Printing of Electronic Nanoinks by Laser Forward Transfer

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Abstract

Laser forward transfer processes are capable of directly generating patterns and structures of functional materials for the rapid prototyping of electronic, optical and sensor devices. These processes, also known as laser induced forward transfer or LIFT, offer unique advantages and capabilities for digital microfabrication. A key advantage of laser forward transfer techniques is their compatibility with a wide range of materials, surface chemistries and surface morphologies. These processes have been demonstrated in the fabrication of a variety of microelectronic elements such as interconnects, passives, antennas, sensors, power sources and embedded circuits. Overall, laser forward transfer is perhaps the most flexible digital microfabrication process available in terms of materials versatility, substrate compatibility and range of speed, scale and resolution. Recently, laser forward transfer of thin film-like structures with excellent lateral resolution and thickness uniformity using metallic nanoinks has been shown at NRL using a technique named laser decal transfer. The high degree of control in size and shape achievable with laser decal transfer has been applied to the digital microfabrication of 3-dimensional stacked assemblies and freestanding structures for MEMS applications. This paper will describe the unique advantages and capabilities of laser decal transfer of electronic nanoinks, discuss its applications and explore its role in the future of digital microfabrication.

Introduction

Lithography and etching processes have dominated the micro and nanofabrication areas since the beginning of the microelectronics industry. There are considerable challenges, however, in adapting lithographic processes to new applications requiring processing on plastic or flexible substrates, production of small batch sizes and customization or prototype redesign. In these cases, the complexity, significant capital investment and high operating costs of the equipment involved, combined with the limited range of materials that can be patterned represent significant shortcomings. Furthermore, the use of lithographic techniques requiring the vacuum deposition of a thin film and its subsequent etching to achieve a desired pattern from a given material is not practical for many applications requiring the modification, and/or repair of existing microelectronic devices or circuits. As a result, there is a pressing need for the development of new microfabrication techniques and approaches that avoid these limitations.

An alternative to lithography is provided by direct-write techniques. Direct-write techniques are digital microfabrication processes that allow the formation of patterns or structures under complete computer control. Examples of direct-write techniques include inkjet, laser chemical vapor deposition or LCVD and laser direct-write or LDW. In general, these non-lithographic techniques allow the deposition of individual 3-dimensional pixels or "voxels" of virtually any type of material at precisely defined locations to generate a given pattern or shape with little or no material waste. For applications requiring the modification or repair of an existing microelectronic circuit or device, direct-write techniques offer the best chance for success. However, most direct-write techniques are not capable of depositing patterns of electronic materials with placement precision under a micron, with uniform thickness of a few hundred nanometers and with feature morphology and size similar to the surrounding thin film structures already present in the lithographically processed device or circuit. This has limited their use and implementation outside the laboratory.

Laser forward transfer or LIFT is a type of LDW process compatible with a wide range of materials and substrates. The Naval Research Laboratory (NRL) has developed LDW techniques with unique capabilities ranging from the non-phase transformative direct printing of complex suspensions or inks [1] to the "lase-and-place" of entire semiconductor devices [2]. More recently, the use of high viscosity metallic nano-inks with LDW has allowed the direct printing of thin film-like structures with excellent lateral resolution and thickness uniformity [3]. This process has been named laser decal transfer or LDT.

Background

LDW is not limited by the constraints encountered in LCVD or inkjet. The term laser direct-write includes various techniques such as laser-based modification, subtraction and addition processes that can create patterns of materials directly on substrates without the need for lithography or masks. In additive mode, laser-forward transfer processes are used for the deposition of voxels, i.e. 3D pixels, of metals, oxides, polymers and composites under ambient conditions onto virtually any type of surface. This laser printing process has been used with great success in the fabrication of sensors, microbatteries, interconnects, antennae and solar cells [4-6]. When combined with other laser forward transfer processes, LDW can be used for fabricating embedded electronic devices and circuits [7]. LDW is also capable of transferring entire devices such as semiconductor IC's inside a pocket or recess in a substrate, similar to pick-and-place machines used in circuit board assembly [8]. No other direct-write technique offers this broad range of capabilities for the rapid prototyping of electronic circuits on a single platform. A schematic illustrating the basic components of a laser direct-write system is shown in Figure 1. More recently, laser forward transfer of thin film-like structures with excellent lateral resolution and thickness uniformity using metallic nanoinks has been shown by LDT. The high degree of control in size and shape achievable with LDT has been applied to the digital microfabrication of 3-dimensional stacked assemblies and freestanding structures such as microbridges and microcantilevers without the use of sacrificial layers [9].

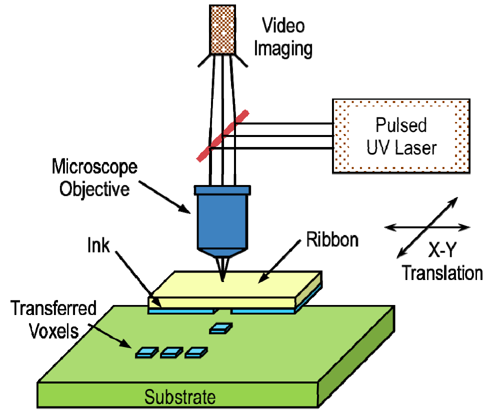

Figure 1. *Schematic showing the basic components of a laser direct-write system.*

Experimental

The laser used for the transfers performed in this work was a frequency tripled Nd:YVO_4 laser operating at 355 nm with pulse energies of a few hundred µJ at kHz repetition rates. Typical laser energies used for laser transfer were ~ 2 to 10 nJ (30 ns FWHM) resulting in a fluence of 8 to 40 mJ/cm^2 at the ribbon. The substrate was placed on top of a computer- controlled X-Y stage motion control system. The ribbon was made from a 50 mm x 75 mm glass microscope slide to which a suspension of silver nanoparticles (called the ink) was applied using doctor blading and placed with the ink layer side parallel and facing the receiving substrate separated by a 10 to 50 microns adjustable gap. The laser spot was focused onto this ink layer and a series of voxels were laser decal transferred by translating the ribbon to a new area after each laser pulse. Transfers were performed on a variety of surfaces including polyimide, glass and p-type Silicon. The surface of the substrates was not pre-treated by any special techniques other than rinsing with organic solvents (acetone and isopropanol) and dried with nitrogen. After transfer, the samples were placed in a convection oven for 30 min. at 150 °C for thermal curing.

Optical microscopy was used to characterize the transfers before and after curing and also to characterize the ribbon before and after the transfers. Once cured, the thickness, width and surface morphology of the transfers were determined using contact profilometry (KLA Tencor P-10), atomic force microscopy or AFM (Digital Instruments Dimension 3100), and scanning electron microscopy or SEM (LEO 1550). The adhesion and chemical resistance were evaluated by subjecting the transfers to tape peel tests and immersion in solvents (water and isopropanol) respectively, and afterwards measuring any changes in morphology or electrical properties of the transferred patterns. Characterization of the electrical properties of sample lines transferred between Au-pads on glass substrates was performed using standard 4-probe measurement techniques using a Keithley 2400 sourcemeter with 200 µA input current.

Results and Discussion

With LDT, the size of the removed material on the ribbon is identical to the size of the transfer demonstrating that the laser transfer generates a 1-to-1 correspondence in size and shape between the laser spot illuminating the ribbon and the transferred voxel. The SEM image in Figure 2 shows an example of the control in shape and size achievable with LDT. This is very important for repair applications, since specific voxel lengths and forms can be generated with a variable shape aperture, allowing the transfer of a complete repair pattern with one single laser pulse. In general, the thickness of the transfers depended on the thickness of the ink layer on the ribbon and ranged between 100 nm and 1 µm. For any given thickness, however, AFM analysis of the transfers demonstrated the excellent edge definition and thickness uniformity of the laser transfers. Such features are similar to those obtained by lithographically patterning and then etching a vacuum deposited thin film layer of similar thickness. To our knowledge, no other laser forward transfer technique can generate the kind of thin film-like patterns that can be achieved using the LDT process.

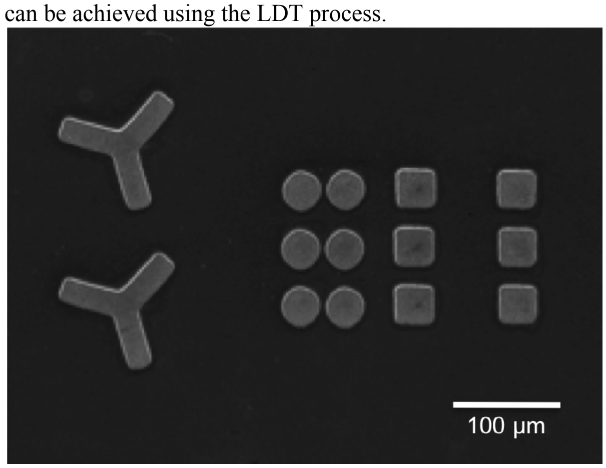

Figure 2. *SEM image revealing the control in shape and resolution of silver nanoinks deposited on a Si substrate by LDT.*

The use of high viscosity nanoparticle suspensions (1,000 to 100,000 cP) as inks for the ribbon plays an important role in the ability to perform the decal transfers. To date, most of the nano-inks used in laser transfers by other groups have been of relatively low viscosities (< 100 cP) and the resulting transfers form droplets when released from the ribbon. As the droplets reach the substrate surface, patterns of varying shape and thicknesses tend to be generated analogous to those formed by inkjet, but with surrounding debris. By using nanoparticle suspensions of much higher viscosities, it is possible to take advantage of shear thinning effects that prevent the breakup of the transfer into a discontinuous ensemble [3]. In order to characterize the electrical properties of the laser decal transfers, multiple sets of continuous lines across gold pads on glass substrates were printed and then oven cured. Electrical characterization using 4-probe measurements revealed resistivities for some of these lines to be as low as 3.4 μΩ cm, which corresponds to about 2.1 times the resistivity of bulk silver metal (1.6 μΩ cm at room temperature). The ability to laser decal transfer complex fluids and suspensions without degrading their properties while maintaining their shape and thickness once released from the ribbon is crucial for printing highly conductive thin-film-like patterns devoid of discontinuities, interfaces or steps.

Since laser decal transfer is able to generate patterns with high edge definition and low debris outside the transferred region, it is also well suited for the deposition of patterns or lines in close proximity or with small gaps. This is very important for fabricating high density interconnects and electrodes for organic thin film transistors. For example the source and drain inter-digitated electrodes can be laser decal transferred onto a pentacene layer for making organic thin film transistor devices [10].

The high degree of control in size and shape of the transferred voxels achievable with laser decal transfer can in principle also be used to build 3-dimensional stacked structures as those required for interconnects. An example of this capability can be found in the SEM images on Figure 3. In order to fabricate the structure shown in this figure, a series of Ag voxels were laser decal transferred onto Au pads on the surface of a glass substrate to build two pillars out of plane, which in turn supported an Silver interconnect rectangular slab deposited across them by LDT as well. The 3D structure allowed the electrical connection of the outside pads without touching the central Au electrode line patterned on the substrate. The complete assembly was made by LDT without the use of sacrificial layers required to support the freestanding rectangular Ag interconnect. Such capability represents a true digital microfabrication process by which complex geometries can be generated and assembled voxel by voxel. This capability is unique and opens the possibility for the digital microfabrication of other types of structures such as MEMS on low temperature substrates, which are impossible to generate by lithographic techniques.

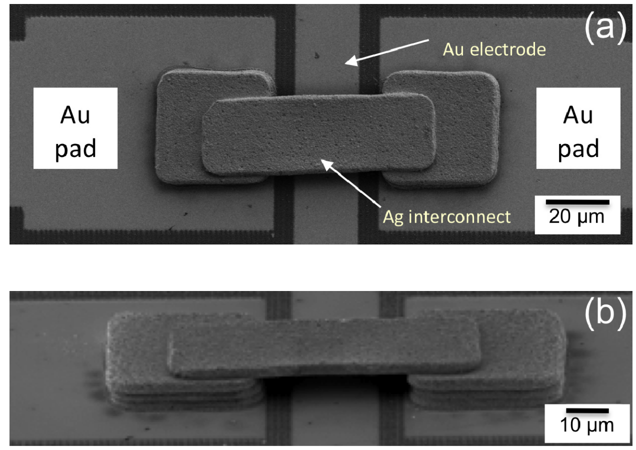

Figure 3. *SEM image showing a sample interconnect built by LDT on a patterned glass substrate. (a) Top view and (b) glancing angle view, revealing the freestanding nature of the top Ag interconnect.*

Summary

Laser decal transfer of high viscosity inks results in digitally microfabricated patterns that exhibit extremely uniform thickness, show precise edge definition and are free of debris. Given that laser decal transfer allows the printing of different shapes and sizes, any given pattern can be deposited in just a few steps, thus allowing further optimization of the writing time. In fact, laser decal transfers correspond to a form of digital microfabrication processes where the shape and size of each "bit" can be changed at will. The resulting decal transfers are well suited for the repair, modification and customization of microelectronic circuits, such as TFT-FPD's, photovoltaics, integrated circuits and other semiconductor devices, as well as the direct-write of MEMS-like three-dimensional structures.

Acknowledgements

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