Laser-Induced Forward Transfer Direct-Write of Miniature Sensor and Microbattery Systems

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Direct-Write techniques have the potential to revolutionize the way miniature sensor devices and microbattery systems are designed and fabricated. The Naval Research Laboratory has developed an advanced laser-based forward transfer process for direct writing novel structures and devices comprising of metals, ceramics, polymers and composites under ambient conditions on both ceramic and plastic substrates. Using this forward transfer technique, we have demonstrated the ability to rapidly prototype various types of physical and chemical sensor devices, and microbatteries. The laser forward transfer process is computer controlled which allows the design of the devices to be easily modified and adapted to any specific application. Furthermore, the same process enables the fabrication of complete sensor or power-source systems by incorporating the passive electronic components required for sensor readout or power management. Examples are provided of various types of miniature sensors, and prototype alkaline and Li-ion microbatteries fabricated using this technique.

Keywords: Laser transfer, MAPLE Direct-Write, Direct-Write of sensors, Direct-Write of microbatteries

1. Introduction

Current trends for developing advanced electronic and sensor systems place emphasis in achieving performance levels generally associated with integrated circuits. This requires further miniaturization, while enhancing the functionality and reliability of existing components. It also requires new strategies to eliminate the long lead times required for the fabrication of prototypes and evaluation of new materials and designs. In particular, for sensor and micro-power sources development, the trend is toward the fabrication of micron-scale devices which can be incorporated into any type of platform.¹⁾

Direct-write techniques, which do not require photolithographic processing steps, provide an alternative for the development and fabrication of the above described systems. Direct-write technologies do not compete with photolithography for size and scale, but rather complement it in specific applications requiring rapid turnaround and/or pattern iteration, conformal patterning, or for modeling difficult circuits.¹⁾ Examples of direct-write technologies for fabricating or modifying metallic interconnects and/or other electronic passive elements include ink jet printing,²⁾ direct-write of ceramic slurries (Micropen®),³⁾ laser trimming⁴⁾ and laser chemical vapor deposition (LCVD).⁵⁾ However, none of the above techniques is capable of operating in air and at room temperature while maintaining

sub-10- μm resolution and without requiring *ex situ* processing. Furthermore, more than one technique must be used to deposit and process the range of materials employed for the fabrication electronic, sensor and power generation devices.

Over the past decade, various laser-based direct-write techniques have been developed for depositing different types of materials such as metals for interconnects and mask repair. More recently, a new laser-based direct-write technique, called MAPLE DW, for Matrix-Assisted Pulsed-Laser Evaporation Direct-Write, has been used for the direct-write of conformal electronic devices,⁶⁻⁹⁾ phosphor materials,¹⁰⁾ microbatteries^{11,12)} and even viable biomaterials.^{13,14)} In this paper, we describe the use of the MAPLE DW technique for the fabrication of temperature, strain and chemical sensors as well as prototype alkaline and Li-ion microbatteries.

2. Background

MAPLE DW, is a laser-based processing technique that was originally developed to fabricate and rapidly prototype mesoscopic electronic devices utilizing matrices containing metallic, dielectric or resistive materials.⁵⁾ This approach, however, is gentle enough to successfully form patterns and three-dimensional structures of a wide variety

of organics, including chemically sensitive polymers, active proteins and antibodies as well as viable cells.^{13,14)}

MAPLE DW involves the forward transfer of materials from a UV-transparent support to a receiving substrate. The transfers are performed by mixing the active, or sensitive material in a UV-absorbent matrix to form an “ink”. The ink is then applied to the UV-transparent support to form the “ribbon” as shown in Figure 1. A focused UV laser pulse is directed through the backside of the ribbon so that the laser energy interacts with the matrix at the support interface. The UV microscope objective that focuses the laser at the interface also serves as an optical guide to determine the region of the ribbon to be transferred. Layers of matrix near the support interface evaporate due to localized heating from the laser-material interaction. This vaporization releases the remaining ink by gently and uniformly propelling it away from the support. In this manner, MAPLE DW is capable of producing passive electronic devices (i.e., interconnects, resistors, capacitors) with line widths of the order of 10 μm . By removing the ribbon and allowing the laser pulse to interact with the substrate, this approach is also able to micromachine channels and through vias into polymer, semiconductor, and metal surfaces as well as trim deposited structures to meet design specifications. All micromachining and material transfer can be controlled by computer (CAD/CAM), which enables this tool to rapidly fabricate complex structures without the aid of masks or moulds. This technique, therefore, has the potential to fabricate by a single tool, complete prototype systems on a single substrate including the sensor coating, transducer, support electronics and even the microbatteries required to power the whole assembly.

Figure 1. Schematic diagram of the MAPLE DW process.

3. Experimental

3.1 MAPLE DW Ribbon Preparation

Borosilicate glass discs, double side polished, 5.0 cm diameter x 3mm thick were used as ribbon supports. For the fabrication of the temperature and strain sensors, a screen printable silver paste (Parmod RRA-100, from Paralec, Inc.) was applied to one side of the discs using a

#4 wire-coater (Gardner, Inc.) to form an ink layer about 5-10 μm thick. For the fabrication of the cathodes for the alkaline microbatteries, powders of MnO_2 (< 425 mesh, JEC) and Ag_2O (< 325 mesh, Alfa) were each mixed with 5 to 20 wt% of acetylene carbon black (Alfa). The resulting powders were mixed with a solution comprised of equal parts of 0.1 N KOH and glycerol (Alfa) by weight until forming a uniform paste to make the MnO_2 and Ag_2O inks respectively. For the fabrication of the anodes, Zn powders (3 μm dia., GoodFellow), were mixed with a solution of equal parts by weight of 9N KOH and glycerol until forming a uniform paste. These pastes were then applied to one side of the borosilicate glass discs using a #4 wire-coater to form a 510 μm thick ink layer. Inks for the Li-ion electrodes were comprised of lithium cobalt oxide, KS6 carbon and an organic binder (polyvinylidene fluoride or PVDF) for the cathode and MCMB 2528 carbon with PVDF for the anode. Both electrodes were made into a slurry by adding 1-methyl-2-pyrrolidinone as a solvent and cast onto the ribbon as described above. In the case of the chemical sensors, the ribbons were prepared by spray coating a solution containing 0.1 gm of polyepichlorohydrin (PECH, average MW = 700000, Aldrich) and 0.01 gm of acetylene carbon black (Alfa) mixed in 50 ml of chloroform.

The coated side of the ribbons was kept at a distance of 100-200 μm from the substrate with a spacer. Both the substrate and the ribbon were held in place using a vacuum chuck over the X-Y substrate translation stage. The third harmonic emission of a Nd:YAG laser, $\lambda = 355 \text{ nm}$ (Spectra Physics), was directed through a circular aperture and a 10x objective lens, resulting in a 85 mm diameter spot at the ribbon. The laser fluence varied between 0.1 – 1.0 J/cm^2 depending on the material being transferred, and was estimated by averaging the total energy of the incident beam over the irradiated area.

3.2 Temperature and Strain Sensor Fabrication and Testing

Silver conductive lines were transferred from the silver paste ribbons by MAPLE DW onto polyimide substrates and used as temperature and strain sensors. The length and layout of the lines was easily modified via computer control in order to achieve ~ 10- μm thick and ~ 100- μm wide patterns. The silver ink was dried at 100 $^\circ\text{C}$ on a hot plate to remove excess solvent and then cured at 280 $^\circ\text{C}$ in an oven for 10 min to decompose the organic silver precursors in order to form conductive patterns. Patterns in the form of serpentine lines were evaluated as temperature sensors by comparing their change in resistance to the response of a type K thermocouple. One of the MAPLE DW serpentine patterns and a thermocouple were mounted next to each other and exposed to heat pulses generated by a heat gun over a temperature range of 24 to 60 $^\circ\text{C}$. A second pattern was evaluated as a strain sensor by measuring its resistance change as a function of deflection

due to an applied force. The resistance of the serpentine was measured using a computer controlled 34401A digital multimeter (Agilent).

3.3 Chemical Sensor Fabrication and Testing

For the chemical sensors, 1 mm x 4 mm pads of PECH/carbon were deposited by MAPLE DW over silver interdigitated electrodes. To verify the operation of the MAPLE DW sensors, similar pads of PECH/carbon were spray coated onto a second set of silver electrodes. The silver electrodes were deposited by MAPLE DW onto polyimide substrates in the same way as the serpentine lines. The response of the PECH/carbon sensors was evaluated by challenging them with controlled exposures of toluene and dimethylmethylphosphonate (DMMP) vapor streams. The carrier air temperature and humidity were controlled with a Miller Nelson HCS-301 air-humidity generator. An automated Harvard 22 liquid syringe pump system was utilized to generate analyte vapor by injecting the liquid analyte into a heated evaporation plate system. The resulting vapor was mixed with humidified carrier air and passed into a test chamber housing the chemical sensors. The test chamber consisted of a hermetic enclosure with opposite inlet and outlet gas ports, to allow vapor flow over the sensors.

3.4 Microbattery Fabrication and Testing

Separate MnO_2 and Ag_2O pads 2 mm x 3 mm in area and 40 μm thick were laser transferred onto 1 cm^2 gold-coated glass substrates. The pads were heated to 150 $^\circ\text{C}$ in an oven for 30 min to remove the glycerol. Then a 4 mm x 5 mm x 2 μm thick film formed by drop casting separate layers of ethyl cellulose (Aldrich) and Nafion[®] was prepared over each of the MnO_2 and Ag_2O pads to serve as the separator between the metal oxide cathode and the Zn anode. A Zn layer was then laser transferred onto the ethyl cellulose in the form of a 2 mm x 25 mm x 20 μm pad. At this point, the resulting MnO_2 /separator/Zn and Ag_2O /separator/Zn structures were ready for evaluation.

The lithium-ion electrodes were fabricated onto separate substrates as pads 3 mm x 3 mm x 40 μm thick. Lithium cobalt oxide was transferred onto aluminum substrates while the carbon electrode was transferred onto a copper

substrate. After transfer, the electrodes were dried in a vacuum oven for 12 hours at 110 $^\circ\text{C}$. The electrodes were then submerged in a 1 M LiClO_4 /propylene carbonate electrolyte solution for 12 hours prior to their electrochemical evaluation. Half-cell measurements for determining the charging and discharging characteristics were performed at a 12-hour rate in free electrolyte versus a Li/Li^+ reference electrode and lithium counter electrode.

Chronopotentiometry of the zinc/ MnO_2 alkaline microbatteries and lithium-ion electrodes was performed using an EG&G PAR 263 potentiostat driven with M270 software. The thickness of both the ink ribbons and the dried pads were determined via stylus profilometry (Tencor P10).

4. Results and Discussion

4.1 Temperature and Strain Sensors

Using MAPLE DW, we have demonstrated a simple temperature sensor on a polyimide substrate. A silver serpentine line about 10 cm long, occupying a 5 mm x 5 mm area and with a resistance of about 93 ohms was made by MAPLE DW as shown in Figure 2(a). The response of the MAPLE DW temperature sensor to a heat pulse from a heat gun mirrored that of an adjacent thermocouple and it is shown in Figure 2(b). The variation in resistance as a function of temperature was calibrated against a type K thermocouple resulting on a $\Delta R/\Delta T$ of 0.21 ohms/K for the sensor element. The same device was then mounted on a cantilever and its resistance was monitored as a function of the deflection caused by various weights. The response of this simple strain sensor is shown on Figure 2(c). A linear fit of the data reveals a 5.2 ohm/N resistance over applied force response.

4.2 Chemiresistor Gas Sensor

By using dispersions of conductive materials such as carbon and non-conductive chemoselective polymers, gas sensors based on conductimetric techniques^{15,16)} can be fabricated. In the correct ratio, the polymer/carbon composite becomes conductive and its resistance will change when exposed to different vapors, as shown

Figure 2. (a) Photograph of a temperature sensor made by MAPLE DW of a silver serpentine line on a polyimide substrate. (b) Response of this sensor to a heat pulse. (c) Response of the sensor as a function of deflection caused by various weights (the straight line shows a linear fit to the data).

schematically in Figure 3(a). These types of chemical sensors are known as chemiresistors and are extremely simple to operate and ideally suited for miniaturization and manufacture in array form. For this work, PECH was selected since it is a polymer with a range of solubilities to numerous analytes, making it well suited for the fabrication of chemical gas sensors with broad applicability to a variety of different types of analytes.

Figure 3. (a) Schematic showing the basic operation of a chemiresistor sensor. (b) Optical micrograph of a chemiresistor gas sensor element fabricated entirely by MAPLE DW.

Figure 3(b) shows a micrograph of a typical PECH/carbon chemiresistive pad fabricated by MAPLE DW across a set of silver interdigitated electrodes also made by MAPLE DW on a polyimide substrate. To evaluate the performance of the chemiresistors made by MAPLE DW, similar PECH/carbon pads were fabricated by spray coating and placed side-by-side and exposed to calibrated concentrations of analyte vapors. Toluene and DMMP were used as analytes. Toluene and DMMP cover a range of solubility properties from a low polarity hydrocarbon to a polar and hydrogen-bond basic phosphonate ester. Toluene is a chemical present in diesel vapor, while DMMP is a simulant and precursor for chemical nerve agents. The results of the vapors tests indicated that the response of the MAPLE DW and that of the spray coated chemiresistors were similar and showed sensitivities of the order of parts per million (ppm). The response of both chemiresistors when exposed to various concentrations of toluene and DMMP vapors are shown in Figure 4.

The real potential of MAPLE DW is made clear when a complete sensor system consisting of a single sensor element, interconnects and passive electronic components is fabricated using this laser direct-write technique. An

actual working example is provided in Figure 5 which shows a photograph of a complete self contained chemical sensor system manufactured on a 5 cm x 5 cm polyimide substrate. The majority of the components shown on this image, including the chemiresistor, the Ag interconnects and the polymer thick film resistors, but not the LED's and the 4-quad comparator IC (which were soldered to the circuit afterwards), were fabricated by MAPLE DW. Future plans include the fabrication of multiple sensor elements in the form of arrays and the addition of microbatteries all made by MAPLE DW.

4.3 Alkaline Microbatteries

An schematic showing the cross-section of the MAPLE DW stacked alkaline microbattery is shown in Figure 6(a). Figure 6(b) shows a top view micrograph of a zinc/MnO₂ alkaline microbattery made this way on top of a gold-

Figure 4. Response of a spray coated and a MAPLE DW PECH/carbon chemiresistor sensors to various concentrations of (a) toluene and (b) DMMP vapors. The spikes on the toluene response signals are due to the syringe pump system used to generate the calibrated vapor exposures.

coated glass substrate. We have also successfully fabricated stacked alkaline microbatteries in which the top Zn layer overlays the electrolyte and is in contact with the

Figure 5. Photograph of a working chemiresistor sensor system made by MAPLE DW. The photograph shows all the elements of the sensor except for the batteries which are mounted on the back.

bottom electrode.¹²⁾ After the zinc pad is laser deposited, a small carbon paper current collector is placed on top of the zinc and the microbatteries are ready to be tested. The zinc/MnO₂ alkaline microbatteries have the expected cell voltage of 1.5 V, while the zinc/Ag₂O microbatteries showed the expected voltage of 1.6 -1.8V.

Figure 6. (a) Cross section schematic of the stacked alkaline microbatteries made by MAPLE DW. (b) Optical micrograph of a Zn/MnO₂ microbattery.

It should be pointed out that none of the alkaline

microbatteries fabricated for this work were packaged and thus the KOH electrolyte solution would evaporate with time. Figure 7 shows the discharge and charge characteristics of a zinc/MnO₂ alkaline microbattery. The specific energy of these batteries is approximately ten times lower than expected, due to the high resistance of the ethyl cellulose/Nafion® separator. Despite this, one of the zinc/MnO₂ alkaline microbatteries was connected to a digital watch and was able to power it for over 10 minutes as shown in Figure 8.

Figure 7. Charge Discharge behavior of a Zn/MnO₂ microbattery made by MAPLE DW.

Future work will focus in increasing the specific energy of these alkaline microbatteries by using other materials as separator layers, and in developing and testing various packaging schemes.

Figure 8. Photograph showing a prototype Zn/MnO₂ alkaline microbattery powering a digital watch.

4.4 Li-ion Microbatteries

The laser transferred lithium-ion electrodes show favorable charge and discharge characteristics on early cycles as shown on Figure 9. Figure 9(a) depicts the 4th cycle of charging a lithium cobalt oxide cathode and superimposed on the same figure is its discharge behavior. The electrode was successfully cycled between 4.18 V and 3 V and

exhibited near theoretical capacity.¹⁷⁾ The 6th cycle of the carbon anode charge (to 50 mV) and discharge (to 1 V) is shown in Figure 9(b). Although the efficiency of the carbon anode is not as high as that of the lithium cobalt oxide cathode, it shows satisfactory performance at early cycles before break-in is complete. It is important to note that near theoretical charging capacities were obtained. A prototype Li-ion microbattery was assembled in a dry environment by placing a lithium gel electrolyte between the electrodes and then pressing them together. The resulting structure was then attached to a circuit for testing and evaluation. Figure 10 shows a photograph of a prototype Li-ion microbattery connected to a blinking LED circuit. At the time of writing this paper, this Li-ion

Figure 9(a) C/12 charge and discharge behavior on the 4th cycle of a laser transferred LiCoO₂ cathode in 1 M LiClO₄ between 3.0 and 4.18 V vs. Li/Li⁺. Figure 9(b) C/12 charge and discharge behavior on the 6th cycle of a laser transferred LiCoO₂ cathode in 1 M LiClO₄ between 1.0 and 0.05 V vs. Li/Li⁺.

microbattery had not been tested.

5. Summary

MAPLE DW is an ideal process for the direct-write of sensors and microbatteries since it operates in air and at low temperatures. It is compatible with many types of substrates and conditions which are ideal for the processing of the numerous and dissimilar materials required for the fabrication of physical and chemical

sensors as well as microbatteries. MAPLE DW has been used for rapid prototyping of custom-engineered sensors and microbatteries in various types of geometries. The versatility and CAD/CAM features of the MAPLE DW technique allow sensor elements and complete sensor systems to be easily reconfigured and integrated with other components. This same approach is also useful for the fabrication of microbatteries in various configurations in order to meet the desired power requirements of a microelectronic system. The microbatteries so far

Figure 10. Photograph of a Prototype Li-ion microbattery connected to a blinking LED circuit.

demonstrated by MAPLE DW are not yet optimized and extensive work in developing appropriate current collectors and packaging schemes is still needed before any of these devices can be integrated into microelectronic circuits. However, the potential for the MAPLE DW technique to play a significant role in the development of the next generation of micropower sources is clear.

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