

# Chapter 10

## Direct Write Technologies

### 10.1 Direct Write Technologies

The term “Direct Write” (DW) in its broadest sense can mean any technology which can create two- or three-dimensional functional structures directly onto flat or conformal surfaces in complex shapes, without any tooling or masks [1]. Although beam deposition, direct printing, extrusion-based and other AM processes fit this definition; for the purposes of distinguishing between the technologies discussed in this chapter and the technologies discussed elsewhere in this book, we will limit our definition of DW to those technologies which are designed to build freeform structures in dimensions of 5 mm or less, with feature resolution in one or more dimensions below 50  $\mu\text{m}$ . This “small-scale” interpretation is how the term direct write is typically understood in the additive manufacturing community. Thus, for the purposes of this chapter, DW technologies are those processes which create meso, micro, and nano-scale structures using a freeform deposition tool.

Although freeform surface modification using lasers and other treatments in some cases can be referred to as direct write [2] we will only discuss those technologies which add material to a surface. A more complete treatment of direct write technologies can be found in books dedicated to this topic [3].

### 10.2 Background

Although the initial use of some DW technologies predate the advent of AM, the development of DW technologies was dramatically accelerated in the 1990s by funding from the U.S. Defense Advanced Research Projects Agency (DARPA) and its Mesoscopic Integrated Conformal Electronics (MICE) program. DARPA recognized the potential for creating novel components and devices if material deposition technologies could be further developed to enable manufacture of complex electronic circuitry and mesoscale devices onto or within flexible or complex three-dimensional objects. Many different DW technologies were developed or improved

following funding from DARPA, including Matrix-Assisted Pulsed Laser Evaporation (MAPLE), nScript 3De, Maskless Mesoscale Materials Deposition (M<sup>3</sup>D, now known as Aerosol Jet), and Direct Write Thermal Spraying. As a result, most people have come to consider DW technologies as those devices which are designed to write or print passive or active electronic components (conductors, insulators, batteries, capacitors, antennas, etc.) directly from a computer file without any tooling or masks. However, DW devices have found broad applicability outside the direct production of circuitry and are now used to fabricate structures with tailored thermal, electrical, chemical, and biological responses, among other applications.

DW processes can be subdivided into five categories, including ink-based, laser-transfer, thermal spray, beam deposition, liquid-phase, and beam tracing processes. Most of these use a 3D programmable dispensing or deposition head to accurately apply small amounts of material automatically to form circuitry or other useful devices on planar or complex geometries. The following sections of this chapter describe these basic approaches to DW processing and commercial examples, where appropriate.

### 10.3 Ink-Based DW

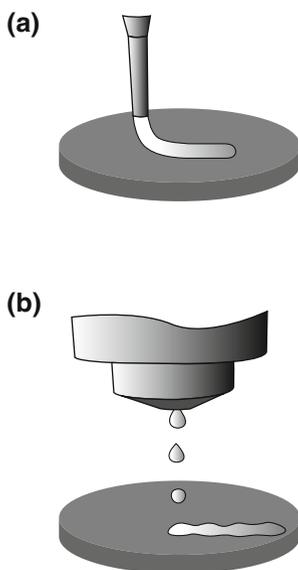
The most varied, least expensive, and most simple approaches to DW involve the use of liquid inks. These inks are deposited on a surface and contain the basic materials which become the desired structure. A significant number of ink types are available, including, amongst others:

- Colloidal inks
- Nanoparticle-filled inks
- Fugitive organic inks
- Polyelectrolyte inks
- Sol-gel inks.

After deposition, these inks solidify due to evaporation, gelation, solvent-driven reactions, or thermal energy to leave a deposit of the desired properties. A large number of research organizations, corporations, and universities worldwide are involved in the development of new and improved DW inks.

DW inks are typically either extruded as a continuous filament through a nozzle (see Chap. 6) or deposited as droplets using a printing head (see Chap. 7). Important rheological properties of DW inks include their ability to (1) flow through the deposition apparatus, (2) retain shape after deposition, and (3) either span voids/gaps or fill voids/gaps, as the case may be. To build three-dimensional DW structures it is highly desirable for the deposited inks to be able to form a predictable and stable 3D deposition shape, and to bridge small gaps. For 2D electronic structures built onto a surface, it is highly desirable for the deposited inks to maintain a constant and controllable cross-section, as this will determine the

**Fig. 10.1** Schematic illustration of direct ink writing techniques: (a) continuous filament writing and (b) droplet jetting [4] (courtesy nScript)



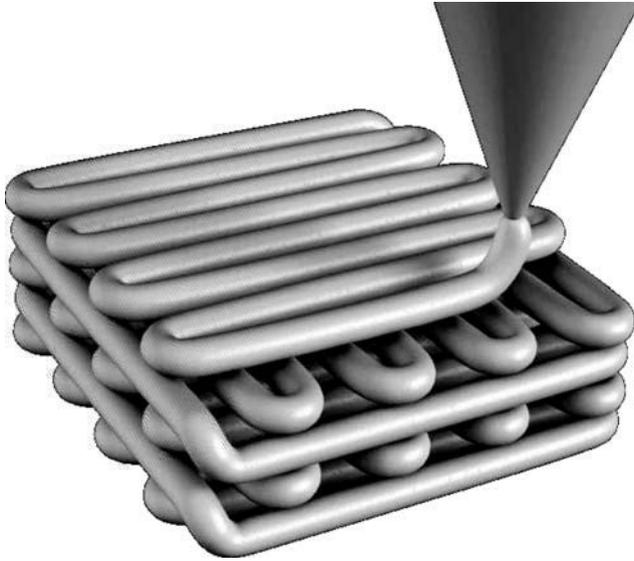
material properties (e.g., conductivity, capacitance, etc.). In general, this means that viscoelastic materials which flow freely under shear through a nozzle but become rigid and set up quickly after that shear stress is released are preferred for DW inks.

DW inks must be transformed after deposition to achieve the desired properties. This transformation may be due to the natural environment surrounding the deposit (such as during evaporation or gelation) but in many cases external heating using a thermal source or some other postprocessing step is required.

Figure 10.1 illustrates the two most common methodologies for DW ink dispensing. Continuous dispensing, as in (a), has the merits of a continuous cross-sectional area and a wider range of ink rheologies possible. Droplet dispensing, as in (b), can be parallelized and done in a very rapid fashion; however, the deposit cross-sections are discontinuous, as the building blocks are basically overlapping hemispherical droplet splats, and the rheological properties must be within a tighter range (as discussed in Sect. 7.4). Nozzle dispensing and quill processes both create continuous deposits from DW inks. Printing and aerosol deposition processes both create droplets from DW inks. These four approaches are discussed in more detail below.

### 10.3.1 Nozzle Dispensing Processes

Nozzle DW processes are technologies which use a pump or syringe mechanism to push DW inks through an orifice for deposition onto a substrate. A 3-axis motion



**Fig. 10.2** A schematic drawing showing the deposition of a scaffold using a nozzle process [4] (courtesy nScript)

control system is typically used with these nozzle systems to enable deposition onto complex surfaces or to build-up scaffolds or other 3D geometry, as illustrated in Fig. 10.2. Some nozzle devices are packaged with a scanning system that first determines the topology of the substrate on which the deposit is to be made, and then deposits material conformally over that substrate surface based on the scan data.

For nozzle processes, the main differentiating factors between devices are the: (1) nozzle design, (2) motion control system, and (3) pump design. Nozzle design determines the size and shape of the deposit, directly influences the smallest feature size, and has a large effect on the types of inks which can be used (i.e., the viscosity of the ink and the size and type of fillers which can be used in the inks). The motion controller determines the dimensional accuracy and repeatability of the deposit, the maximum size of the deposit which can be made, and the speed at which deposition can occur. The pump design determines the volumetric control and repeatability of dispensing, how accurately the deposits can be started and stopped, and the speed at which deposition can occur. The difference between these three factors for different manufacturers and designs determines the price and performance of a nozzle-based DW process.

Micropen and nScript are two companies with well-developed extrusion nozzles and deposition systems for DW. Micropen stopped selling machines in 2008 and currently sells DW services and solutions; however, many of their machines are still used by existing customers. nScript markets and sells nozzles, pumps, and

**Table 10.1** nScript Tabletop Series system and specifications (courtesy nScript)

Travel (x,y,z)	300 mm × 150 mm × 100 mm
Resolution (x,y,z)	±0.5 μm
Repeatability (x,y)	±2 μm
Repeatability (z)	±1 μm
Accuracy (x,y,z)	±12 μm
Volumetric control	Optional 20 pL or 100 pL control
Maximum travel speed	300 mm/s



integrated scanning, dispensing and motion control systems for DW. Both companies have a wide range of nozzle designs, and have feedback systems in place to make sure that the stand-off distance between the nozzle and the substrate remains substantially constant; to enable repeatable and accurate deposition of traces across conformal surfaces.

One characteristic of nScript systems is their Smart Pump<sup>TM</sup> design, which has 20 pL control of deposition volume and has an aspirating function, causing the material to be pulled back into the print nozzle at the end of a deposition path. This aspiration function enables precise starts and stops. In addition, a conical nozzle design enables a large range of viscous materials to be dispensed. The pump and nozzle design, when combined, enable viscosities which are processable over six orders of magnitude, from 1 cp to 1,000,000 cp (the equivalent of processing materials ranging from water to peanut butter). This means that virtually any electronic ink or paste can be utilized. This is one of the greatest strengths of the nScript system design and nozzle-based systems in general. Table 10.1 shows an nScript Tabletop Series nozzle deposition system along with its technical specifications.

Simple DW nozzle devices can be built using off-the-shelf syringes, pumps, and three-axis motion controllers for a few thousand dollars, such as by using the Fab@Home system developed at Cornell University [6]. These enable one to experiment with nozzle-based DW processes for a relatively low capital investment (~\$2,000). Fully integrated devices with multiple nozzles capable of higher dimensional accuracy, dispensing repeatability, and wider range of material viscosities can cost significantly more than \$250,000.

Nozzle DW processes have successfully been used to fabricate devices such as integrated RC filters, multilayer voltage transformers, resistor networks, porous chemical sensors, biological scaffolds, and other components. Three aspects of nozzle-based processes make them interesting candidates for DW practitioners: (1) these processes can deposit fine line traces on nonplanar substrates, (2) they work with the largest variety of inks of any DW technology and (3) they can be built-up from interchangeable low-cost components, and integrated easily onto various types of multiaxis motion control systems. The main drawback of nozzle based systems is that the inks must typically be thermally postprocessed to achieve the robust properties desired for most end-use applications. Thus, a thermal or laser postdeposition-processing system is highly beneficial. Although the types of

materials which have been deposited successfully using nozzle-based processes are too numerous to list, examples include [5]:

- Electronic Materials – metal powders (silver, copper, gold, etc.) or ceramic powders (alumina, silica, etc.) suspended in a liquid precursor that after deposited and thermally postprocessed forms resistors, conductors, antennas, dielectrics, etc.
- Thermoset Materials – adhesives, epoxies, etc. for encapsulation, insulation, adhesion, etc.
- Solders – lead-free, leaded, etc. as electrical connections.
- Biological Materials – synthetic polymers and natural polymers, including living cells.
- Nanomaterials – nanoparticles suspended in gels, slurries, etc.

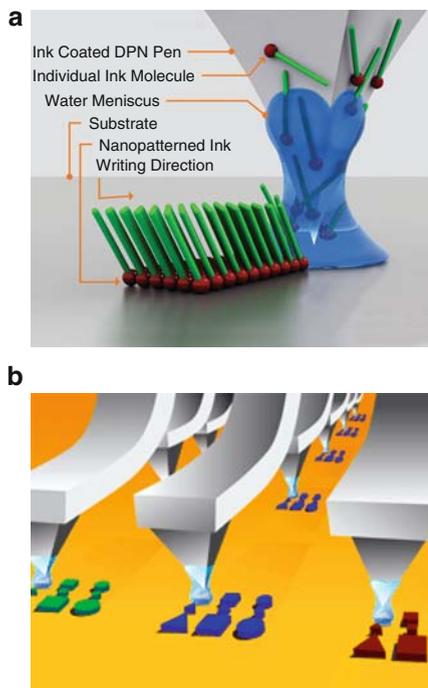
### ***10.3.2 Quill-Type Processes***

DW inks can be deposited using a quill-type device, much like a quill pen can be used to deposit writing ink on a piece of paper. These processes work by dipping the pen into a container of ink. The ink adheres to the surface of the pen and then, when the pen is put near the substrate, the ink is transferred from the pen to the substrate. By controlling the pen motion, an accurate pattern can be produced. The primary DW method for doing this is the dip-pen nanolithography (DPN) technique developed by a number of universities and sold by Nanoink, Inc. This process works by dipping an atomic force microscope (AFM) tip into an inkwell of specially formulated DW ink. The ink adheres to the AFM tip, and then is used to write a pattern onto a substrate, as illustrated in Fig. 10.3a.

Dip-pen nanolithography is capable of producing 14 nm line widths with 5 nm spatial resolution. It is typically used to produce features on flat surfaces (although uneven topography at the nm scale is unavoidable even on so-called flat surfaces). Various 1D and 2D arrays of pen tips are available, with some 1D 8-pen designs capable of individual tip actuation (either “on” or “off” with respect to each other by lifting individual AFM tips using a thermal bimorph approach) so that not all print heads produce the deposition pattern being traced by the motion controller or so that unused pens can be used for AFM scanning. The largest 2D print array, the 2D nano PrintArray™, has 55,000 AFM quills in a square centimeter, which enables 55,000 identical patterns to be made at one time. This array, however, does not enable individual tip actuation.

One use of dip-pen nanolithography is the placement of DNA molecules in specific patterns. DNA is inherently viscous, so the pens used for these materials must be stiffer than for most nano inks. Also, unique inkwell arrays have been developed to enable multiple tips to be charged with the same ink, or different inks for different tips. When combining a multimaterial inkwell with an actuated pen array, multimaterial nano-scale features can be produced. NanoInk offers two types of inks, mercaptohexadecanoic acid and octadecanethiol, for basic DPN

**Fig. 10.3** (a) A schematic showing how an AFM tip is used to write a pattern on a substrate. (b) An illustration of a 2D array of print heads (55,000 per  $\text{cm}^2$ ) [7] (courtesy NanoInk)



experiments. They also recommend the purchase of self-assembling molecules from Asemblon, Inc. Based on the physics of adhesion to AFM tips at very small length scales, most inks developed for other DW processes can not be used with dip-pen nanolithography.

### 10.3.3 Inkjet Printing Processes

A significant number of organizations around the world have investigated the deposition of DW precursor inks using inkjet printing [3, 8]. This is primarily done to form complex electronic circuitry on flat surfaces, as deposition onto a conformal substrate is difficult. The inkjet printing approach to DW fabrication is comparable to the direct printing class of additive manufacturing technologies discussed in Chap. 7. In the case of DW, the print heads and motion control systems are optimized for printing high accuracy electronic traces from DW inks onto relatively flat substrates rather than the build-up of three-dimensional objects from low-melting-point polymers or photopolymers.

The primary benefits of inkjet approaches to direct write are their speed and low cost. Parallel sets of inkjet print heads can be used to very rapidly deposit DW inks. By setting up arrays of print heads, very large areas can be printed rapidly. In addition, there are numerous suppliers for inkjet print heads.

The primary drawbacks of inkjet approaches to direct write are the difficulty inherent with printing on conformal surfaces, the use of droplets as building blocks, more stringent requirements on ink rheology than other ink processes, and a limited droplet size range. Since inkjet print heads deposit material in a droplet by droplet manner, the fundamental building block is hemispherical (see Fig. 10.1b). In order to produce consistent conductive paths, for instance, the droplets need a repeatable degree of overlap. This overlap is relatively easy to control between droplets that are aligned with the print head motion, but for deposits that are at an angle with respect to the print head motion there will be a classic “stair-step” effect, resulting in a change in cross-sectional area at locations in the deposit. This can be overcome by using only a single droplet print head and controlling its motion so that it follows the desired traces (similar to the Solidscape approach to direct printing). It can also be overcome using a material removal system (such as a laser) to trim the deposits after their deposition to a highly accurate, repeatable cross-section, giving consistent conductivity, resistivity or other properties throughout the deposit. However, these solutions to stair stepping mean that one can’t take advantage of the parallel nature of inkjet printing, or a more complicated apparatus is needed.

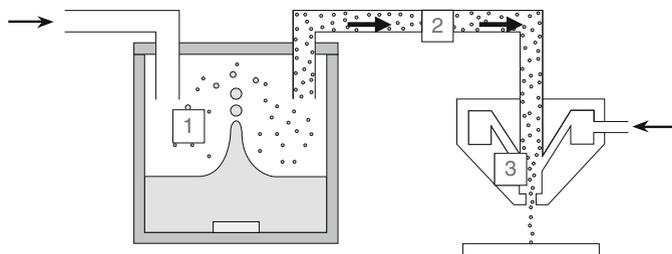
Most inkjet print heads work best with inks of low viscosity at or near room temperature. However, the rheological properties (primarily viscosity) which are needed to print a DW ink can often only be achieved when printing is done at elevated temperatures. The modeling introduced in Chap. 7 is useful for determining the material types which can be considered for inkjet DW.

### ***10.3.4 Aerosol DW***

Aerosol DW processes make deposits from inks or ink-like materials suspended as an aerosol mist. The commercialized version of this approach is the Aerosol Jet process developed by Optomec (which also sells the LENS process discussed in Chap. 9). The Aerosol Jet process begins with atomization of a liquid molecular precursor or a colloidal suspension of materials, which can include metal, dielectric, ferrite, resistor, or biological materials. The aerosol stream is delivered to a deposition head using a carrier gas. The stream is surrounded by a coaxial sheath air flow, and exits the chamber through an orifice directed at the substrate. This coaxial flow focuses the aerosol stream onto the substrate and allows for deposition of features with dimensions as small as 5  $\mu\text{m}$ . Typically either laser chemical decomposition or thermal treatment is used to process the deposit to the desired state.

The Aerosol Jet process can be controlled to be gentle enough to deposit living cells. A schematic illustration of the Aerosol Jet process is shown in Fig. 10.4.

The Aerosol Jet process was initially conceived as a process which made use of the physics of laser guidance. When photons of light interact with free-floating or suspended small particles there is a slight amount of “force” applied to these particles, and these particles move in the direction of photon motion. When applied to aerosol DW, a laser is transmitted through the mist into a hollow fiber optic.



**Fig. 10.4** Aerosol Jet System. (1) Liquid material is placed into an atomizer, creating a dense aerosol of tiny droplets 1–5  $\mu\text{m}$  in size. (2) The aerosol is carried by a gas flow to the deposition head (with optional in-flight laser processing). (3) Within the deposition head, the aerosol is focused by a second gas flow and the resulting high velocity stream is jetted onto the substrate creating features as small as 10  $\mu\text{m}$  in size (Courtesy of Optomec)

The laser propels tiny droplets from the mist into and through the hollow fiber, depositing the droplets onto a substrate where the fiber ends [9]. Laser guidance, however, entrains and moves droplets slowly and inefficiently. To overcome this drawback, further iterations with the technology involved pressurizing the atomizer and using a pressure drop and flow of gas through the tube between the atomizer and the deposition head as the primary means of droplet propulsion. Lasers can still be used, however, to provide in-flight energy to the droplets, or to modify them thermally or chemically. The ability to laser-process the aerosol droplets in-flight and/or on the substrate enables the deposition of a wider variety of materials, as both untreated and coaxially laser-treated materials can be considered.

One benefit of a collimated aerosol spraying process is its high stand-off distance and large working distance. The nozzle can be between 1 and 5 mm from the substrate with little variation in deposit shape and size within that range. This means that repeatable deposits are possible on substrates which have steps or other geometrical features on their surface. The Aerosol Jet process is also more flexible than inkjet printing processes, as it can process a wide range of material viscosities (0.7–2,500 cPs), it has variable line widths from 5 to 5,000  $\mu\text{m}$ , and layer thicknesses between 0.025 and 10  $\mu\text{m}$ . The main drawback of the Aerosol Jet process is its complexity compared to other ink-based processes. However, since the Aerosol Jet process has been parallelized to include 40 printheads in an array, and it could be parallelized to an even greater extent, the process can be made quite fast and flexible, in spite of its complexity.

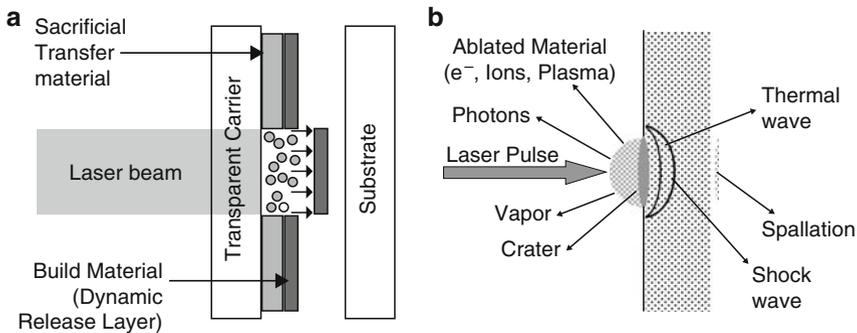
Table 10.2 summarizes the key benefits and drawbacks of ink-based approaches to DW.

## 10.4 Laser Transfer DW

When a focused high-energy laser beam is absorbed by a material, that material may be heated, melted, ablated, or some combination thereof. In the case of

**Table 10.2** Key benefits and drawbacks of ink-based approaches to DW

Manufacturer	Nozzle	Quill	Inkjet printing	Aerosol
	nScript	Nanoink	Various	Optomec
Key benefits	Greatest range of viscosities, simplicity, capable of 3D lattice structures	Nano-scale structures, massive parallelization is possible	Speed due to parallelization of print heads, numerous manufacturers	Widest range of working distances and line widths, coaxial laser treatment
Key drawbacks	Knowledge of surface topography needed to maintain constant stand-off distance	Only relevant at very small length scales, requires precise motion controllers and custom inks	Need flat plates or low-curvature substrates, limited ink viscosity ranges	Complex apparatus. Requires inks which can be aerosolized



**Fig. 10.5** (a) Mechanism for laser transfer using a sacrificial transfer material (based on [10]). (b) Mechanism for laser transfer using thermal shock and spallation (based on [11]) (courtesy Douglas B. Chrisey)

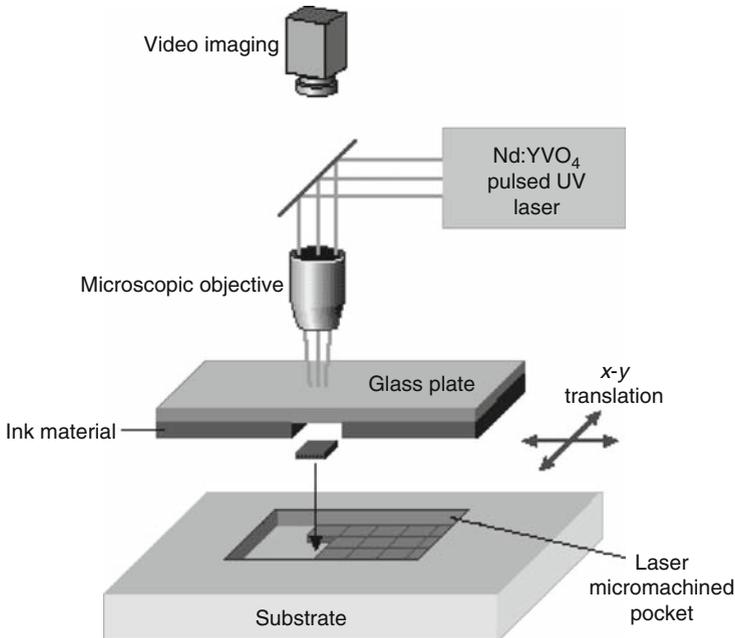
ablation, there is direct evaporation (or transformation to plasma) of material. During ablation, a gas or plasma is formed, which expands rapidly as further laser energy is added. This rapid expansion can create a shock wave within a material or it can propel a material. By focusing the expansion of the material during ablation; utilizing shock waves produced by laser ablation; or taking advantage of rapid thermal expansion inherent with laser heating, materials can be accurately transferred in a very repeatable and accurate manner from one location to another. Laser transfer DW makes use of these phenomena by transferring material from a foil, tape, or plate onto a substrate. By carefully controlling the energy and location of the impinging laser, complex patterns of transferred material can be formed on a substrate.

Two different mechanisms for laser transfer are illustrated in Fig. 10.5. Figure 10.5a illustrates a laser transfer process where a transparent carrier (a foil

or plate donor substrate which is transparent to the laser wavelength) is coated with a sacrificial transfer material and the dynamic release layer (the desired build material). The impinging laser energy ablates the transfer material (forming a plasma or gas), which propels the build material toward the substrate. The material impacts the substrate and adheres, forming a coating on the substrate. When using a pulsed laser, a precise amount of material can be deposited per pulse.

Figure 10.5b shows a slightly different mechanism for material transfer. In this case the laser pulse ablates a portion of the surface of a foil. This ablation and absorption of thermal energy creates thermal waves and shock waves in the material. These waves are transmitted through the material and cause a portion of the material on the opposing side to fracture from the surface in a brittle manner (known as spallation). The fractured material is propelled toward the substrate, forming a deposit coating on the substrate (not shown).

The U.S. Naval Research Laboratory and Potomac Photonics participated in the DARPA MICE program to develop the Matrix-Assisted Pulsed Laser Evaporation Direct Write (MAPLE DW) process [12]. A schematic of the MAPLE DW process is shown in Fig. 10.6. In this process, a laser transparent quartz disc or polymer tape is coated on one side with a film (a few microns thick), which consists of a powdered material that is to be deposited and a polymer binder. The coated disc or tape is placed in close proximity and parallel to the substrate. A laser is focused onto the coated film. When a laser pulse strikes the coating, the polymer is



**Fig. 10.6** Matrix-Assisted Pulsed Laser Evaporation Direct Write (MAPLE DW) process [13] (Courtesy PennWell Corp., Laser Focus World)

evaporated and the powdered material is deposited on the substrate, firmly adhering to it. By appropriate control of the positions of both the ribbon and the substrate, complex patterns can be deposited. By changing the type of ribbon, multimaterial structures can be produced.

Laser transfer processes have been used to create deposits of a wide variety of materials, including metals, ceramics, polymers, and even living tissue. The main drawbacks of a laser transfer process are the need to form a tape with the appropriate transfer and/or deposit materials, and the fact that the unused portions of the tape are typically wasted. However, for materials which easily form films, this is only a minor drawback.

The benefits of the laser transfer process are that it produces a highly repeatable deposit (the deposit is quantized based on the laser pulse energy), it can be as accurate as the laser scanners used to manipulate the laser beam, and the deposited materials may not need any further postprocessing. In addition, the laser can be used to either simply propel the material onto the substrate without thermally affecting the substrate or it can be used to laser treat the deposit (including heating, cutting, etc.) to modify the properties or geometry of the deposit during or after deposition. In the case of a rigid tape (such as when using a glass plate) the plate is typically mechanically suspended above the substrate. When a flexible polymer tape is used, it can be laid directly onto the substrate before laser processing and then peeled from the substrate after laser processing, leaving behind the desired pattern.

## 10.5 Thermal Spray DW

Thermal spray techniques for DW have been demonstrated by researchers at the State University of New York at Stony Brook and commercialized by a spin-off company, MesoScribe Technologies, Inc [14]. Thermal spray is a process that accelerates material to high velocities and deposits them on a substrate, as shown in Fig. 10.7. Material is introduced into a combustion or plasma flame (plume) in powder or wire form. The plume melts and imparts thermal and kinetic energy to the material, creating high velocity droplets. By controlling the plume characteristics and material state (e.g., molten or softened) it is possible to deposit a wide range of metals, ceramics, polymers, or composites thereof. Particles can be deposited in a solid or semisolid state, which enables the creation of useful deposits at or near room temperature.

A deposit is built-up by successive impingement of droplets, which yield flattened, solidified platelets, referred to as splats. The deposit microstructure, and thus its properties, strongly depends on the processing parameters utilized. Key characteristics of thermal spray DW includes: (1) a high volumetric deposition rate, (2) material flexibility, (3) useful material properties in the as-deposited state (without thermal treatment or curing), and (4) moderate thermal input during processing, allowing for deposition on a variety of substrates.

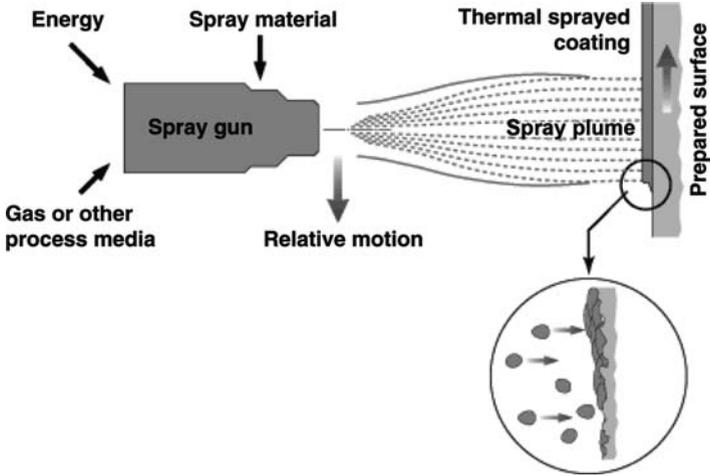


Fig. 10.7 General apparatus for thermal spray [15] (Courtesy of and (C) Copyright Sulzer Metco. All rights reserved)

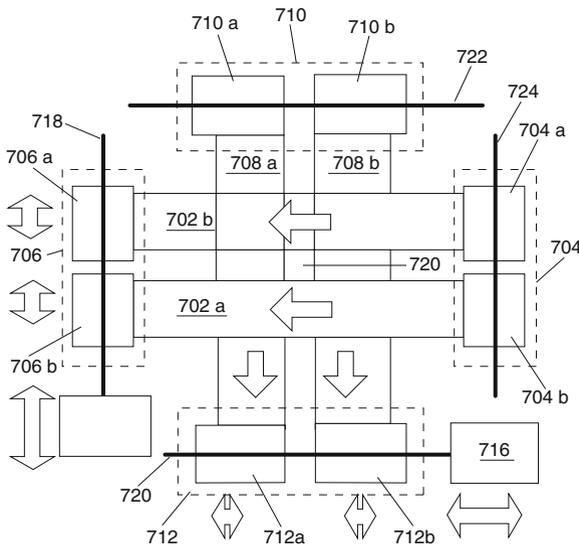


Fig. 10.8 Schematic aperture apparatus for direct write thermal spray (U.S. patent 6576861). Foils 702a, b and 708a, b are in constant motion and are adjusted to allow different amounts of spray to reach the substrate (through hole 720 in the center)

DW thermal spray differs from traditional thermal spray in that the size and shape of the deposit is controlled by a unique aperture system. A schematic apertures system from an issued patent is shown in Fig. 10.8. This aperture is

made up of adjustable, moving metal foils (702a and 702b moving horizontally and 708a and 708b moving vertically) which constrain the plume to desired dimensions (region 720). The distance between the moving foils determines the amount of spray which reaches the substrate. The foils are in constant motion to avoid overheating and build-up of the material being sprayed. The used foils become a waste product of the system.

Because the temperature of the substrate is kept low and no post treatment is typically required, DW thermal spray is well-suited to produce multilayer devices formed from different materials. It is possible to create insulating layers, conductive/electronic layers, and further insulating layers stacked one on top of the other (including vias for signal transmission between layers) by changing between various metal, ceramic, and polymer materials. DW thermal spray has been used to successfully fabricate thermocouples, strain gages, antennas, and other devices for harsh environments directly from precursor metal and ceramic powders. In addition, DW thermal spray, combined with ultrafast laser micromachining, has been shown to be capable of fabricating thermopiles for power generation [16].

## 10.6 Beam Deposition DW

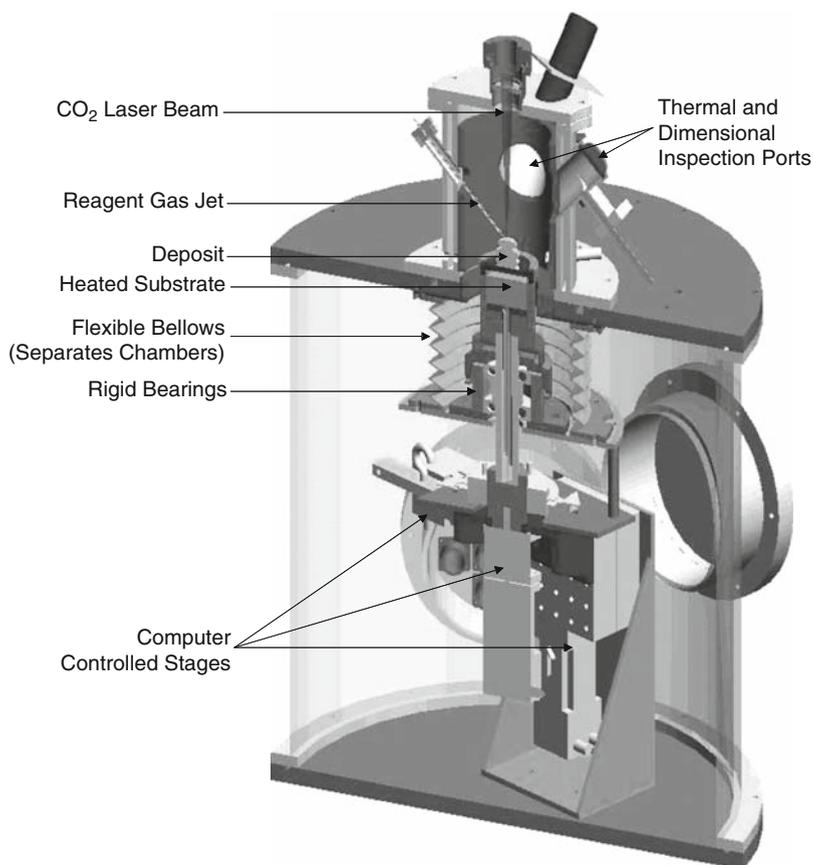
Several direct write procedures have been developed based upon vapor deposition technologies using, primarily, thermal decomposition of precursor gases. Vapor deposition technologies produce solid material by condensation, chemical reaction or conversion of material from a vapor state. In the case of chemical vapor deposition (CVD), thermal energy is utilized to convert a reactant gas to a solid at a substrate. In the regions where a heat source has raised the temperature above a certain threshold, solid material is formed from the surrounding gaseous precursor reactants. The chemical composition and properties of the deposit are related to the thermal history during material deposition. By moving a localized heat source across a substrate (such as by scanning a laser) a complex geometry can be formed. A large number of research groups over almost 20 years have investigated the use of vapor deposition technologies for additive manufacturing purposes [17]. A few examples of these technologies are described below.

### 10.6.1 Laser CVD

Laser Chemical Vapor Deposition (LCVD) is a DW process which uses heat from a laser to selectively transform gaseous reactants into solid materials. In some systems, multiple gases can be fed into a small reactant chamber at different times to form multimaterial structures; or mixtures of gases with varying concentrations can be used to form gradient structures. Sometimes flowing jets of gas are used to create a localized gaseous atmosphere, rather than filling a chamber with the gaseous precursor materials.

The resolution of a LCVD deposit is related to the laser beam diameter, energy density and wavelength (which directly impact the size of the heated zone on the substrate) as well as substrate thermal properties. Depending on the gases present at the heated reactive zone, many different metals and ceramics can be deposited, including composites. LCVD has been used to deposit carbon fibers and multilayered carbon structures in addition to numerous types of metal and ceramic structures.

A LCVD system developed at the Georgia Institute of Technology is displayed in Fig. 10.9. This design constrains the reactant gas (which is often highly corrosive, and/or biologically harmful) to a small chamber that is separated from the motion controllers and other mechanisms. This small, separated reaction chamber has multiple benefits, including an ability to quickly change between reagent gas materials for multimaterial deposition, and better protection of the hardware from corrosion. By monitoring the thermal and dimensional characteristics of the



**Fig. 10.9** The LCVD system developed at Georgia Tech

deposit, process parameters can be controlled to create deposits of desired geometry and material properties.

Georgia Tech's LCVD system has deposited materials such as carbon, silicon carbide, boron, boron nitride, and molybdenum onto various substrates including graphite, grafoil, zirconia, alumina, tungsten, and silicon [18]. Direct write patterns as well as fibers have been successfully deposited. A wide variety of materials and deposit geometries makes LCVD a viable technology for further direct write developments. LCVD is most comparable to microthermal spray, in that deposits of metals and ceramics are directly formed without posttreatment, and without the "splat" geometry inherent in thermal spray. The benefits of LCVD are the unique materials and geometries it can deposit. However, LCVD has a very low deposition rate and a relatively high system complexity and cost compared to most DW approaches (particularly ink-based technologies). High temperature deposition can be another disadvantage of the process. In addition, the need to deposit on surfaces that are contained within a controlled-atmosphere chamber limits its ability to make deposits on larger pre-existing structures.

LCVD can be combined with layer-wise deposition of powders (similar to the binder printing techniques in Chap. 7) to more rapidly fabricate structures than when using LCVD alone. In this case the solid material created from the vapor phase is used to bind the powdered material together in regions where the laser has heated the powder bed. This process is known as Selective Area Laser Deposition Vapor Infiltration (SALDVI). In SALDVI, the build-rates are much higher than when the entire structure is fabricated from LCVD-deposited materials only; but the resultant structures may be porous and are composite in nature. The build-rate difference between LCVD and SALDVI is analogous to the difference between binder-based printing as practiced by ZCorp and direct printing as practiced by Objet Geometries or 3D Systems.

### ***10.6.2 Focused Ion Beam CVD***

A focused ion beam (FIB) is a beam of ionized gallium atoms created when a gallium metal source is placed in contact with a tungsten needle and heated. Liquid gallium wets the needle, and the imposition of a strong electric field causes ionization and emission of gallium atoms. These ions are accelerated and focused in a small stream (with a spot size as low as a few nanometers) using electrostatic lenses. A FIB is similar in conceptualization to an electron beam source, and thus FIB is often combined with electron beams, such as in a dual-beam FIB-scanning electron microscope system.

FIB processing, when done by itself, can be destructive; as high-energy gallium ions striking a substrate will cause sputtering and removal of atoms. This enables FIB to be used as a nanomachining tool. However, due to sputtering effects and implantation of gallium atoms, surfaces near the machining zone will be changed

by deposition of the removed material and ion implantation. This sputtering and ion implantation, if properly controlled, can also be a benefit for certain applications.

Direct-write deposition using FIB is possible in a manner similar to LCVD. By scanning the FIB source over a substrate in the presence of CVD gaseous precursors, solid materials are deposited onto the substrate (and/or implanted within the surface of the substrate) [19, 20]. These deposits can be submicron in size and feature resolution. FIB CVD for DW has been used to produce combinations of metallic and dielectric materials to create three-dimensional structures and circuitry. In addition, FIB CVD is being used in the integrated circuits (IC) industry to repair faulty circuitry. Both the machining and deposition features of FIB are used for IC repairs. In the case of short-circuits, excess material can be removed using a FIB. In the case of improperly formed electrical contacts, FIB CVD can be used to draw conductive traces to connect electrical circuitry.

### ***10.6.3 Electron Beam CVD***

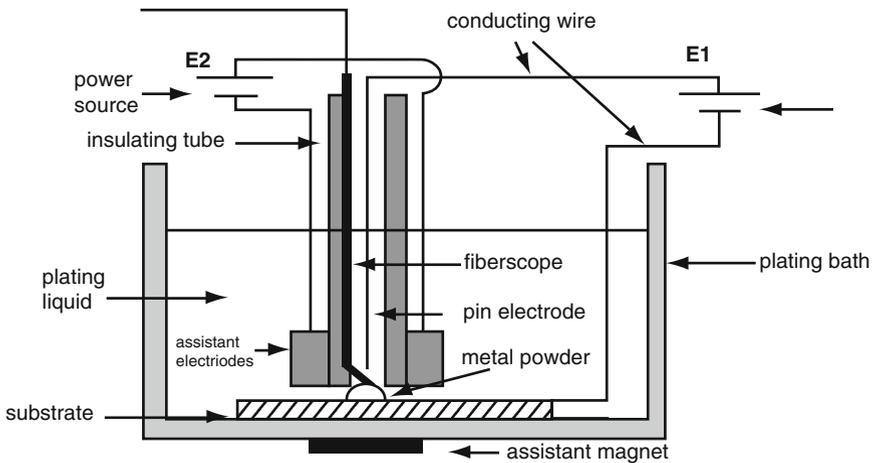
Electron beams can be used to induce CVD in a manner similar to FIB CVD and LCVD. Electron beam CVD is slower than laser or FIB CVD; however, FIB CVD and electron beam CVD both have a better resolution than LCVD [21].

## **10.7 Liquid-Phase Direct Deposition**

Similarly to the vapor techniques described above, thermal or electrical energy can be used to convert liquid-phase materials into solid materials. These thermochemical and electrochemical techniques can be applied in a localized manner to create prescribed patterns of solid material.

Drexel University illustrated the use of thermochemical means for DW traces using ThermoChemical Liquid Deposition (TCLD). In TCLD, liquid reactants are sprayed through a nozzle onto a hot substrate. The reactants thermally decompose or react with one another on the hot surface to form a solid deposit on the substrate. By controlling the motion of the nozzle and the spraying parameters, a 3D shape of deposited material can be formed. This is conceptually similar to the ink-based DW approaches discussed above, but requires a high-temperature substrate during deposition.

A second Electrochemical Liquid Deposition (ECLD) approach was also tested at Drexel. In ECLD, a conductive substrate is submerged in a plating bath and connected to a DC power source as the cathode, as in Fig. 10.10. A pin made up of the material to be deposited is used as the anode. By submerging the pin in the bath near the substrate and applying an appropriate voltage and current, electrochemical decomposition and ion transfer results in a deposit of the pin material onto the substrate. By moving the pin, a prescribed geometry can be traced. As electrochemical



**Fig. 10.10** Schematic of an electrochemical liquid deposition system [22] (MATERIALS & DESIGN by Zongyan He, Jack G. Zhou and Ampere A. Tseng. Copyright 2000 by Elsevier Science & Technology Journals. Reproduced with permission of Elsevier Science & Technology Journals in the format Textbook via Copyright Clearance Center.)

plating is a slow process, the volumetric rate of deposition for ELCD can be increased by putting a thin layer of metal powder in the plating bath on the surface of the substrate (similar conceptually to SALDVI described above). In this case, the deposited material acts as a binder for the powdered materials, and the volumetric rate of deposition is significantly increased [22].

Thermochemical and electrochemical techniques can be used to produce complex-geometry solids at small length scales from any metal compatible with thermochemical or electrochemical deposition, respectively. These processes are also compatible with some ceramics. However, these approaches are not available commercially and have few benefits over the other DW techniques described above. Drawbacks of TCLD-based approaches are the need for a heated substrate and the use of chemical precursors which may be toxic or corrosive. Drawbacks of ECLD-based approaches include the slow deposition rate of electrochemical processes and the fact that, when used as a binder for powders, the resultant product is porous and requires further processing (such as sintering or infiltration) to achieve desirable properties.

## 10.8 Beam Tracing Approaches to Additive/Subtractive DW

By combining layer-wise additive approaches with freeform beam (electron, FIB, or laser) subtractive approaches, it is possible to create DW features. Many coating techniques exist to add a thin layer of material to a substrate. These include physical vapor deposition, electrochemical or thermochemical deposition, chemical vapor

deposition, and other thin film techniques used in the fabrication of integrated circuits. Once these layers are added across the surface of a substrate, a freeform beam technology can be used to trim each layer into the prescribed cross-sectional geometry. These micro- or nanodiameter beams are used to selectively cure or remove materials deposited in a layer-by-layer fashion. This approach is conceptually similar to the bond-then-form sheet lamination techniques discussed in Chap. 8.

### ***10.8.1 Electron Beam Tracing***

Electron beams can be used to either cure or remove materials for DW. Standard spin-on deposition coating equipment can be used to produce thin films between 30 and 80 nm. These films are then exposed to a prescribed pattern using an electron beam. Following exposure, the uncured material is removed using standard IC-fabrication techniques. This methodology can produce line-edge definition down to 3.3 nm. A converse approach can also be used, whereby the exposed material is removed and the unexposed material remains behind. In the case of curing, low-energy electrons can be utilized (and are often considered more desirable, to reduce the occurrence of secondary electron scattering). These techniques fit well within existing IC fabrication methodologies and enable maskless IC fabrication.

Another variant of electron beam tracing is to produce a thin layer of the desired material using physical vapor deposition or a similar approach and then to use high-powered electron beams to remove portions of the coating to form the desired pattern.

Electron beams are not particularly efficient for either curing or removing layers of material, however. Thus, electron beam tracing techniques for DW are quite slow.

### ***10.8.2 Focused Ion Beam Tracing***

As discussed above, a focused ion beam can be utilized to machine materials in a prescribed pattern. By combining the steps of layer-wise deposition with layer-wise FIB machining, a multilayer structure can be formed. If the deposited material is changed layer-by-layer, then a multimaterial or gradient structure can be formed.

### ***10.8.3 Laser Beam Tracing***

Short-wavelength lasers can be utilized to either cure layers of deposited materials or ablatively remove materials to form micro and nano-scale DW features. To overcome the diffraction limit of traditional focusing optics, a number of

nanopatterning techniques have been developed to create features that are smaller than half the optical wavelength of the laser [23]. These techniques include multiphoton absorption, near-field effects, and Bessel beam optical traps. Although these techniques can be used to cure features at the nano scale, inherent problems with alignment and positioning at these length scales make it difficult to perform subwavelength nanopatterning in practice.

These laser approaches are conceptually identical to the electron beam and FIB-based additive plus subtractive approaches just mentioned. Some of the benefits of lasers for beam tracing DW are that they can process materials much more rapidly than electron beams, and they can do so without introducing FIB gallium ions. The main drawback of lasers is their relatively large spot size compared to electron and focused ion beams.

## 10.9 Hybrid Technologies

As in most additive manufacturing techniques, there is an inherent trade-off between material deposition speed and accuracy for most DW processes. This will remain true until techniques are developed for line-wise or layer-wise deposition (such as is done with microstereolithography using a DLP system, as described in Chap. 4). Thus, to achieve a good combination of deposition speed and accuracy, hybrid technologies are often necessary. Some examples of hybrid technologies have already been mentioned. These include the additive/subtractive beam tracing methods described above and the use of a laser in the Aerosol Jet aerosol system.

The primary form of hybrid technology used in DW is to form deposits quickly and inexpensively using an ink-based technique and then trim those deposits using a short-wavelength laser. This results in a good combination of build speed, accuracy, and overall cost for a wide variety of materials. In addition, the laser used to trim the ink-based deposits has the added benefit of being an energy source for curing the deposited inks, when used in a lower power or more diffuse manner. If DW is integrated with an AM process that includes a laser, such as stereolithography, the laser can be used to modify the DW traces [24].

## 10.10 Applications of Direct Write Technologies

The applications of DW processes are growing rapidly [25]. There is a growing variety of materials which are available; including semiconductors, dielectric polymers, conductive metals, resistive materials, piezoelectrics, battery elements, capacitors, biological materials, and others. These can be deposited onto various substrate materials including plastic, metal, ceramic, glass, and even cloth. The combination of these types of materials and substrates means that the applications for DW are extremely broad.



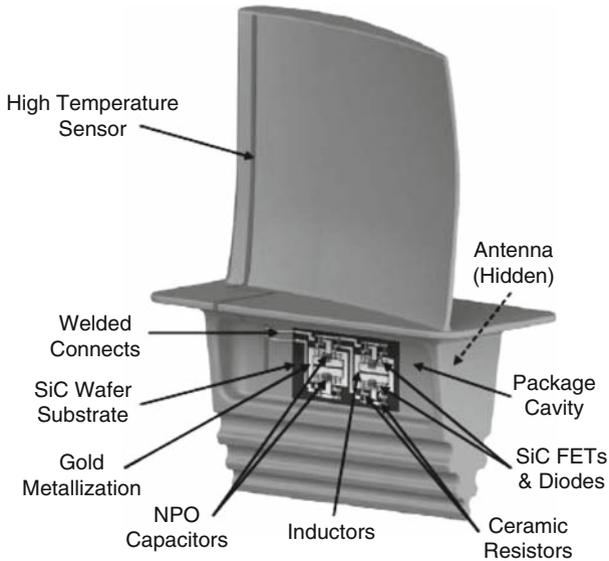
**Fig. 10.11** 35-GHz fractal antenna design (*left*) and MAPLE-DW printed antenna on the abdomen of a dead drone honeybee (*right*). (Courtesy Douglas B. Chrisey)

The most often cited applications for DW techniques are related to the fabrication of sensors. DW approaches have been used to fabricate thermocouples, thermistors, magnetic flux sensors, strain gages, capacitive gages, crack detection sensors, accelerometers, pressure gages, and more [3, 14, 16, 26].

A second area of substantial interest is in antenna fabrication using DW. Since DW, like other AM techniques, enables fabrication of complex geometries directly from CAD data, antenna designs of arbitrary complexity can be made on the surface of freeform objects; including, for instance, fractal antennas on conformal surfaces. Figure 10.11 illustrates the fabrication of a fractal antenna on the abdomen of a worker honeybee using MAPLE-DW.

Another area of interest for DW is as a freeform tool to connect combinations of electronic components on freeform surfaces. One area where this is particularly useful is in harsh environments, as shown in Fig. 10.12. In this example, direct write thermal spray is used as a method for producing and connecting a series of electronic components that monitor and feed back information about the state of a turbine blade. A thermocouple, labeled High Temperature Sensor in the figure, is deposited on the hot region of the blade, whereas the supporting electronics are deposited on the cold regions of the blade. DW-produced conductors are used to transmit signals between regions and components.

DW companies have demonstrated approaches for depositing robust sensors in a freeform manner onto complex-geometry substrates. The next step is for these systems to be made portable to enable, to some degree, the ability to bring a DW “sensor fabricator” to the specimen rather than always needing to bring the specimen to the sensor fabricator. These portable DW systems would need the ability to deposit conductors, insulators, and sensor-required metal and ceramic materials. For this approach to be adopted widely, however, software tools that contain generic descriptions of useful sensor types, including a set of rigorously tested sensor designs that conform to a set of performance and repeatability standards, must be developed. These software tools must be intelligent and enable the deposition of these sensor designs conformally onto complex surfaces. When this type of sensor fabricator and associated software is developed; it will enable existing infrastructure (e.g., power plants, paper mills, mining equipment, etc.) to be



**Fig. 10.12** A direct write sensor and associated wiring on a turbine blade structure. Signal conditioning electronics are positioned on a more shielded spot (Courtesy MesoScribe Technologies, Inc. and Arkansas Power Electronics Int.)

upgraded with new process control systems by adding intelligent feedback where there is currently no integrated sensor capability.

Although most DW processes can produce thermal and strain sensors, there is still opportunity for improved conductors, insulators, antennas, batteries, capacitors, resistors and other electronic circuitry. In addition, in every case where a conductive path is not possible between a power source and a deposited sensor, some form of local power generation is necessary. Several researchers have demonstrated the ability to create systems which use electro-magnetic or thermopile power generation schemes using DW [16]. If designs for energy harvesting devices can be made robustly using DW, then the possibility for remote monitoring and sensing of components and parts becomes possible. For instance, the ability to create a thermal sensor with integrated power harvesting and antenna directly onto an internally rotating component (such as a bearing) within a transmission could provide feedback to help optimize performance of systems from power plants to motor vehicles to jet engines. In addition, this type of remote sensing could notify the operator of thermal spikes before catastrophic system failure, thus saving time and money.

Overall, DW techniques for additive manufacturing remain an area of great potential. The rapidly expanding number of publications related to DW, and the ongoing investments in DW R&D indicate these technologies will mature quickly into highly capable and robust methods for creating nano-, micro-, and meso-scale features.

### 10.10.1 Exercises

1. From an internet search, identify two DW inks for conductive traces, one ink for resistors and one for dielectric traces that are commonly used in nozzle-based systems. Make a table which lists their room-temperature properties and their primary benefits and drawbacks.
2. For the inks identified in problem 1, estimate the printing number (7.6). List all of your assumptions. Can any of the inks from problem 1 be used in an inkjet printing system?
3. Would you argue that DW techniques are a subset of AM technologies (like PBF or BD) or are they more an application of AM technologies? Why?
4. Two techniques for accelerating DW were discussed in this chapter where DW deposition was used to bind powders to form an object. What other DW techniques might be accelerated by the use of a similar approach? How would you go about doing this? What type of machine architecture would you propose?
5. Research thermocouple types that can withstand 1,000°C. Based on the materials that are needed, which DW techniques could be used to make these thermocouples and which could not?

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