Inkjet Printing of Materials as a Mimic of Biological Growth

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Abstract

Inkjet printing is familiar as a method for printing ink on absorbent paper. In principle the method can be used to print multilayer devices, but we will then need to be able to control the structure of material deposited onto hard surfaces and to overprint different materials on one another. This paper deals addresses the approaches available to form materials by reaction between successive ink layers. The short diffusion distances allow uniform structures to form instead of interfacial barriers or precipitates that would result on a larger scale. Many aspects of these processes can be compared to those that occur during growth of biological tissues. Thus, biology may be a fruitful source of ideas on how to exploit this technology.

Multilayer Manufacturing and Biological Growth

The manufacture of silicon electronic devices depends on a series of steps to add or remove material on a wafer surface in patterns. Inorganic materials are typically deposited by vapor-phase processes and are patterned using photoresists. Most polymers cannot be vapor-deposited and so are spin-coated, patterned by exposure to UV light and the excess washed away. Many of the processes are thus subtractive rather than additive. As each layer is deposited, it must not react or otherwise change during the processing of subsequent layers.

There is much current interest in making multilayers of polymers and small-molecule organic materials for OLEDs (organic light-emitting diodes) and OTFTs (organic thin-film transistors). The available processes are more limited because there is no large chemical contrast between resists and organic active materials. Thus, controlled removal to form patterns is much more difficult. Many groups are developing printing methods to form these devices. The general approach is to use printing to pattern one layer and to deposit the others as uniform layers by spin coating or vapor deposition. Available printing methods include microcontact printing, inkjet printing, silk screen printing and others. Each has its advantages and disadvantages in terms of speed, resolution and range of useable materials. An alternative is to use conventional methods to pattern an inorganic substrate and then deposit all the organic layers as uniform sheets.

Our group has had a long interest in biomimetic materials and processes. Many biological growth processes also depend on the serial deposition of materials with complex structures. The layerwise nature of tree growth is evident as tree-rings. Bones, teeth, shells, tendon, skin and many other materials form by variations of this approach. Often, a layer of cells exports reagents into a thin layer of liquid or gel, which separates the cells from the material being built. There is a parallel with a vapor source delivering material across a vacuum to a substrate on which deposition is occurring. This parallel suggests that it should be possible to form both 3-dimensional device structures and large objects by some sort of repetitive printing process using only mild conditions. There is a concern about growth rates but some biological materials, such as deer antler, form at centimeters/day, which must be comparable with vapor deposition rates.

In order to explore the potential of this approach, we need a method to mimic cells, that is to deliver sequences of reagents to a substrate in a layerwise manner. We chose inkjet printing because the nozzle size is comparable with that of an animal cell (20-50 microns) and the system lends itself readily to many dilute aqueous solutions.

Inkjet Printing of Materials

Efforts to inkjet print materials have been reviewed recently.[1] The process has been studied in some detail in the context of printing ceramic powders to make alumina and zirconia parts. There have also been extensive studies of printing binder into layers of ceramic powder as a freeform fabrication method.[2] Metal lines have been printed via a printed palladium salt followed by metallization using electroless plating methods.[3] Dielectric layers and many organic compounds have also been printed.

For commercial printheads, the main requirements for the ink are that the viscosity be comparable with that of water and that the surface tension be adjusted to limit wetting of the faceplate around the outside of the nozzle. The ink must be in a solvent that does not attack the cartridge, either through dissolution or corrosion. It is common to add a humectant, a water-soluble, high boiling point liquid such as glycerol. This prevents hard drying of the ink in the nozzle. In piezoelectric printheads, where the drive voltage is high, there may be a problem if the ink is electrically conducting. In thermal inkjet heads there is a concern about degradation as the ink is boiled to expel the drop. However, the heating time is only a few microseconds so the major concern may be contamination of the heated surface.

The resolution of inkjet printing is normally in the range of 50-100 microns with a drop size of 25-50 microns. Printing on a hard substrate can be quite different to printing onto absorbent paper but there has been little study of the details of the wetting and drying process. The drop sizes of commercial inkjet printers are decreasing in order to attain higher resolution. In conventional printing there is a constraint that printing times should not increase too much. If a printer were designed specifically for device manufacture, this constraint might be relaxed. Recently it has been shown that prepatterned substrates can be used to make very fine (5 microns) features by differential wetting.[4]

Our studies have mainly been carried out using refilled Hewlett Packard thermal inkjet heads mounted in an x-y-z stage. Pulses are applied to an individual nozzle in order to form single drops under control as the head is moved over the substrate.

Multilayer Inkjet Printing

In building multilayer structures by inkjet printing, there are a number of concerns. One wants to be able to print individual dots, lines and areas. One wants to be able to make thick layers by repetitive printing. One wants to be able to build layers of different materials without them mixing. It may be necessary to wash away reaction by-products at intermediate stages without destroying the device. Since it is desirable to use flexible organic substrates for organic devices, one wants to achieve good adhesion and properties without high temperature steps.

Overprinting of Lines

A dilute suspension of conducting polymer, poly(2,3 dihydrothieno-1,4-dioxin/poly(styrenesulfonate), (PEDOT) was printed onto glass slides as a sequence of dots spaced to form a line. As shown in figure 1, sequential printing over a single line gives a linewidth of about 150 microns that does not change as 30 layers are printed. Individual dots are in the size range of 50-100 microns and the greater width of the lines may be due to fluctuations in droplet placement. About 100nm of material is added for each layer. Conductivities were measured in the range of 1-5 $S.cm^{-1}$, which gives a resistance of about 10 kohm/cm for a line 2 microns thick.

In figure 2, lines are printed side-by-side in order to produce a conducting area. The result is shown for printing the lines with an offset of 50 and 100 microns. In the latter case, we obtain a flat area of conductor about 700 microns wide and 2 microns thick with a thickness variation of ½ micron. AFM studies of these areas suggest that there may be pinholes through the film.

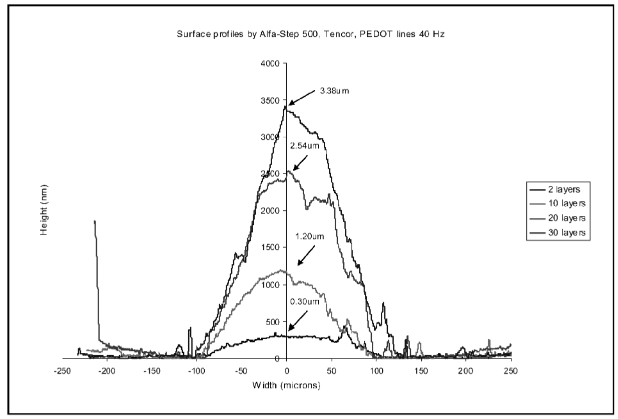


Figure 1. Profiles of inkjet printed PEDOT lines with 2 to 30 layers. Each layer is about 100 nm thick.

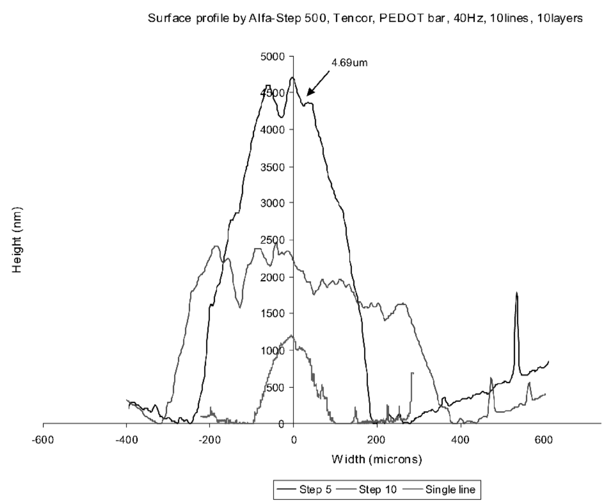


Figure 2. PEDOT lines printed side-by-side to form a layer. 10 lines printed each offset by 12 microns (high peak) or 25 microns (flat profile). Compared with 10 overprinted lines (small peak).

Reaction Between Layers

By inkjet printing it is possible to deposit layers of differing materials on top of one another. By sequentially printing two reactive components it is possible to form an adherent solid film by diffusion and reaction. This film can trap other species. If the solid product is not strongly swollen by water, the film will become a dense substrate for deposition of further materials. In this way, multilayer devices may be built.

By printing multiple layers of a water-soluble epoxide, diglycidylglycerol, and a water soluble amine, triethylenetetramine, we have formed cross-linked epoxies which are water-swellable but not soluble. These layers can be printed onto silicon wafers, which then allow infra-red spectroscopy to monitor the curing reaction of the amine and epoxy.

Figure 3 shows that the epoxy peaks in the region of 800-900 cm^{-1} are consumed when the amine is overprinted.

This is a diffusion-and-reaction process, which we have modeled with a simple finite-difference method. As shown in figure 4, two layers each 5 microns thick are allowed to react. The central peak shows the gelled reaction product building up as the epoxy and amine diffuse together. By varying the reaction kinetics or the diffusion rate, the gel may form a uniform layer (fast diffusion) or may form a dense barrier between the two layers (slow diffusion).

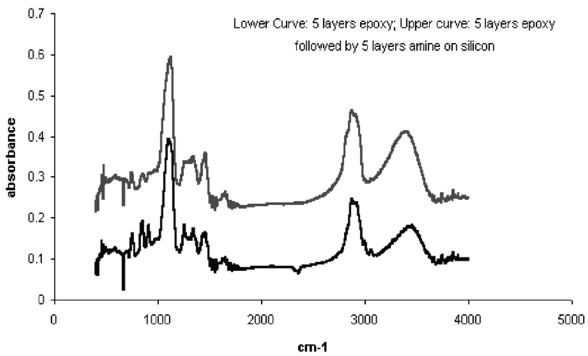


Figure 3. Infrared spectra of 5 printed layers of epoxy solution (lower curve) and after overprinting and reaction 5 layers of amine (upper curve).

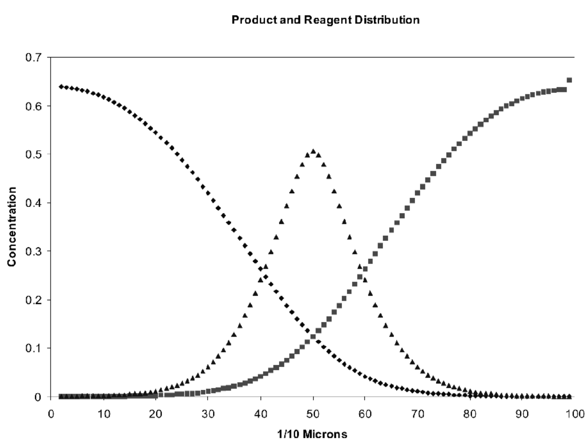
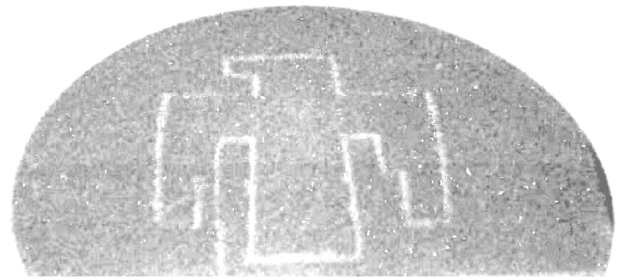


Figure 4. Model for layers of two reagents, each 5 microns thick, that diffuse and reaction to form a product at the interface (central peak).



(central peak).

Figure 5. Fluorescent image of labeled bovine serum albumin printed and immobilized in a printed epoxy gel.

In the biological growth processes, mentioned above, the tissue is not formed by two layers of reactants but by reactants emitted from a single layer of cells. In this case it is not immediately obvious how tissue formation can be controlled, except directly at the cell surface. The models show that combinations of fast-diffusing reagents and slow moving inhibitors or catalysts, coupled with timed release, can give rise to layers of products at a distance from the source. In principle the same ideas could be applied to inkjet printed layers in order to form products within or below the topmost layer of material. Thus, it should be possible to form buried layers.

In addition to the epoxy system outlined above, we have printed successive layers of cationic polymer (polydimethyldiallyammonium chloride) and anionic polymer (sodium polystyrenesulfonate). In this case there is no simple spectroscopic method to follow the reaction. As initially deposited the layers can be readily redissolved in water. After annealing in a humid atmosphere at 50°C overnight, the layers become insoluble, presumably because the two polymers diffuse and form an ionic complex.

Immobilization of Polymers and Particles

We have also explored the use of printed gels to provide a matrix in which other materials can be immobilized. We have printed densely packed layers of alumina particles by combining layers of epoxy, of amine and of a suspension of 0.3 micron alumina in water. The gelation of the polymer serves to prevent subsequent redispersion of the alumina. The same system can be used to trap proteins in a printed gel. Figure 5 shows a printed pattern of fluorescent bovine serum albumin immobilized in an epoxy resin matrix.

Conclusions

Inkjet printing has the potential to be a versatile technology for many types of organic devices. As with conventional printing, we can expect different methods to be used depending on the required resolution and the number of parts being made. In the context of our previous work on freeform fabrication, inkjet methods should allow components to be incorporated into parts to give combinations of mechanical and sensing functions more similar to those of animals.

Acknowledgements

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