A Micromachined Printhead for the Direct Evaporative Patterning of Organic Materials

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Abstract

We investigate the use of microsystems (MEMS) in the direct patterning of materials needed for organic optoelectronic devices on large area low-cost substrates.

We present a new high-resolution printing technique for depositing molecular organic semiconductor materials on substrates. By depositing the materials directly from the gas phase, without liquid phase coming in contact with the substrate, we aim at avoiding the limitations encountered when inkjet printing such materials.

One of the main advantages of this technique is that it does not require a vacuum, which is very significant for achieving low-cost fabrication.

Our micromachined printhead was used, in conjunction with inkjet technology for the delivery of liquid phase material, to print patterns of organic material.

Introduction

Organic optoelectronic devices can be fabricated on a variety of substrates due to their low-temperature processing. However, it still remains a challenge to develop suitable fabrication techniques to pattern organic thin films on low-cost, large-area substrates [1].

Small molecular weight organic materials are typically deposited by vacuum thermal evaporation and patterned through shadow masks. However, shadow masking, is not scalable to very large area substrates, because the flatness requirements are difficult to achieve for thin shadow masks on large areas. Organic materials can be deposited by ink-jet printing, but this technique limits the achievable film morphology and is difficult to apply to the fabrication of multilayers, because the solvent used to deposit one layer can partially redissolve the previous layer. The interface between layers is therefore modified in an unpredictable way. This has serious practical implications since optoelectronic devices need well defined heterostructure contacts between specified materials of specified thicknesses. Moreover, some materials, such as pentacene which is used for Organic Field Effect Transistors (OFETs), exhibit very different functionalities when inkjet printed and when evaporated. When the presence of solution is deleterious to the performance of the material, one solution to the problem is to use evaporation to deposit the material. We offer another solution in this paper by jetting the material from a porous region.

We previously demonstrated the direct patterning of thermally evaporated organic materials in vacuum using micromachined printheads [2,3]. We used an electrostatically actuated micromachined shutter integrated with an x-y-z manipulator to modulate the flux of evaporated materials in a vacuum chamber and generate patterns of the deposited materials. We successfully printed both small molecular weight organic materials and metals, and printed an array of 30 micron organic light emitting devices [4].

Principle of the printing

In our new printing technique, we also deposit materials on substrates directly from the gas phase, but without the use of moving micromachined parts. Most importantly, this technique does not require a vacuum ambient during printing.

The micromachined printhead consists of a silicon membrane comporting a central area with macropores, which are 2 micron diameter through holes, and a surrounding thin film platinum heater. The microfabricated device is shown in Figure 2.

The material to be printed is first delivered from the back side of the chip onto the central porous region of the silicon membrane. The delivery can be performed either in gaseous phase, through evaporation, or in liquid phase, with the use of a solvent. The material then deposits inside the pores. During this phase, the solvent evaporation can be precisely controlled by using the integrated microheater at low power. In the second step of the printing, the integrated heater is then used to heat up the porous area and the material is re-evaporated from the pores onto the substrate.

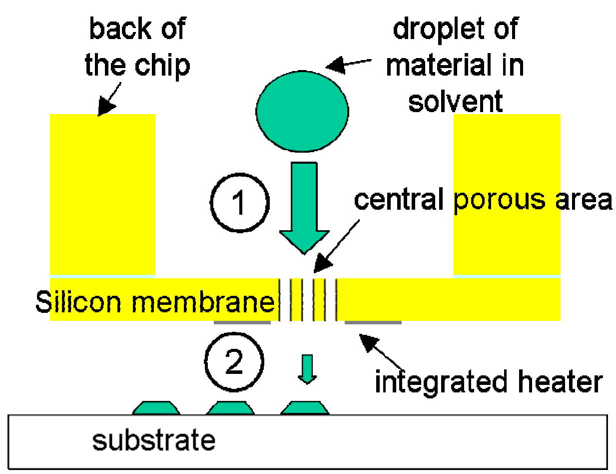

Figure 1. *Schematic of the printing principle*

Compared to our previous printing technique, the problems of crashing and stiction associated with the moving microshutter are avoided, since there is no moving part. Clogging of the aperture is also limited since the material is removed during each printing cycle. Other advantages include the smaller quantity of organic material used, and the reduced substrate heating.

A very important advantage of this technique is that it doesn't require a vacuum ambient during printing. The printing can be

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performed in a glove box under nitrogen ambient, or even under standard ambient conditions with a gas flow providing a local controlled environment.

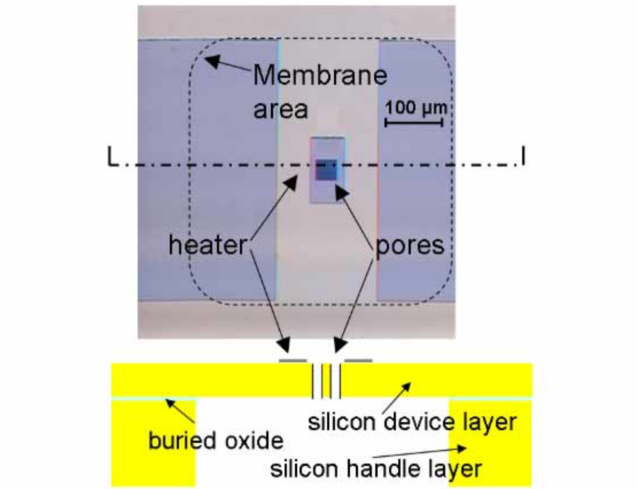

***Figure 2**. Microscope picture and cross-section schematic of the microfabricated printhead chip*

Fabrication of the printheads

The fabrication of the printheads starts from a Silicon-On-Insulator (SOI) wafer, with a 20 micron silicon device layer, a 1 micron buried oxide layer and a 500 micron base layer (see Fig.3).

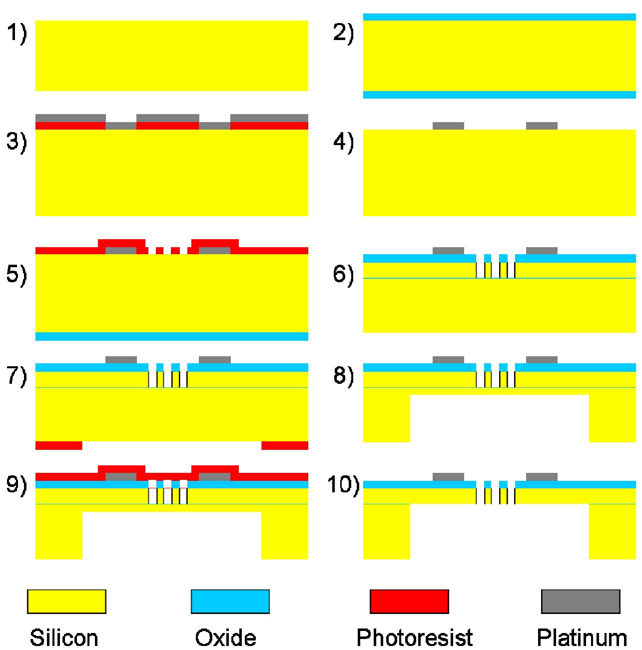

***Figure 3**. Illustration of the fabrication process*

We fabricated two different kinds of printheads. The first ones didn't have a silicon dioxide layer between the silicon substrate and the metal layer. The fabrication of the second kind is presented here.

First, 1000 Angstroms of silicon dioxide are thermally grown on the SOI wafer (2). Then, the metal layer (10 nm Ta and 200 nm Pt) is deposited by e-beam evaporation and patterned by lift-off (3 and 4). The silicon dioxide layer is patterned by a wet etch in Buffered Oxide Etch (BOE) and the pores are etched through the silicon device layer using Deep Reactive Ion Etching (DRIE) (5 and 6). The membrane is then created by etching the back side of the wafer through DRIE to the buried oxide layer which acts as an etch stop (7 and 8). Finally, the front side is protected with photoresist and the buried oxide layer is removed from the back of the membrane through a wet etch in BOE (9 and 10).

Results

Thermal characterization

We first present results for the first kind of printheads, without the oxide layer.

We measured the temperature of the device under different actuation currents using a Quantum Focus Instrument "InfraScope II" infrared microscope. The temperature profile measured for an actuation current of 0.85A is shown on Fig. 4.

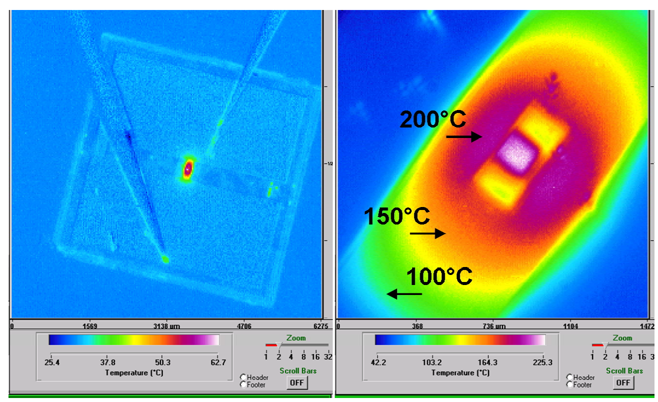

***Figure 4**. Temperature profile of the microfabricated printhead chip obtained with the InfraScope II. Left: view of the whole chip and probes. Right: View of the membrane region for an actuation current of 0.85A.*

We also measured the temperature using two other techniques: using a thermocouple, and measuring the resistance of the device which allows calculating the temperature given the Temperature Coefficient of Resistance (TCR) of the metal. We used a value of 1/292 K^{-1} for the TCR of the Ta/Pt stack, that was previously measured in our laboratory.

We compared those measurements to simulation results obtained using the software CoventorWare. The results are shown on Fig. 5. The device reaches a temperature of 200°C at about 0.9A of current and 5W of electrical power.

The second kind of printheads exhibits better temperature performance, reaching almost 500°C for about 0.8A of current and 5 Watts of power as shown on Fig. 6.

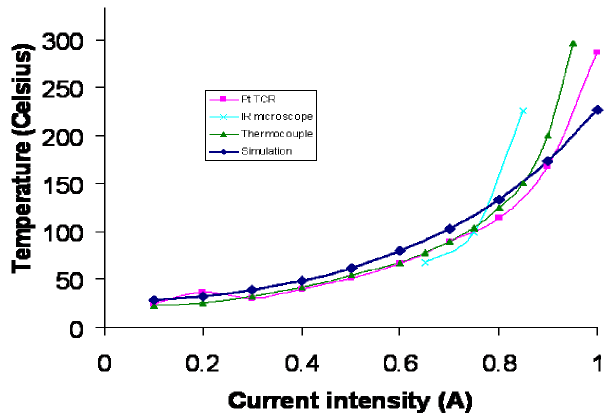

Figure 5. *Temperature of the first kind of printheads obtained by different measurement techniques, and compared to simulation results.*

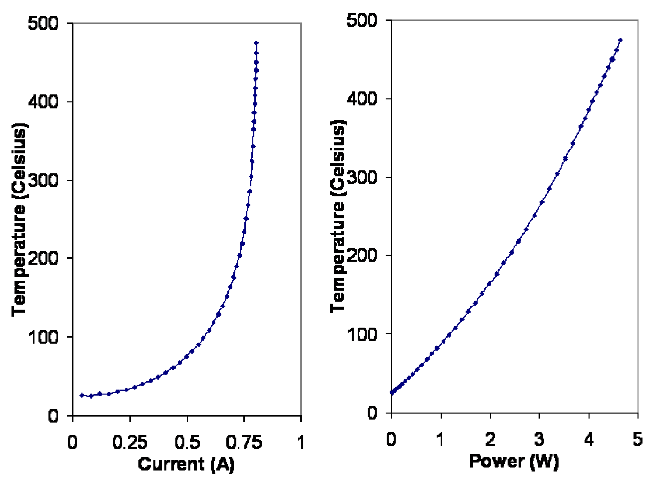

Figure 6. *Temperatureof the second kind of device obtained by electrical resistivity measurement.*

Heater failure

The temperature range of our printheads is limited by the failure of the metal layer.

For the devices without oxide, this failure occurs between 225°C and 300°C. The central part of the heater, which reaches the highest temperature during operation, appears roughened after failure (see Fig. 7). Auger analysis shows that there are discrete layers of Pt, Ta, and Si in the smooth areas, while the roughened areas show a Pt-Ta-Si layer over Si with a broad diffusion-type interface. The failure therefore appears to initiate from partial silicidation of the Pt film or Pt-Si interdiffusion, and the Ta layer is not sufficient as a diffusion barrier between Pt and Si.

The devices with an oxide barrier reach a higher maximum temperature as seen on Fig.6. A cross-section of a failed heater was obtained by focused ion beam (FIB) and is shown on the SEM picture of Fig.8. It shows that the oxide layer is intact and therefore functions well as a barrier layer, even when the temperature is high enough for the platinum layer to partially melt or dewet from the substrate.

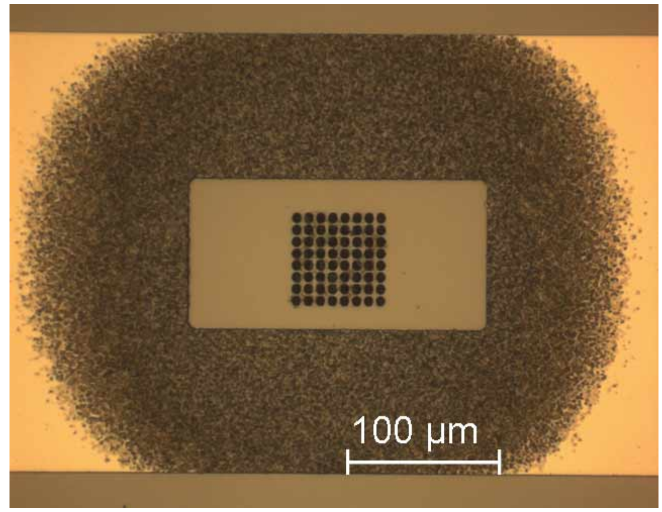

Figure 7. *Microscope image of the platinum heater and porous area at the center of the membrane after failure.*

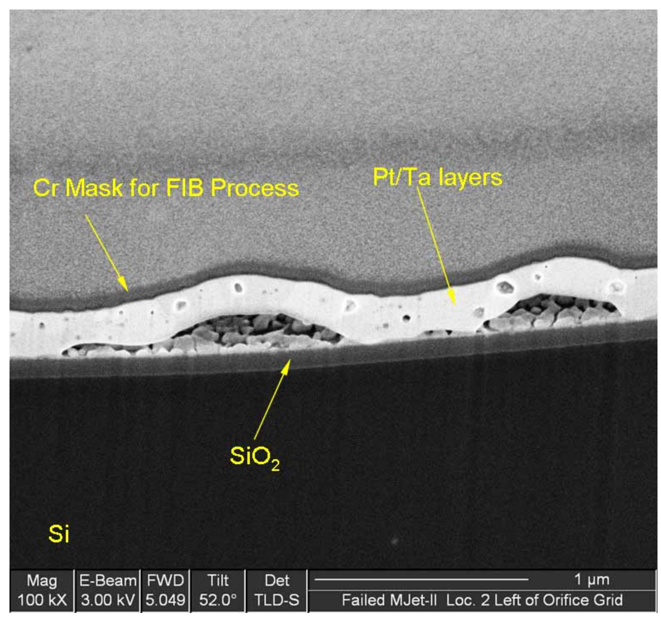

Figure 8. *SEM picture of a FIB cross-section of a second kind of device after failure.*

Thermal time constant

The thermal time constant of the device was estimated by applying a voltage step across the device to heat it up while keeping the current constant by means of a temperature-independent resistor of higher value placed in series. The resistance of the device is therefore proportional to the voltage across it, and it is linearly related to the temperature, through the thermal coefficient of resistance, up to 1000°C for platinum. The thermal time constant is found to be on the order of 1 millisecond (see Fig. 9).

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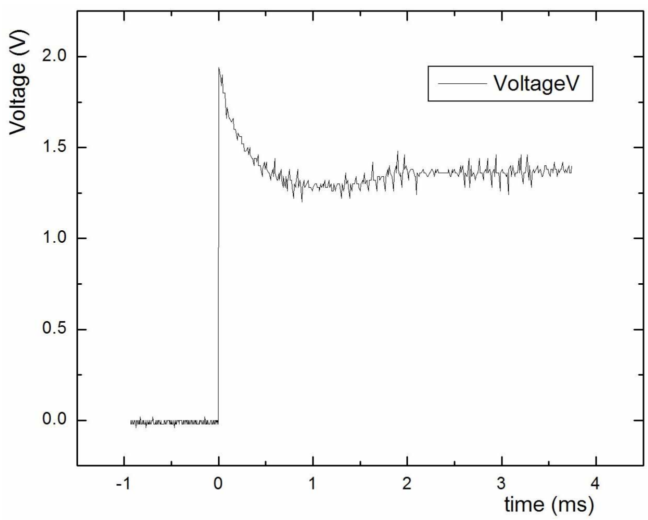

***Figure 9**. Voltage (linearly related to temperature) across a heater submitted to a voltage pulse.*

Material loading and re-evaporating

A drop of organic material Alq3 in solvent was deposited on the back of the device as in Fig. 1. Fig. 10(a) shows a fluorescent microscope image of the porous region seen from the front of the device after this loading step. Green fluorescent material Alq3 is loaded in the pores.

The integrated metal heater was then used to heat up the central area of the silicon membrane, in order to re-evaporate material from the porous area. Fig. 10(b) shows an optical microscope image of the porous region of the device illuminated from the back. It can be seen that the pores are empty, and therefore the material has successfully been removed.

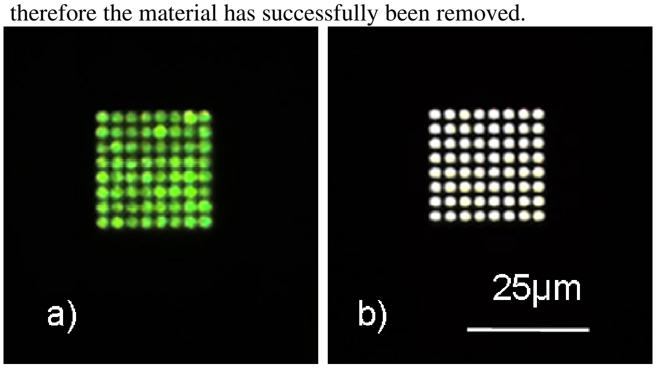

***Figure 10**. Images of the porous area seen from the front of the device: (a) fluorescent microscope image after loading Alq3 into the pores and (b) back illuminated optical microscope picture after heating*

Printing

This printhead was used to print small molecular organic material Alq3. Ink-jet technology was used for the delivery of liquid phase material into the porous region. For printing results, see [5] at this conference.

Conclusion

We presented a new high-resolution printing technique for depositing molecular organic semiconductor materials on substrates directly from the gas phase. Unlike typical evaporation of organic materials, this fabrication technique does not require a vacuum.

The printing technique utilizes a micromachined printhead with a silicon membrane comporting macropores (2 microns in diameter) and an integrated thin film platinum heater for local evaporation of the materials.

The fabrication process of the printheads was described, as well as their temperature performance. We demonstrated the ability to load organic material into the porous region and evaporate it onto the substrate under ambient conditions using the integrated heater.

This printhead was used, in conjunction with inkjet technology for the delivery of liquid phase material, to print patterns of organic material.

Since this printing technique does not require a vacuum, it can lead to low-cost fabrication of organic devices.

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Author Biography

Valérie Leblanc received the diplôme d'ingénieur from Ecole Polytechique, Palaiseau, France in 2002. She is currently working toward the PhD degree in materials science and engineering at the Massachusetts Institute of Technology, Cambridge, MA. Her research focuses on the use of microsystems for the printing of organic optoelectronic devices.