radii can be difficult to prepare by IJP because they can easily break by unstable flow patterns aroused by the sharp kinks in the ink lines.

Although LIFT is a maturing technology, its potential for industrial application is still under development. Main challenges are the currently still limited processing speeds and process reliability, which is mainly due to the lack of reliable large-area coating mechanisms, which can supply donor substrates of extremely homogenous thickness.

If the laser is used in combination with a dynamic release layer, the donor material “only” undergoes a pressure wave lifting the material to the receiver

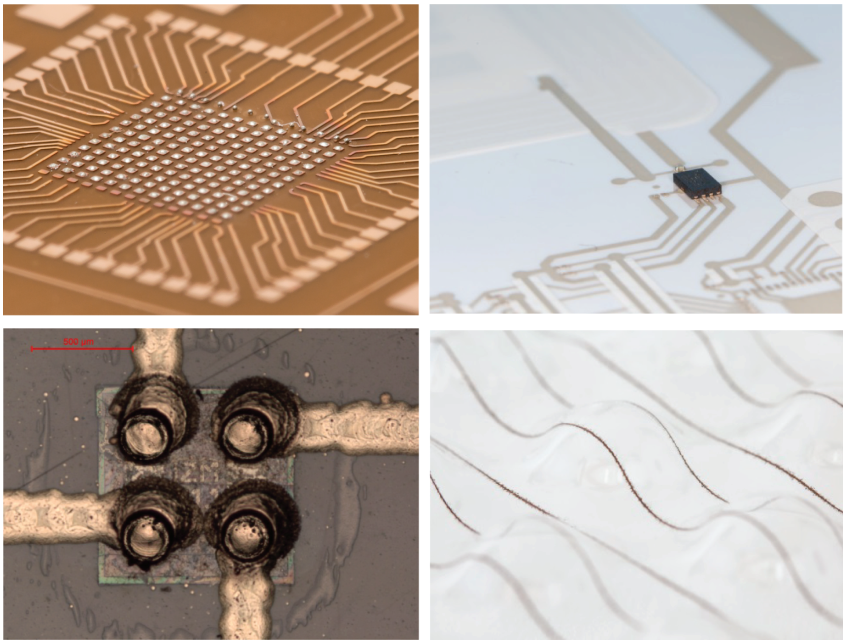

Figure 1.5 Examples of LIFT-printed interconnects and conformal lines on a curved surface.

substrate. This process is mainly adiabatic (room temperature) and does not harm the donor material. Hence, also living tissue cells and other temperature-sensitive (bio)materials can be printed in this way [66].

1.3.2.1 Toward 3D Printing

In addition to 2D features, the LIFT technology was also successfully applied to 3D printing. Examples include the transfer of solder pastes for 3D IC stacking, PCB bonding, and interconnect applications. An example is given in Figure 1.5 with 100 μm LIFT transferred features for PCB bonding and conformal printing on a curved surface, an achievement that is highly challenging for other printing technologies.

1.3.3 Contact Printing Technologies

Contact printing technologies make use of stencils or moulds with a predefined pattern to deposit ink onto the substrate and therefore offer less design and process compensation flexibility than, for example, IJP. On the other hand, these technologies can process higher viscosity and larger particle inks and are particularly well suited for industrial large volume production. In offset, gravure, and flexo printing, ink is transferred onto target substrates by means of printing rolls. These printing technologies involve a number of ink transfers from one to another carrier roll. Consequently, the amount of ink that is finally deposited on the target substrate is highly dependent on its relative affinities to the intermediate carrier roll materials. Printed layer thicknesses thus can vary considerably and can be controlled by the selection of the roll materials' surface properties. As intrinsic roll-to-roll processes, offset, gravure, and flexo printing are all particularly well suited for continuous and high-throughput industrial production.

In offset printing, the surface of the printing roll is chemically patterned such that some surface sections attract the ink, while others repel it. The surface chemistry and the ink properties need to be well matched to create the required contrast in ink wettability. Although the entire roll surface is exposed to the ink, it will stick only to the parts where there are strong interactions and where it wets and spreads well, resulting in a thin film of ink on these spots. The contrast in surface wettability determines among others the printing properties such as layer thickness transfer, printing resolution, and feature definition. High printing speeds and rather good resolutions of down to 5 μm [67] can be achieved with offset printing, as long as the ink properties and printing parameters are in the correct range. Viscosities for ink formulations processed by offset printing are usually quite high, in the order of 40 – 100 Pa s.

In flexographic (or flexo) printing, the print pattern is present as a protruding relief on a printing roll, which is typically made out of a soft, rubber-like material (Figure 1.6). The ink is first transferred from a reservoir onto the printing roll by means of an anilox cylinder. This anilox cylinder consists of a metal roll with regularly engraved indentations (ink cells). Although these cells are present everywhere on the anilox surface, ink transfer occurs only to the elevated parts of the printing roll from where it is subsequently deposited onto the substrate. However, the pressures applied need to be kept rather low, to prevent excessive mechanical deformations of the protrusions, and consequently a decreased printing quality. Typical viscosities for flexo inks are rather low, between the values typical for IJP and offset printing (roughly 50 – 500 mPa s).

Microcontact printing (soft lithography) is somewhat similar to flexography and is the patterned transfer of a material onto a substrate by means of a relief silicone stamp [70]. Although in most cases self-assembled monolayers have been transferred using microcontact printing, it has also been applied directly for the patterned deposition of functional nanomaterials [71]. The striking feature of this approach is the impressive line width that can be achieved (below 1 μm), which is

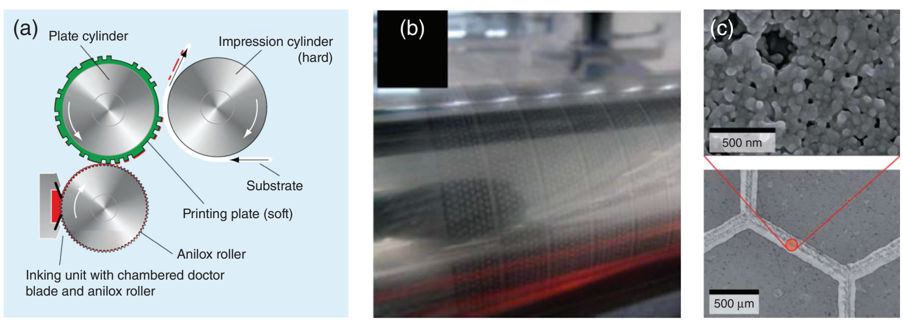

Figure 1.6 Schematic principle of flexo printing (a). (Kipphan (2001) [68]. Reproduced with permission of Springer.) Foil on roll with flexo printed silver ink (b) and microscopic images of the resulting conductive grid structure (c). (Yu *et al*. (2012) [69]. Reproduced with permission of Royal Society of Chemistry.)

unprecedented by other technologies. Upscaling to industrial production, however, has until now been a challenge.

In contrast to flexo printing, gravure printing makes use of a predefined pattern of indents engraved in a metal or plastic roll [15]. Ink transfer rollers are used to coat the gravure roll with the functional nanomaterial dispersion, and a squeegee or doctor blade knife is used to remove the excess of ink from the drum. The roller material needs to be rather rigid in order to allow proper ink removal from the roller surfaces. Ink viscosities need to be in the same range as for flexo printing. Advantages of the technology include high printing speeds and good printing resolutions. Due to the possibility of engraving different depths into the printing roller, printing of different layer thicknesses during one single printing run is easily possible, something which cannot be achieved with offset or flexo printing. A disadvantage of the technology is that large features need to be printed via a number of smaller cells, which are separated by cell walls. In particular for functional features and device functionality (for instance in the case of conductive tracks), these walls can form a serious shortcoming. Due to the high costs of the gravure roll, this technology is especially suited for industrial mass printing of large numbers of identical samples. At this moment, gravure printing is not yet a widely introduced manufacturing technology for functional nanomaterials but might become more attractive once printed electronic or biomedical devices are maturing.

A completely different approach is screen printing, in which the ink is pushed through a fine mesh of metal or polymer wires (Figure 1.7) [73]. Pattern definition is achieved by local closure of the mesh openings by means of a polymer film (emulsion). Structuring of this emulsion is typically carried out by selective removal of polymeric material using lithographic techniques. The transfer of the ink is achieved by a squeegee, which moves over the screen at a predefined speed and pressure, to squeeze the ink through the prepatterned mesh. As a consequence of this process, screen printing formulations are usually pastes with high viscosity (typically at least several pascal seconds [74]). Therefore, their solid loads can be very high, which, in combination with the thickness of the screens, results in feature heights unequaled by any other printing technology. The typical range is between 5 and 30 μm height, but extreme values of more than 100 μm have been shown for single-pass printing. Under laboratory conditions, line widths of 20 μm have been demonstrated [75], whereas for industrial processes the current limit is about 30–40 μm. This combination of line width and height results in the possibility to produce functional structures with large aspect ratios (around one), which can be very useful for a number of applications, for example, when high currents need to be transported through conductive lines of limited width/surface coverage. The most preferred screen printing pastes are generally shear thinning formulations, which display lower viscosities under shear, that is, when being squeezed through the mesh but solidify as soon as the shear is released, that is, after they have been deposited on the substrate [74]. Due to these rheologic characteristics, they allow the production of very well-defined structures, e.g., by limiting underflow, the unwanted deposition of paste underneath the covered areas of the screen. Although screen printing is by no means limited to the deposition of nanomaterials, it is widely used for this

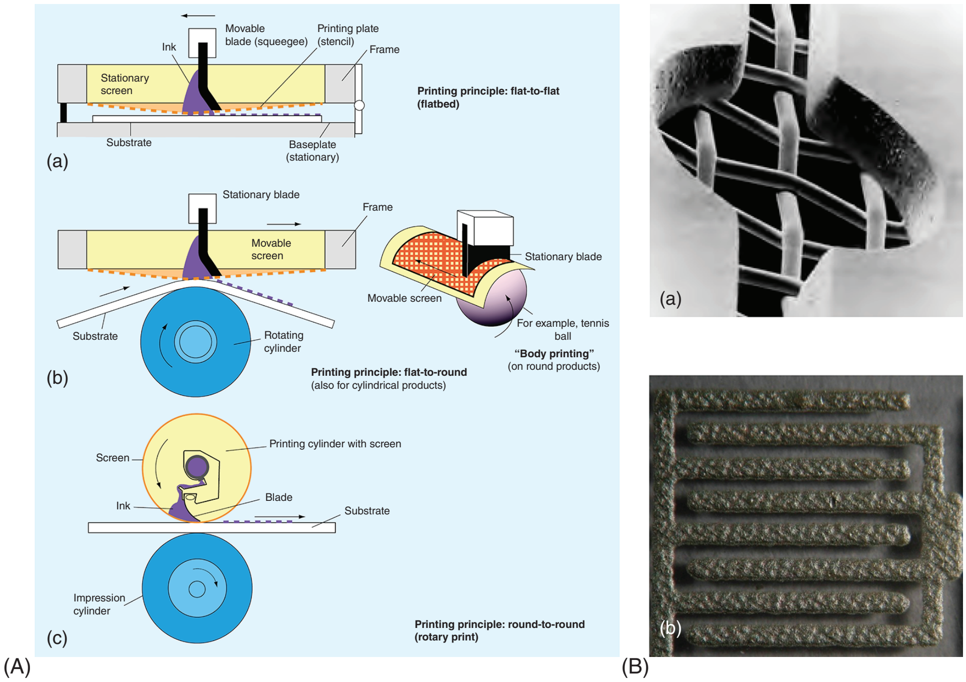

Figure 1.7 Schematic representation of various embodiments of screen printing (A). Electron microscopic image of a screen mesh partially covered with emulsion (B). (Kipphan (2001) [68]. Reproduced with permission of Springer.) Electrode pattern for a pressure sensor consisting of screen-printed graphene sheets and carbon nanotubes [72]. (Janczak (2014) http://www.mdpi.com/1424-8220/14/9/17304/htm. Used under CC BY 3.0 http://creativecommons.org/licenses/by/3.0/.)

class of materials, if the desired functionality dictates so. Since the technology is well established in industry, robust, highly reliable, and fast, screen printing has especially high prospects for applications in the mass manufacturing of functional devices based on functional nanomaterials. Roll-to-roll applicability when rotary screens instead of flatbed screens are used is an additional benefit, which allows continuous production at high speeds (up to 25 $m\,min^{-1}$ [16, 76]).

The commercial success of printing as a feasible method for functional nanomaterials depends highly on the ability to be integrated in industrial mass production processes, which demand some critical conditions to be fulfilled. Printing technologies need to be superior in overall performance to the competing more traditional approaches, such as subtractive manufacturing. In order to achieve this, large amounts of products need to be produced at high fabrication speeds, which demands fast and large-area-compatible printing technologies. In this respect, roll-to-roll compatible technologies are especially interesting candidates to be considered, since they allow continuous processing to be applied [15, 16, 76–79]. At the same time, high process reliability with regard to process stability and consistent end-product performance are also crucial prerequisites. Under certain economic and technical boundary conditions, sheet-to-sheet processing can outcompete roll-to-roll manufacturing, since the former approach can typically yield somewhat higher end-product qualities in terms of structural definition and resolution.

1.3.4 Photopolymerization

Vat photopolymerization (or SLA) is an optical manufacturing technology based on the selective and layer-by-layer photopolymerization of photocurable monomers. In the case of vat photopolymerization, the 3D product is built by light exposure of a film of resin through a baseplate and release of the exposed and cured part from the baseplate to allow new uncured resin to flow between the built part and the baseplate. This process is repeated numerous times to yield the final layer-by-layer manufactured part. In another embodiment, the exposure is from the top, and the product is step-by-step immersed in a vat of resin. These two embodiments are depicted in Figure 1.8. A major drawback of bottom-up vat photopolymerization is that the product needs to be carefully separated from the baseplate after each exposure to prevent damage. Novel solutions were developed to accelerate the separation without damaging the build. TNO developed a force feedback solution, which is based on the measurement of the force needed to separate the product from the plate and to use this information to accelerate the building process [80]. Carbon3D invented a process based on an inhibition layer between the baseplate and the part, preventing the adhesion of the part to the baseplate and thus accelerating the building process (even toward a continuous 3D print process) [81].

The technology allows for resolutions in the micrometer scale and below and for good dimensional stability. Challenges are in the field of productivity, part robustness, thermal stability, long-term stability, limited mechanical properties, outgassing, and biocompatibility.

The conventional systems were based on classical light sources, such as single beam laser, or digital light processors (switchable mirrors). The introduction of laser-array exposure in combination with advanced coating technologies has led to a new concept for photopolymerization. The system combines the

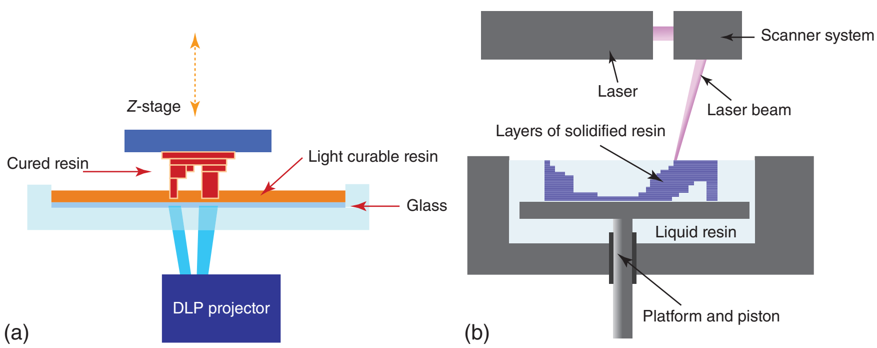

Figure 1.8 Two embodiments of photopolymerization: DLP in which a layer of resin is exposed by a pattern generated by a so-called digital light processor (a) and SLA where the pattern is created by a scanning laser beam (b).

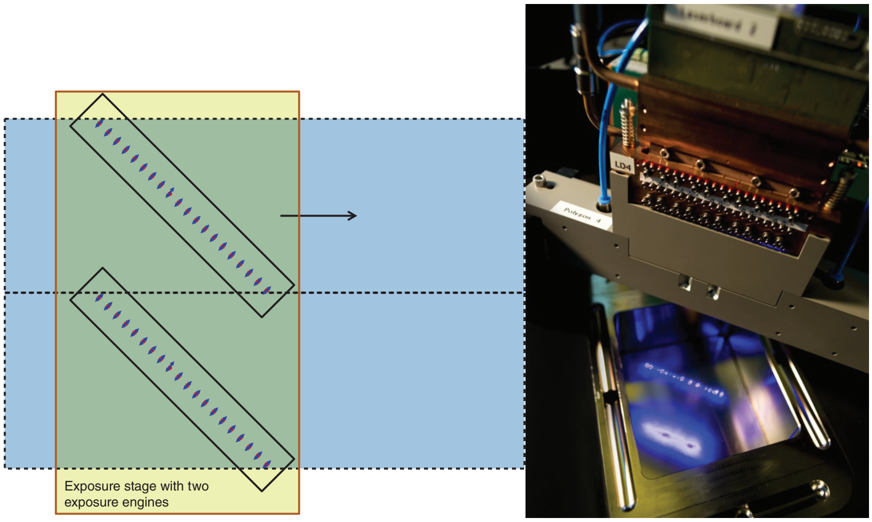

Figure 1.9 Sketch and picture of light engine based on multiple laser sources for high-resolution and large-area 3D printing [82].

advantages of high-resolution patterning (10–20 μm), fast single-pass exposure, large area exposure (the laser arrays are stitched to enable wide single-pass exposures), and coating of high-viscosity materials. The layout and a picture of the exposure engine are shown in Figure 1.9.

In general, four classes of vat photopolymerization materials are distinguished. The polymeric materials formed by photocuring of a (mainly organic) resin formulation are most commonly used. Typically, these materials consist of acrylate-based, acrylate–epoxy, or acrylate–oxetane hybrid formulations to meet application requirements. Challenges such as polymerization shrinkage and limited mechanical properties are addressed by organic–inorganic composites. In addition, 3D products can be made with composite resins, in which functional metal or ceramic (nano)particles are dispersed into an organic binder. The organic binder photopolymerizes and determines the part shape during the 3D build process. After 3D manufacturing, the binder material is thermally or chemically removed and the remainder is densified to reveal the final ceramic or metal part. A third class of materials is used for making moulds for metal or ceramic castings. Finally, photocurable materials are used as functional coatings applied on polymeric products. The main challenges in this field are adherence, layer consistency, and (mechanical and thermal) matching of materials.

Parts produced by photopolymerization are typically 100% dense but might have nonuniform properties and uncured resin fragments. Mechanical properties are inferior to nylon type materials used in thermal AM processes. To increase mechanical robustness (impact strength, modulus, etc.), photopolymers are nowadays reformulated and reengineered to adhere to the requirements imposed by high-tech applications, such as dental parts and high-tech parts.

Resins used in AM photopolymerization technologies have typically high covalent cross-link densities, leading to inferior mechanical properties (brittleness) and mechanical deformations during the building process (because of internal stresses, warpage, and incomplete curing). Studies into improved mechanical properties target for improved polymer chemistry and additions.

1.3.5 Powder Bed Technology

Powder bed fusion (PBF) is a thermal process based on fusion or melting of particles to form 3D products. PBF is used is to make metal and polymer parts. The process is based on the consecutive deposition of thin layers of powder via a roller or a coater process. A focused laser beam is used to locally melt or fuse the powder according to the predefined digital pattern. In this way, a digital image is transferred in a 3D part. Only the thermally affected material is fused into the 3D object, the unaffected material remains in the powder bed or is removed during the cleaning of the part. The key challenges of the PBF technology are part quality, production yield, dimensional stability, and material properties.

Because PBF is a thermal process, the material properties of the 3D printed part are determined by the temperature-time profile of each voxel inside the part. Voxels are typically heated multiple times, by cross-talk during exposure of adjacent and following tracks. In particular in the case of metal PBF, heat accumulation in the build product gives rise to thermally induced internal stresses and eventually to mechanical part deformation. Proper design of support structures to control the heat release from the part and laser scan strategies to better control the heating of the voxels have proven to improve the part quality significantly. However, further thermal control via optimized write strategies (with pulsed lasers and variable power settings) improved design strategies and in-line monitoring are required elements for obtaining part quality levels comparable to that obtained with conventional machining.

The particle characteristics, such as shape, size, and size distribution, determine to a great extent the mechanical properties and the surface quality of the printed part. Particle sizes typically range between 10 and 60 μm, depending on the material and application. Very small particles form clusters and prevent uniform recoating, while very large particles reduce the maximum layer packing density. The particle distribution determines the amount of absorbed laser light, the melting characteristics, the formation of pores and thereby the quality of the formed material, and the possible porosity of the final product. In most of the PBF technologies, a bimodal mixture of small and larger monodispersed powders is preferred for optimum printing performance, where the small particles fill the voids between the larger particles [83].

The lateral resolution is determined by the laser spot size and the thermally affected zone. The height resolution is also determined by the layer thickness of the deposited material. Layer thickness variation accumulates and impacts the following layers as well. This in turn may lead to incomplete sintering or melting with altered mechanical properties or porosity.

Binder jetting is a smart combination of selective deposition of a binder material in a powder bed. The binder locally binds the powder particles to reveal a green product. In a postprocessing step, heat treatment is used to release the binder and to further compact the 3D printed part.

1.4 Summary and Conclusions

The many different printing technologies currently available are a versatile toolbox for materials scientists and industry alike to deposit functional nanomaterials into well-defined patterns and structures both on flat surfaces and in three dimensions. They therefore form a highly valuable alternative to processing methods based on subtractive approaches or deposition from the vapor phase. The technical applications encompass biological and biomedical, electronic, catalytic, and a range of other functionalities. In order to allow an efficient printing process that best suits the envisioned functionality, the complex interplay of the nanomaterials with other ink ingredients, the printing technology, the substrate, and possible postdeposition treatments need to be well understood and carefully considered. Ink and paste formulations can be adjusted such that chemical and physical stability of the dispersed nanomaterials and a good processability are ensured. Depending on the specific requirements for the eventual materials or device properties, feature definition and resolution, layer thicknesses, and surface topologies, the choice for a particular printing technique can vary. Other important factors that determine which printing method suits a certain process best are its design flexibility, the mechanical stability of the used substrate (noncontact vs contact printing), and the intended production speed and volume. The recent progress in the field of functional nanomaterials processing to apply not only traditional printing techniques in two dimensions but also to include 3D printing has opened a wide and promising field for novel applications and devices.

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