

Direct writing of electronic and sensor materials using a laser transfer technique

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We present a laser-based direct write technique termed matrix-assisted pulsed-laser evaporation direct write (MAPLE DW). This technique utilizes a laser transparent fused silica disc coated on one side with a composite matrix consisting of the material to be deposited mixed with a laser absorbing polymer. Absorption of laser radiation results in the decomposition of the polymer, which aids in transferring the solute to an acceptor substrate placed parallel to the matrix surface. Using MAPLE DW, complex patterns consisting of metal powders, ceramic powders, and polymer composites were transferred onto the surfaces of various types of substrates with <10 micron resolution at room temperature and at atmospheric pressure without the use of masks.

Current trends for developing advanced electronic and sensor systems place great emphasis in achieving performance levels generally associated with integrated circuits. This requires further miniaturization, while enhancing the functionality and reliability of existing systems. New strategies are needed in order to eliminate the long lead times required for the fabrication of prototypes and evaluation of new materials and designs. The use of rapid prototyping techniques such as direct write, which do not need photolithographic processing, provide a solution to the above requirements. Direct write technologies do not compete with photolithography for size and scale but rather add a complementary tool for specific applications requiring rapid turnaround and/or pattern iteration, conformal patterning, or modeling difficult circuits. Examples of direct write technologies for fabricating or modifying metallic interconnects and/or other electronic passive elements include ink jet printing,¹ direct write of ceramic slurries (Micropen),² laser trimming,³ and laser chemical vapor deposition (LCVD).⁴ However, none of these techniques is capable of operating in air and at room temperature while maintaining sub-10- μm resolution and without requiring *ex situ* processing, as well as being compatible with the broad classes of materials needed for electronic and sensor systems.

Over the past decade, various laser-based direct write techniques have been developed for depositing different types of materials. Laser ablation transfer (LAT) has been used to generate high-resolution color images by means of laser transferring pigments of different colors for printing applications.⁵ Similarly, laser-induced forward transfer (LIFT) has shown the ability to direct write metals for interconnects and for mask repair and also simple dielectric materials such as metal oxides.^{6,7} LIFT is a technique that employs a focused pulsed laser beam to vaporize a thin film from a laser transparent donor substrate in air and at room temperature.⁸ The material then condenses onto an acceptor substrate placed in close proximity (25–50 μm) to the donor substrate. The area coated per laser pulse depends on the size of the laser spot striking the film as well as the gap between both substrates. However, because LIFT causes the vaporization of the material being transferred, it is not useful for direct writing of complex multicomponent metal oxides, polymers, and composite materials.

In this rapid communication, a laser transfer technique similar in implementation to LIFT but different in mechanism is described. The technique evolved from the combination of LIFT with a laser-based vacuum deposition technique for transferring organic and polymeric materials called matrix-assisted pulsed-laser evaporation (MAPLE).⁹ Specific examples of the MAPLE process are described elsewhere.¹⁰ Briefly, MAPLE utilizes a

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frozen target made from a dilute solution of the organic material to be deposited and a volatile solvent. When the laser pulse strikes the surface of the target, the solvent is vaporized and pumped away, while the organic material is released and collected over a substrate placed opposite to the target, thus forming a highly uniform thin film with minimal organic decomposition. The combination of the mechanistic aspects of MAPLE, in the form of a matrix-coated ribbon, with LIFT's laser transfer process resulted in MAPLE direct write (MAPLE DW). In MAPLE DW, a quartz disc is coated on one side with a 1–10 microns thick film of a matrix of the material to be transferred. The matrix usually consists of a homogeneous mixture of the material in powder form and a polymeric binder. The fundamental mechanism for the transfer in MAPLE DW is the evaporation of the binder when the laser pulse is absorbed at the interface between the quartz disc and the matrix coating. The confined vapor that forms between the substrate and the coating propels the later toward the acceptor substrate. Using MAPLE DW, the transferred material is not vaporized, which allows for the transfer of complex compounds without affecting their composition, phase, and functionality. Because MAPLE DW utilizes a modified laser micromachining system, it can operate in various direct writing forms. The process can be both additive as in LIFT and also subtractive as in laser micromachining. Furthermore, the laser can be used to perform *in situ* material processing operations such as annealing and pretreatment of surfaces.

Fused silica discs, double-side polished, 5.0 cm in diameter with thickness ranging between 2 and 6 mm were used as ribbon supports as shown in Fig. 1. Powders containing spherically shaped particles ranging from 100 nm to 2 microns in diameter were utilized. The powders were prepared in solutions containing 1 g of powder and 0.05 gm of poly(butyl methacrylate) (PBMA, $M_w = 320,000$, Aldrich Chemical Company, Inc., Milwaukee, WI) in 10 ml of chloroform and mixed by sonication. PBMA was selected as the polymer because when exposed to ultraviolet (UV) radiation under 253 nm, it decomposes 100% into its volatile monomer, butyl ester.¹¹ These solutions were spin coated over the disks so as to form a uniform powder/PBMA matrix coating about 2–4 microns thick. The coated quartz disc is referred to as the ribbon. For the experiments here described, the coated side of the ribbon was separated from the substrate by $-25 \mu\text{m}$ using a polyimide spacer. Both the substrates and ribbons were held in place using a vacuum chuck over the X-Y substrate translation stage (see Fig. 1). Various substrates were used for the transfer experiments including alumina, glass, silicon, and various types of printed circuit boards such as FR-4 and Rogers RO4003 (RO4003). An excimer laser operating with a KrF mixture (248 nm, 20-ns pulse) was used for the transfer experiments. The laser beam was spatially

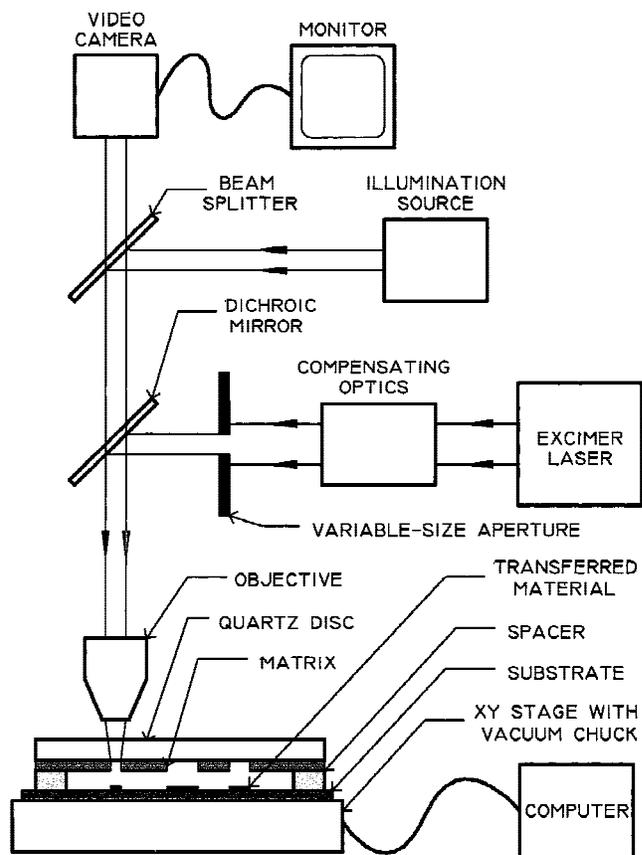


FIG. 1. Schematic diagram illustrating the basic elements of the MAPLE DW system.

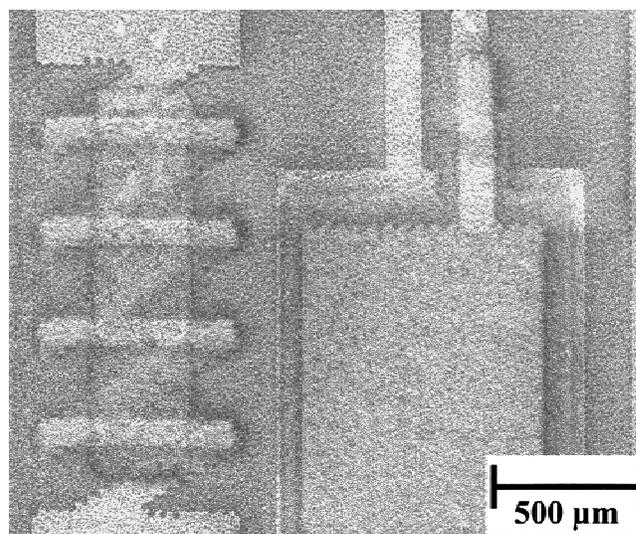
filtered and then directed through a variable-size circular aperture. A $10\times$ objective lens, antireflective (AR) coated for 248 nm, with a 0.25 numerical aperture and 1.5 cm working distance was used. Changing the aperture size generated beam spots with diameters ranging from 8 to $200 \mu\text{m}$. The laser fluence was estimated by averaging the total energy of the incident beam over the irradiated area. Figure 1 shows the arrangement for each of these components.

The transfer of metal powders was evaluated using a silver ribbon and a $30\text{-}\mu\text{m}$ -diameter laser spot with a fluence of $500 \text{ mJ}/\text{cm}^2$. Patterns consisting of lines and pads were fabricated onto silicon, glass, alumina, and RO4003 substrates. The adhesion of the silver pads to various substrates was evaluated with tape tests. Tape tests are shear-type tests that can discriminate between complete lifting, partial adhesion, or complete adhesion relatively easily.¹² The transfers over silicon and glass did not survive the tests, while the transfers over alumina and RO4003 substrates were partially removed by the tape. Using the above conditions, $400 \times 150 \times 16 \mu\text{m}$ thick silver lines were fabricated across gold evaporated electrodes on RO4003 substrates. The resistivity of the lines was evaluated at 1 MHz using a HP4284A LCR (Hewlett Packard, Palo Alto, CA) meter. The average resistivity of

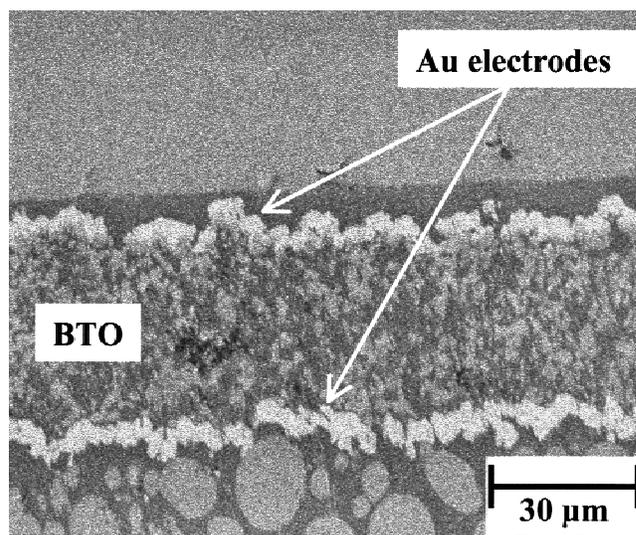
these lines was about 1000 times higher than bulk silver. The high resistivities were caused by poor contact among the transferred silver powders due to contamination from the residual polymeric binder.

Four pairs of parallel plate capacitor structures and a four turn flat inductor were fabricated by the MAPLE DW technique using a hybrid approach. The hybrid approach consisted of a combination of laser micromachining of the bottom gold electrode, MAPLE DW of the BaTiO_3 (BTO) or $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) pads and LIFT of the gold top electrode. The above steps were performed using the setup shown in Fig. 1 with the appropriate ribbons in the case of LIFT or MAPLE DW. Laser micromachining was performed by removing the ribbon altogether and adjusting the objective to focus the laser at the substrate surface. For the capacitors, a 25- μm laser spot at a fluence of 400 mJ/cm^2 was used to fabricate pairs of 20–30- μm -thick BTO pads with areas of 0.8×0.8 and $1.6 \times 1.6 \text{ mm}^2$, respectively, over RO4003 substrates. The purpose of these experiments was to evaluate the scaling of the capacitance of these devices with area. For the four turn flat inductor, similar parameters were used to fabricate a $1.0 \times 0.3 \text{ mm}^2$ YIG core 20 μm thick. In both cases, the morphology and thickness of the BTO and YIG layers were quite uniform, and the surface roughness variations were due primarily to the imperfections of the underlying substrate. Figure 2(a) shows a 45° glancing angle scanning electron microscope (SEM) image of one of the capacitors and the inductor made for this work. The parallel plate capacitors and the inductor were evaluated at frequencies ranging from 1 MHz to 1.8 GHz using a HP4291A impedance analyzer.

The capacitance ratio between each pair of large and small capacitors was close to their area ratio (4:1) as expected with some variations attributed to nonuniformities in the BTO transfers. Their capacitance ranged from 2 to 40 pF with dissipation factors between 0.11 and 0.17. These capacitors were then annealed in air at 200 °C for 2 h. After the annealing step, the capacitance drops by about 40% while the dissipation factors decreased by 1 order of magnitude. From these results, the effective dielectric constant of the capacitors was estimated to be around 25 after the annealing step. In the case of the four turn flat inductor, the measured inductance for the YIG core was 9 nH at 1 MHz. The inductor exhibited a Q of <1 , indicative of very high losses, and the effective permeability was estimated, without taking into account any loss effects, to be about 70. The cause for the lower than bulk dielectric constant values obtained for the BTO transferred powders, as well as the lower than bulk magnetic permittivity obtained with the YIG transferred powder, can be attributed to the large fraction of air gaps present in both cases.¹³ The presence of PBMA within the transferred BTO powders was verified after the annealing experiments performed with the



(a)



(b)

FIG. 2. (a) Glancing angle SEM image of a parallel plate capacitor and flat inductor made by MAPLE DW with gold electrodes made by LIFT. (b) SEM cross section micrograph of a parallel plate capacitor made by MAPLE DW.

capacitors. At 200 °C, PBMA decomposes into its volatile monomer and in the process is replaced with air, lowering the effective dielectric constant of the capacitor but at the same time lowering its loss. The existence of a large fraction of air gaps, estimated at 50% for these samples, was confirmed by performing cross-sectional SEM analysis on one of the capacitors as shown in Fig. 2(b).

A simple gas sensor based on conductimetric techniques¹⁴ was fabricated using composites made from a 20% by weight dispersion of micron-sized graphite powder and a chemoselective nonconducting polymer. This loading resulted in a conductive matrix near the percolation threshold that swells reversibly in the presence of a gaseous solvent, disrupting the conductive pathway and

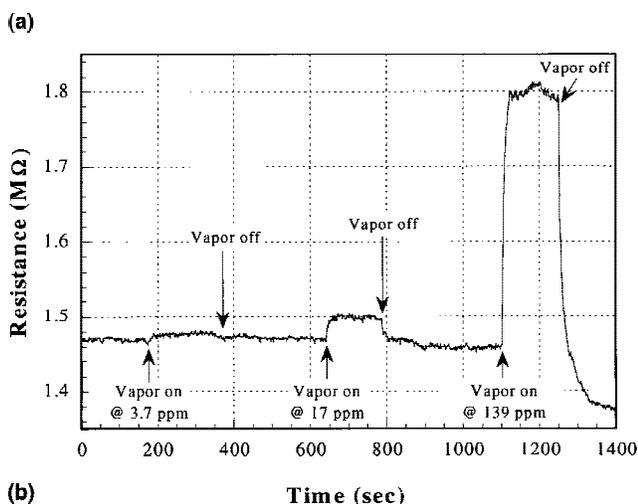
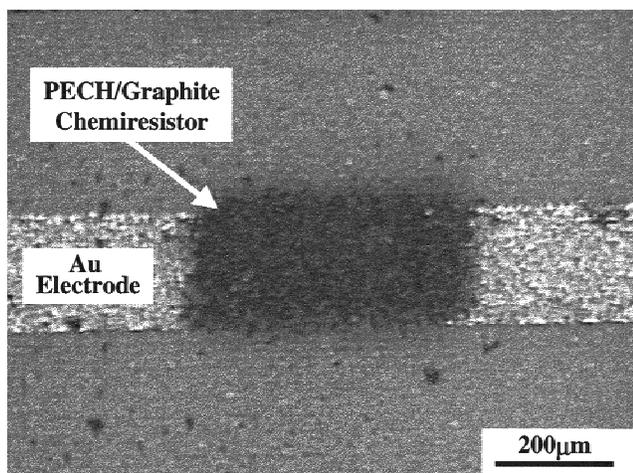


FIG. 3. (a) Micrograph showing a PECH/graphite conductive pad made by MAPLE DW. (b) Resistance versus time graph of the same pad showing the change in resistance when challenged with various vapor concentrations of the mustard gas simulant bis-chloroethylether (CEE). Notice the rapid response when the vapor is turned on and the recovery time once the vapor is turned off.

causing an increase of the resistance. A ribbon made with a 4- μm -thick layer of poly(epichlorohydrin) (PECH, $M_w \sim 700,000$, Aldrich) mixed with graphite (Pelco graphite paint, Ted Pella, Inc., Redding, CA) was used in order to test the ability of the MAPLE DW process to transfer fragile polymer materials as well as composites. A series of conductive patches across gold electrodes, see Fig. 3(a), which exhibited sensitivities of the order of parts per million (ppm) when exposed to several gases, as shown in Fig. 3(b), were fabricated using MAPLE DW. The changes in resistance while the gas vapors are off were due to temperature and humidity variations and are completely reversible. This clearly demonstrates that MAPLE DW can also be used for direct writing of functional polymer materials as well as composites.

In summary, we have demonstrated the efficacy of a laser-driven, maskless deposition technique termed MAPLE DW. This technique allows the direct writing of

various materials including metals, ceramics, and polymeric materials onto different types of substrates. The laser transfer process is spatially highly selective, because the area covered with transferred material depends on the incident laser beam, which can be focussed or patterned. Various types of device configurations such as capacitors, inductors, and chemoresistors were demonstrated using this technique. The structures made by MAPLE DW showed a high degree of porosity and a lack of adhesion between the transferred powders. Future research will be focused on reducing the porosity, increasing the adhesion and minimizing the contamination between the transferred powders by replacing the currently used polymer binders with lower molecular weight organic binders and organic precursors, as well as using a second laser to anneal the materials once they have been transferred.

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