

A novel laser transfer process for direct writing of electronic and sensor materials

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Abstract. MAPLE direct write (MAPLE DW) is a new laser-based direct-write technique which combines the basic approach employed in laser-induced forward transfer (LIFT) with the unique advantages of matrix-assisted pulsed-laser evaporation (MAPLE). MAPLE DW utilizes an optically transparent substrate coated on one side with a matrix consisting of the material to be transferred mixed with a polymer or organic binder. As in LIFT, the laser is focused through the transparent substrate onto the matrix. When a laser pulse strikes the matrix, the binder decomposes and aids the transfer of the material of interest to an acceptor substrate placed parallel to the matrix surface. MAPLE DW is a maskless deposition process which operates in air and at room temperature. Powders of Ag, BaTiO₃, SrTiO₃, and Y₃Fe₅O₁₂ with average diameters of 1 μm were transferred onto the surfaces of alumina, glass, silicon, and printed circuit board substrates. Parallel-plate and interdigitated capacitors and flat inductors were produced by MAPLE DW over Rogers RO4003 substrates. MAPLE DW was also used to transfer polymer composites for the fabrication of gas sensor chemoresistors. One such composite chemoresistor fabricated with polypichlorohydrin/graphite was used to detect organic vapors with a sensitivity of parts per million.

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In the last ten years, the use of electronic systems has increased dramatically. In concert, the demand for faster and smaller products has placed enormous emphasis on miniaturization and increased functionality. In order to fabricate electronic assemblies with reduced weight, volume, cost, and time, new materials and/or tools to process them must be developed. Until now, limited progress in the miniaturization of electronic and sensor components has been achieved

by using surface-mounted components. Surface-mount technologies are based on a three-fold strategy of first designing, then patterning, and finally mounting each of the system components on a circuit board. Modifications to an existing device require time-consuming iterations of the above steps. The use of rapid prototyping techniques can provide a solution to these time-consumption problems. With a rapid prototyping processes, it is possible to direct write elements and components onto the wide variety of surfaces called for in circuit design, essentially eliminating multiple steps and time constraints. Furthermore, the fact that direct-write techniques are compatible with current computer software for integrated design and manufacture (CAD/CAM) is an added advantage.

This article presents a novel direct-write technique that combines the positive advantages of laser-induced forward transfer (LIFT) and matrix-assisted pulsed-laser evaporation (MAPLE). This technique is called MAPLE direct write (MAPLE DW). An overview of the MAPLE DW process, along with its advantages, is presented. We give experimental results from various devices made by MAPLE DW such as parallel-plate and interdigitated capacitors, flat inductors, conducting lines, resistors, and chemoresistive gas sensors.

1 Background

1.1 Laser-induced forward transfer (LIFT)

Over the past decade, many direct-write techniques based on laser-induced processes have been developed to deposit materials for a variety of applications. Among these techniques, LIFT has shown the ability to direct write metals for interconnects and mask repair and also simple dielectric materials such as metal oxides. LIFT was first demonstrated with metals such as Cu and Ag over substrates such as silicon and fused silica by utilizing excimer or Nd: YAG lasers [1, 2]. LIFT is a relatively simple technique that employs laser radiation to transfer a thin film from an optically transparent support onto a substrate placed below and parallel to it. Patterning is achieved by moving the laser beam (or substrate) or

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by pattern projection. The former is a method of direct writing patterns.

LIFT has several experimental requirements that can have significant effects on the quality of the pattern or device fabrication. The laser fluence should be adjusted so that the process is carried out near the energy threshold to transfer only the film material. Target films typically do not exceed a thickness of a few 100 nm. The distances between the target film and the substrate must be controlled, generally within 25 to 75 μm . Overall, LIFT has proven to be a simple and effective technique that can be used on a wide variety of metals, and some simple oxides, but not with complex multi-component materials such as ferroelectrics.

1.2 Matrix-assisted pulsed-laser evaporation (MAPLE)

A new, laser-assisted, vacuum deposition technique, known as MAPLE [3] has been developed at NRL for depositing thin, uniform layers of chemoselective polymers [4–6] and other organic materials, such as carbohydrates [7]. The hybrid laser transfer mechanism associated with MAPLE enables the deposition of complex organic molecules into thin films that cannot be used in conventional PLD processing.

In MAPLE, an organic compound is dissolved in a matrix material, generally a volatile solvent such as an alcohol, to form a solution. This solution is frozen to $\sim -100^\circ\text{C}$ in order to form a laser target (2.5-cm-diameter disc, 1 cm thick). When the laser strikes the surface of the target, it causes rapid vaporization of the solvent molecules. Part of the thermal energy absorbed by the solvent is transferred to the organic molecules. When these molecules are exposed to the gas–target interface, they are transported into the gas phase with sufficient kinetic energy to be desorbed from the target surface without significant decomposition. A film will be formed on a substrate placed opposite the target; the solvent is pumped out.

1.3 MAPLE direct write (MAPLE DW)

The MAPLE DW technique utilizes all of the advantages associated with LIFT and MAPLE to produce a laser-driven direct-write process capable of transferring materials such as metals, ceramics, and polymers onto polymeric,

metallic, and ceramic substrates at room temperature. The overall write resolution for this technique is currently on the order of 10 μm . Since MAPLE DW uses a highly focused laser beam, it can easily be utilized for micromachining, drilling, and trimming applications, by simply removing the ribbon from the laser path. The flexible nature of MAPLE DW allows the fabrication of multilayered structures in combination with patterning. Thus, MAPLE DW is both an additive as well as *subtractive* direct-write process. MAPLE DW can also be adapted to operate with two lasers of different wavelengths where the wavelength from one laser has been optimized for the transfer and micromachining operations (i.e. UV), whereas the second laser is used modify the surface and anneal either the substrate or any of the already deposited layers (i.e. IR or visible) [8].

In MAPLE DW, a laser-transparent substrate such as a quartz disc is coated on one side with a film a few microns thick. The film consists predominantly of a mixture or matrix of a powder of the material to be transferred and a photo-sensitive polymer or organic binder. The polymer assists in keeping the powders uniformly distributed and well adhered to the quartz disc. The coated disc is called the ribbon and is placed in close proximity (25 to 100 μm) and parallel to the acceptor substrate. As with LIFT, the laser is focused through the transparent substrate onto the matrix coating (see Fig. 1). When a laser pulse strikes the coating, a fraction of the polymer decomposes into volatile byproducts which propel the powders to the acceptor substrate. In MAPLE DW, the material to be transferred is not vaporized, because the laser fluences required to decompose the photo-sensitive polymer are below the ablation threshold of the powders. By avoiding the vaporization of the material, complex compounds can be transferred without modifying their composition, phase, and functionality. Furthermore, there is no heating of the substrate on which the material is transferred.

Both the acceptor substrate and the ribbon are mounted onto stages that can be moved by computer-controlled stepper motors. By appropriate control of the positions of both the ribbon and the substrate, complex patterns can be fabricated. By changing the type of ribbon, multicomponent structures can easily be produced. Furthermore, because the laser in the MAPLE DW system can also be focused onto the substrate, operations such as micromachining, drilling, trimming, and

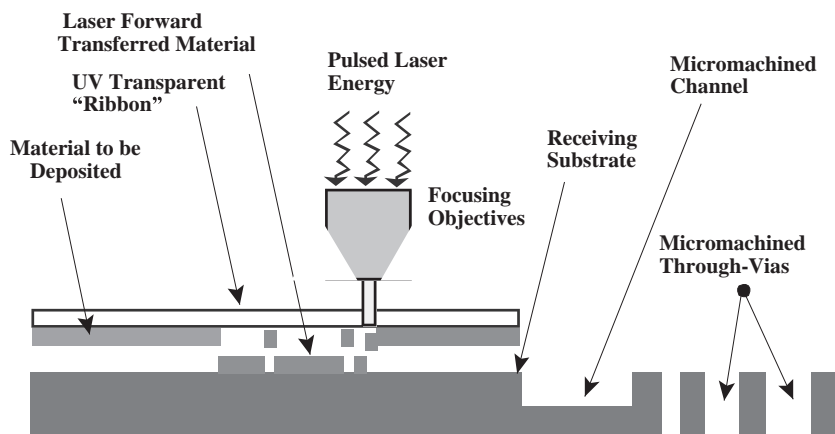


Fig. 1. Schematic representation of the MAPLE DW process

annealing can be performed by simply removing the coated ribbon from the laser path.

2 Experimental

Fused silica quartz discs, double-side polished, 5.0 cm in diameter and with thickness ranging from 2 to 6 mm were used as ribbon supports. Two types of ribbons coated on one side were used for this work. The first type were coated by e-beam evaporation with 150-nm-thick gold or nichrome layers for the LIFT experiments. The second type were spin-coated with a matrix film. The matrices were prepared by mixing powders (1 to 2 μm average grain size) with poly(butyl methacrylate) (PBMA, average $M_w = 320\,000$, Aldrich) in a chloroform solution. Typical solutions contained about 1 gm of powder and 0.05 gm of PBMA mixed by sonication in 10 to 20 ml of chloroform. When these solutions were spin-coated at 3000 rpm over the quartz discs, a uniform powder/PBMA coating 2–4 μm thick was formed once the chloroform had evaporated. Ribbons with Ag, BaTiO₃ (BTO), SrTiO₃ (STO), and Y₃Fe₅O₁₂ (YIG) powders were prepared.

For all the transfers performed in this work, a 25- μm spacer was used to separate the coated side of the ribbons from the substrates. Both the substrate and ribbon were held in place by using a vacuum chuck over the X-Y substrate translation stage. An excimer laser operating with a KrF mixture (248 nm, 20 ns pulse width) was used for the transfer experiments. The laser beam was spatially filtered and then directed through a circular aperture. A mirror that is highly reflecting at 45° (at 248 nm) and transparent in the visible was used to direct the laser beam into the objective lens and for imaging through the objective into a camera. A 10 \times objective lens, AR coated for 248 nm, with a 0.25 numerical aperture

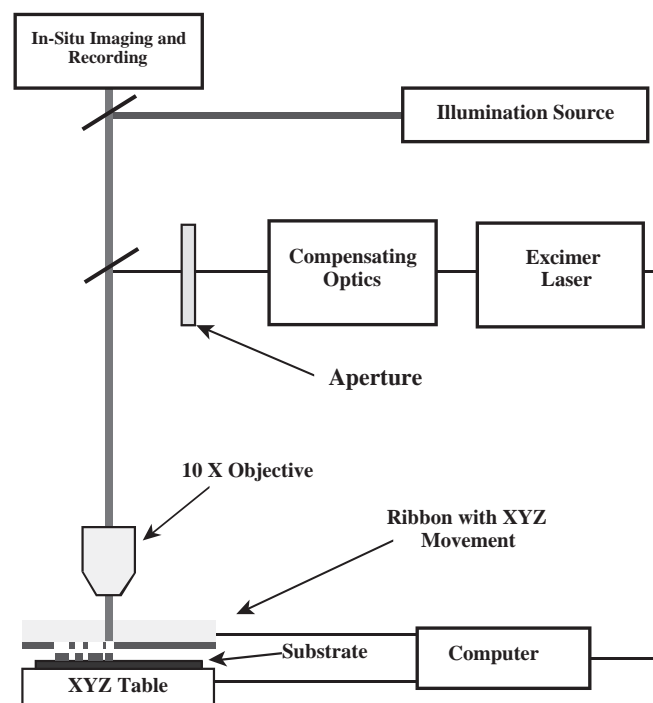


Fig. 2. Schematic diagram of the MAPLE DW apparatus

and 1.5 cm working distance was used. By changing the aperture size, beam spots from 8 μm to 200 μm were generated. The laser fluence was estimated by averaging the total energy of the incident beam over the irradiated area. Figure 2 shows how each of these components were arranged in our system. Various substrates were used for the transfer experiments, including silicon, glass, alumina, polyimide, and various types of printed circuit boards such as bare FR-4 and bare Rogers RO4003 (RO4003). Each of these substrates presented various degrees of surface finish, ranging from the epi-polished finish of the silicon substrates to the very rough finish of the bare FR-4 and bare RO4003. Transfer tests were performed by using Ag and BTO ribbons over each of these substrates. The adhesion of the transferred material varied from poor, on silicon, to good, over RO4003 substrates, as evaluated with standard tape tests.

2.1 Conductive lines and coplanar resistors

0.35-mm-long silver conductive bridges, connecting gold pads on alumina substrates, were fabricated by MAPLE DW by using 2- μm -thick Ag/PBMA matrix ribbons. A 100- μm -diameter laser spot with a fluence of 500 mJ/cm^2 was used for these experiments. About 10 passes were required in order to produce a 10- μm -thick silver line. By using the e-beam gold-coated ribbons, Au conducting lines were deposited by LIFT on glass, alumina, FR-4, and RO4003 substrates. An optical micrograph of the gold lines deposited on a RO4003 substrate is shown on Fig. 3a. The lines were generated by overlapping the 25- μm -diameter laser spots, each with a fluence of 550 mJ/cm^2 . In order to generate 10- μm -thick gold

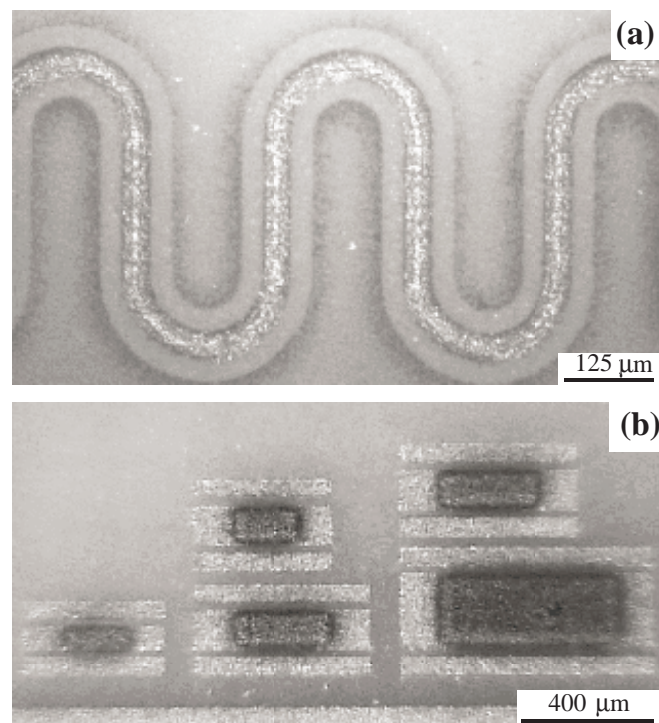


Fig. 3. **a** lines deposited by LIFT on RO4003 circuit board. The Au line is approximately 30 μm wide after a final laser trimming step, performed along both sides of the line. **b** Optical micrograph of nichrome coplanar resistors made by LIFT on RO4003

Table 1. Summary of experimental parameters used for this work

Devices	Transfer process	Material dia. (μm)	Spot Size (mJ/cm^2)	Fluence	No. of passes	Thickness (μm)
Ag lines	MAPLE DW	Ag	100	500	10	10
Au lines	LIFT	Au	25	550	100	10
NiCr resistors	LIFT	NiCr	25	1500	100	10
Parallel-plate capacitors	MAPLE DW (dielectric)	BTO	25	500	25	20–25
Interdigitated capacitors	MAPLE DW	STO	25	500	20	5–20
Flat inductor	MAPLE DW (ferrite)	YIG	25	550	25	20
Chemoresistor	MAPLE DW	PECH/graphite	25	250	N/A	

lines, about 100 passes were required. The five coplanar resistors shown in Fig. 3b were made by LIFT of the nichrome ribbons over RO4003. The overlap between successive passes was optimized in order to improve the uniformity of the nichrome structures. Again, a $25\text{-}\mu\text{m}$ spot with a fluence of $1500\text{ mJ}/\text{cm}^2$ was used. The final thickness of the nichrome resistors was about $10\text{ }\mu\text{m}$ after 100 passes. Table 1 lists the experimental parameters from these experiments.

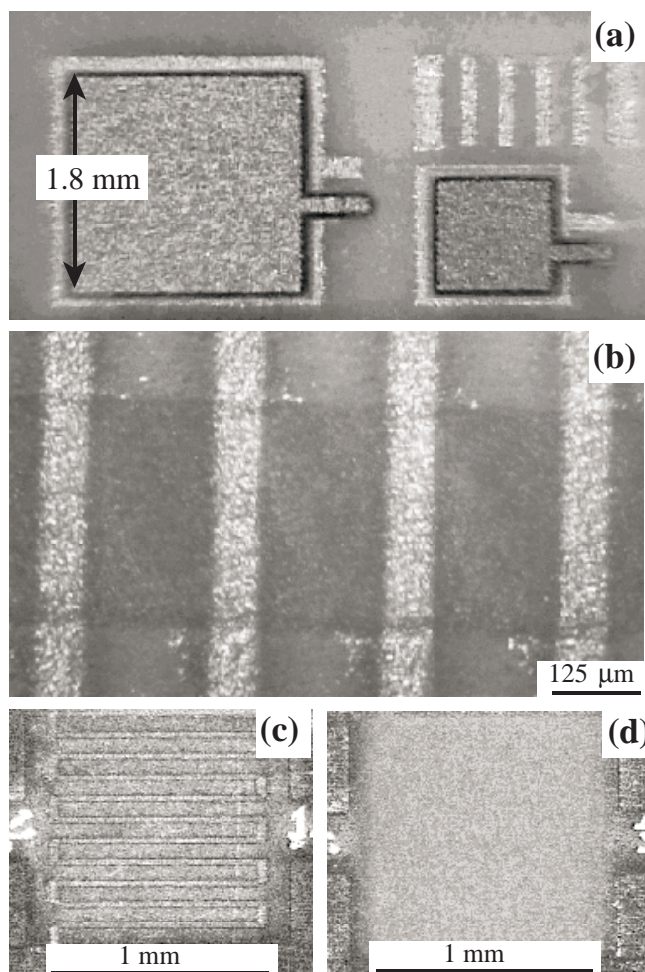


Fig. 4. **a** Optical micrograph showing two parallel-plate capacitors with BTO dielectric layers made by MAPLE DW. **b** Optical micrograph showing a four-turn flat inductor with a YIG core deposited by MAPLE DW. **c** and **d** Optical micrographs of an interdigitated capacitor before and after depositing a STO dielectric layer by MAPLE DW

2.2 Multilayer capacitors and inductors

For the fabrication of the parallel plate capacitors, interdigitated capacitors, and flat inductors a hybrid approach was used. First, a $3\text{-}\mu\text{m}$ -thick gold layer was e-beam deposited onto a RO4003 substrate. The bottom electrodes were then patterned with the laser. The ablation patterning was performed with a $25\text{-}\mu\text{m}$ laser spot and a fluence of $3\text{ J}/\text{cm}^2$. Next, for the parallel-plate capacitors, a layer 20 to $25\text{ }\mu\text{m}$ thick of BTO was deposited. In the case of the interdigitated capacitors, layers 5 to $20\text{ }\mu\text{m}$ thick of BTO or STO were deposited, and for the flat inductor a $20\text{-}\mu\text{m}$ -thick layer of YIG was fabricated. Each of these layers were generated by overlapping $25\text{-}\mu\text{m}$ laser spots. Table 1 list details for each material. Finally, $10\text{-}\mu\text{m}$ -thick top Au electrodes were deposited by LIFT under the same conditions employed for making the

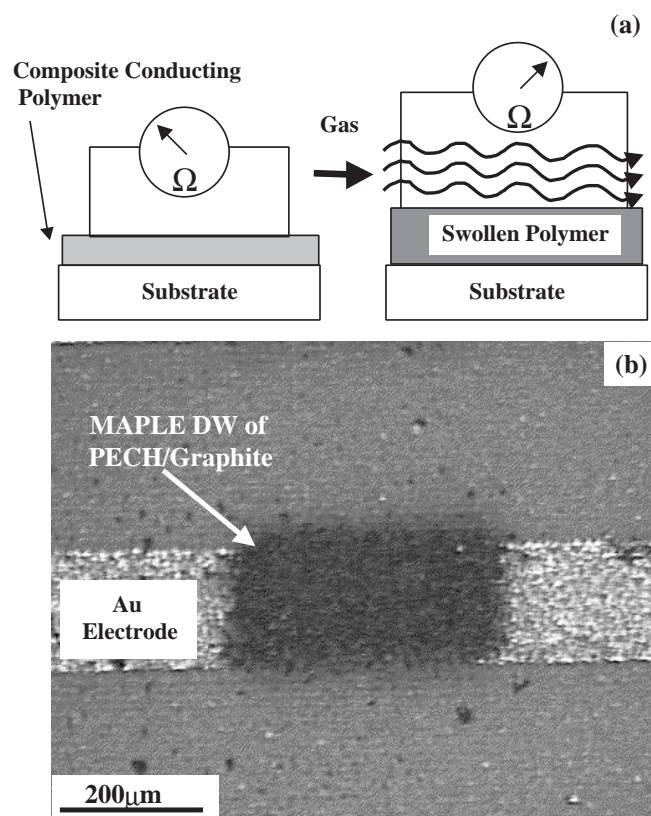


Fig. 5. **a** Principle of operation of a chemoresistor. **b** Optical micrograph of PECH/graphite chemoresistor patch made by MAPLE DW

conduction lines (this last step was not required for the interdigitated capacitors). Figure 4a shows an optical micrograph of two BTO parallel-plate capacitors, and Fig. 4b shows a micrograph of a YIG core flat inductor. Figure 4c,d show optical micrographs of an interdigitated capacitor before and after MAPLE DW of a STO pad.

2.3 Chemoresistor gas sensors

By using dispersions of a conducting material such as graphite and non-conducting chemoselective polymers, gas sensors based on conductimetric techniques [9,10] can be fabricated. In the correct ratio, the graphite/polymer composite is conductive and its resistance will change when exposed to different vapors, as shown schematically in Fig. 5a. A 4- μm -thick ribbon was spin-coated from a solution containing 0.1 gm of polyepichlorohydrin (PECH, average $M_w = 700\,000$, Aldrich) and 0.01 gm of graphite powder mixed in 50 ml of chloroform. This ribbon was used in order to test the ability of the MAPLE-DW process to transfer polymer materials as well as composites. A series of conductive patches across gold electrodes were produced, one of which is shown in Fig. 5b.

3 Results and discussion

3.1 Metal lines

The resistivity of the silver lines deposited by MAPLE DW was measured to be about 10^3 times higher than that of bulk silver. SEM analysis indicated that the silver lines were porous. As a comparison, the average resistivity of the gold lines deposited by LIFT was measured to be $75\ \mu\Omega\ \text{cm}$ at room temperature, which is about 30 times higher than that of bulk Au ($2.4\ \mu\Omega\ \text{cm}$). With LIFT, each laser shot resulted in the transfer of an approximately 0.1- μm -thick spot, whereas with MAPLE DW, each laser shot produced a 1- μm -thick spot. The poor conductivity of the MAPLE DW silver lines is probably due to the large fraction of air gaps present and polymer residue that did not decompose after the transfer.

The measured resistance of the LIFT-deposited nichrome resistors ranged from 65 to 190 Ω and their properties scaled with respect to the cross section and length as expected. The calculated resistivity was considerably larger than that of bulk nichrome and is likely to be due to oxidation of the alloy during transfer. Despite the poor conductivity of the silver MAPLE DW lines, these initial results demonstrate fabrication of conductive structures with MAPLE DW. By using silver powders with controlled particle size distributions, in order to improve filling between particle grains, and by adjusting the silver powder to the polymer content in the matrix, improvements in the conductivity of the metals produced by MAPLE DW should be possible.

It is worth noting that the transfer rate per laser shot for the MAPLE DW process is about an order of magnitude higher than that for LIFT. In LIFT, ribbons with relatively thin coatings must be used in order for the coating to be vaporized and transferred, which is not the case for MAPLE DW.

3.2 Capacitors and inductor

Both the parallel-plate and interdigitated capacitors were evaluated at frequencies ranging from 1 MHz up to 1.8 GHz by using a HP4291A impedance analyzer. The capacitance ratio between the large and small parallel-plate capacitors was close to a 4:1 area ratio as expected, with some variations attributed to nonuniformities on the BTO transfers. The measured capacitance of the devices ranged from 2 to 40 pF and the effective dielectric constants ranged from 22 to 40 with $\tan \delta$ between 0.11 and 0.17. The interdigitated capacitors with BTO layers had capacitances of about 1 pF, and those with STO were about 0.5 pF. The interdigitated capacitors had dielectric constants of 41 and 10 for the BTO and STO layers, as found by using a conformal mapping technique.

All the BTO capacitors were annealed in a furnace at 200 °C for two hours. After the annealing step, the measured capacitance decreased by as much as 40%. For the parallel-plate capacitors, $\tan \delta$ decreased by an order of magnitude as well. After annealing, the effective dielectric constants for the parallel-plate capacitors ranged from 12 to 25, and for the BTO layers they were about 30. Figure 6 shows a plot of the capacitance vs. frequency for one of the parallel-plate capacitors before and after the annealing step. The as-deposited BTO shows large dielectric relaxation with onset at ~ 10 MHz and dielectric saturation at ~ 1 GHz. After annealing, the BTO exhibits a smaller dielectric constant with the onset of the dielectric relaxation shifting to near 2 GHz. Earlier work by this group has shown that by assuming a ferroelectric/polymer/air composite dielectric layer for these capacitors and by applying a logarithmic mixing rule, it is possible to explain the low dielectric constants measured [11]. Based on this premise, we assigned dielectric constants of 2000 and 4 to the BTO powder and PBMA, respectively. Then we assumed that the BTO/PBMA/air volume percentages of the as-deposited and annealed layers were 40:20:40 and 40:0:60, respectively (all the PBMA had de-

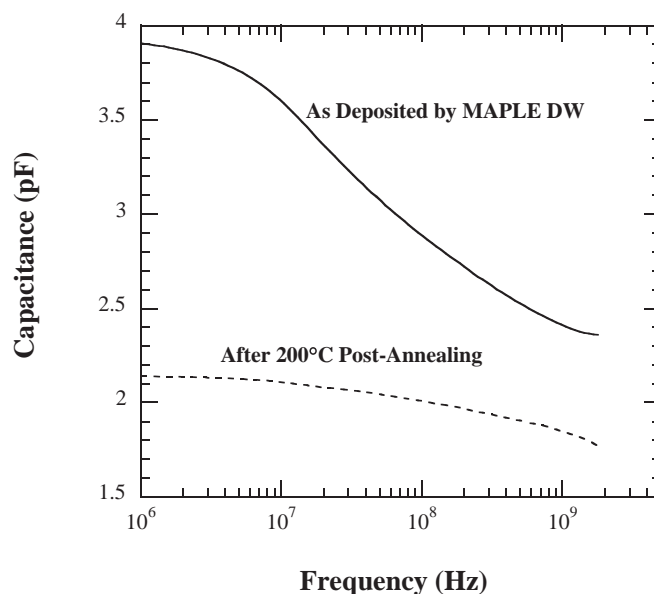


Fig. 6. Capacitance vs. frequency for a BTO parallel-plate capacitor before and after being annealed at 200 °C for 2 hours

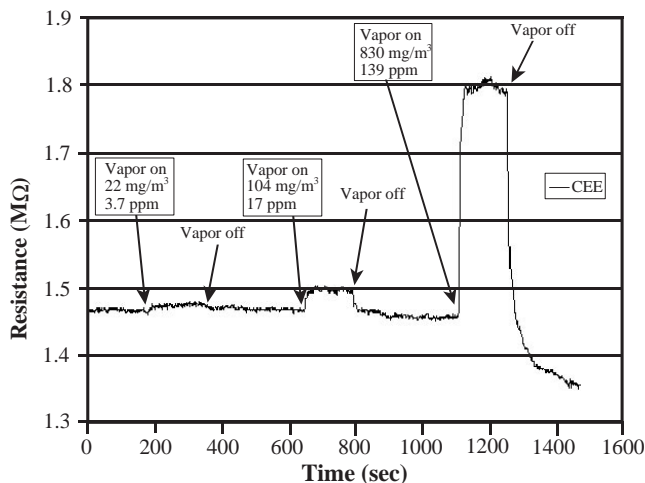


Fig. 7. Change in resistance as a function of time for a PECH/graphite pad made by MAPLE DW when exposed to various concentrations of CEE vapors

composed after annealing). With the above assumptions, the logarithmic mixing rule predicts a dielectric constant of 28 prior to and 21 after annealing, which is a drop of 25% and is close to observation.

The four-turn YIG core flat inductor had a measured inductance of 9 nH at 1 MHz. The inductor exhibited very high losses and the effective permeability was estimated to be about 70. This result can be attributed to the fact that the fabricated inductor had a porous YIG core with a large number of air gaps. In all cases the morphology and thickness of the BTO, STO, and YIG layers was quite uniform, and the surface roughness variations were due primarily to the imperfections of the underlying substrate.

3.3 Chemoresistor

The MAPLE DW PECH/graphite bridges had resistances of the order of 1 to 4 MΩ. When exposed to vapors from solvents such as acetone, toluene, and xylene, the resistance increased rapidly, but once the vapor was removed, the resistance returned to the original level in a few seconds, which is the expected behavior of a chemoresistor. When measured against calibrated concentrations of toluene and a mustard gas simulant, bis-chloro-ethylether (CEE), the MAPLE DW chemoresistors showed sensitivities of the order of parts per million (ppm). These results are preliminary, and more detailed analysis will follow. However, they clearly demonstrate

that MAPLE-DW can also be used for direct writing of polymer materials and composites without damaging their functional behavior. Figure 7 shows the response of the MAPLE DW chemoresistor when exposed to various concentrations of CEE vapor.

4 Conclusion

We have demonstrated the efficacy of a novel laser-driven direct-write technique, MAPLE DW. This technique allows the direct writing of various materials, including metals, ceramics, and polymeric materials, onto different types of substrates, such as alumina, glass, silicon, polyimide, and printed circuit board in air and at room temperature. Various types of device configurations, such as capacitors, inductors, and chemoresistors, were demonstrated using this technique. For this work, parallel-plate capacitors and flat inductors, each with gold electrodes made by LIFT and MAPLE DW BTO dielectric and YIG ferrite layers, respectively, and interdigitated capacitors with MAPLE DW STO pads were demonstrated. Furthermore, miniature chemoresistor gas chemical sensors were also fabricated by MAPLE DW and demonstrated ppm sensitivity to organic vapors.

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