Inkjet Printing for Materials and Devices

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Inkjet printing is familiar as a method of printing text and images onto porous surfaces. In the last few years it has been used as a free-form fabrication method for building three-dimensional parts and is being explored as a way of printing electrical and optical devices, especially where these involve organic components. Inkjet printers are also being used to produce arrays of proteins and nucleic acids. The need for a versatile inkjet technology for free-forming materials and for multilayer devices raises a number of materials problems that do not apply to conventional printing of images. Higher resolutions will be needed if organic transistors are to be printed. Also, it must be possible to print pinhole-free layers to avoid shorting of devices. Multiple layers must be printed such that they mix and react to form a single material or such that they form discrete unmixed layers. Printing on dense rather than porous substrates will be the norm. This article reviews the range of materials that has been printed and the issues that arise as the ink interacts with the substrate.

Introduction

Inkjet printing is familiar as a method for printing computer data onto paper or transparencies. Industrially, it is also widely used to print date information onto cans and bottles. The recent development of free-form fabrication methods for building parts layer-by-layer[1] has led to interest in fabrication of multilayer parts and circuits by inkjet printing. The past few years have seen growing efforts, especially in organic transistors, light-emitting diodes, ceramics, and biopolymer arrays. This review will briefly summarize inkjet technology and then will survey applications in materials.

Printer Technology

Le[2] has reviewed current inkjet technology. The original continuous jet printers used electrostatic plates to deflect drops to the paper or to a reservoir for recycling. These have largely been superseded by drop-on-demand systems. Canon and Hewlett-Packard developed similar systems where a heated plate causes a vapor bubble to form and eject a droplet of ink through a nozzle. The current pulse lasts a few microseconds and raises the plate temperature to about 300 °C. The main problem is to avoid clogging of the nozzle by dried ink. Commercial piezoelectric printers frequently use a glass tube squeezed by a surrounding cylinder of piezoelectric ceramic. The Epson printers use an array of piezoelectric plates, which drive the droplet in bend or push mode. In both printer types, nozzle sizes are in the range of 20−30 μm. Smaller nozzles allow smaller droplets and higher resolution. Droplets are in the range of 10−20 pL.

Ink viscosity and surface tension are crucial parameters in the design of a printer.[3] As a droplet is expelled, energy goes into viscous flow, surface tension of the drop, and kinetic energy. The viscosity must also be low enough to allow the channel to be refilled in about 100 μs. The surface tension must be high enough, and the pressure low enough, to hold the ink in the nozzle without dripping. A major concern in ink design is the "first drop problem", which is the clogging of nozzles by partly dried ink. Clogging has also been the main reason soluble dye inks are used in preference to colloidal dispersions of pigment.[3]

In general, ink properties will be matched to the performance of a specific printer. A typical ink has a viscosity up to 2 cP but printers can be designed to handle liquids up to 100 cP. Where polymeric additives are used to improve dye bonding to the paper, other additives are used to reduce the chain expansion and viscosity. Humectants, low-volatility water miscible liquids such as ethylene glycol, are added at 10−20% to prevent drying and clogging. The surface tension should not be lowered by surfactants because this leads to the ink wetting the faceplate around the nozzles and also prevents formation of a stable droplet stream.[3] The minimum surface tension is about 35 $mN \cdot m^{-1}$.

When the droplet hits the paper, it will be absorbed.[4] Specially coated papers can limit the spread of the ink, and so improve resolution, by adsorbing the dye.[5,6] Resolution can also be improved by the use of pigments (solid particles) in inks in place of soluble dyes. The particulate color will spread less on a microporous paper. Printing of polymer latex allows an oil-soluble dye to be incorporated in the polymer phase and thus limits spreading on the paper. However, the need to retain stability of the latex does make ink formulation much more difficult.[7,8]

Overhead transparencies will not absorb ink and so are coated with a hydrophilic polymer and may be patterned to provide a rough surface on which the ink

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will not spread.[9] An ink layer, thick enough to give good color on a transparency, takes several minutes to dry. The porous film is effectively dry in 15 s. Industrial printing onto hard surfaces relies on solvent evaporation. "Phase change" inks can also be used on hard surfaces or paper. These are waxes, which freeze rapidly to a hemispherical drop and then are cold-rolled to make a bonded layer. The viscosities are again in the range of a few centipoise. There is also much interest in UV-curable inks for printing on dense surfaces.[10]

Sol−Gel Materials

Sol−gel glass materials are used in spin coating[11] and can also be inkjet-printed. Printing patterns onto ceramics has been described.[12] Organic−inorganic hybrid lenses, with a diameter of 50 μm, have been printed and photopolymerized.[13] Self-assembling hybrid layered nanostructures have been printed using sol−gel and monomer solutions in a mixture of water and alcohol.[14]

As formed, sol−gel layers are porous agglomerates of nanoparticles. For many applications they are then sintered at temperatures over 500 °C to densify the layer. Sintering is incompatible with structures on a polymer substrate or containing organic materials. Laser densification may be possible but would probably be too slow for large areas. Alternatively, an organic−inorganic hybrid could be printed but the polymeric matrix may often detract from the desirable properties of the inorganic material.

Organic Light-Emitting Diodes

There is intense current interest in light-emitting diodes with polymer or small-molecule organic charge carrier layers. Such devices are typically four-layer structures with a cathode, electron conductor, hole conductor, and anode. Starting with an indium tin oxide coated conducting glass anode, the subsequent layers can be spin-coated or evaporated.

In many cases it is desirable to pattern the device as an array of pixels or as a design. Silk-screen printing has been used for the hole-conducting layer, which is frequently a solution of dye in polymer.[15]

So far, it has not proved possible to inkjet print pinhole-free layers but several groups have printed the dyes or a second polymer layer onto an existing spin-coated layer.[16,17] Pinholes will lead to shorting of the device. Assuming that they have a common solvent, the printed material generally mixes into the existing layer. For multilayer printing, there is a problem if the dyes redistribute between layers while the droplet is wet.[18]

Since the resolution of displays is similar to that of printed paper, inkjet printing should readily lend itself to OLEDs once a wider range of materials and multiple layers become possible.

Organic Transistors

A useful comparison of the potential of inkjet printing for organic transistors has been published.[19,20] A major problem has been the relatively large size of inkjet dots (>50 μm) and no actual devices seem to have been reported in the scientific literature before a report from Cambridge University in 2000.[21,22] In this case, fine lines were obtained by printing on a stepped surface, such that the ink was pulled into the step as it dried. The source and drain electrodes were printed in a conducting polythiophene in this way and then the semiconducting polymer layer was spin-coated on top. Printing an electrode on either side of a lithographically defined 5-μm polyimide barrier allowed a 5-μm channel length to be defined, despite the drops being printed with a resolution of 50 μm.

Conducting Polymers

De Rossi has reported printing patterns of conducting polymers.[23] Several strategies were tried. Polymer solution was printed onto a solid substrate and then doped to the conducting form with iodine vapor. Polymer was also printed onto a layer of a dopant ($Fe(ClO_4)_3$) to induce conductivity and monomer was similarly printed onto an oxidant layer to induce polymerization and doping. Resolution was about 50 μm. Printing these solutions required a special solvent-resistant print head. It should also be noted that inkjet printing is very vulnerable to blockage due to solvent drying; hence, a printing method that relies on rapid evaporation of solvent is intrinsically difficult to maintain.

There is also a report of the use of inkjet printing solvent onto a film of a polythiophene to induce a phase change that could, in principle, be used for data storage.[24]

Structural Polymers

True polymers are too viscous to print via an inkjet except as a dilute solution or a colloidal dispersion (latex). Hot melt adhesives are short-chain polymers with molecular weights of a few thousand Daltons. They combine fairly low melt viscosity with moderate toughness. Waxes have molecular weights of a few hundred, flow and print easily but are weak and brittle. UV or thermal treatments can be used after printing to increase the molecular weight and strength. Within these limitations, an inkjet system can be tuned to an application. As mentioned in the Introduction, one form of inkjet image printing uses hot colored waxes (phase change materials).[2]

Several companies have developed rapid prototyping methods based on inkjet printing of wax or low molecular weight polymer.[25,26] Compared to other rapid prototyping methods, the precision and simplicity of the process is balanced against the weaker final parts and slower building.

For electronic applications, systems have been developed for printing UV-curable thermosetting polymers for dielectric coatings and adhesives[27,28] (Figure 1). Printed UV-curable epoxies have also been used to form microlenses with diameters from 20 to 140 μm.[29] Inkjet printing has also been used to deposit resist layers.[30] The layer, which is free of pinhole defects, is patterned by exposure and development in the normal way.

The printing of latex inks has been described.[8] This has the advantage of presenting a high molecular weight polymer in a highly concentrated but low viscosity form. Polymer latex has also been printed onto a powder bed as a binder for forming ceramics; see below.[31] High molecular weight polymers have similarly

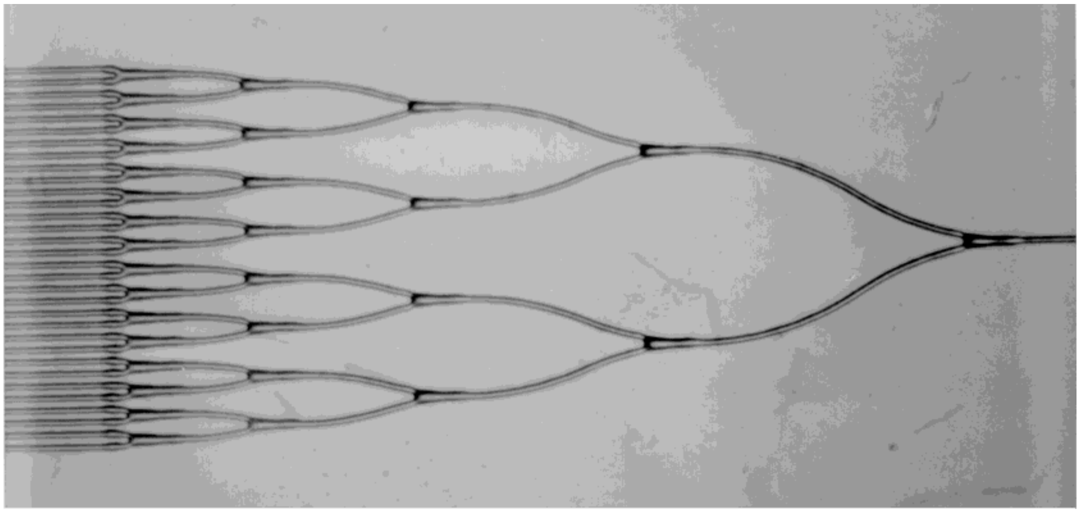

Figure 1. Thirty-two channel splitter printed onto glass using inkjet technology. The individual waveguides are 100-μm diameter. Courtesy, Microfab Inc., Plano, TX (http://microfab.com/).

been formed by printing solvent droplets into a series of layers of polymer powder.[32]

Ceramics

The application of structural ceramics, such as silicon nitride and silicon carbide, has been hampered by the high cost of processing material that is sufficiently flaw-free. In these brittle materials, flaws of 20 μm or more will significantly reduce the strength. Instead of eliminating flaws, it is also possible to increase the strength by increasing the toughness but strategies to do this have been only partly successful. Layerwise manufacturing (free-form fabrication) methods have been intensively developed as a possible low-cost route to high-strength ceramics.[33] Among the approaches developed has been three-dimensional printing in which a binder is inkjet-printed into successive layers of ceramic powder and direct inkjet printing of ceramic powders.

While structural ceramics have failed to live up to their promise, electronic applications of ceramics have developed into a major industry. This includes hermetic packages for semiconductors and substrates for thin film circuits. Here, the ceramic, usually alumina, provides electrical resistance with good thermal conductivity. Ceramic capacitors are based on multiple layers, each several microns thick, of high dielectric constant ceramics, frequently barium titanate. Piezoelectric actuators and sensors are typically lead zirconate titanate. In addition, there are applications for antennae, frequency filters, and other devices based on ceramic thin films. Tape casting and screen printing are often used for these purposes but inkjet printing should be applicable.

Inkjet printing of ceramics was developed by a group at Brunel University. A dilute dispersion of zirconia and polyvinylbutyral binder in solvent was printed and dried to a 60 vol % ceramic dispersion that could be burnt out and sintered to dense ceramic.[34] The system used was a continuous inkjet printer, which is normally a faster and lower resolution method than most drop-on-demand printers. To build solid structures, speed and high throughput are necessary. Aqueous suspensions of zirconia have also been printed with both conventional thermal and piezoelectric inkjet printers.[35,36]

A problem with this approach is the need for low-viscosity inks, which requires very good particle dispersion but also high dilution. Common experience is that it is much harder to obtain good drying to uniform dense green bodies from a dilute suspension. As a result, the final sintered product tends to be weak. In contrast, the "Robocasting" system writes 100-μm lines and layers from aqueous suspensions of around 60 vol % alumina. The resulting material is well-packed and sinters to high density. The Brunel group has put considerable effort into achieving good particle dispersion in their inks but have still been limited to 5 vol %.[37]

The printing of superconducting thick films directly from solutions of metal oxides or nitrates in organic acids has been reported.[38] There is also a report of using an inkjet system to build pillars by putting drops one on the other.[39] In fact, wormlike hollow tubes were formed about 1-mm high by 100-μm diameter. This strange morphology derives from the drying process.

Inkjet printing has also been used on suspensions of alumina in wax.[40] This has the advantage that the drying shrinkage is avoided. On the other hand, the suspensions are fairly dilute, which makes it difficult to achieve good fired density.

The 3D printing system has proved very successful for making sintered ceramic molds for metal casting.[41] A binder is inkjet-printed into a layer of powder, a new layer of powder is rolled onto the top, and more binder is printed. The final shape is shaken loose form the powder bed and sintered. In this process the coarse powder size needed for the rolling step limits the quality of the ceramic product. Fine powder can be used by inkjet printing first a uniform layer of powder and then printing binder as a second step.[42] In this case the printing must be adjusted to ensure uniform binder diffusion into the powder bed to avoid density variations in the final part. The process has also been applied to stainless steel powder to make tooling for injection molding.[43] The layerwise approach has the advantage that the curved cooling channels that follow the inner surface can be designed into the mold.

The same process of inkjet printing liquid into powder has been used to prepare tablets with graded pharmaceutical contents to give predictable release profiles.[44]

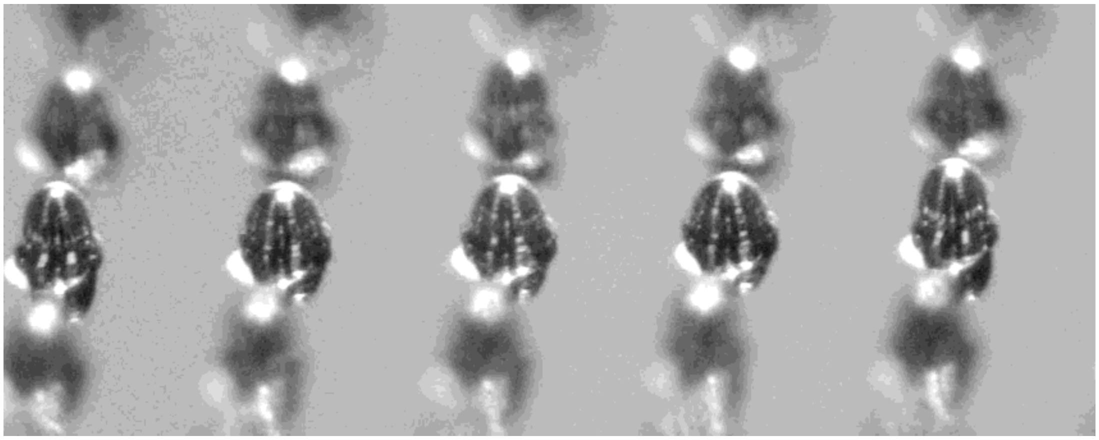

Figure 2. Solder drops (100) placed onto 250-μm pitch pads at a rate of 400 s^{-1}.

Nanoparticles

Many of the materials previously discussed can be printed as fine particles or as solutions. Since sedimentation must be avoided in inks, particle sizes should be less than a micrometer. The dispersion must be very good to avoid any aggregation that would increase the viscosity and this starts to severely limit the maximum particle volume fraction for very small (<100 nm) particles. The advantages of particulate suspensions include the greater chemical stability of crystal over solutions, the higher concentration of active species for most partially soluble compounds, and the greater ease of immobilizing species within a printed layer.

There is much interest in conventional inkjet printing with nanoparticle inks.[45,46] One obvious target is to print nanoparticulate suspensions of gold or other metals to form conductors for electronics but there is little reported work in this area. There are two Japanese reports discussing this.[47,48] The method has also been applied to printing electrodes for photovoltaic cells.[49] Diamond grit has also been printed.[50]

Magnetic inks are used for printing checks, normally using laser printers with a magnetic toner. Nanoparticulate magnetic inks have been developed for inkjet printing.[51,52] In this case, presumably, the particles must be small enough to be in the superparamagnetic state to avoid clumping in the ink but must dry to a densely packed magnetic film. It has also recently been suggested that a magnetic fluid could be jetted with much higher resolution without using a nozzle.[53]

Metals

As a low-viscosity liquid, solder is an obvious target for inkjet printing to allow printing of solder bumps onto circuit boards or semiconductor packages. A system for delivering uniform 100-μm droplets has been described[54] (Figure 2). There have also been efforts to use liquid metal jets in free-form fabrication.

It is also possible to form electrodes by printing a solution of a metal precursor, followed by conversion to metal. Silver metallorganic ink has been described which converts to metal below 300 °C.[55] Multilayer printing, with firing steps between layers, has been used to deposit silver electrodes with a resistance of 1 $\Omega/\square$ for photovoltaic cells. Bismuth was added to improve adhesion and further heat treatment was needed to achieve low contact resistance.[56] More recently, copper contacts have been printed using a precursor route.[57]

Electroless plating has also been used to deposit metal by inkjet printing a colloidal platinum suspension onto polyester transparencies. This was followed by a copper/formaldehyde solution that produced copper lines 100-μm wide. Layers peeled off various coated and uncoated transparencies but remained attached to transparencies which had been etched in sodium hydroxide. Resistivities of the order of 10^{-6} Ωm were obtained with thicknesses of less than 1 μm.[58]

Nucleic Acid and Protein Arrays

"Gene chips" are normally formed using a split-nib pen to pick up a drop of dilute solution and deposit it onto a pretreated slide with a resolution of about 100 μm. The DNA becomes covalently bonded to the slide. Starting from an array of sample tubes, a robotic system can print a DNA library onto a series of slides.[59] Applied to this system, an inkjet printer would need to be able to aspirate samples from the tubes and to clean the head between samples. A number of companies are developing commercial systems of this type (for example, Packard Bioscience, http://www.packardbiochip.com/products/biochip_arrayer.htm). A recent review has compared technologies for printing arrays.[60]

Reports in the literature include using conventional printers to deposit DNA onto membranes at 300 dpi,[61] using a bubble-jet printer, apparently without degradation of the DNA, to print onto glass,[62] printing a circular array of antigens onto a polycarbonate CD for immunoassay,[63] and printing enzyme arrays onto filter paper.[64]

An alternative to depositing oligonucleotides is to print the reagents to synthesize the oligonucleotides in situ in each drop on the slide.[65] To meet the requirements of combinatorial chemistry, a valve-controlled inkjet printer has been developed, which delivers 48 reagents from separate reservoirs to a row of delivery nozzles.[66]

Arrays are normally read under uniform fluorescent illumination. One report concerns addressing inkjet-printed spots with a laser coupled into a planar waveguide on the surface of the slide and scanned.[67]

Inkjet printing has also been applied to the manufacture of biosensors.[68−70]

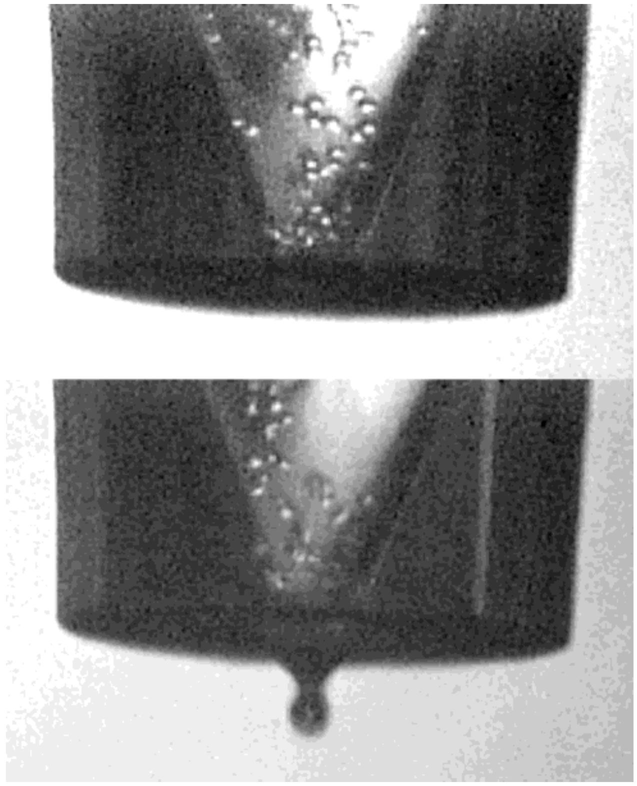

Figure 3. Human liver cells being jetted in a phosphate buffer. Courtesy, Microfab Inc., Plano, TX (http://microfab.com/).

Protein arrays are more problematic than DNA arrays because the printing and binding process must not cause denaturation and loss of activity of the protein. Denaturation would be the expected result if the system is allowed to dry or if the surface bonding is too tight. One approach is to print the protein into a gel layer on a slide. It would also be necessary to avoid drying during the process. A recent paper describes making arrays using a contact printing robot and methods for limiting denaturation.[71] It has been shown that alkaline phosphatase retains it activity after being printed onto glass.[72]

There are also obvious applications for inkjet printing of matrixes for tissue engineering. The process has been used to modify polymer surfaces to permit or prevent local attachment of cells.[73] The direct inkjet printing of cells in suspension has also been demonstrated (Figure 3).

Prospects for Inkjet Printing of Structures and Devices

The examples given above illustrate the wide range of materials that can be inkjet-printed. Almost all these applications concern single layers of a material printed from solvent or suspension. There is need for a rapid direct-write technology that can be used to form devices of low-temperature materials, including organic semiconductors, polymers, and biopolymers. These will require several layers of different materials to be overprinted. It will be critical that the properties of these layers are comparable with those of sintered materials. There will also be pressure for much higher resolution than that obtainable with current printers.

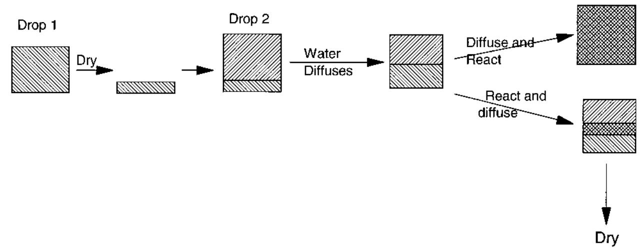

Figure 4. Models for reaction between serially printed layers of epoxy and amine curing agent.

As well as the devices being organic, much of the need is for them to be formed on flexible polymeric substrates. The low surface energy of polymers makes the wetting more difficult and the flexing of the substrate implies a need for toughness in the device materials.

When ink is printed onto a nonadsorbent surface, it will tend to bead up rather than form a uniform layer. In printing on transparencies, this can be controlled by use of a swelling polymer layer, a transparent but porous layer, and a roughened surface. If a material is to be built from many deposited layers, then these wettability questions must be resolved for inks on a previous layer of ink.

The problems of retaining good adhesion between metals and polymers have been addressed in making flexible printed circuit boards, but these will normally depend on high-energy methods for deposition of the metal or high-temperature lamination. If we are to print circuits onto polymers at low temperatures, there will need to be some development of bonding chemistry and printable adhesive layers.

Printing of multiple ink layers onto a hard surface, with a drying time between layers, will result in redissolution, resuspension, or remelting of each previous dry layer of ink in the new liquid. A mechanism is needed to harden or insolubilize each layer before the next one is deposited. Examples given above include UV curing and thermal treatment. This can also be achieved by printing a pair of inks that react to form a solid layer, by curing, or by the sol–gel reaction. In addition, this insoluble layer may be dense or may be a layer of porous matrix that will take up an active material. It is thus quite possible, through combinations of materials chemistry, to either form a single layer through the interaction of several inks or to form a stack of solid layers.

Recent work at the University of Arizona has focused on inkjet printing multiple layers of polymers and ceramics.[74] IR spectroscopy has been used to monitor the reaction of a water-soluble epoxy (diglycidylglycerol) and amines printed as successive layers. Small molecules diffuse and react completely, whereas a larger polyetheramine appears to form a reacted barrier film between the layers that limits further reaction (Figure 4). Large uniform films can be readily printed with these liquids but lines and patterns break up into droplets on most substrates. It is possible to print patterns by first printing an acceptor layer of alumina powder and then printing in dyes or reagents (Figure 5).

Many device technologies depend on uniform insulating layers separating active components. However, inkjet-printed layers often contain pinholes. There is one report above of defect-free layers being formed by inkjet printing[30] but several groups have found it difficult to

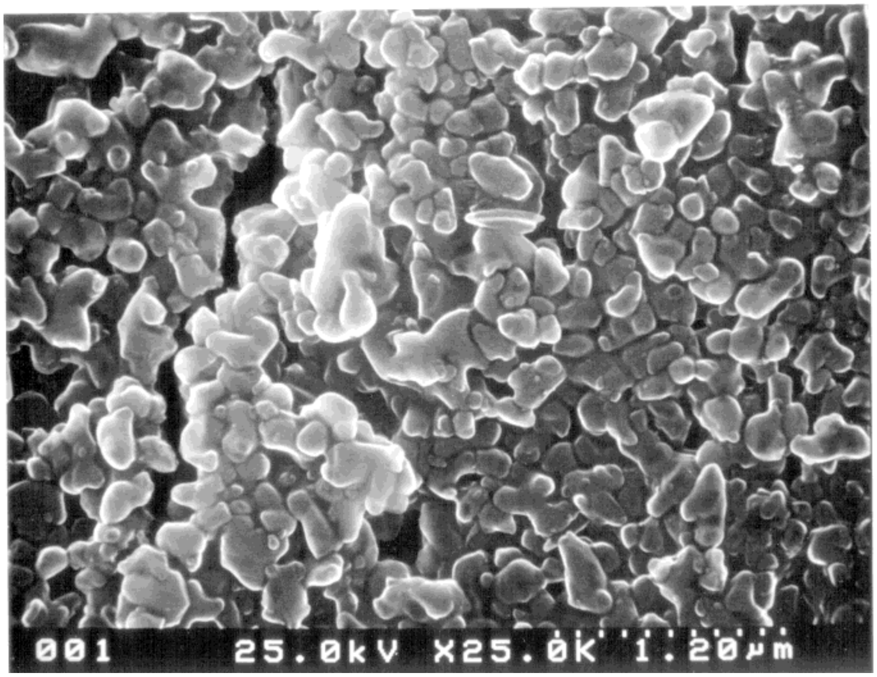

Figure 5. Alumina particles, 0.2 μm, printed from dilute aqueous suspension and bonded by an overprinted epoxy solution.

prevent shorting between layers. A good understanding of the formation of pinholes in printed layers will certainly be necessary if the technique is to be used for device manufacture.

Resolution is being addressed aggressively in the context of photoprinting but here the issue is partly a trade-off between drop size and speed that would not necessarily affect printing of devices. This favors systems with a variable drop size to print sharp edges slowly and large areas quickly. While droplet diameter will decrease from the current 20−30 μm, the constraints arising from viscous flow through a small hole would seem to make unlikely direct printing to line widths of <10 μm. However, there is certainly the possibility to use controlled wetting on patterned surfaces to reduce line width,[21] although it remains to be shown how this could be applied to subsequent layers of a more complex structure. In making any direct comparison between inkjet printing and photolithography, it should be kept in mind that multilayer printing methods are more truly three-dimensional and should allow many more layers to be added. Assuming ink with a solids volume fraction of about 10%, layer thicknesses are of the order of a few micrometers.

One clear materials challenge is that of attaining high-conductivity metal electrodes. A printed nanoparticle layer would also need good particle−particle contact to reach high conductivity but nanoparticle suspensions have surfactant layers on the particle surface. The metal precursor route is successful but requires temperatures that are too still high for many active materials and substrates. In addition, the electrode layer has to be strongly adherent and flexible. The same issues arise if it is desired to print layers with a high dielectric constant, with a strong piezoelectric response or with semiconducting properties; the properties of a film made by low-temperature chemistry are usually inferior to those of an evaporated or sintered material.

Inkjet printing is only one of a large group of techniques for building layers. Screen printing has long been applied to thick-film electronics and has recently been applied to light-emitting diodes.[15] Thick-film pastes may also be written directly onto a substrate.[75] Spin coating is a familiar method for photoresist deposition. Microcontact printing and the family of soft-lithography techniques offer excellent resolution but it is relatively difficult to pattern multiple layers.[76] It is certainly possible to envisage a combination of additive processes to be used to make organic devices, especially inkjet printing, spin coating, and microcontact printing. Subtractive processes, such as dissolution or etching, would almost certainly lead to damage of previous layers.

The thin layers and dilute inks make building of parts by inkjet printing very slow. 3D printing avoids this by printing only binder into fairly thick powder layers. Inkjet printing of waxes is notably slow compared to other free-forming methods but does offer higher resolution. If multiple layers are to be printed, each layer must be hardened to avoid redissolution in the next layer. Any such chemical reaction could probably not take less than 1 min and this would then limit the speed of the overall process. In rapid prototyping, 1 min per layer is a fairly typical minimum time and the build time for a large object can then be estimated on the basis of the thickness of each layer and the height of the object. One minute per layer would seem to be quite adequate for building devices.

Outside of optics and electronics, the area where inkjet printing of materials may well be readily applicable is in matrixes for tissue engineering. Here, the ability to handle dilute solutions of gelling materials will be important.

Conclusions

Inkjet printing has the potential to be applied to organic electronic devices, to direct writing of electronics onto flexible substrates, and to biotechnology and biomedical materials. The process of delivering the ink to the surface is well-understood. The processes that control the formation of multiple layers with controlled structures have not been much considered.

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